

SÃO PAULO STATE UNIVERSITY “JÚLIO DE MESQUITA FILHO” (UNESP)

Postgraduate Program in Materials Science and Technology (POSMAT)

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**DIELECTRIC PROPERTIES OF ORGANIC-BASED THIN FILMS
INTEGRATED INTO ROLLED-UP CAPACITORS**

BAURU-SP

JANUARY 2023

RICARDO MAGNO LOPES DA SILVA

Dielectric properties of organic-based thin films integrated into rolled-up capacitors

Doctoral thesis presented to the Postgraduate Program in Materials Science and Technology (POSMAT), at the São Paulo State University (UNESP), as one of the requirements to obtain the title of Ph.D.

Advisor: Dr. Carlos Cesar Bof Bufon.

BAURU-SP

JANUARY 2023

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Propriedades dielétricas de filmes finos de composição orgânica integrados a microcapacitores enrolados

Tese de doutorado apresentada ao Programa de Pós-Graduação em Ciência e Tecnologia de Materiais (POSMAT), da Universidade Estadual Paulista “*Júlio de Mesquita Filho*” (UNESP), como um dos requisitos para obtenção do título de Doutor.

Orientador: Dr. Carlos Cesar Bof Bufon

BAURU-SP

JANEIRO DE 2023

S586d

Silva, Ricardo Magno Lopes da

Dielectric properties of organic-based thin films integrated into rolled-up capacitors / Ricardo Magno Lopes da Silva. -- Bauru, 2023
149 p. : il., tabs.

Tese (doutorado) - Universidade Estadual Paulista (Unesp),
Faculdade de Ciências, Bauru

Orientador: Carlos Cesar Bof Bufon

1. organic/hybrid electronics. 2. low- dielectrics. 3. metal-organic frameworks (MOFs). 4. nanomembrane-based capacitors. I. Título.

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Aos 08 dias do mês de fevereiro do ano de 2023, às 09:00 horas, por meio de Videoconferência, realizou-se a defesa de TESE DE DOUTORADO de RICARDO MAGNO LOPES DA SILVA, intitulada **Dielectric properties of organic based thin films integrated into rolled-up capacitors**. A Comissão Examinadora foi constituída pelos seguintes membros: Prof. Dr. CARLOS CÉSAR BOF BUFON (Orientador(a) - Participação Virtual) do(a) Instituto Presbiteriano Mackenzie / Instituto Presbiteriano Mackenzie, Prof. Dr. RAFAEL FURLAN DE OLIVEIRA (Participação Virtual) do(a) Laboratório Nacional de Nanotecnologia (LNNano) / Centro Nacional de Pesquisa em Energia e Materiais (CNPEM), Prof. Dr. VARLEI RODRIGUES (Participação Virtual) do(a) IFGW / Unicamp – Campinas, Prof. Dr. CARLOS FREDERICO DE OLIVEIRA GRAEFF (Participação Virtual) do(a) Departamento de Física / Faculdade de Ciências - Unesp/Bauru, Prof. Dr. JOSÉ ROBERTO RIBEIRO BORTOLETO (Participação Virtual) do(a) Departamento de Engenharia de Controle e Automação / Instituto de Ciência e Tecnologia - Unesp/Sorocaba. Após a exposição pelo doutorando e arguição pelos membros da Comissão Examinadora que participaram do ato, de forma presencial e/ou virtual, o discente recebeu o conceito final: APROVADO. Nada mais havendo, foi lavrada a presente ata, que após lida e aprovada, foi assinada pelo(a) Presidente(a) da Comissão Examinadora.


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To my parents, Ricardo and Maristela, my sister Marcely, and my partner for life Luciana. For they always believed in me, even when I did not.

ACKNOWLEDGEMENTS

There were many people involved in the accomplishment of this work, both helping directly and indirectly ways. Therefore, I would like to mention some of them, specifically thanking to:

My family, for all the love and support, dispensed in my lifetime of studies. Thank you for all the good thoughts and for praying for me. I love you.

My fiancée, for all the patience, love, and affection during my doctoral journey. Thank you for sharing your life experiences with me.

My supervisor, Prof. Dr. Carlos Cesar Bof Bufon, for all the opportunities and encouragement he gave me during all the seven years working together, six of them at the LNNano, in CNPEM. The leader of the Nano and Microfabrication Division in LNNano, Dr. Rafael Furlan, for providing me with the conditions and incentive to keep my experiments, besides the conversation and advisement on my career. Also, my supervisor Prof. Dr. Flávio Leandro de Souza, for welcoming me into his research group and for providing me with opportunities to remain in the Academy.

My friends from the university, who are real companions for life, for always being there when I needed to, in academic and non-academic matters. Also, my friends and colleagues in the research group for their direct contributions to my research and the insights in the coffee break talks.

The institution LNNano – CNPEM, always welcomed me and provided the conditions I needed to complete my academic research projects.

The CAPES foundation, for the financial support to my studies during this journey.

The POSMAT – UNESP, for providing the source of knowledge and the academic degree for my learning and graduation title.

Finally, the Examination Board for this doctoral thesis defense, the yet not mentioned: Prof. Dr. Carlos Frederico de Oliveira Graeff, Prof. Dr. José Roberto Ribeiro Bortoleto, and Prof. Dr. Arlei Rodrigues; also, the already previously mentioned Dr. Rafael Furlan and Prof. Dr. Carlos Cesar Bof Bufon. For the disposition and contribution to my work and this life stage conclusion.

“There is nothing noble in being superior to some other man. True nobility is in being superior to your previous self.”

Ernest Hemingway.

SILVA, Ricardo Magno Lopes da. **Dielectric properties of organic-based thin films integrated into rolled-up capacitors**. 2023. 149p. Thesis (Ph.D. in Science and Technology of Materials) – UNESP, School of Science, Bauru, 2023.

ABSTRACT

The knowledge of organic semiconductor thin-film polarization effects brings benefits to developing novel electronic devices. However, the incorporation of few-molecule active layers into functional hybrid devices by establishing a top electrical contact, and yet preserving their overall integrity, is still an obstacle. An effective approach to circumvent this issue using conventional microfabrication techniques consists of using self-rolled nanomembranes, which provide a mechanical reliable contact between molecular ensembles and metal electrodes via the controlled releasing of planar structures from the substrate. This work begins by reporting the integration of 5 nm-thick metal-phthalocyanine ensembles (viz. CuPc, CoPc, and F₁₆CuPc) into self-rolled nanomembrane-based capacitors, posteriorly characterized by impedance spectroscopy measurements as a function of temperature (from 6 to 300 K), for the investigation of the dielectric polarization on the ensembles of organic semiconductors. At low temperatures, the permittivity of the molecular ensembles is found temperature-independent, but strongly dependent on the organic/inorganic hybrid interfaces, while the calculated relaxation times are more likely related to each single-molecule polarization. These results also support the deterministic design of the nanomembrane-based capacitor as a reliable alternative for the study of the dielectric properties for molecular-composed thin films, stimulating the exploitation of further complex, newer, and intrinsically challenging materials as dielectrics in the nanoscale thickness incorporated into the rolled-up capacitors. In this context, the next material chosen for investigation in such device structure belongs to the class of porous hybrid materials called Surface-Supported Metal-Organic Frameworks (SURMOFs), a promising group that rises to solve the demand for robust insulators in the interlayer dielectrics technology. The suitability of SURMOFs for electronics originates from their low cost, high versatility, low- κ , excellent morphology control, and robust mechanical properties. However, their intrinsic porosity represents an obstacle to the establishment of a reliable top electrode for the electric investigation of thin films for such materials. Therefore, ultrathin films of HKUST-1 SURMOF are integrated into the nanomembrane-based capacitors to access their dielectric properties with considerable accuracy. A low- κ value of 2.0 ± 0.5 and robust breakdown strength of 2.8 MVcm^{-1} are obtained for films with thicknesses below 80 nm. Furthermore, the spontaneous self-encapsulated structure provides good protection for the SURMOF towards different hazardous exposure. Based on the experimental data, finite-element calculations were employed to compare the HKUST-1 performance as the dielectric layer with well-established insulators applied in electronics (SiO_2 and Al_2O_3), and the results indicate that HKUST-1 exhibits better dielectric performance between interconnect structures, placing it as a promising candidate for application as an interlayer dielectric for novel electronics. The new results obtained in this study provide the basis for novel applications of such materials in organic and hybrid electronics.

Keywords: organic/hybrid electronics; low- κ dielectrics; metal-organic frameworks; nanomembrane-based capacitors.

SILVA, Ricardo Magno Lopes da. **Propriedades dielétricas de filmes finos de composição orgânica integrados a microcapacitores enrolados**. 2023. 149p. Tese (Doutor em Ciência e Tecnologia de Materiais) – UNESP, Faculdade de Ciências, Bauru, 2023.

RESUMO

O conhecimento dos efeitos de polarização em filmes finos de semicondutores orgânicos traz grandes benefícios para o desenvolvimento de novos dispositivos eletrônicos. No entanto, a incorporação de conjuntos moleculares em dispositivos híbridos funcionais, estabelecendo um contato elétrico superior que preserve a sua integridade, ainda é um desafio. Uma abordagem eficaz para contornar esse problema usando técnicas convencionais de microfabricação em 2D consiste no uso de nanomembranas autoenroladas, que proporcionam um contato mecânico confiável entre conjuntos moleculares e eletrodos metálicos através da liberação controlada de estruturas planares do substrato. Este trabalho começa relatando a integração de conjuntos de metal-ftalocianinas (viz. CuPc, CoPc e F₁₆CuPc) de 5 nm de espessura em capacitores baseados em nanomembranas autoenroladas, posteriormente caracterizados por medidas de espectroscopia de impedância em função de temperatura (de 6 a 300 K), para a investigação da polarização elétrica dos conjuntos de semicondutores orgânicos. Para baixas temperaturas, tais filmes apresentam permissividade independente da temperatura, mas fortemente dependente das interfaces híbridas orgânico/inorgânico, enquanto os tempos de relaxação calculados são mais provavelmente relacionados a polarização de cada estrutura molecular. Estes resultados também suportam o design determinístico dos capacitores baseados em nanomembranas como uma alternativa confiável para o estudo das propriedades dielétricas de conjuntos moleculares, o que estimula a exploração de materiais mais complexos, novos e intrinsecamente desafiadores como dielétricos com espessuras na nanoescala incorporados aos capacitores enrolados. Neste contexto, o próximo material escolhido para investigação em tais dispositivos pertence à classe de materiais híbridos porosos denominados estruturas metal-orgânicas suportadas em superfície (SURMOFs), um grupo promissor que surge para atender a demanda por isolantes robustos para a tecnologia de dielétricos entrecamadas. A adequação dos SURMOFs para a eletrônica vem de seu baixo custo, alta versatilidade, *low-κ*, excelente controle de morfologia e propriedades mecânicas robustas. Porém, sua porosidade intrínseca representa um obstáculo para o estabelecimento de contato superior confiável para investigação elétrica de filmes finos desses materiais. Portanto, filmes ultrafinos de HKUST-1 SURMOF são integrados aos capacitores baseados em nanomembranas para acessar suas propriedades dielétricas com considerável precisão. Um valor de κ igual a $2,0 \pm 0,5$ e uma robusta resistência à ruptura de $2,8 \text{ MVcm}^{-1}$ são obtidos para os filmes com espessuras abaixo de 80 nm. Além disso, a estrutura autoencapsulada fornece uma boa proteção para o SURMOF em relação a diferentes exposições perigosas. Com base nos dados experimentais, cálculos de elementos finitos foram empregados para comparar o desempenho do HKUST-1 com isolantes já aplicados na eletrônica (SiO₂ e Al₂O₃) como camada dielétrica e indicam que o HKUST-1 apresenta melhor desempenho em estruturas de interconexão, revelando um candidato promissor para aplicação como dielétrico entrecamadas para novos eletrônicos. Os resultados obtidos neste estudo fornecem uma base para novas aplicações desses materiais na eletrônica orgânica e híbrida.

Palavras-chave: eletrônica orgânica/híbrida; *low-k*; MOFs; capacitores autoenrolados.

LIST OF FIGURES

Figure 1: Schematic of dielectric loss mechanisms for dielectric materials. Source: (QIN; ZHANG; WU, 2022).	24
Figure 2: Representation of the molecular structures of the CuPc, CoPc, and F ₁₆ CuPc (respectively, from left to right). As illustrated, the molecules present a planar configuration. Source: adapted from (SILVA; MERCES; BOF BUFON, 2020).	28
Figure 3: Representation of the growth of MOF thin films. a) Deposition of a MOF precipitated directly on a substrate (above) and onto a substrate functionalized with a SAM (below). b) Epitaxial growth of a SURMOF by LbL-deposition technique onto a substrate functionalized with a SAM. Source: extracted from (GLIEMANN; WÖLL, 2012).	29
Figure 4: Schematic representation of the HKUST-1 MOF structure; (a) the top-left panel shows the metallic node and organic linker – copper atom and BTC, respectively – precursor components of the building-block units (bottom-left panel) for the HKUST-1 MOF structure formation. A unit cell of the crystal is evinced; (b) crystal structure of HKUST-1 built onto a substrate, showing the deposition steps of one LbL-deposition cycle. Source: adapted from (MONTAÑEZ et al., 2019).	30
Figure 5: Representation of nanomembrane-based rolled-up functional devices as: (a) magnetic inductor; (b) battery; (c) biosensor; (d) VOFET; (e) OFET; (f) capacitors. Source: adapted from, respectively, (FERRO et al., 2021; KARNAUSHENKO et al., 2018; LIU et al., 2018a; MINATO GAU FERRO et al., 2020; NAWAZ et al., 2020; PETRINI et al., 2018; TORIKAI et al., 2018).	32
Figure 6: The variation of different types of polarization with time under a step-function electric field E. Source: extracted from (KAO, 2004).	36
Figure 7: Zener breakdown (left panel) and collision, or avalanche, breakdown (right panel). Source: (MORTON, [s.d.]).	43
Figure 8: Schematic illustrations of dielectric loss mechanisms. Source: adapted from (QIN; ZHANG; WU, 2022).	45
Figure 9: The complex components of relative permittivity – dielectric constant in the top panel and respective loss factor at the bottom panel – as functions of frequency. Source: adapted from (KAO, 2004).	46
Figure 10: Diagram representing potential signals applied and respective equations of Ohm's Law, for (a) DC voltage (V_{DC}), in a direct current circuit and (b) AC voltage (V_{AC})	

on a sinusoidal wave shape. (c) Representation of current response to a V_{AC} applied with an angular frequency ω . Source: adapted from (CHOI et al., 2020).	47
Figure 11: Electric circuit modeling and graphical representation. (a) The most used equivalent circuit model to analyze impedance data, namely Randles and Erschler model. (b) Impedance spectrums in the form of Nyquist plots for circuits from (a) depending on the rate of charge transfer at the electrode/electrolyte interface. (c) The circuit elements dominate at different frequencies. Source: adapted from (CHENG; HSU; YUNG-CHEN WU, 2017).	55
Figure 12: Picture of a sample with a 6 x 14 device array (84 devices), restricted into the inner square of the chip (center panel), side-by-side with a regular Brazilian 1 real coin 27 mm-diameter (left panel). In the right panel, an amplification of the sample with the rolled-up devices is shown. Source: the author.	57
Figure 13: Illustration of: (a) sequential growth process of the HKUST-1 SURMOF onto Al_2O_3 substrate functionalized with the SAM PHDA; (b) illustration of Au substrate functionalized with the SAM MHDA, after 2 and 6 cycles of HKUST-1 SURMOF growth. Source: adapted from (SILVA et al., 2022; WANG; WÖLL, 2018).	59
Figure 14: Illustration of the MSM samples configuration. The films thickness is not in scale. Source: adapted from (SILVA et al., 2022).	61
Figure 15: Fabrication processes for rolled-up capacitors. (a) Substrate cleaning; (b) patterning of the Ge layer; (c) thermal treatment for the Ge oxidation, forming the GeO_x sacrificial layer; (d) patterning of the stressed metallic NM consisting of Au/Ti/Cr (5/10/10 nm) onto the sacrificial layer; (e) deposition of Al_2O_3 (10 nm) onto the metallic NM; (f) patterning of the Cr (10 nm) layer on Al_2O_3 , configuring a conventional parallel-plate capacitor; (g) deposition of Al_2O_3 (10 nm) onto the parallel-plate capacitor; (h) patterning and wet etching (with HF) for accessing the electric contacts; (i) deposition of the electric contacts of Cr/Au; (j) patterning and wet etching of the trench for accessing the GeO_x layer, for the roll-up; (k) patterning of anchors for the tubes protection on the rolling of the NM; (l) deposition of the MBTF onto the capacitor (MPc evaporation or HKUST-1 SURMOF growth); (m) immersion of the sample in the roll-up solution; (n) dissolution of the GeO_x sacrificial layer, enabling the roll-up process; (o) r-NM-based capacitor (h-rCap) formed. Source: adapted from (SILVA; MERCES; BOF BUFON, 2020).	62
Figure 16: Fabrication of the <i>r</i> -NM-junction. The process comprises the determination of the: (a) dielectric mesa (by SiO_2 substrate corrosion) to elevate the bottom electrode;	

(b) Au bottom electrode (finger-shaped). (c) sacrificial layer (GeO_x); (d) strained metallic NM consisting of Au/Ti/Cr. (e) electric contacts. (f) HKUST-1 SURMOF (active area). (g) The roll-up process occurs by dissolving the sacrificial layer and releasing the NM. (h) Final configuration of the <i>r</i> -NM-junction, established with the tubular top contact. Source: adapted from (SILVA et al., 2022).....	64
Figure 17: Scheme illustrating the process of roll-up – controlled removal of a sacrificial layer to the directional release of a stressed NM. The strained NM is liberated in a way to promotes a tubular-shaped structure. Source: adapted from Carlos C. B. Bufon courtesy animation.	65
Figure 18: Instruments used for the optical microscopies performed in this work. (a) Conventional optical microscope Zeiss Axio Imager. (b) LSCM from Keyence VK-X200. Source: Images acquired and adapted from the official LNNano site (https://lnnano.cnpem.br/instalacoes-e-divisoas/divisao-de-nanomateriais/laboratorio-de-microscopia-eletronica-de-varredura-duplo-feixe/ , at 18/03/2023).	68
Figure 19: AFM equipment used for the topological exploration of the dielectric films. (a) NaioAFM Nanosurf. (b) Park Systems – NX10. Source: images acquired and adapted from the official LNNano site (https://lnnano.cnpem.br/instalacoes/microscopia-e-criomicroscopia/microscopia-de-forca-atomica/ , at 18/03/2023).	69
Figure 20: Scanning Electron Microscope (FEG-SEM) Inspect F50 from FEI (Japan). Source: the author.....	70
Figure 21: Demonstration of the electric characterization set-up and equipment used: (a) Probe station cascade (4-tip probes) with detail on the atmosphere-controlled box (inset); (b) LakeShore system for cryostat-support station (4-tip probes) with detail on the sample chuck (inset); (c) Keithley 4200 for IxV measurements; (d) Solartron 1260A for impedance analysis; (e) Keysight E4980A for impedance analysis. Source: the author.....	71
Figure 22: Illustrative representation of the domain for the FEM simulation performed. (a) 3D demonstration of the interconnections (out of scale) on the dielectric substrate. (b) Cross-section of the interconnections, with illustrative opposite-charged electric potential applied. (c) Mesh structure for the Lagrange elements. (d) Example of electric field distribution on the mash after applied potentials. (e) Different structure created for the simulation, with the dielectric as a wall for the interconnections, besides their substrate. Source: the author.....	74

Figure 23: AFM image of a 400-nm-thick Al ₂ O ₃ film, presenting an RMS value of ≈ 4.0 nm. Source: extracted from (SILVA; MERCES; BOF BUFON, 2020).	75
Figure 24: Atomic force microscopy (AFM) images of 10-nm-thick MPc films: (a) CuPc, (b) CoPc, and (c) F ₁₆ CuPc. Source: Reprinted with permission from (SILVA; MERCES; BOF BUFON, 2020).	76
Figure 25: STEM images of the stages for the lamella preparation of an MSM device with a layer of 100 cycles of the HKUST-1 SURMOF between metallic electrodes using the FIB technique. (a) Image of one MSM device with the region etched by the ion beam. (b) Zoomed into the upper view of the etched region, with the arrows indicating the (c) angular perspective of the etched region. (d) Prepared lamella (highlighted) detached and soldered to a micromanipulator. (e) Lamella (highlighted) attached (soldered) to the grid for probing. (f) Zoomed in the (rough) lamella on the grid, with a respective top view (inset). (g) Lamella after ion beam polishing procedure for STEM and EDS characterization. (h) Zoom on the polished lamella. (i) Detail of the HKUST-1 SURMOF layer sandwiched by the electrodes in the MSM structure. Source: the author.....	77
Figure 26: Bright Field STEM image of a 100 cycles film of the HKUST-1 SURMOF in MSM device, after the cut and preparation of a lamella of the sample by FIB technique. Source: the author.	78
Figure 27: EDS for the MSM junction. Source: the author.....	79
Figure 28: GIXRD pattern for different deposition cycles on functionalized Al ₂ O ₃ surface. Source: Extracted from (SILVA et al., 2022).	80
Figure 29: XRD patterns of 20 cycles of HKUST-1 SURMOF film grown onto Al ₂ O ₃ substrates functionalized with PHDA SAM. The image depicts the comparison between diffractograms of the film: pure, immersed in 60% ethanol / 40% water v/v solution for 3 h, and immersed in DI water for 3 h. Source: the author.....	81
Figure 30: (a) Profile of the HKUST-1 SURMOF thickness for 10 deposition cycles obtained from the 20 μm x 40 μm AFM topography image shown in (b). (c) Profile HKUST-1 SURMOF thickness for 40 deposition cycles obtained from the 20 μm x 40 μm AFM topography image shown in (d). Source: extracted from (SILVA et al., 2022).	82
Figure 31: 5 μm x 5 μm AFM topography images of the HKUST-1 SURMOF films for: (a) 10 deposition cycles of a black and white threshold-created treated image showing a cluster size of about 5 nm, with its respective (b) original AFM image; (c) 40 deposition cycles of a black and white threshold-created treated image showing a cluster size of	

about 0.5 μm , with its respective (d) original AFM image. Source: extracted from (SILVA et al., 2022).	83
Figure 32: Cover page of Applied Materials & Interfaces, volume 12, number 26 (top panel), and article divulgation image (bottom panel) of the article entitled Temperature-Independent Polarization of Ultrathin Phthalocyanine-Based Hybrid Organic/Inorganic Heterojunctions. Source: adapted from (SILVA; MERCES; BOF BUFON, 2020).	86
Figure 33: SEM images of the devices: (a) i-pCap, (b) i-rCap, and (c) h-rCap. The SEM images were artificially colored. The scale bars in panels (a-c) are 40 μm long. The cross-sectional view of each device is illustrated in panels (d-f) below the respective SEM image. Each dielectric layer is considered as an impedance (Z) in the system – see each equivalent-circuit expansion as insets in the panels (d-f) . Source: extracted from (SILVA; MERCES; BOF BUFON, 2020).	87
Figure 34: Impedance phase (θ) as a function of f at 6 K and 300 K for (a) i-pCap, (b) i-rCap, and (c) h-rCap. Inset: Respective impedance modulus ($ Z $) as a function of f at 6 K and 300 K. Source: extracted from (SILVA; MERCES; BOF BUFON, 2020).....	88
Figure 35: $I \times V$ plot graph for i-pCap with Al_2O_3 dielectric layer, showing the leakage current through the film at 6K and 300K. Source: the author.	89
Figure 36: (a) Capacitance as a function of f for each device architecture at 6 and 300 K. (b) Capacitance as a function of T for $f = 10^3$ Hz. Source: extracted from (SILVA; MERCES; BOF BUFON, 2020).	90
Figure 37: Relative permittivity for a 15-nm-thick Al_2O_3 film <i>i-pCap</i> . The top panel exhibits the diagram of permittivity as a function of f (abscissa axis) and T (ordinate axis). The color scale bar is shown in the bottom panel along with the permittivity-frequency plot obtained at 6 and 300 K. Source: extracted from (SILVA; MERCES; BOF BUFON, 2020).	93
Figure 38: (a) Real and (b) imaginary part of the capacitance of the Al_2O_3 , relative to the geometric capacitance value of the parallel-plates device, both at 6 and 300 K. The lines are curves fitted by the respective Debye model, exhibited as inset panels. Source: extracted from (SILVA; MERCES; BOF BUFON, 2020).	94
Figure 39: Relative permittivity diagrams of 5-nm-thick molecular ensembles of (a) CuPc, (b) CoPc, and (c) F_{16}CuPc , as a function of f and T . (d) Permittivity values calculated for $T < T'$ and $f < 10^4$ Hz and the color scale bar. The respective relaxation times are exhibited in panel (e) . Source: extracted from (SILVA; MERCES; BOF BUFON, 2020).	95

Figure 40: MPc relative permittivity at $T = T'$. The lines are curves fitted by the Havriliak-Negami model with $\alpha = \beta = 1$. Source: adapted from (SILVA; MERCES; BOF BUFON, 2020)	97
Figure 41: Graphical abstract of the work exploiting HKUST-1 ultrathin layers incorporated into r-NM capacitors. Source: extracted from (SILVA et al., 2022).....	99
Figure 42: Parallel-plate capacitors-based HKUST-1 SURMOF in MIM structures. (a) Optical microscopy image showing an array of 9 devices on a chip. The active area of about 0.2 mm^2 is determined through the area of the circular top gold electrode. (b) Photography showing the entire $9 \times 9 \text{ mm}^2$ chip with 121 MSM devices fabricated. Source: extracted from (SILVA et al., 2022).	100
Figure 43: Histogram phase degree for different MSM devices with HKUST-1 SURMOF. (a) 30, (b) 40, (c) 50, (d) 75, and (e) 100 deposition cycles. The counts are the phase values of 22 different MSM devices for each SURMOF thickness, covering the frequency range from 1 kHz to 50 mHz (10 points/decade). Source: extracted from (SILVA et al., 2022).	101
Figure 44: Histogram phase degree for different MSM devices with HKUST-1 SURMOF deposited for 20 cycles. (inset) Mean values and respective standard errors of impedance phase spectroscopies for the same structures. The counts were performed considering the phases of 20 different MSM devices covering the frequency range from 1 kHz to 50 mHz (24 points/decade). Source: extracted from (SILVA et al., 2022). .	102
Figure 45: Layout and layer composition of the devices. (a)-(b) Illustration of the i-pCap and h-rCap device structures. The roll-up process starts after the GeO_x dissolution; the top electrical contact on the SURMOF is accomplished as the outermost surface of the strained tri-metallic layer curls. (c) Respective layer sequence for the regions indicated in the dotted rectangles for i-pCap and h-rCap. (d) SEM image of a couple of h-rCap devices, highlighting the reduction of the device footprint area. (e) LSCM image from an array of 18 devices shows the reproducibility and scalability of the fabrication process of the h-rCap structures. Source: reprinted from (SILVA et al., 2022).	103
Figure 46: Impedance characteristics for MSM and h-rCap devices in N_2 atmosphere condition. (a)-(b) Typical impedance θ and C_p as a function of frequency for devices comprising 20 LPE deposition cycles of HKUST-1. (c) θ as a function of frequency for h-rCap devices with different LPE deposition cycles. The highlighted region indicates the frequency range where the devices exhibit typical capacitor behavior; (inset) the measured C_p in this region. (d)-(e) Equivalent circuit for MSM and h-rCap devices.	

(f) Area/Capacitance as a function of HKUST-1 SURMOF thickness. **Source:** extracted from (SILVA et al., 2022). 105

Figure 47: Influence of the environmental conditions on the dielectric properties of 40-cycles HKUST-1 SURMOF films. (a)-(b) Illustration of MSM and h-rCap devices exposed to different environments. (c)-(d) Respective θ and (e)-(f) C_p as a function of frequency for MSM and h-rCap devices. The **inset** in (e) shows the C_p at high frequencies after NH_3 exposition for the MSM device. The laboratory condition (amb) involves a relative humidity of around 70% and a temperature of 25°C. **Source:** extracted from (SILVA et al., 2022). 107

Figure 48: Dielectric response of the *h-rCap* devices with 10-deposition cycles of HKUST-1 SURMOF measured at different environmental conditions. (a)-(b) θ and capacitance as a function of frequency. The minor variation in the θ and capacitance response is related to the low SURMOF thickness (~ 20 nm) for 10-deposition cycles, which allows a better-compacted structure after the rolled-up process. **Source:** extracted from (SILVA et al., 2022). 108

Figure 49: (a) Percentage changes of θ at 10 kHz for MSM and h-rCap devices relative to the N_2 atmosphere condition. (b) κ values for HKUST-1 obtained in this work compared to previously reported works. The error bars indicate the uncertainty of the data, which is not reported in most cases. (c) A survey of the inverse of footprint area versus the inverse of the thickness of the active layer, comparing the results from the devices in this work, and other device in the literature. (d) Typical current versus applied electric field for MSM and r-NM-junction. (e) Breakdown electric-field versus κ for this work compared with other low- κ materials reported in the literature. In (c) and (e) MOFs are open circles and SURMOFs are solid circles. **Source:** adapted from (SILVA et al., 2022). 109

Figure 50: FEM simulations for HKUST-1, SiO_2 , and Al_2O_3 . (a) Illustration of two parallel interconnects on HKUST-1 as substrate. V_{DC} and GND correspond to the force and sense terminals for an applied DC electric potential. (**inset**) Respective electric field lines distribution for cross-section. (b) Electric field (in modulus) between the two parallel interconnects (vertical line, $x = 0$) for HKUST-1, SiO_2 , and Al_2O_3 as substrate. (c) Representation of the setup for simulation, considering the respective dielectrics as sidewalls for both parallel interconnects. (d) Electric field (in modulus) between the two parallel interconnects (vertical line, $x = 0$) for different dielectrics as substrate and sidewalls. (e) Experimental dielectric loss spectroscopy for HKUST-1 and Al_2O_3 as the

dielectric layer in a MIM configuration. In **(b)** and **(d)**, solid and dotted data lines represent grounded and float configurations for the sense electrode. **Source:** adapted from (SILVA et al., 2022). 112

Figure 51: The electric field in the x-axis at 1 μm below the surface of the HKUST-1 substrate, for the simulated cross-section area of parallel interconnections, 40-nm-apart from each other. **Source:** adapted from (SILVA et al., 2022). 113

Figure 52: Graphical abstracts of the scientific contributions to the literature from this author and project. The titles of the papers are: **(a)** Surface-Supported Metal–Organic Framework as Low-Dielectric-Constant Thin Films for Novel Hybrid Electronics (SILVA et al., 2022); **(b)** Ambipolar Resistive Switching in an Ultrathin Surface-Supported Metal–Organic Framework Vertical Heterojunction (ALBANO et al., 2020); **(c)** Temperature-Independent Polarization of Ultrathin Phthalocyanine-Based Hybrid Organic/Inorganic Heterojunctions (SILVA; MERCES; BOF BUFON, 2020); **(d)** Hybrid nanomembrane-based capacitors for the determination of the dielectric constant of semiconducting molecular ensembles (PETRINI et al., 2018). 118

LIST OF TABLES

Table 1: Impedance spectroscopy parameters and their relation.....	48
Table 2: Frequency dependences and phase shifts of some impedance pure elements.....	53
Table 3: Calculated charge induced and capacitance from the <i>FEM</i> simulations considering the sense terminal grounded.....	114
Table A1: Estimation of the individual between-electrodes area for the CTVJ devices, and their respective C_p measured by impedance spectroscopy.....	137
Table A2: Main results on the VNA measures for the micro-scaled antennas.....	146

LIST OF ABBREVIATIONS AND SYMBOLS

AFM – atomic force microscopy	LSCM – 3D laser scanning confocal microscopy
C_p – parallel capacitance	MBTF – molecular-based thin-films
CoPc – cobalt phthalocyanine	MHDA – mercaptohexadecanoic acid
CPE – constant phase element	MIM – metal/insulator/metal
CuPc – copper phthalocyanine	MIS – metal/insulator/semiconductor
DFT – density functional theory	MOFs – metal-organic frameworks
EDS – energy-dispersive x-ray spectroscopy	MPcs – metal-phthalocyanines
ϵ' – electrical permittivity	MSM – metal/SAM-SURMOF/metal
ϵ'_r – relative electrical permittivity	NM – nanomembrane
F₁₆CuPc – copper hexadecafluoro phthalocyanine	OFETs – Organic Field-Effect Transistors
FEG-SEM – Field Emission Gun Scanning Electron Microscope	OLEDs – Organic Light-Emitting Diodes
FEM – finite-element modeling	OPVs – Photovoltaics
FIB – focused ion beam	OSC – organic semiconductor
GIXRD – Grazing Incidence X-Ray Diffraction	PDEs – Partial Differential Equations
<i>h-rCap</i> – hybrid rolled nanomembrane-based capacitor (with MPc or SURMOF)	PHDA – phosphonohexadecanoic acid
HKUST-1 – Hong Kong University of Science and Technology – Cu ₃ (BTC) ₂	R – resistance
<i>i-pCap</i> – inorganic planar capacitor	R_p – parallel resistance
<i>i-rCap</i> – inorganic rolled nanomembrane-based capacitor	<i>r-NMs</i> – rolled-up nanomembranes
IC – integrated circuits	RMS – root-mean-square
ILD – interlayer dielectric	SAM – self-assembled monolayer
IS – impedance spectroscopy	SEM – scanning electron microscopy
κ – dielectric constant	STM – Scanning Tunneling Microscopy
LbL – layer-by-layer	SURMOFs – surface metal-organic frameworks
LNLS – Brazilian Synchrotron Light Laboratory	<i>tan δ</i> – loss tangent
LPE – Liquid Phase Epitaxy	τ – dielectric relaxation
	VOFETs – Vertical Organic Field-Effect Transistors
	XPS – X-ray Photoelectron spectroscopy

TABLE OF CONTENTS

CHAPTER I: INTRODUCTION	23
1.1. ORGANIC AND HYBRID MATERIALS FOR ELECTRONICS.....	23
1.1.1. Metal Phthalocyanines	27
1.1.2. Surface-Supported Metal-Organic Frameworks.....	28
1.2. NANOMEMBRANE-BASED DEVICES	31
1.3. MOTIVATION AND OBJECTIVES	33
CHAPTER II: THEORETICAL BACKGROUND	35
2.1. ORIGINS OF POLARIZATION IN MATERIALS.....	35
2.2. DIELECTRIC PROPERTIES OF MATERIALS.....	37
2.2.1. Capacitance and Polarization for Dielectrics.....	37
2.2.2. Permittivity in Dielectrics	39
2.2.3. Dielectric Relaxation in Materials.....	40
2.2.4. Dielectric Breakdown	42
2.2.5. Complex Permittivity: Dielectric Constant and Loss Factor	45
2.3. IMPEDANCE SPECTROSCOPY	47
2.3.1. Impedance Principles	49
2.3.2. Linear Response Theory	50
2.3.3. Elements for Modeling Impedance Systems	52
CHAPTER III: SAMPLES FABRICATION – FACILITY AND TECHNIQUES	57
3.1. CONVENTIONAL METHODS FOR MICROFABRICATION.....	57
3.1.1. Facility – Cleanroom Laboratory	58
3.1.2. Step-by-Step HKUST-1 SURMOF Growth	58
3.1.3. Devices Fabrication	60
3.2. <i>r</i>-NM-BASED FORMATION: NM RELEASING / ROLL-UP PROCESS	65

3.2.1. Tubes Formation for the MPcs Capacitors.....	66
3.2.2. Tubes Formation for the HKUST-1 SURMOF Capacitors.....	66
3.2.3. Tubes Formation for HKUST-1 SURMOF <i>r</i> -NM-junctions	66
CHAPTER IV: CHARACTERIZATION METHODS.....	68
4.1. MORPHOLOGICAL CHARACTERIZATION OF THE FILMS AND SAMPLES.....	68
4.1.1. Optical microscopies of the films and devices.....	68
4.1.2. Atomic force microscopy (AFM).....	69
4.1.3. Electron Microscopies and Spectroscopy	70
4.2. ELECTRICAL CHARACTERIZATION OF THE SAMPLES	70
4.2.1. Electrical Characterization of the <i>h-rCap</i> Devices with MPcs	71
4.2.2. Electrical Characterization of the MSM and <i>h-rCap</i> Devices with HKUST-1 SURMOF.....	72
4.3. FEM SIMULATIONS OF DIELECTRICS FOR INTERCONNECTIONS	73
CHAPTER V: STRUCTURAL ANALYSIS FOR THIN FILMS OF THE DIELECTRIC MATERIALS.....	75
5.1. Surface Topography Characterization of the Al ₂ O ₃ films	75
5.2. Surface Topography Characterization of the MPcs films	75
5.3. Structural Characterization of the HKUST-1 SURMOF Films.....	76
5.3.1. Electrical Microscopies and Spectroscopy	76
5.4. Grazing Incidence X-Ray Diffraction (GIXRD)	79
5.4.1. Atomic Force Microscopy	82
CHAPTER VI: MPc THIN FILMS INTO ULTRACOMPACT CAPACITORS	84
6.1. ON THE MICRO / NANOSCALE CAPACITIVE DEVICES	84
6.2. DEVICES ENSEMBLE	85
6.3. PHTHALOCYANINES AS DIELECTRIC LAYERS	85

6.3.1.	Design of Each Capacitive Structure Assayed	86
6.3.2.	Impedance Spectroscopy vs. Temperature.....	88
6.3.3.	Capacitive Response at Low- T	89
6.3.4.	Modeling the Electric Permittivity of the Active Materials.....	91
6.3.5.	Dielectric Properties of the Ultrathin Semiconducting Molecular Ensembles 94	
6.3.6.	The Role of Pc Structure on Molecular-Ensemble Dielectric Properties....	96
CHAPTER VII: HKUST-1 SURMOF DIELECTRIC INVESTIGATION		99
7.1.	INTRODUCING THE CHALLENGE	99
7.2.	MORPHOLOGY OF THE HKUST-1 SURMOF THIN FILMS.....	99
7.3.	HKUST-1 SURMOF INTO DEVICES.....	100
7.3.1.	Dielectric Layers in MIM (MSM) Structures	100
7.3.2.	Dielectric Layers in h - r Cap Devices	102
7.3.3.	Self-Encapsulation of r -NM-based Capacitors Exposed to Diverse Atmospheres	106
7.3.4.	FEM Simulations	111
CHAPTER VIII: FINAL CONSIDERATIONS		116
8.1.	CONCLUSIONS	116
8.1.1.	MPcs in h - r Cap Devices.....	116
8.1.2.	HKUST-1 SURMOF in h - r Cap Devices	117
8.2.	SCIENTIFIC CONTRIBUTIONS	118
8.2.1.	Periodical Peer-Reviewed Publications	118
8.2.2.	Event and Congress Participations	119
REFERENCES		121
APPENDIX		135

CHAPTER I: INTRODUCTION

1.1. ORGANIC AND HYBRID MATERIALS FOR ELECTRONICS

Molecular ensembles present plenty of envisioned applications to electronics that require a pack of properties and characteristics poorly found in the classic inorganic components, such as mechanical flexibility, lightweight, low-temperature processing, and high throughput manufacturing at low cost (LIAO et al., 2015; TORIKAI et al., 2018). In mesoscopic physics, the electron position in molecules implies smaller electrostatic screening than in inorganic electronic materials, which helps the buildup of steep electrical potential gradients.

Conceptually speaking, one single molecule describes a 0D system, working as a quantum dot. A small molecule connected to electrodes can perform the function of a nanowire. Molecular monolayers or ensembles (≤ 5 nm) describe 2D systems (VILAN; ASWAL; CAHEN, 2017). The composition of molecules usually consists of small (“lightweight”) atoms, which perform small spin-orbit coupling, increasing the spin memory for electrons, which is a useful property in spintronics (ATZORI et al., 2016). In solar cells, for example, there is a huge claim for organic semiconductors, and the dielectric properties of molecules with semiconductor-like behavior are extremely relevant (ARMIN et al., 2017). Molecular engineering can allow the achievement of closer-to-ideal conditions for charge separation in molecular ensembles and, as consequence, more efficient charge generation from the sunlight. Therefore, the investigation of the dielectric properties in thin films of organic semiconductors, for example, holds great importance for physical and electronic applications.

Organic and inorganic elements can be arranged to form hybrid frameworks, engineered at the nanoscale. Such structures have been widely employed in current electronics, braving the challenge of continuous miniaturization of functional systems and devices (BOF BUFON et al., 2010; CHOI et al., 2018; VILAN; ASWAL; CAHEN, 2017). Such organic and inorganic building blocks, combined to form hybrid (organic-inorganic, *i.e.*, molecular-based) systems, offer several benefits for electronics when compared to intrinsic inorganic-based structures (LIANG et al., 2018). Currently, the application of organic or hybrid materials embraces organic field-effect transistors (OFETs) (CHOI et al., 2018), photovoltaics (OPVs) (ZHOU; HUANG, 2018), diodes (OLEDs) (SONG et al., 2018), batteries (ZHAO et al., 2018), and

molecular-based supercapacitors (LIU et al., 2018b), among others (ARMIN et al., 2017; BUENO, 2018). A pivotal interest in developing novel organic/hybrid technologies relies on the branch of flexible, bendable, and rollable electronics (LI et al., 2019; LIM et al., 2019). In this scenario, molecular materials have been largely exploited to address the function of inorganic circuitry components – *e.g.* envisioning pressure sensing applications to build up interactive electronic devices and e-skins (MERCES; DE OLIVEIRA; BOF BUFON, 2018; SURMENEV et al., 2019; WANG et al., 2019). To support the technological development of organic and molecular-based electronics, the investigation of the dielectric properties of such materials is a fundamental task for the branch of hybrid systems. The control of the functionalities emerging from the hybrid interfaces is an important key to efficiently incorporating the nanoscale properties of molecules and nanomaterials into electronics (REZVANOV et al., 2018; VILAN; CAHEN, 2017). Understanding the dielectric polarization and loss mechanisms of materials provides us the tools to tailor the electric field absorbing performance for such systems (QIN; ZHANG; WU, 2022), mostly for the organic and hybrid materials applied as dielectrics in energy storage devices. **Figure 1** shows a schematic for types of dielectric loss in the complex structures created on hybrid electronics.

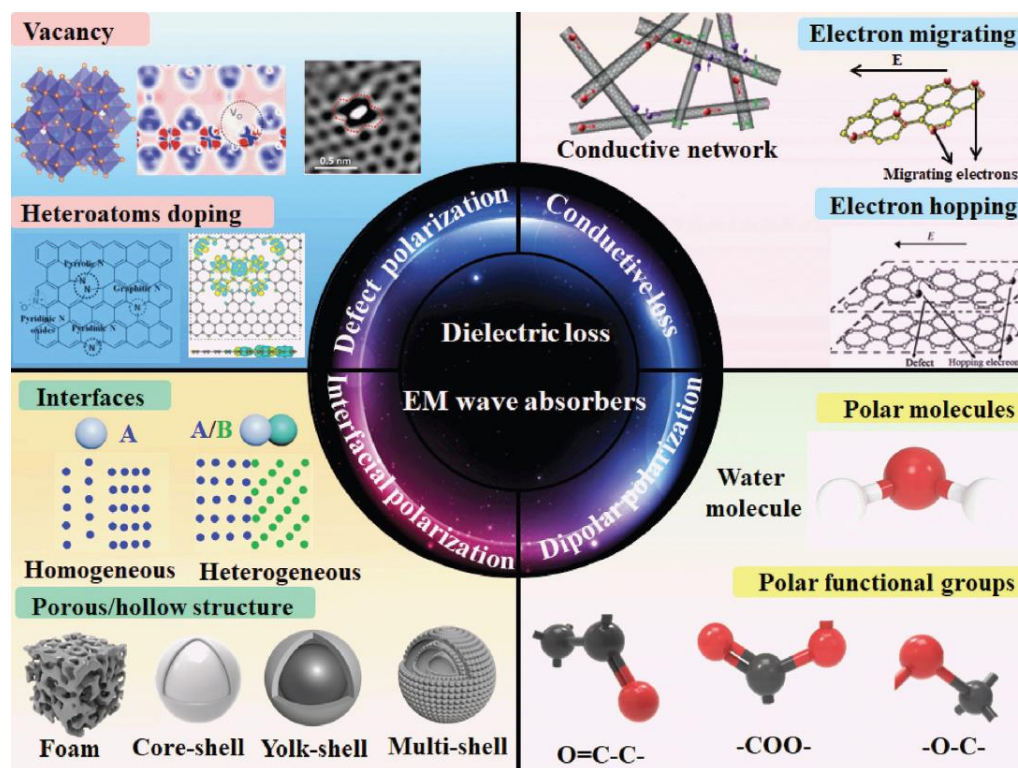


Figure 1: Schematic of dielectric loss mechanisms for dielectric materials. **Source:** (QIN; ZHANG; WU, 2022).

Nowadays, the development of compact energy storage devices is crucial for the new demands based on portable, wearable, and implantable electronics. However, in a conventional approach, the dependence of geometric parameters for these passive electronic devices (*e.g.*, area and wire windings) makes miniaturization a challenging process. Furthermore, for the effective integration of these systems, they must be capable to access the properties of thin films of organic and molecular-based hybrid materials, *i.e.*, molecular-based thin films, *MBTF* (XIANG et al., 2016). By controlling the properties of single molecules or molecular ensembles (building blocks), specific functionalities can be further explored (JEONG et al., 2017). For example, the highly localized electronic charges can be controlled through the molecular configuration, opening new horizons for exploring unprecedented quantum effects. Also, the inherent reduced size and flexibility of such *MBTF* materials may affect positively the properties of passive electronics, *e.g.*, either by increasing the capacitance owing to the ultrathin film thicknesses or extending their useful life associated with the good mechanical properties. In addition, the reduction of power consumption and heat generation can also be easily achieved. These findings point out molecular/hybrid electronics in a highlighted position for the current demands of electronic device miniaturization.

Another rising issue on the miniaturization in electronics rises from the parallelism of integrated circuits (IC). The number of active components in ICs has been exponentially increasing with the miniaturization of electronic devices, with a reduction of more than 30% of the footprint area of devices on a chip every 2-3 years (ADVANCING TECHNOLOGY FOR HUMANITY, 2020). The corresponding decrease in transistor size and increase of their density on chips brings with it other issues such as increased resistance of the interconnect wires, propagation delay, and crosstalk between the wires. These problems can be solved by the introduction of interlayers of low- κ dielectric materials (MENDIRATTA et al., 2015). The incorporation of organic elements increase the low- κ aspects of the material over the neat oxide layers, owing to their limited polarizability, they also increase the free volumes, diminishing their density (HATTON et al., 2006; VOLKSEN; MILLER; DUBOIS, 2010). In both cases (organic based and oxide layers), intrinsic disorder and high porosity lead to poor thermal properties (ERICKSON et al., 2015; KIM et al., 2015; XIE et al., 2016), where heat management is critical. Recently, advances in boron nitride placed 2D materials as a promising class of materials to be considered for low- κ dielectrics (HONG et al., 2020; KNOBLOCH et al., 2021). However, the current lack of suitable 2D insulators and integration difficulties into silicon technology limit new advances (ILLARIONOV et al., 2020).

To circumvent this issue, porous-hybrid materials, specifically metal-organic frameworks (MOFs), rise as promising candidates for low- κ dielectrics (ADVANCING TECHNOLOGY FOR HUMANITY, 2020). The introduction of highly ordered porosity and the evacuation of polar guest molecules suggest that MOFs represent an ideal replacement as an interlayer dielectric (ILD) material. There is evidence that uniform, ordered porous structures can have improved mechanical properties compared with disordered structures (HATTON et al., 2006). At the current stage, addressing the many issues related to the design and fabrication of devices would be highly desirable (MENDIRATTA et al., 2015). Despite the potential of MOFs for applications as low- κ dielectrics, a major obstacle is the fabrication of monolithic, surface anchored MOF thin films. In this context, Surface-Supported Metal-Organic Frameworks (SURMOFs) prepared with layer-by-layer (LbL) deposition by a dip coating method offer unique opportunities for a better incorporation of such structures into devices (SHEKHAH et al., 2007). This approach provides MOF films with well-controlled features, including thickness, homogeneity, morphology, and defect density with improved adhesion onto desired substrates (HEINKE; WÖLL, 2019). In addition, the crystallinity can be deterministically tailored on both metallic and insulating surfaces by selecting the chain length of the self-assembled monolayer (SAM) (VELLO et al., 2020). This unique set of properties projects exciting new possibilities for the integration and development of novel electronic devices (ALBANO et al., 2020, 2021; CHANDRESH et al., 2021). Nevertheless, their potential as low- κ dielectrics has not yet been entirely accessed. A detailed electronic-access investigation of the SURMOFs dielectric properties incorporated into electronic devices at the micro-nanoscale has not been successfully established and reported up to date. Several limitations on measurement techniques and device architectures hinder the accurate determination of their dielectric constant values. Among the main difficulties, the reliable fabrication of electrically conducting top contacts and the full integration in a suitable manufacturing platform are the most significant challenges owing to the high intrinsic porosity and ultrathin thicknesses of the films. Simple evaporation of metallic patches using, *e.g.*, physical vapor deposition must be abandoned owing to the interdiffusion of metal atoms during the deposition process.

In this scenario, this work explores the full integration of HKUST-1 SURMOF thin films into functional devices (with an unconventional architecture) exhibiting reliable contact of the upper electrode to the material, for the investigation of their dielectric properties for

application as ILD. This represents exciting possibilities for contribution to the advance of electronics.

1.1.1. Metal Phthalocyanines

For the last few years, molecules based on alternating double-and-single (π -conjugated) bonds integrated into functional devices have attracted much interest. Some examples rely on flexible devices, reduced manufacturing temperatures, and low cost-production (YUVARAJA et al., 2020). As the organic materials have reached the nanoscale, they brought new fundamental interesting properties to the new generation of devices, such as interfacial organic-inorganic functionalities (LIU; XU; NOH, 2015; POZZOLI et al., 2020; SILES et al., 2016). Therefore, the investigation of the role of molecular orientation (MAS-TORRENT; ROVIRA, 2011), and electrode configuration (MERCES et al., 2017b), in the charge accumulation and transfer across organic-inorganic interfaces has enabled the development of new functional device concepts with precise control of their electronic properties (FAHLMAN et al., 2019; MERCES et al., 2021).

The choice of studying metal phthalocyanine-based (MPc-based) films in a few-nanometer thickness is based on how well explored and underpinned their properties are, in addition to still fostering further study and investigation on its functionalities. Even recently, it was revealing a new metal / π -conjugated MPc-based hybrid system that displays interesting features toward electrochemistry and organic-electronics recent advances (BATISTA et al., 2022; FERRO et al., 2021; SERGI LOPES et al., 2020).

The ultrathin layers MPc-based used as the dielectrics here were the copper phthalocyanine (CuPc), copper hexadecafluoro phthalocyanine (F₁₆CuPc), and cobalt phthalocyanine (CoPc). The molecules form organic semiconductive structures: CuPc and CoPc behaves as p-type and F₁₆CuPc acts as n-type semiconductor (CHEN; MA, 2010; LIAO; SCHEINER, 2001). Besides, CuPc and CoPc presents interesting magnetic response depending on the substrate used (WANG; LI; YANG, 2019). **Figure 2** shows the molecular structures of each MPc chosen.

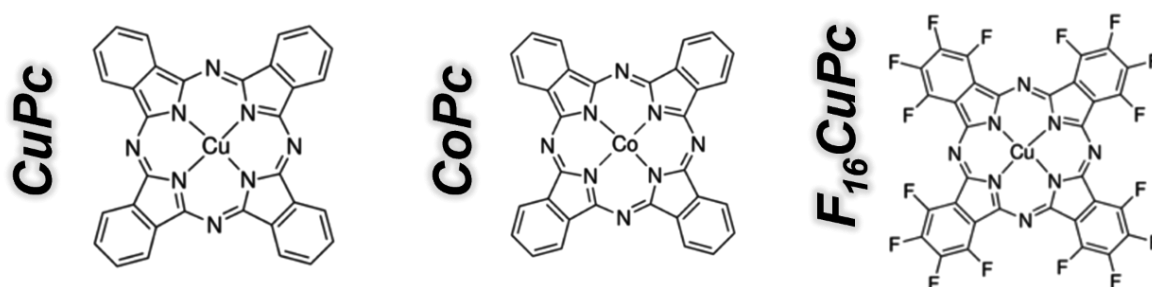


Figure 2: Representation of the molecular structures of the CuPc, CoPc, and F₁₆CuPc (respectively, from left to right). As illustrated, the molecules present a planar configuration. **Source:** adapted from (SILVA; MERCES; BOF BUFON, 2020).

The three molecules compose materials considered as model building blocks for organic devices (DE OLIVEIRA et al., 2016; MELVILLE; LESSARD; BENDER, 2015). Furthermore, the study of such a well-established molecule in the electronics endorses the validation of the unconventional capacitive device used here (*r*-NM-based platform), thus allowing the exploitation of further audacious structures as dielectric layers incorporated into the ultracompact capacitors (*i.e.*, SURMOFs).

1.1.2. Surface-Supported Metal-Organic Frameworks

Typically, MOFs are hybrid and tridimensional structures composed of metal ions or clusters connected by organic linkers. Such a class of material is highly versatile, being used for different applications, *e.g.*, catalysis (YANG; GATES, 2019), drug delivery (LAWSON; WALTON; CHAN, 2021), gas storage (XUE et al., 2018), and water splitting (ZHANG et al., 2021), among others (ALBANO et al., 2020; CHU et al., 2021). In addition, a specific application can be targeted either by adjusting its porous size or through post-synthetic reactions. The step-by-step growth of these structures on functionalized substrates (SURMOFs), has opened new possibilities for their application in electronic devices (ALBANO et al., 2020; SILVA et al., 2022). Through the SURMOF approach, the thickness and homogeneity can be better accessible, ensuring effective integration into electronic devices. **Figure 3** illustrates the growth of a MOF film directly onto a surface functionalized with SAM, and the growth of a SURMOF film by the LbL-deposition technique.

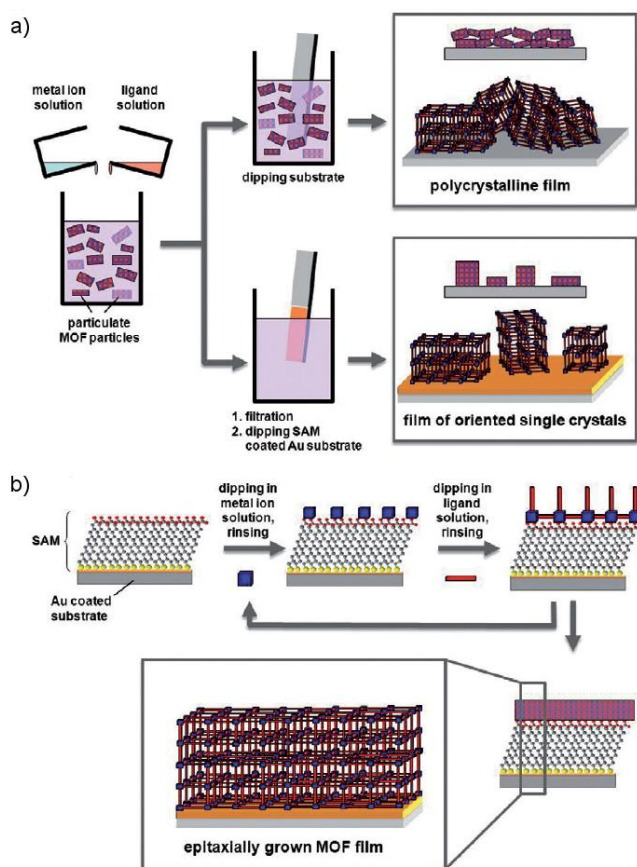


Figure 3: Representation of the growth of MOF thin films. **a)** Deposition of a MOF precipitated directly on a substrate (above) and onto a substrate functionalized with a SAM (below). **b)** Epitaxial growth of a SURMOF by LbL-deposition technique onto a substrate functionalized with a SAM. **Source:** extracted from (GLIEMANN; WÖLL, 2012).

Nevertheless, the understanding of the accumulating properties of these structures remains a challenging process owing to the low thicknesses and the intrinsic high porosity. Despite the high resistive switching at low applied voltages by only using conventional rolled-up nanomembranes (*r-NMs*), such an employed architecture does not allow the investigation of SURMOF dielectric properties because of its geometric limitations. Thus, the *r-NM*-based capacitors depict a suitable architecture to evaluate such properties (BOF BUFON et al., 2010; PETRINI et al., 2018). This architecture is based on the self-rolling of capacitors plates, where the bottom metallic plate mechanically touches the top target layer after the selective dissolution of a sacrificial layer. Examples of *r-NM*-based capacitors for

evaluating dielectric properties at molecular scales can be found in the literature, for example, Bufon *et al.* determined the dielectric constant of SAMs with different chain lengths immobilized on Al_2O_3 thin film (BOF BUFON et al., 2010). Also, recently, the dielectric constant of semiconducting molecular ensembles has been investigated (PETRINI et al., 2018).

In this sense, a detailed investigation of the dielectric properties of the SURMOF $\text{Cu}_3(\text{BTC})_2$, also known as HKUST-1 (Hong Kong University of Science and Technology) (CHUI et al., 1999), is reported in this work. The HKUST-1 is formed of copper paddlewheels as metallic nodes, connected by trimesic acid (BTC) as organic linkers. According to the literature, the surface area (BET and Langmuir), total pore volume, and density of synthesized Cu-BTC are $692.2 - 2302 \text{ m}^2/\text{g}$, $0.333 - 0.76 \text{ cm}^3/\text{g}$ and $0.495 - 1.22 \text{ g/cm}^3$, respectively (CHOWDHURY et al., 2009, 2009; CHUI et al., 1999; DATHE et al., 2005; GARCÍA-PÉREZ et al., 2009; LEE; LI; JAGIELLO, 2005; LIU et al., 2007; MIN WANG et

al., 2002; NAJAFI NOBAR, 2018; SENKOVSKA; KASKEL, 2008; VISHNYAKOV et al., 2003). A schematic of the MOF HKUST-1 composition units, structure, and LbL-grown onto a substrate is represented in **Figure 4**.

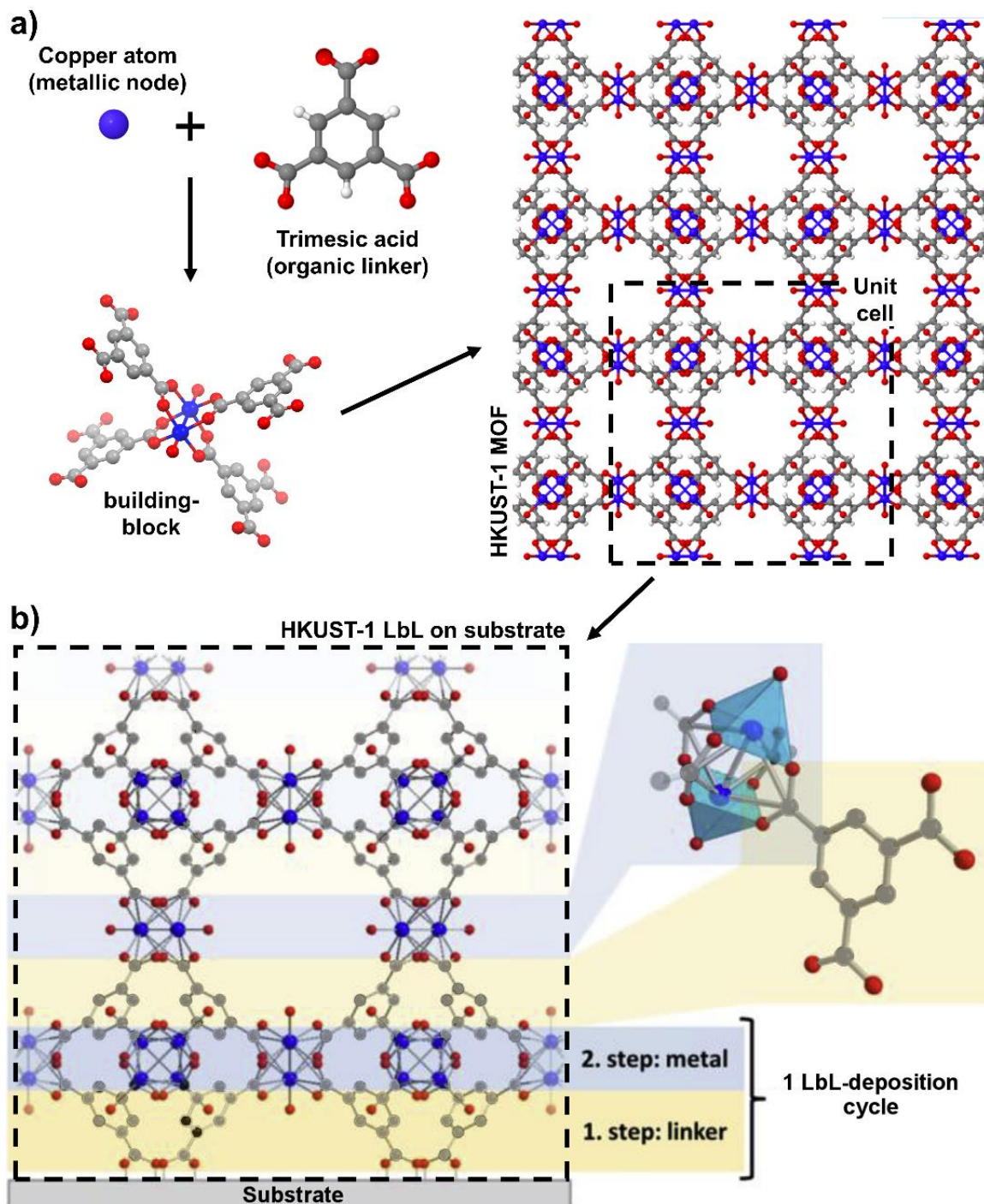


Figure 4: Schematic representation of the HKUST-1 MOF structure; **(a)** the top-left panel shows the metallic node and organic linker – copper atom and BTC, respectively – precursor components of the building-block units (bottom-left panel) for the HKUST-1 MOF structure formation. A unit cell of the crystal is evinced; **(b)** crystal structure of HKUST-1 built onto a substrate, showing the deposition steps of one LbL-deposition cycle. **Source:** adapted from (MONTAÑEZ et al., 2019).

The material is explored as ultrathin films in micro-scaled heterojunctions. The HKUST-1 SURMOF is grown onto SAM functionalized substrates of Al_2O_3 and Au, for the different architectures of the investigated devices. Parameters such as SAM chain length, temperature, humidity, crystalline orientation, and roughness of substrate also play an essential role in the SURMOF morphology (OHNSORG; BEAUDOIN; ANDERSON, 2015; SUMMERFIELD et al., 2015; VELLO et al., 2020). The films grown here are produced in ambient temperature ($\sim 20^\circ\text{C}$), ambient humidity (Relative Humidity, *i.e.*, RH from 40%-50%), onto mercaptohexadecanoic acid (MHDA) functionalized Al_2O_3 films, deposited on SiO_2 substrates, depicting a relatively cheap fabrication method, compatible with the basic electronics production. The intrinsic dielectric properties are accessed by the integration of these structures in *r-NM*-based capacitors. The SURMOF dielectric constant for different thicknesses is determined by modeling the impedance characteristics obtained in the function of frequency using electrical equivalent circuit models. The implemented rolled-up architecture also allows a self-encapsulation of SURMOF films against hazardous agents and UV irradiation. Furthermore, a substantial reduction of footprint device area up to 90% is obtained. The potential of the HKUST-1 SURMOF as ILDs is demonstrated by performing finite-element modeling (FEM) simulations and compared with traditional dielectrics widely used in the semiconductor industry (*i.e.*, SiO_2 and Al_2O_3).

1.2. NANOMEMBRANE-BASED DEVICES

One of the main challenges for the successful integration of molecular electronics is the establishment of reliable electric top contacts. Conventional approaches based on the sublimation of metal contacts may lead to the diffusion of metallic atoms into the molecular film (SANG; PEMBERTON, 2019; ZHANG et al., 2015). Considering such a scenario, different alternatives have been employed to circumvent such an issue on molecular ensembles and consequently access their electrical properties. Some proposed alternatives are based on Scanning Tunneling Microscopy (STM) for the electronic characterization of single molecules and monolayers. However, the STM has as the main limitations the complexity of sample preparation and the need for highly sophisticated instrumental tools (KAISER; GROSS; SCHULZ, 2019; KANO; TADA; MAJIMA, 2015). Other alternatives have shown interesting prospects, *e.g.*, direct metal electrode transfer, photoreduction of silver cations to metallic silver nanoparticles, and liquid metal electrodes (MAKITA et al., 2020; MARTÍN et al., 2016; YI et

al., 2019). The main limitations of these alternatives are related to incompatibility with the real device manufacturing processes, including parallelism and scalability. Furthermore, some of the mentioned methodologies do not allow low-temperature investigation, which is essential for charge transport understanding at such a molecular scale (LIU et al., 2015).

In this context, the *r*-NMs emerge as a potential tool for accessing the fundamental properties of molecular ensembles through the effective integration of such materials into different functional devices. The *r*-NM approach is based on the controlled strain of a metallic nanomembrane (NM) deposited on a sacrificial layer. By properly dissolving the sacrificial layer, the strain of the free-standing NM enables a self-winding conformation. This conformation may occur on, *e.g.*, molecular ensembles or porous-hybrid materials, performing a damage-free, reliable, and soft top contact (ALBANO et al., 2020, 2021; SERGI LOPES et al., 2020). Usually, the NM is composed of two or three different metallic layers, its release and self-confirmation are mainly caused by the elastic energy stored owing to the strain created between the layers during the deposition. Besides, the *r*-NMs technology is highly versatile, adopting several structures and configuring different functional and integrable devices, *e.g.*, (those represented in **Figure 5**, respectively) magnetic inductors (KARNAUSHENKO et al., 2018), batteries (LIU et al., 2018a), biosensors (FERRO et al., 2021; MINATOGAU FERRO et al., 2020), horizontal/vertical organic field-effect transistors (OFETs and VOFETs) (NAWAZ et al., 2020; TORIKAI et al., 2018), capacitors (PETRINI et al., 2018), among others.

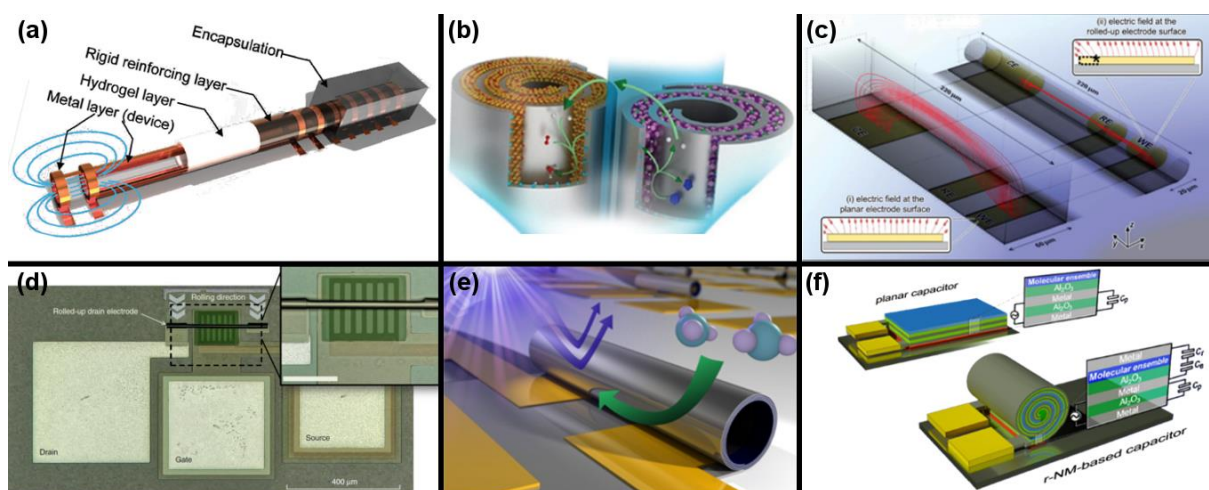


Figure 5: Representation of nanomembrane-based rolled-up functional devices as: **(a)** magnetic inductor; **(b)** battery; **(c)** biosensor; **(d)** VOFET; **(e)** OFET; **(f)** capacitors. **Source:** adapted from, respectively, (FERRO et al., 2021; KARNAUSHENKO et al., 2018; LIU et al., 2018a; MINATOGAU FERRO et al., 2020; NAWAZ et al., 2020; PETRINI et al., 2018; TORIKAI et al., 2018).

The capability of *r*-NMs in performing electrical top contacts on molecular ensembles has been further explored through the years. A capacitive structure based on the roll-up of NMs is a well-established method to explore thin films of top-layer as dielectrics (BOF BUFON et al., 2010; PETRINI et al., 2018; SHARMA et al., 2014). By using such an approach, the charge accumulation on thin films of organic semiconductors has been elucidated. Also, the elaboration of *r*-NMs to contact ultrathin (< 30nm) molecular ensembles enabled accessing the polarization in organic semiconductors into a functional capacitive NM-based device. Regardless all the benefits provided by the *r*-NM-based approach for the incorporation into devices and investigation of organic and hybrid materials, the roll-up technique still presents limitations, such as the requirement for compatibility between the material of interest and the roll-up solution. Here, water-based solutions are used for the sacrificial layer removal. Despite most materials are water-stable, some (HKUST-1, for instance) present water-instability. For what it's worth, here we found an alternative solution for the specific case of the incorporation of the HKUST-1 SURMOF into the structure without damaging the material (the details of this parameterization are presented later in this manuscript). The schematics and equivalent circuit of the *r*-NM-based capacitor are shown in **Figure 5(f)**. In addition, the capacitive *r*-NMs have been shown as a platform suitable for molecular ensembles and hybrid materials characterized as dielectrics.

1.3. MOTIVATION AND OBJECTIVES

The main goal of the investigation of *MBTF* dielectric properties incorporated into devices is the application of new materials, with exciting properties, in electronics. While the deposition of films of SURMOFs onto solid substrates is widely explored, their incorporation into functional electronic devices as thin films, in general, still lacks exploitation.

The objective of this project is, firstly, to establish the *r*-NM-based capacitors as a reliable platform for the dielectric investigation of *MBTF*, by the evaluation of well-explored molecular ensembles of CuPc, CoPc, and F₁₆CuPc. The study of thin films of such molecules allows the determination of their dielectric permittivity and relaxation into functional devices. Then, the HKUST-1 SURMOF can be incorporated into the capacitor structures as ultrathin films of dielectric layers. The HKUST-1 films grown by the quasi-epitaxial growth method (LbL-deposition), are to be submitted to impedance spectroscopies (IE), allowing the

exploitation of their behavior as dielectrics. The polarization of SURMOF dielectric films is to be investigated in several atmospheres, for the HKUST-1 behavior can be studied under different guest-molecule conditions. Among the motivations for this work are the promising prospects that SURMOFs offer for new electronics and the lack of experimental reports regarding their dielectric properties from electronic devices at the nanometric-thick scale, mainly due to the high intrinsic porosity of the MOF.

The results of the dielectric properties for HKUST-1 SURMOF are to be used in simulations, with thin layers of the material modeled as ILD for comparison with other oxide materials performing the same role.

CHAPTER II: THEORETICAL BACKGROUND

2.1. ORIGINS OF POLARIZATION IN MATERIALS

The effect of polarization on materials can be described as the separation of opposing charges relative to a common center. Overall neutral particle, polarized by an electric field, will become a dipole consisting of two charges equal in magnitude but opposite in polarity, $+q_d$ and $-q_d$, separated by a small directional distance δ . Such charge separation forms an electric dipole moment $\langle \mathbf{p} \rangle$ (KAO, 2004) – Note that in the referenced book, the electric dipole moment is denominated $\mathbf{u}$.

$$\langle \mathbf{p} \rangle = \langle q_d \cdot \delta \rangle \quad (1)$$

In this Chapter, bold emphasis is used for indicates vectorial magnitudes. The study of the polarization of materials relies on the mechanisms of dipole formation and alignment occurring in its components. It depends on the capacity of the elements in the material when exposed to an electric field, to form (or already possess) positive-negative pairs of poles, and the capability to rearrange/orient these poles. Some materials contain an intrinsic dipole in their composition, prevenient of the bond character, and arrangement of its components. This feature yields the material an additional contribution to the overall polarization capacity, but the total mechanisms of dipole formation go beyond that, and practically all matter presents at least one of the dipole formation phenomena, given certain conditions.

The polarization mechanisms are modeled on the study of materials as dielectrics, and their investigation provides information to predict their behavior in electric systems, essential for its incorporation in new electronic technologies.

In **Figure 6**, a general representation of the polarization mechanisms and their usual time responses is demonstrated.

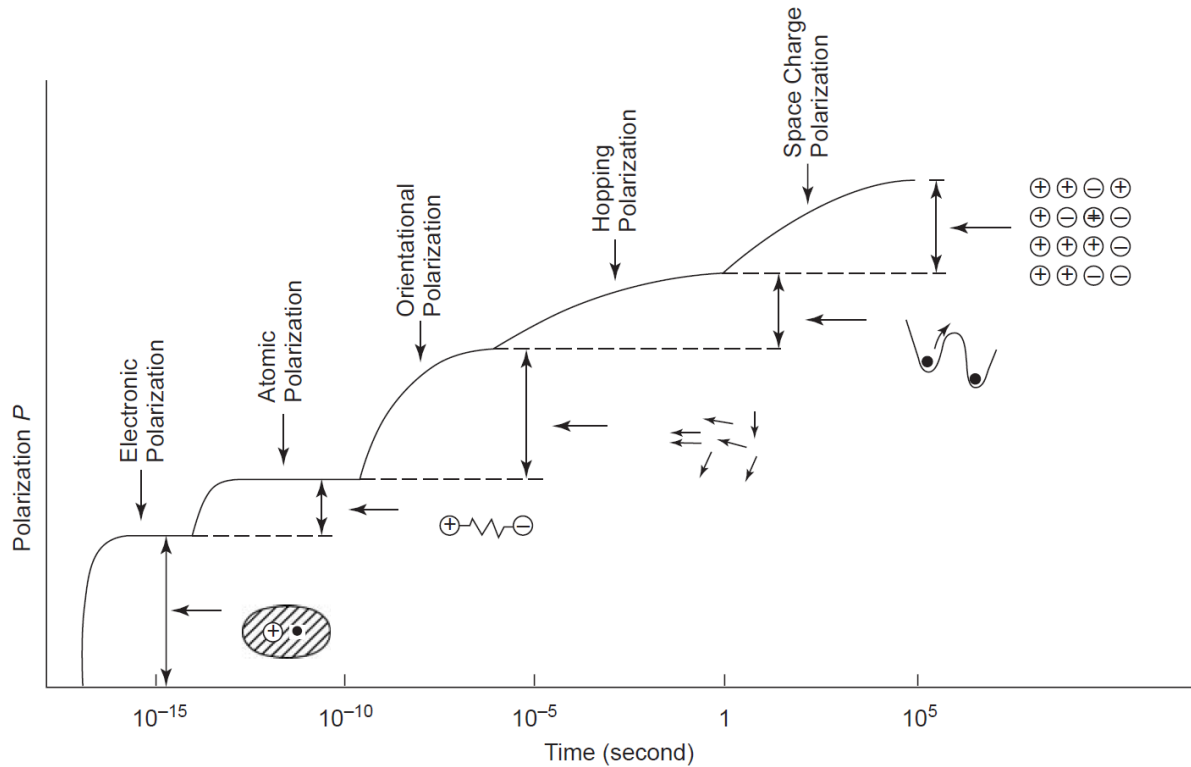


Figure 6: The variation of different types of polarization with time under a step-function electric field E .
Source: extracted from (KAO, 2004).

To sum up, electronic polarization is always present in atoms or molecules in all kinds of materials. Ionic polarization is present only in materials made of two or more different kinds of atoms that form ions due to the sharing of the valence electrons of one or more atoms with the others. For both electronic and ionic polarizations, the dipole moments are induced by electric fields, so they are classified as induced dipole moments. In short, both electronic and ionic polarizations are due to the translation (or deformation) of the valence electron clouds from their original thermal equilibrium state to a new equilibrium state. Such mechanisms of polarization are intramolecular phenomena, and therefore, slightly dependent on temperature. However, orientational polarization occurs only in the materials composed of molecules with an asymmetrical structure in which the centroid of the negative charge (mainly electrons) and that of the positive charge (mainly nuclei) are not coincident, so they possess permanent dipole moments in the absence of external fields. The formalism in this Section is mostly adapted from (BARSOUKOV, 2018; KAO, 2004).

2.2. DIELECTRIC PROPERTIES OF MATERIALS

Some figures of merit mostly describe the dielectric properties of materials. Some of them can be commonly found as: (i) relative permittivity (ϵ_r); (ii) loss tangent ($\tan \delta$); (iii) breakdown field. First parameters (i) and (ii) refer to how the material dipoles follow the electric fields applied, at frequency-dependence, giving the conditions of which mechanisms are contributing and when each one stops contributing to the total polarization. The third parameter (iii) is related to the intensity of the electric field applied at which the other dielectric parameters of the material become invalid, describing the maximum value before the material stops behaving as a dielectric.

2.2.1. Capacitance and Polarization for Dielectrics

By placing a slab of insulator material between two parallel plates of conductors connected to opposing potentials, the charges in the conductor plates increases. The additional charge arises from the induced polarization of the insulator material between the plates. The principle of charge induced in two parallel conductor plates submitted to different potentials, is the definition of electric capacitance of the system described. The consequent relation between alternated (sinusoidal) potential and current response are defined in the equations below:

$$C = \frac{Q}{V} \quad \Rightarrow \quad dQ = C \cdot dV \quad (2) \quad \frac{dQ}{dt} = I \quad \Rightarrow \quad I_C = C \cdot \frac{dV}{dt} \quad (3)$$

$$I_C = C \cdot \frac{d[V_{max} \cdot \sin(\omega \cdot t)]}{dt} = \omega \cdot C \cdot V_{max} \cdot \cos(\omega \cdot t) \quad (4)$$

The extra charge induced by the polarization of a dielectric placed between the plates is considered in the total capacitance calculated by the multiplication of a factor and the capacitance in the plates without the dielectric. This factor is related to the polarization of the dielectric material, defined by relative permittivity (ϵ_r), giving $C = \epsilon_r \cdot C_0$, where $C_0 = \epsilon_0 \cdot A/d$ and are related to the capacitance in the vacuum. The electric displacement field vector (electric flux density vector $\mathbf{D}$) is defined as the combined vector of the electric field applied ($\mathbf{E}$) and the field resulting from the polarization of the material ($\mathbf{P}$).

$$\mathbf{D} = \epsilon_0 \cdot \mathbf{E} + \mathbf{P} \quad (5)$$

This brings us to the interpretation that, when submitted to an electric field, the material induces free charges in the metal plates ($\mathbf{D}_0 = \epsilon_0 \cdot \mathbf{E}$) which are there even in the vacuum between the electrodes, and the polarization of the dielectric material during the time of field

applied, induces bound charges in the electrodes, which are related to the image-charges induced in the conductive plates to balance the interfacial dipolar charges in the dielectric (with a total dipole vector $\mathbf{P}$, also given as σ_b or density of bounded charges). The bound charges are related and proportional to the bulk-polarized dipoles $\mathbf{p}$ in Equation 1, as described in Equation 6:

$$\mathbf{P} = \sigma_b = n \cdot \langle \mathbf{p} \rangle = n \cdot q_d \cdot \delta = n \cdot \alpha \cdot \mathbf{E}_{loc} \quad (6)$$

for a dielectric material with dipole formation, where n is the volumetric density of atoms (or molecules) per unit volume of the material, $\mathbf{p}$ is an individual dipole moment in the material, δ is the distance between the polarized charges, α is the polarizability of the material, and $\mathbf{E}_{loc}$ is the local electric field. The polarization magnitude is given by surface charge density unit $P = q/A = \sigma_s$, in the units of $[C/m^2]$. Therefore, the polarization is proportional to a parameter related to the material only (n, α), and a parameter related to the material when an external electric field is applied ($\mathbf{E}_{loc}$). We can generalize such relation as $\mathbf{P} = n \cdot \alpha \cdot \mathbf{E}_{loc} = \chi \cdot \epsilon_0 \cdot \mathbf{E}$, where $\mathbf{P}$ is a direct relationship between the electric susceptibility χ (characteristic of each dielectric material), which is a dimensionless parameter, proportional to the permittivity of the material related to the permittivity in the vacuum (ϵ_0), and the externally applied field $\mathbf{E}$. Thus,

$$\mathbf{P} = \chi \cdot \epsilon_0 \cdot \mathbf{E} \quad \Rightarrow \quad \mathbf{D} = \epsilon_0 \cdot \mathbf{E} + \chi \cdot \epsilon_0 \cdot \mathbf{E} = \epsilon_0 \cdot (\chi + 1) \cdot \mathbf{E} \quad (7)$$

$$\mathbf{D} = \epsilon_0 \cdot \epsilon'_r \cdot \mathbf{E} = \epsilon \cdot \mathbf{E} \quad D = \sigma_s [C/m^2] \quad (8)$$

where ϵ_0 is the permittivity of the vacuum and χ is the electric susceptibility of the dielectric, relating to the proportional amount of electric field induced by the material referent to the amount of electric field in the vacuum, and ϵ'_r is the real part of the relative permittivity in the material. The $\mathbf{D}$ is the electric displacement, also given as charge surface density or electric flux density. Therefore, assuming $\mathbf{P}$ and $\mathbf{E}$ aligned in the same direction, the real part of the permittivity in the material (ϵ') is related as:

$$\mathbf{D} = \epsilon' \cdot \mathbf{E} = \epsilon_0 \cdot \mathbf{E} + \mathbf{P} \quad \Rightarrow \quad \epsilon' \cdot E = \epsilon_0 \cdot E + P \quad (9)$$

$$\epsilon' = \epsilon_0 + \frac{P}{E} \quad \Rightarrow \quad \frac{\epsilon'}{\epsilon_0} = 1 + \frac{P}{\epsilon_0 \cdot E} \quad (10)$$

$$\epsilon'_r = \frac{P}{\epsilon_0 \cdot E} + 1 = \frac{n \cdot \alpha}{\epsilon_0} + 1 \quad \alpha = \frac{\chi \cdot \epsilon_0}{n} \quad (11)$$

The parameter ϵ'_r measures the proportional permittivity of the material (ϵ') referent to the permittivity of the vacuum (ϵ_0). The formalism in this Section is adapted from (BARSOUKOV, 2018; KAO, 2004).

2.2.2. Permittivity in Dielectrics

To understand the frequency response of these polarization mechanisms, we approach the problem with a microscopic theory of polarization and understand how the polarizability of particles in a certain effective field relates to measurable parameters such as ϵ_r^* : The polarization induced at some point in our dielectric material is proportional to the local electric field, as described in Equation 6. We must calculate the local electric field at some point when this will include the polarization of the surrounding material. One may consider a sphere (radius r) around the point where we must calculate the polarization. Considering a spherical symmetry, an electric field in the direction r is produced at the center of the sphere by a small surface area of sphere δA with polarization P (along z):

$$\delta E_r = \frac{P \cdot \cos \theta}{4 \cdot \pi \cdot \epsilon_0 \cdot r^2} \cdot \delta A \quad (12)$$

$$E_S = \iint_S \delta E_r \cdot \cos \theta \Rightarrow E_S = \frac{P}{3 \cdot \epsilon_0} \quad (13)$$

The total electric field at some point within the material is the sum of this contribution from the surrounding polarization and the applied electric field E .

$$E_{loc} = E + \frac{P}{3 \cdot \epsilon_0} \quad (14)$$

By combining this result with Equations 6 and 11 we obtain the Clausius-Mossotti relation:

$$\frac{\epsilon_r' - 1}{\epsilon_r' + 2} = \frac{n \cdot \alpha}{3 \cdot \epsilon_0} \quad \frac{\epsilon_r' - 1}{\epsilon_r' + 2} = \frac{\rho N_A \cdot \alpha}{M \cdot 3 \cdot \epsilon_0} \quad (15)$$

The term α in the Clausius-Mossotti relation represents the overall polarization of a material relating to the effective local field. The analogous relation (right) substitutes the number of atoms or molecules per unit of volume n for the parameters ρ and M , respectively the density and molecular weight of the material, and the Avogadro constant $N_A = 6.023 \times 10^{23}$. This relation describes how a macroscopic (measurable) quantity ϵ_r' is obtained from the local microscopic responses for material, by its polarizability α .

Debye (and Onsager, later) used a statistical method to solve only part of the polarization problem by considering the whole dielectric medium as a continuum where there is no correlation between molecules (molecular interactions) in deformational (or induced) polarization and in orientational polarization. Statistical-mechanical approaches to the

polarization problem, considering the interaction between nearest dipoles, were first used by Kirkwood and, later, by Frohlich. Frohlich developed a more rigorous expression, considering the correlation between molecules in both orientational and deformational polarizations employing a statistical–mechanical approach. The general Frohlich formalism is given by Equation 16:

$$\frac{(\varepsilon_S - \varepsilon_\infty) \cdot (2 \cdot \varepsilon_S + \varepsilon_\infty)}{\varepsilon_S \cdot (\varepsilon_\infty + 2)^2} = \frac{N_V \cdot g \cdot p^2}{9 \cdot \varepsilon_0 \cdot k_B \cdot T} \quad (16)$$

where N_V is the number of dipoles within the spherical region of volume V , g is a measure of the local ordering in the material (the correlation factor), p is the dipole moment of an individual molecule, ε_S is the relative dielectric constant in a very low electric field variation (approximately static), and ε_∞ is the relative dielectric constant in the infinite. In the model of Frohlich, both the short-range interaction between molecules and the deformational polarization is considered. Frohlich also considered a spherical region within an infinite, homogeneous dielectric continuum of static dielectric constant ε_S . This region contains dipoles whose behavior is governed by statistical–mechanical laws. Frohlich also treated the internal and reaction fields in a macroscopic manner, which is more realistic than the Onsager model.

2.2.3. Dielectric Relaxation in Materials

When an electric field E is applied to an insulating material, the resulting polarization P may be divided into two parts according to the time constant of the response: (i) a high-frequency almost instantaneously polarization response, mostly assigned to electronic and ionic polarization $P_\infty = P_e + P_i = (\varepsilon_\infty - 1) \cdot \varepsilon_0 \cdot E$ denominating relative dielectric constant in the infinite ε_∞ ; (ii) a time-dependent polarization P'_t , from the orientation of dipoles in the electric field that, when the time is infinite (or long enough to the saturation), originates a static dielectric constant ε_S . From Equation 11, both are assigned in Equations 18 and 19.

$$P_{t \rightarrow \infty} = P_\infty + P_S = (\varepsilon_\infty - 1) \cdot \varepsilon_0 \cdot E + (\varepsilon_S - 1) \cdot \varepsilon_0 \cdot E \quad (17)$$

$$\varepsilon_\infty - 1 = \frac{P_\infty}{E \cdot \varepsilon_0} \quad (18)$$

$$\varepsilon_S - 1 = \frac{P_S}{E \cdot \varepsilon_0} \quad (19)$$

and so, when considering a system with a single-relaxation time τ (first-order kinetics),

$$\frac{dP_{(t)}}{dt} = \frac{-P_{(t)}}{\tau} \quad (20)$$

$$P_{(t)} = (\varepsilon_S - \varepsilon_\infty) \cdot \varepsilon_0 \cdot E \cdot e^{\frac{-t}{\tau}} \quad (21)$$

Applying a step voltage u :

$$P_{(t)} = (\varepsilon_S - \varepsilon_\infty) \cdot \varepsilon_0 \cdot E \cdot \left(1 - e^{\frac{-t}{\tau}}\right) \quad (22)$$

$$dP_{(t-u)} = (\varepsilon_S - \varepsilon_\infty) \cdot \varepsilon_0 \cdot \left(1 - e^{\frac{t-u}{\tau}}\right) \cdot dE_{(u)} \quad (23)$$

$$dP_{(t-u)} = dP_{\infty(t-u)} + dP_{S(t-u)} \quad (24)$$

$$dP_{(t-u)} = (\varepsilon_\infty - 1) \cdot \varepsilon_0 \cdot dE_{(u)} + (\varepsilon_S - \varepsilon_\infty) \cdot \left(1 - e^{\frac{t-u}{\tau}}\right) \cdot \varepsilon_0 \cdot dE_{(u)} \quad (25)$$

$$P = (\varepsilon_\infty - 1) \cdot \varepsilon_0 \cdot E_{(t)} + (\varepsilon_S - \varepsilon_\infty) \cdot \varepsilon_0 \cdot \int_0^t \frac{E_{(t)}}{\tau} \cdot e^{\frac{t-u}{\tau}} \cdot du \quad (26)$$

We can simplify this approach by using Equation (27):

$$P_S = P_\infty + P'_{(t=\infty)} \quad (27)$$

Applying a step voltage $u_{0(t)}$, where the initial ($t = 0$) polarization is due only to “instant responsive” mechanisms (P_∞), and applying the Laplace transforms on both sides of the Equation (27):

$$\mathbf{P} = \mathbf{P}_\infty \cdot u_{0(t)} + \mathbf{P}'_{(t)} \quad \Rightarrow \quad \mathcal{L}\{\mathbf{P}\} = \mathcal{L}\{\mathbf{P}_\infty \cdot u_{0(t)} + \mathbf{P}'_{(t)}\} \quad (28)$$

$$\mathcal{L}\{\mathbf{P}\} = \frac{\mathbf{P}_\infty}{(p + \omega_0)} + \frac{\omega_0 \cdot \mathbf{P}_S}{p \cdot (p + \omega_0)} \quad (29)$$

where $\omega_0 = \tau^{-1}$. Therefore, the displace current is given by:

$$\mathbf{i} = \frac{d\mathbf{D}}{dt} = \frac{d(\varepsilon_0 \cdot \mathbf{E} + \mathbf{P})}{dt} \quad (30)$$

$$\mathcal{L}\{\mathbf{i}\} = p \cdot \mathcal{L}\{\mathbf{P}\} - \mathbf{P}_{(t=\infty)} \quad \Rightarrow \quad \mathcal{L}\{\mathbf{i}\} = \mathbf{P}_\infty + \frac{\omega_0 \cdot (\mathbf{P}_\infty - \mathbf{P}_S)}{(p + \omega_0)} \quad (31)$$

and therefore:

$$\mathbf{i}_{(t)} = \mathbf{P}_\infty \cdot \delta_{(t)} + \frac{(\mathbf{P}_S - \mathbf{P}_\infty)}{\tau} \cdot e^{\frac{-t}{\tau}} \quad (32)$$

Taking that $\mathcal{L}\{E\} = 1/p$, we have the admittance:

$$Y = \frac{\mathcal{L}\{i\}}{\mathcal{L}\{E\}} = \varepsilon_\infty \cdot \varepsilon_0 \cdot p + (\varepsilon_\infty \cdot \varepsilon_S) \cdot \varepsilon_0 \cdot \frac{\omega_0 \cdot p}{p + \omega_0} \quad (33)$$

$$\varepsilon^* = \frac{Y}{j \cdot \omega \cdot \varepsilon_0} \Rightarrow \varepsilon^* = \left[\varepsilon_\infty + \frac{(\varepsilon_S - \varepsilon_\infty)}{1 + \omega^2 \cdot \tau^2} \right] - j \cdot \left[\frac{\omega \cdot \tau \cdot (\varepsilon_S - \varepsilon_\infty)}{1 + \omega^2 \cdot \tau^2} \right] \quad (34)$$

The real and imaginary parts of Equation 34 are the Debye relaxation relations, which have remained the basic model of dielectric relaxation since their inception (Debye, 1929). In this Section, the formalism for the complex permittivity is demonstrated as a function of the admittance, emphasizing that the real parameter measured in the impedance analyzers is the current response of the circuit, which relates directly to the admittance of the system (electric current, *i.e.*, electrons that managed to be transported through the circuit, responding the V_{AC} applied). However, as the films here are measured as dielectrics (treated as insulators), the formalism of the equations developed here are expanded using the impedance as the variable quantity for the determination of the materials parameter, so much that it is the quantity calculated and given by the equipment. The variable substitution is achieved by the complex relation between the quantities $Y^* = (Z^*)^{-1}$. The formalism in this Section is adapted from (BARSOUKOV, 2018; KAO, 2004).

2.2.4. Dielectric Breakdown

The dielectric breakdown in insulators is quantifiable in values of dielectric strength or breakdown strength, which is the electric field value along the length of the material that causes its dielectric to break down. There are two non-catastrophic breakdown mechanisms associated with insulators/semiconductors which might therefore be applicable: (i) Zener breakdown and (ii) avalanche breakdown.

Typically, an electron in the valence band lacks the energy to enter the conduction band. However, as in the Zener breakdown, a strong electric field causes the energy bands bend with distance and an electron can hop from the valence to conduction band by changing its position (see **Figure 7**). In even larger electric fields an electron, once in the conduction band, may acquire very large amounts of kinetic energy in between collisions. It may be that when it does experience a collision, sufficient energy can be given to a valence-band electron to promote it into the conduction band. The original electron loses some kinetic energy but stays in the conduction band. There are now two electrons (and two holes) which can then generate more, producing an “avalanche” effect.

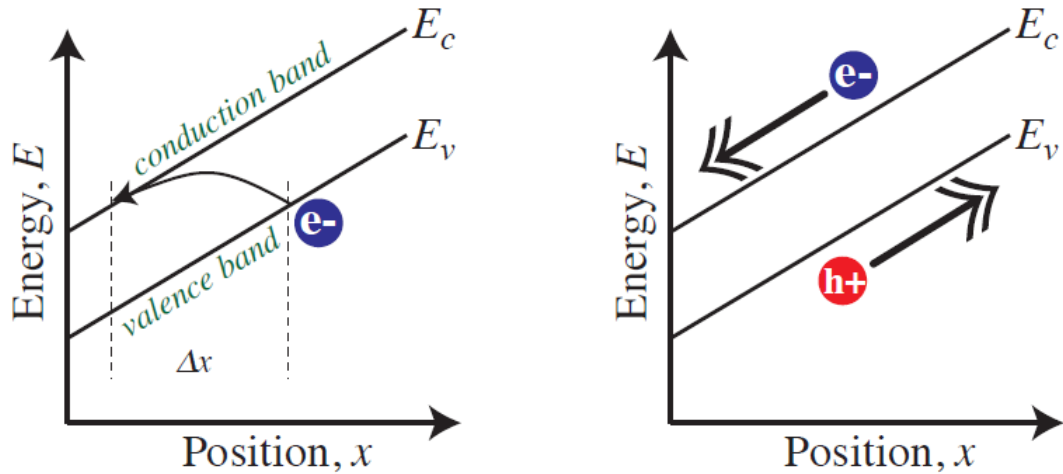


Figure 7: Zener breakdown (left panel) and collision, or avalanche, breakdown (right panel).
Source: (MORTON, [s.d.]).

Breakdown in insulators is usually classified under the following five headings: (i) collision breakdown, (ii) thermal breakdown, (iii) gas-discharge breakdown, (iv) electrolytic breakdown, and (v) dipole breakdown. Those are described below.

2.2.4.1. Collision breakdown

In the collision breakdown, a similar mechanism as the avalanche breakdown occurs. Although the concentration of electrons in the conduction band of insulators is relatively low ($\sim 10^6 \text{ m}^{-3}$), at high fields these few electrons acquire large amounts of kinetic energy and through collisions, multiply the number of free electrons.

2.2.4.2. Thermal breakdown

Thermal breakdown can occur in DC conditions, where any conduction that starts to take place, ohmic heating will result and, in insulators and semiconductors, higher temperature results in more free carriers and a higher conductivity which can cause more conduction, more heating (even melting) as breakdown ensues. Also, the thermal breakdown can occur under AC conditions, where any loss (lag) mechanism dissipates energy and hence heats the material, leading to breakdown as above.

2.2.4.3. Gas-discharge breakdown

Common lightning is an obvious example of gas-discharge breakdown, though it may also be the dominant mechanism in a solid if the insulator is porous, containing occluded gas bubbles (*e.g.*, interlayer air in some micas). The field experienced by the gas is higher than that in the solid because of the continuity condition on the electric displacement field. Because ϵ_r' of the solid is likely to be significantly greater than ϵ_r' of the gas, a larger electric field E will be present within the gas region. Thus, even if the breakdown strength is higher for the gas, it is likely that the solid will fail at a lower applied field, because of the amplifying effect of its relative permittivity.

2.2.4.4. Electrolytic breakdown

The term “electrolytic breakdown” is used for a breakdown caused by structural imperfections such as dislocation arrays, grain boundaries, and other defects, which produce electrically weaker or conducting paths in the material through which current may pass.

2.2.4.5. Dipole breakdown

Dipole breakdown is related to but distinct from the above mechanism, where structural imperfections stress the dipoles produced when the material becomes highly polarized in such a way as to make them more easily ionized. This increases the concentration of free carriers providing semiconducting paths with significantly lower electrical resistivity.

2.2.4.6. Breakdown mechanisms overview

In actual material, all these mechanisms may be active to some extent. Thermal and collision breakdowns are certainly “the last straw”, giving catastrophic breakdowns in many cases. Zener breakdown and avalanche breakdown mentioned before are two non-catastrophic breakdown mechanisms, associated with semiconductors.

This whole Section regarding dielectric breakdown was adapted from the college material (MORTON, [s.d.]).

2.2.5. Complex Permittivity: Dielectric Constant and Loss Factor

When a time-varying electric field is applied across a parallel-plate capacitor with the plate area of one unit and separation of d between the plates, the total current is given by:

$$J_T = J_C + A \cdot \frac{dD}{dt} = J_C + \varepsilon^* \cdot \frac{dE}{dt} \quad (35)$$

where J_C is the conduction current and ε^* is defined as the complex permittivity, which is introduced to allow for dielectric losses due to the friction accompanying polarization and orientation of electric dipoles. This may be written as:

$$\varepsilon^* = \varepsilon' - j \cdot \varepsilon'' = (\varepsilon'_r - j \cdot \varepsilon''_r) \cdot \varepsilon_0 \quad (36)$$

in which ε'_r is the dielectric constant and ε''_r the loss factor. **Figure 8** illustrates dielectric loss mechanisms prevailing in different types of organic/hybrid material.

Each polarization mechanism in the material has its restriction on the time-response from the variation rate of the field. When the limit frequency response of a mechanism is achieved, a peak in the dielectric loss is observed (denominated absorption or dispersion, depending on the activated mechanisms). The frequency with the

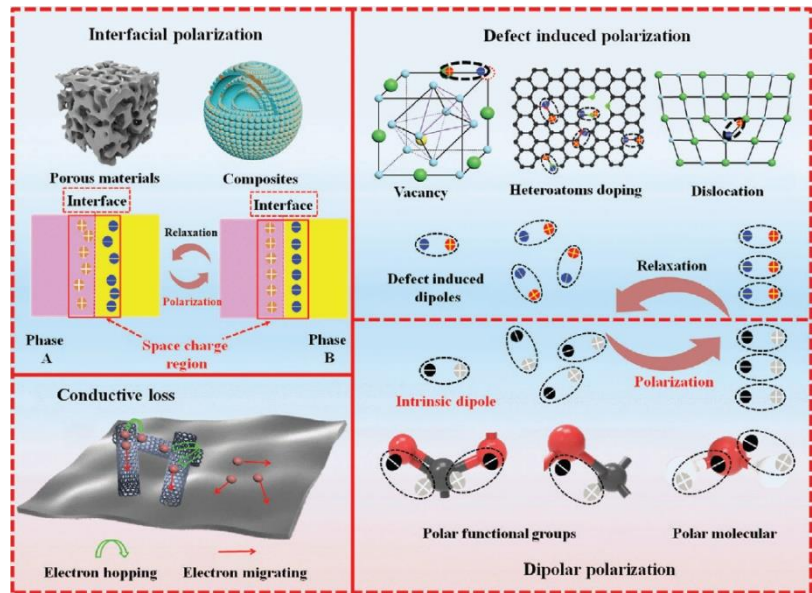


Figure 8: Schematic illustrations of dielectric loss mechanisms.

Source: adapted from (QIN; ZHANG; WU, 2022).

dielectric loss peaks occur is denominated here as ω_0 . **Figure 9** shows the characteristic relative permittivity response to an E frequency range in a material. Such a response is direct related to the polarization mechanisms shown in **Figure 6**.

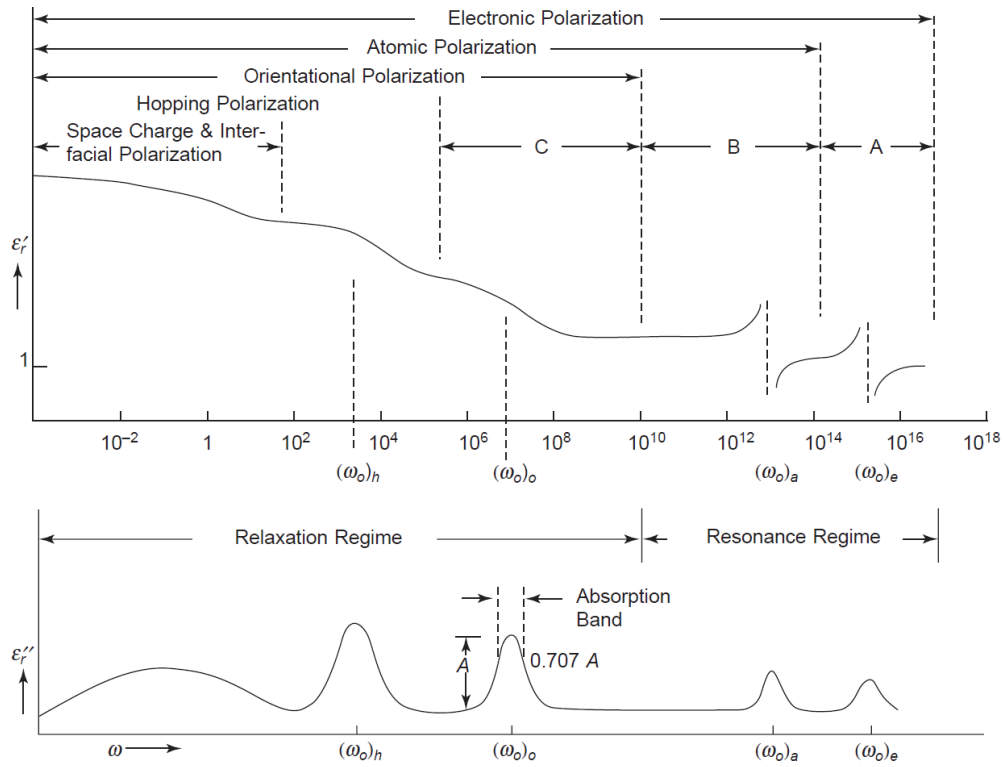


Figure 9: The complex components of relative permittivity – dielectric constant in the top panel and respective loss factor at the bottom panel – as functions of frequency. **Source:** adapted from (KAO, 2004).

In **Figure 9**, the region “A” polarization relates completely to electronic polarization. In region “B”, it is due to the combination of electronic and atomic polarization, and so on. The ω_0 with indexes e , a , o , and h correspond to the resonance/relaxation frequencies from electronic, atomic, orientational, and Hopping polarization, respectively. The frequency spectra of ε'_r and ε''_r are self-explanatory (KAO, 2004).

An arbitrary time-varying field can be resolved into sinusoidal AC fields of a spectrum of frequencies employing the Fourier transformation. For simplicity, we consider the applied field to be monochromatic and a sinusoidal function of angular frequency ω , and by substituting the permittivity and applied electric field in Equation 16, we have:

$$E = E_{max} \cdot e^{j(\omega \cdot t + \varphi_E)} \quad (37)$$

$$J_T = \sigma \cdot E + j \cdot \omega \cdot (\varepsilon' - j \cdot \varepsilon'') \cdot E = [(\sigma + \omega \cdot \varepsilon'') \cdot E] + j \cdot [\omega \cdot \varepsilon' \cdot E] \quad (38)$$

where σ is the electrical conductivity of the material. The formalism in this Section is adapted from (BARSOUKOV, 2018).

2.3. IMPEDANCE SPECTROSCOPY

Impedance spectroscopy analysis is a technique of electric characterization of samples that measures the resistance that interrupts the current flow (I_{AC}) when an AC voltage (V_{AC}) is applied to a circuit. These interruptions are represented by various circuit elements, such as resistors, inductors, and conductors, which constitute the overall impedance in an electric system. Applying relatively small magnitudes of sinusoidal potentials to an impeditive circuit, Ohm's Law is valid, allowing the approximate relation of the input signal to the output current at a steady-state angular frequency ($\omega = 2\pi \cdot f = 1/T$ [rad/s]) dependency, according illustrated in **Figure 10**:

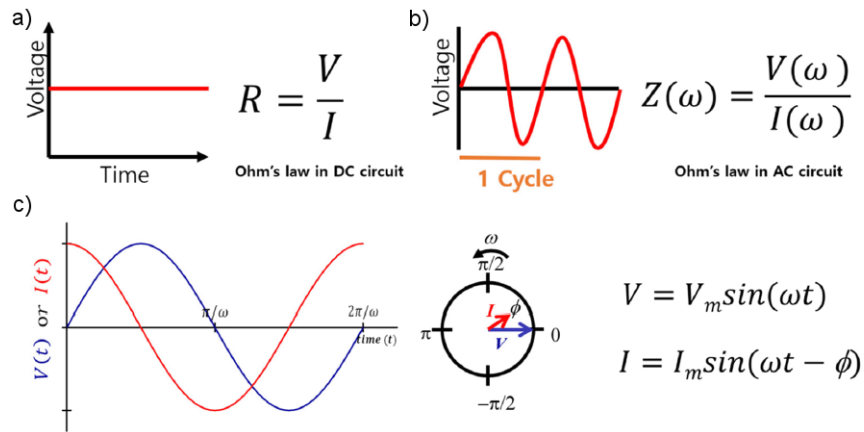


Figure 10: Diagram representing potential signals applied and respective equations of Ohm's Law, for (a) DC voltage (V_{DC}), in a direct current circuit and (b) AC voltage (V_{AC}) on a sinusoidal wave shape. (c) Representation of current response to a V_{AC} applied with an angular frequency ω . **Source:** adapted from (CHOI et al., 2020).

The most common parameters and relations used in impedance spectroscopy analysis are expressed in **Table 1**, considering all the system measured (submitted to a voltage) a single impedance element. The relationship between I_{AC} and V_{AC} is associated with several properties of the single impedance measured and related below. In the **Table 1** below, note that in a general system, $R \neq 1/G$ and $X \neq 1/B$. Also, remember that the simplification of the circuit element terms in **Table 1** is valid for a circuit element of a single impedance, submitted to the applied AC potential.

The formalism in this Section is adapted from (STALLINGA, 2009).

Table 1: Impedance spectroscopy parameters and their relation. Adapted from (STALLINGA, 2009):

Parameter	Relation	Name	Unit (SI)
Y^*	$Y^* = G + i.B$	Admittance	S
Z^*	$Z^* = R + i.X$ $Z^* = (Y^*)^{-1}$	Impedance	Ω
G or Y'	$G = Y' = Re(Y^*)$	Conductance	S
B or Y''	$B = Y'' = Im(Y^*)$	Susceptance	S
R or Z'	$R = Z' = Re(Z^*)$	Resistance	Ω
X or Z''	$X = Z'' = Im(Z^*)$	Reactance	Ω
C for a single Z element	$Y_C^* = i.\omega.C \Rightarrow C = Y_C''/\omega$	Capacitance	F
	$Z_C^* = -i.[1/(\omega.C)] \Rightarrow C = -1/(\omega.Z_C'')$		
	$C = Q/V = dQ/dV$	Static (DC) and dynamic (AC) capacitance, resp.	
L for a single Z element	$Y_L^* = -i.[1/(\omega.L)] \Rightarrow L = -1/(\omega.Y_L'')$	Inductance	H
	$Z_L^* = i.\omega.L \Rightarrow L = Z_L''/\omega$		
$\tan \delta$	$\tan \delta = 1/(\omega.R.C)$	Loss-tangent	-
σ	$\sigma = (t/A).G$	Conductivity*	S.m ⁻¹
ρ	$\rho = (A/t).R$	Resistivity*	$\Omega.m$
ε	$\varepsilon^* = (t/A).C^*$	Permittivity*	F.m ⁻¹
ε_r'	$\varepsilon_r' = \frac{\varepsilon'}{\varepsilon_0}$	Relative permittivity	-
	$\varepsilon_r' = \kappa$	Dielectric constant	
χ	$\chi = 1 - \varepsilon_r$	Susceptibility	-
M	$M = \varepsilon^{-1} = j.\omega.Z.\frac{\varepsilon_0.A}{t}$	Modulus function*	m.F ⁻¹
Q	$Q = \left \frac{X}{R}\right = \left \frac{B}{G}\right $	Quality factor	-
D	$D = \left \frac{R}{X}\right = \left \frac{G}{B}\right $	Dissipation factor	-
τ	$\tau = \frac{X}{[\omega.R]}$	Time constant	s

* In the equations, A is the area of the device, and t is its thickness.

2.3.1. Impedance Principles

Considering a two-terminal circuit with a network N (composed of linear, time-invariant passive circuit elements), where N is driven by a current generator, a generalized sinusoidal input current source $i_{(t)}$, with angular frequency ω :

$$i_{(t)} = I_{max} \cdot \cos(\omega \cdot t + \varphi_I) \quad (39)$$

$$I = I_{max} \cdot e^{j \cdot (\omega \cdot t + \varphi_I)} \quad (40)$$

Note that Equation 40 is the phasor representation of Equation 39. In the sinusoidal steady-state, the voltage $v_{(t)}$ is then also sinusoidal with angular frequency ω , to which a phasor V can be associated:

$$v_{(t)} = V_{max} \cdot \cos(\omega \cdot t + \varphi_V) \quad (41)$$

$$V = V_{max} \cdot e^{j \cdot (\omega \cdot t + \varphi_V)} \quad (42)$$

Therefore, the (driving point) impedance $Z_{(\omega)}$ of a network N at frequency ω can be defined as the ratio of phasors V and I .

$$Z_{(\omega)} = \frac{V}{I} = \frac{V_{max} \cdot e^{j \cdot (\omega \cdot t + \varphi_V)}}{I_{max} \cdot e^{j \cdot (\omega \cdot t + \varphi_I)}} = \frac{V_{max}}{I_{max}} \cdot e^{j \cdot (\varphi_V - \varphi_I)} \quad (43)$$

The SI unit of impedance is the ohm (Ω). As a dual situation, consider the same network N now driven by a sinusoidal voltage source $v_{(t)}$, to which the phasor V is associated, and draw current $i_{(t)}$ having phasor I . We define the (driving point) admittance Y of network N at angular frequency ω as:

$$Y_{(\omega)} = \frac{I}{V} = \frac{I_{max} \cdot e^{j \cdot (\omega \cdot t + \varphi_I)}}{V_{max} \cdot e^{j \cdot (\omega \cdot t + \varphi_V)}} = \frac{I_{max}}{V_{max}} \cdot e^{-j \cdot (\varphi_V - \varphi_I)} \quad (44)$$

The SI unit of admittance is the siemens (S). From both the above definitions, it follows that $Z_{(\omega)} = [Y_{(\omega)}]^{-1}$, for remembering.

Because of the linearity hypothesis, the impedance (admittance) of a network N is dependent on the angular frequency ω but independent of phasor I (or V) of the source current (voltage) signal employed in the definition. The calculation rules for expressing series and parallel arrangements for impedances and admittances, follow the corresponding rules for resistance and conductance, respectively. By determining the phases difference $\varphi_V - \varphi_I = \theta$ and using the Euler's relation, we can represent the impedance in Equation 43 as:

$$Z = \frac{V_{max}}{I_{max}} \cdot e^{j \cdot \theta} \quad (45)$$

$$Z = \frac{V_{max}}{I_{max}} \cdot [\cos(\theta) + j \cdot \sin(\theta)] = Z_0 \cdot [\cos(\theta) + j \cdot \sin(\theta)] \quad (46)$$

In Equation 46, as $Z_{(\omega)}$ is a complex number, the calculation of its modulus (length of the phasor) is acquired by the product $Z \cdot \bar{Z}$, where $\bar{Z}$ is the impedance complex conjugate, Therefore,

$$Z\bar{Z} = \{Z_0 \cdot [\cos(\theta) + j \cdot \sin(\theta)]\} \cdot \{Z_0 \cdot [\cos(\theta) - j \cdot \sin(\theta)]\} \quad (47)$$

$$Z^2 = Z_0^2 \quad \Rightarrow \quad |Z| = \sqrt{Z_0^2} \quad (48)$$

$$Z = |Z| \cdot [\cos(\theta) + j \cdot \sin(\theta)] = |Z|e^{j\theta} \quad (49)$$

$$Re(Z) = Z' = |Z| \cdot \cos(\theta) \quad Im(Z) = Z'' = |Z| \cdot \sin(\theta) \quad (50)$$

We come to that $Z_0 = |Z|$. As one may notice, $Z_0 = V_{max}/I_{max}$ is always ≥ 0 , given that V_{max} and I_{max} are both positive amplitude values. Thus, we can relate the terms in the impedance phasor as:

$$|Z| = [(Z')^2 + (Z'')^2]^{1/2} \quad \theta = \arctg\left(\frac{Z'}{Z''}\right) \quad (51)$$

Such impedance phasor relations are widely used for the data treatment extracted from impedance analyzers equipment. The formalism in this Section is adapted from (BARSOUKOV, 2018; CALLEGARO, 2016).

2.3.2. Linear Response Theory

The theory of linear electrical circuits is traditionally developed with the Laplace transform (CALLEGARO, 2016). Here an alternative equivalent approach, by using Fourier transform, is presented.

Considering a two-terminal element as a signal-processing system, having current $i_{(t)}$ as its input and voltage $v_{(t)}$ as its output. Let us assume that the element is linear, so if $[i_{(t)}, v_{(t)}]$ is a possible input-output signal pair for the element, then any $[k \cdot i_{(t)}, k \cdot v_{(t)}]$ with real k is another possible couple. The equilibrium condition $[i_{(t)} \equiv 0, v_{(t)} \equiv 0]$ exists for all linear elements. The effects on output occur after the input, so $i_{(\tau)}$ affects $v_{(t)}$ only if $\tau \leq t$. Also, the input-output relationship is stable over time, so if $[i_{(t)}, v_{(t)}]$ is an input-output signal couple, $[i_{(t+T)}, v_{(t+T)}]$ for an arbitrary T is another. Therefore, the most general input-output relation can be written as:

$$v_{(t)} = \int_{\tau=-\infty}^t \zeta(t-\tau) \cdot i_{(\tau)} \cdot d\tau \quad (52)$$

Considering that $\zeta(\tau) \equiv 0$ for $\tau < 0$; or, equivalently, that $\zeta(\tau)$ must have the form $\zeta(\tau) = H(\tau) \cdot \xi(\tau)$, where $\xi(\tau)$ is a generic function and $H(\tau)$ is the Heaviside function:

$$H_{(\tau)} = \begin{cases} 1, & \tau \geq 0 \\ 0, & \tau < 0 \end{cases} \quad (53)$$

$$H_{(\tau)} = \int_{-\infty}^{\tau} \delta_{(x)} \cdot dx \quad (54)$$

Thus, Equation 52 becomes a convolution integral in the form:

$$v_{(t)} = \int_{\tau=-\infty}^t \zeta_{(t-\tau)} \cdot i_{(\tau)} \cdot d\tau = \zeta_{(t)} * i_{(t)} \quad (55)$$

Note that the Heaviside function is the integral of the Dirac delta function. The $\zeta(t)$ is denominated in the kernel of the linear relation (the impulsive response of the element), and its unit is given by $[\Omega.s]$.

Therefore, we consider:

$$v_{(t)} = \zeta_{(t)} \cdot i_{(t)} \quad \Rightarrow \quad \mathcal{F}[v_{(t)}] = \mathcal{F}[\zeta_{(t)}] \cdot \mathcal{F}[i_{(t)}] \quad \Rightarrow \quad V_{(f)} = Z_{(f)} \cdot I_{(f)} \quad (56)$$

The definition of impedance can thus be extended beyond the sinusoidal steady state, to the most general voltage and current signals. The impedance function $Z_{(f)}$ gives the relationship between the components at frequency f between signals $i_{(t)}$ and $v_{(t)}$.

From $q_{(t)} = C \cdot v_{(t)}$, the capacitance can be related as:

$$v_{(t)} = \int_{\tau=-\infty}^t \frac{1}{C} \cdot i_{(\tau)} \cdot d\tau = \int_{\tau=-\infty}^{+\infty} \frac{1}{C} \cdot H_{(t-\tau)} \cdot i_{(\tau)} \cdot d\tau \quad (57)$$

giving the relation $\zeta(t) = (1/C) \cdot H_{(\tau)}$, and so, by the Fourier transform:

$$Z_{(f)} = \mathcal{F}\left[\frac{1}{C} \cdot H_{(\tau)}\right] = \frac{1}{2 \cdot C} \cdot \delta_{(f)} - j \cdot \frac{1}{2 \cdot \pi \cdot f \cdot C} \quad (58)$$

In Equation 58, the imaginary part of $Z_{(f)}$ is the capacitive reactance.

$$\chi_{(f)} = -\frac{1}{2 \cdot \pi \cdot f \cdot C} = -\frac{1}{\omega \cdot C} \quad (59)$$

The real part of $Z_{(f)}$, in Equation 58, is related to the infinite memory of the capacitor and thus not strictly linear, since admits many solutions $v_{(t)} = K$ for $i_{(t)} \equiv 0$. It is omitted from

the general representation of an ideal capacitor, by considering that the capacitor is discharged for $t < 0$.

Similarly, the resistance and inductance are described as:

$$v_{(t)} = R \cdot i_{(t)} = \int_{\tau=-\infty}^{+\infty} R \cdot \delta_{(t-\tau)} \cdot i_{(\tau)} \cdot d\tau \Rightarrow \zeta(t) = R \cdot \delta_{(t)} \Rightarrow Z_{(f)} = R \quad (60)$$

$$v_{(t)} = L \cdot \frac{di_{(t)}}{dt} = \int_{\tau=-\infty}^{+\infty} L \cdot \delta'_{(t-\tau)} \cdot i_{(\tau)} \cdot d\tau \Rightarrow \zeta(t) = L \cdot \delta'_{(t)} \Rightarrow Z_{(f)} = i \cdot \omega \cdot L \quad (61)$$

Impedance and admittance of pure elements is a real quantity for resistors, and pure imaginary for inductors and capacitors; at the given frequency ω . The pure elements of the electrical circuits (R , C , and L) can be arranged in parallel or in series to create models for real systems, in which equivalent representations of the network (impedances and admittances) are calculated.

Formerly, all materials placed between two electrodes for impedance spectroscopy analysis can be represented in a circuit by different arrangements composed of these ideal elements (resistor, capacitor, and inductor), according to their electric response. Naturally, more complex systems (regarding the composition of the materials) require more complicated representations of these elements. For instance, the constant phase element (CPE) is an impeditive circuit element used to model inhomogeneous materials, with localized effects of charge transport/accumulation through the material (*e.g.*, metallic clusters diffused into porous materials). Another example is the Warburg element, used to fit mass transport field-responsive dynamics in mediums (widely common in electrochemical measures). Such artifices are necessary to describe the mechanisms of charge behavior for some systems. Determining the charge transport and charge accumulation mechanisms is essential to the proposition of a representative circuit model. After setting a proper model, the properties of the material can be determined and later explored in large-scale technologies. The formalism in this Section is adapted from (CALLEGARO, 2016; STALLINGA, 2009).

2.3.3. Elements for Modeling Impedance Systems

In general, the pure elements are usually used for modeling the response for material layers incorporated to electric systems, describing well enough the elements playing a role in the circuit. However, for some cases the characterization of a system by impedance

spectroscopy results in more complex responses, which requires a more elaborated assembly of the pure elements for modeling the dielectric response of the material. For such, the more commonly used elements are presented below. Those elements of the circuit are, in general, a composition of many pure elements that, when arranged in a certain way, can better describe the system. The composed equation for determining the parameters of such elements is generalized and boundary conditions are used for achieving the mathematical formula describing their circuit behavior.

A general description of the circuit elements for modeling the impedance behavior is presented in **Table 2**.

Table 2: Frequency dependences and phase shifts of some impedance pure elements. Adapted from (CHENG; HSU; YUNG-CHEN WU, 2017, p.):

Impedance element	Description	Phase angle (°)
R	$Z_R = R$	0
C	$Z_C = \frac{1}{\omega \cdot C}$	-90
L	$Z_L = \omega \cdot L$	90
CPE	$Z_{CPE} = \frac{-1}{(j \cdot \omega \cdot C)^\alpha}$	0 – -90
W (semi-finite)	$Z_W = \frac{A_W}{\sqrt{\omega}}(1 - j)$	-45

Therefore, the main goal here is to better understand the phenomena occurring in the selected materials, by impedance spectroscopy characterizations.

The formalism in this Section is adapted from (BARSOUKOV, 2018; CALLEGARO, 2016).

2.3.3.1. For Pure Elements

A resistor is an element that obeys Ohm's law, where $v_{(t)} = R \cdot i_{(t)} \Leftrightarrow i_{(t)} = G \cdot v_{(t)}$ for all t , R is the resistance, and $G = R^{-1}$ is the conductance of the element. The unit of resistance in the SI is the ohm (Ω) and the unit of conductance is the siemens (S). Resistors are perfectly

dissipative elements, so the electrical power absorbed by the element is instantaneously dissipated, following the relation: $p(t) = v(t) \cdot i(t) = R \cdot i(t)^2 = G \cdot v(t)^2 \geq 0$.

An ideal (or pure) capacitor is an element in which electrical charge $q(t)$ and voltage $v(t)$ satisfy the relation $q(t) = C \cdot v(t)$ for all t , and C is the capacitance of the element. In the SI, the unit of capacitance is the farad (F).

A (pure) inductor is an element in which magnetic flux $\Phi(t)$ and current $i(t)$ satisfy the following relation: $\Phi(t) = L \cdot i(t)$, for all t , and L is the inductance of the element. In SI, the unit of inductance is the Henry (H).

Capacitors and inductors are lossless elements: the electrical power $p(t) = v(t) \cdot i(t)$ entering a capacitor or an inductor is not dissipated, but stored as electrostatic energy in capacitors, in the form of $E(t) = q(t) \cdot v(t) = C \cdot v(t)^2 / 2 = q(t)^2 / 2 \cdot C$, or magnetic energy in inductors, in the form of $E(t) = \Phi(t) \cdot i(t) = L \cdot i(t)^2 / 2 = \Phi(t)^2 / 2 \cdot L$. The formalism in this Section is adapted from (CALLEGARO, 2016; STALLINGA, 2009).

2.3.3.2. Nernst impedance (Warburg element)

Electronic systems where a mass flow induces an electric response – such as a diffusion of elements in the components of the device – can be modeled by a component called Nernst impedance or Warburg element (with Z_N given in $\Omega \cdot s^{-1}$). Such a component is mathematically described according to Equation 62.

$$Z_N = A_W \cdot (j \cdot \omega)^{-\alpha} \quad 0 \leq \alpha \leq 1 \quad (62)$$

where A_W is a real constant value. In the original Warburg paper, $\alpha = 1/2$, (45° in the $Z'' \times Z'$ plot), for measurement of electrochemical systems. The “classical” equation describing such a model can be found below.

$$Z_W = A_W \cdot \omega^{1/2} - j \cdot A_W \cdot \omega^{1/2} \quad (63)$$

$$A_W = \frac{R \cdot T}{A \cdot n^2 \cdot F^2 \cdot \sqrt{2}} \cdot \left(\frac{1}{D_O^{1/2} \cdot C_O^b} + \frac{1}{D_R^{1/2} \cdot C_R^b} \right) \quad (64)$$

where R is the ideal gas constant, T is the temperature, F is the Faraday constant, n is the valency, D is the diffusion coefficient of species O and R subscribed (oxidized and reduced species), and C^b the concentration of the species in the bulk.

With a known diffusion length, the finite-length Warburg element (Nernst impedance) is given by:

$$Z_N = \frac{A_W}{\sqrt{j \cdot \omega}} \cdot \tanh \left(\delta \cdot \sqrt{\frac{j \cdot \omega}{D}} \right) \quad (65)$$

where δ is the thickness of the diffusion layer.

An example of the Nernst impedance response is presented in **Figure 11**.

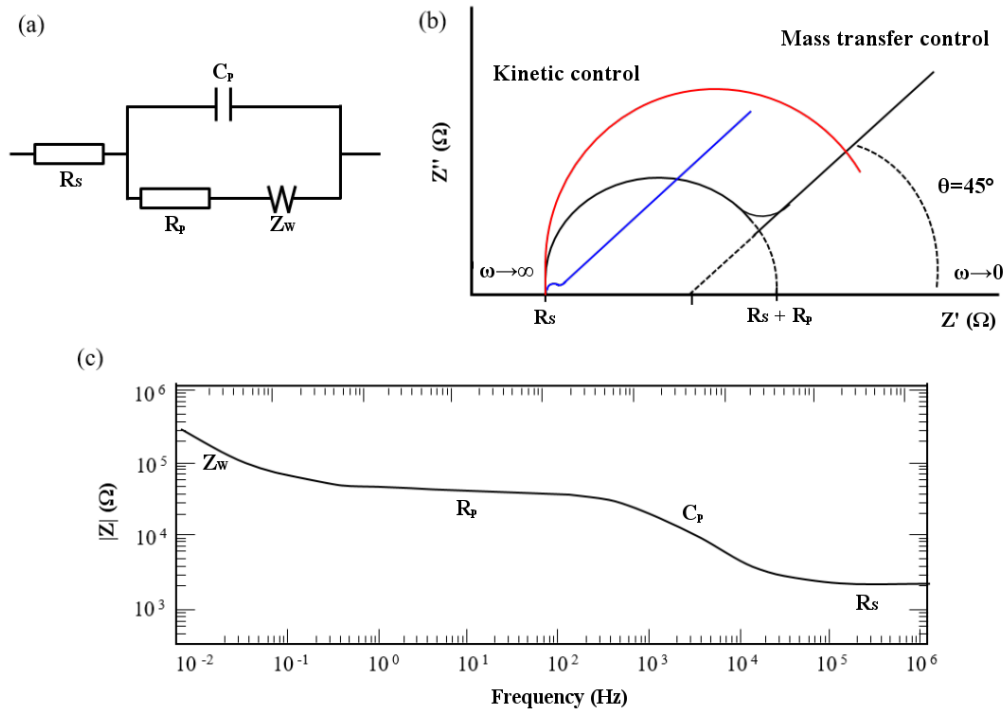


Figure 11: Electric circuit modeling and graphical representation. **(a)** The most used equivalent circuit model to analyze impedance data, namely Randles and Erschler model. **(b)** Impedance spectrums in the form of Nyquist plots for circuits from (a) depending on the rate of charge transfer at the electrode/electrolyte interface. **(c)** The circuit elements dominate at different frequencies. **Source:** adapted from (CHENG; HSU; YUNG-CHEN WU, 2017).

2.3.3.3. Constant phase element (CPE)

The CPE approach arises from the modeling of distributed microscopic properties of materials, such as defects and local charge inhomogeneities. Impedance behavior, corresponding to anomalous capacitance dispersion requiring representation by a CPE, has been examined for a specific form of irregularity or roughness (in electrochemical electrode measures), namely a surface having fractal, that is self-similar geometry on various scales, and

was treated by Mulder *et al.* (1990) and by Pajkossy (1991) (BARSOUKOV, 2018). The general equation to model such behavior is described below.

$$Z_{CPE} = \frac{-1}{(j.\omega.C)^\alpha} \quad 0 \leq \alpha \leq 1 \quad (66)$$

It is depicted by a deviation from ideal capacitance behavior, corresponding to a frequency-dependent phase-angle. The formalism in this Section is adapted from (BARSOUKOV, 2018; CALLEGARO, 2016).

CHAPTER III: SAMPLES FABRICATION – FACILITY AND TECHNIQUES

3.1. CONVENTIONAL METHODS FOR MICROFABRICATION

The electronic microdevices diverge regarding which substrate better suits their functionality. The substrate roughness, as well as particles from the air or from the experimenter (organic or inorganic kind) that happens to end up attached to the surface of the substrate, can determine the viability of the samples, limiting the precision of the functional devices at any step of the fabrication process. These impurities can ruin the proper function of the devices, owing to their micro/nanoscale dimensions. **Figure 12** demonstrates a sample with the fabricated devices side-by-side with a regular 1 real coin, for perspective.

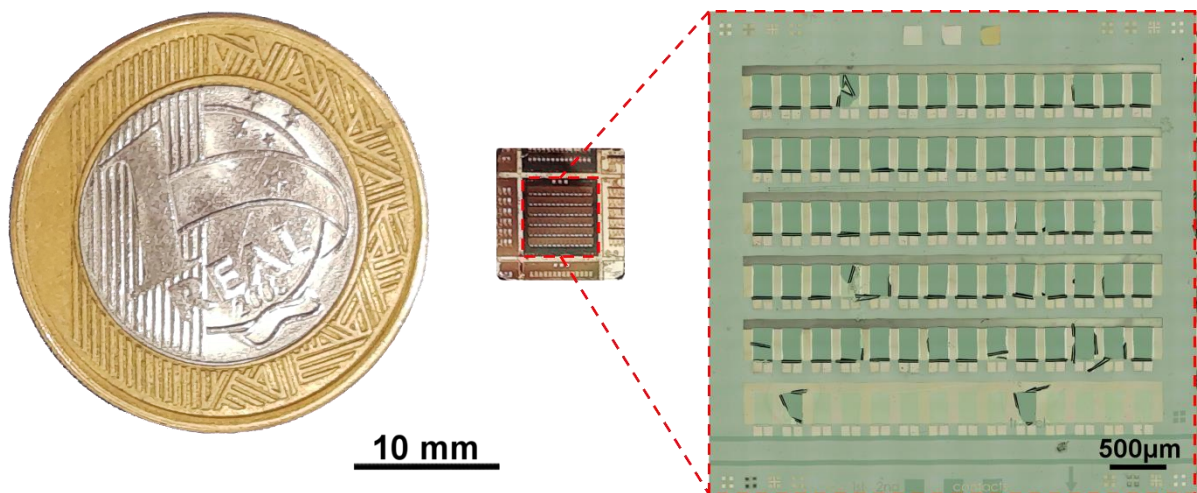


Figure 12: Picture of a sample with a 6 x 14 device array (84 devices), restricted into the inner square of the chip (center panel), side-by-side with a regular Brazilian 1 real coin 27 mm-diameter (left panel). In the right panel, an amplification of the sample with the rolled-up devices is shown. **Source:** the author.

As such, all the fabrication process of the samples was performed in a cleanroom laboratory. The controlled particle number in the lab environment, together with temperature and pressure control of the ambient, provided the proper conditions required for the manufacture of the functional devices, elevating the yield for each sample.

3.1.1. Facility – Cleanroom Laboratory

Cleanrooms are controlled environments used in industries or research laboratories for procedures in which the presence of microorganisms or particulates may modify or interfere somehow with the resultant product or analysis. Such places are completely isolated from other facilities, in a system regulated by standards concerning the activities and interactive techniques. They can be sterilized or not (depending on the purpose – what is developed there), and their main controlled parameters are airflow, pressure, temperature, humidity, noise, vibration, lighting, and contamination from particles and microbes.

Cleanrooms are classified by standards according to the degree of purity of the indoor air and the concentration of particles per unit volume of air. There are some standards to rank a cleanroom. The most common of them (and worldwide officialized) is the ISO 14644-1 (an International Organization for Standardization norm).

For this thesis, the sample fabrication was carried out in the Nanostructured Materials Laboratory (MNL) cleanroom facilities, in the Brazilian Nanotechnology National Laboratory (LNNano) – National Center for Research in Energy and Materials (CNPEM). They are fully equipped for photolithography processes, dry and wet corrosion/etching of films, deposition of organic and inorganic materials, and microscopy for monitoring the fabrication processes. The facility has four neighbor cleanrooms specifically for microfabrication, which are classified according to their level of cleanness – the number and size of particles allowed per volume unit. The innermost room is classified as ISO 5, followed by one ISO 6 and two ISO 7.

3.1.2. Step-by-Step HKUST-1 SURMOF Growth

HKUST-1 SURMOF was grown using a quasi-Liquid Phase Epitaxy (LPE) approach on both Al_2O_3 and Au substrates. On the former substrate, the Al_2O_3 layer was functionalized with a phosphonohexadecanoic acid (PHDA) SAM. The choice of the PHDA relies on the better adhesion of the phosphonic acid onto the Al_2O_3 substrate, and the preferential orientation of the HKUST-1 when grown onto a 16-carbon length SAM (VELLO et al., 2020). The oxide surface functionalization occurred by immersing the sample in 5% (v/v) acetic acid isopropanol solution containing 0.5 mM of PHDA for 1 h at 50°C, followed by 19 h in room conditions. After being washed in isopropanol and dried with gaseous nitrogen ($\text{N}_{2(g)}$), the samples were introduced sequentially in 1 mM copper acetate (2 min) and 1 mM BTC (4 min) ethanolic

solutions, respectively. To remove the non-deposited material, pre-washing and washing steps were employed between the precursor solutions. After the pretending thickness of the film (number of the desired cycles) was reached, the samples were withdrawn under ethanol flood and dried with $N_{2(g)}$ flow. **Figure 13** illustrates the LbL-deposition steps performed on the HKUST-1 SURMOF growth onto the PHDA SAM functionalized Al_2O_3 substrate, and the representation of Au substrate functionalized with the MHDA SAM, followed by 2 and 6 cycles of the HKUST-1 SURMOF growth.

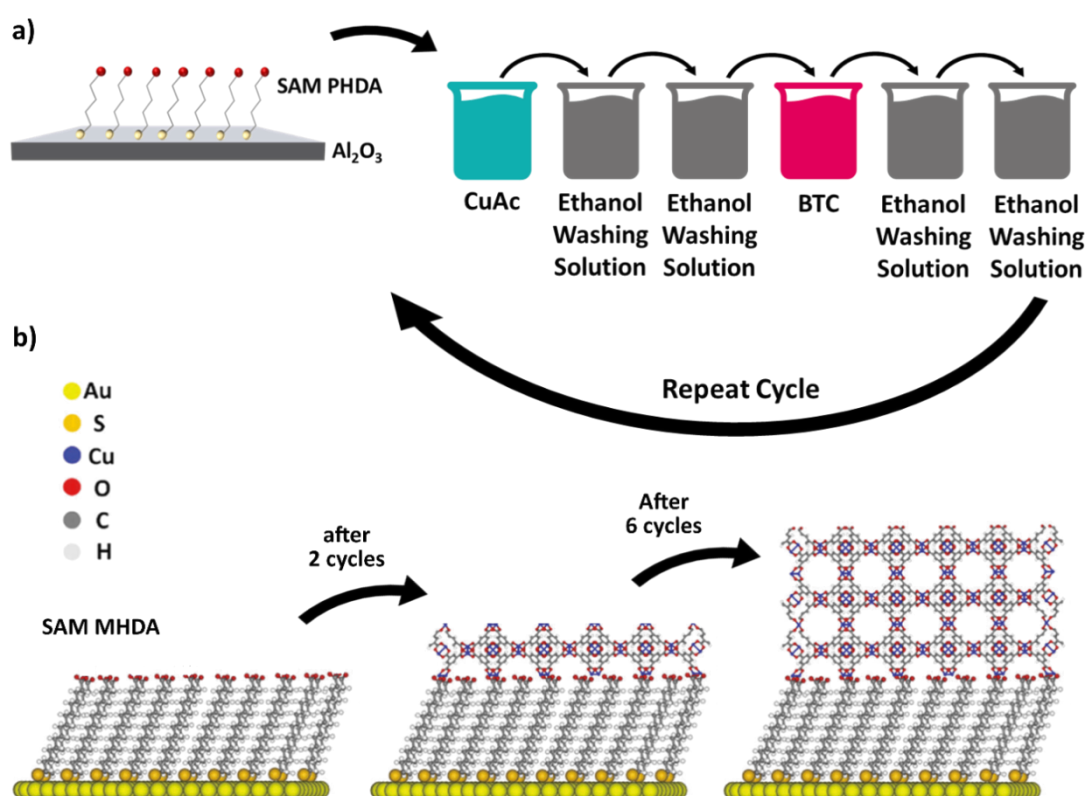


Figure 13: Illustration of: (a) sequential growth process of the HKUST-1 SURMOF onto Al_2O_3 substrate functionalized with the SAM PHDA; (b) illustration of Au substrate functionalized with the SAM MHDA, after 2 and 6 cycles of HKUST-1 SURMOF growth. **Source:** adapted from (SILVA et al., 2022; WANG; WÖLL, 2018).

The growth of HKUST-1 SURMOF onto the Au substrate for a metal/SAM-SURMOF/metal (MSM) approach was performed similarly, differing only on the molecule used as the SAM to functionalize the substrate. For that, the sample was immersed in 10% (v/v) acetic acid ethanolic solution containing 0.5 mM of MHDA SAM for 1 h at 50°C, followed by 19 h in room conditions, and dried with $N_{2(g)}$ in the sequence. More details regarding HKUST-1 SURMOF growth can be found in our previous work (VELLO et al., 2020).

3.1.3. Devices Fabrication

The device manufacturing was based on conventional photolithography processes and thin-film deposition methods. All the patterning were performed using conventional photolithography with AZ 5214E photoresist. Thermal evaporation was employed for the deposition of the metallic layers and the molecular ensembles – by e-beam (ATC-2030-E AJA International, with a distance between the sample and target material of around 40 cm) and resistive thermal evaporation in a Leybold Univex 250, respectively. The depositions were carried out at controlled evaporation rates ($\text{\AA}/\text{s}$), in a high vacuum ($\sim 10^{-7}$ Torr), at room temperature. In the deposition chambers, quartz crystal microbalances were used to monitor the film thicknesses during the evaporations. The Al_2O_3 dielectric layers were grown by atomic layer deposition (ALD) – in an Oxford OpAL reaction chamber using as precursors H_2O and trimethylaluminum 97% (TMA, from Sigma-Aldrich). The option for Al_2O_3 relies on its high dielectric constant ($\sim 6.5 - 9$) and its wide bandgap (~ 2.7 eV) (KHOSA et al., 2018; ROBERTSON, 2004; VANBESIEN et al., 2006). The temperature of the sample stage was kept at 150°C during the Al_2O_3 deposition at a growth rate of 1.6 nm/cycle. The chamber pressure was set between 120–260 mTorr, and argon (Ar) was used as the carrier/purging gas at a flow from 30 to 100 sccm.

Most capacitive devices are produced here as *r*-NM-based devices (3D platform), for the MBTF materials investigations. Some configurations are produced in planar (2D) structures (e.g., in metal-insulator-metal, MIM approach, or planar “pre-rolled” device), for basing and comparison. The rolled nanomembrane-based vertical heterojunctions (*r*-NM-junctions) were fabricated for a better investigation of the dielectric strength of the HKUST-1 SURMOF layer. The fabrication processes for the architectures created here are described further in this Section. Otherwise, other device structures are fabricated, characterized, and described in the Appendix in this work, but not plenty analyzed here. Those structures explore the HKUST-1 SURMOF into collapsed tube capacitors (**Appendix A**), antennas (**Appendix B**), and organic-hybrid NM-based heterojunctions (**Appendix C**).

3.1.3.1. MSM (MIM) capacitors

The MSM devices were fabricated on $9\text{ mm} \times 9\text{ mm}$ Si $\langle 100 \rangle$ substrates covered with a $2\text{-}\mu\text{m}$ -thick of SiO_2 layer. As the bottom electrode, Cr/Au (20/60 nm) were deposited at $0.5\text{ \AA}/\text{s}$ on the entire substrate surface. In the sequence, the Au surface was functionalized with

the MHDA SAM, followed by the HKUST-1 SURMOF growth using LPE. Then, using a shadow mask, Au (40 nm) was deposited at 0.2-0.3 Å/s on the SURMOF surface, configuring the top electrode with active device areas of about 0.2 mm². **Figure 14** illustrates the MSM sample structure formed.

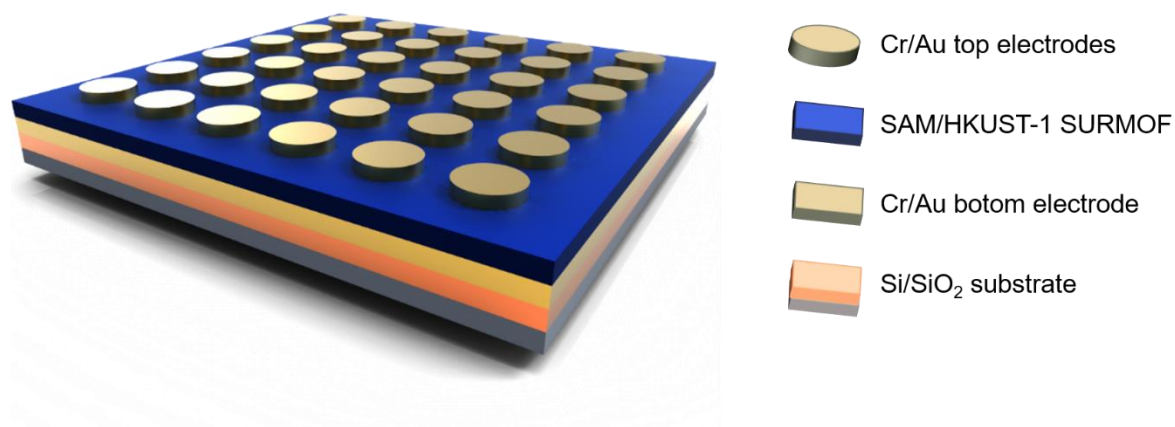


Figure 14: Illustration of the MSM samples configuration. The films thickness is not in scale. **Source:** adapted from (SILVA et al., 2022).

Each sample contains 121 top electrodes (yellow circles). After the fabrication, devices were left to dry for at least 24 h in a vacuum before electrical characterization.

3.1.3.2. Nanomembrane-based capacitors

The capacitors were fabricated on 9 x 9 mm² wide <100> Si/SiO₂ (2-μm-thick) substrates. Onto the Si/SiO₂ substrate, a 20-nm-thick Ge film was patterned and thermally treated for 17h at 60°C to form the sacrificial layer of GeO_x (MINATO GAU FERRO et al., 2020). The fabrication follows with the deposition of the capacitor bottom plate. A strained layer composed of Au (5 nm), Ti (10 nm) and Cr (10 nm) thin films was created. Then, an Al₂O₃ (15-nm-thick) dielectric layer and a Cr (10-nm-thick) top plate were deposited onto the device bottom plate, respectively. At this point, the basic structure of an inorganic parallel-plate capacitor (planar “pre-rolled” device) is ready. Next, an additional 15-nm-thick Al₂O₃ layer (for MPC-based or HKUST-1-based devices, respectively) was deposited on the as-fabricated parallel-plate capacitor to electrically insulate each *NM* winding of the self-rolled device. Notice that without this layer the bottom plate touches the top plate once the *NM* gets released from the sacrificial layer. The step-by-step for the hybrid *MBTF*-based devices are illustrated in **Figure 15**.

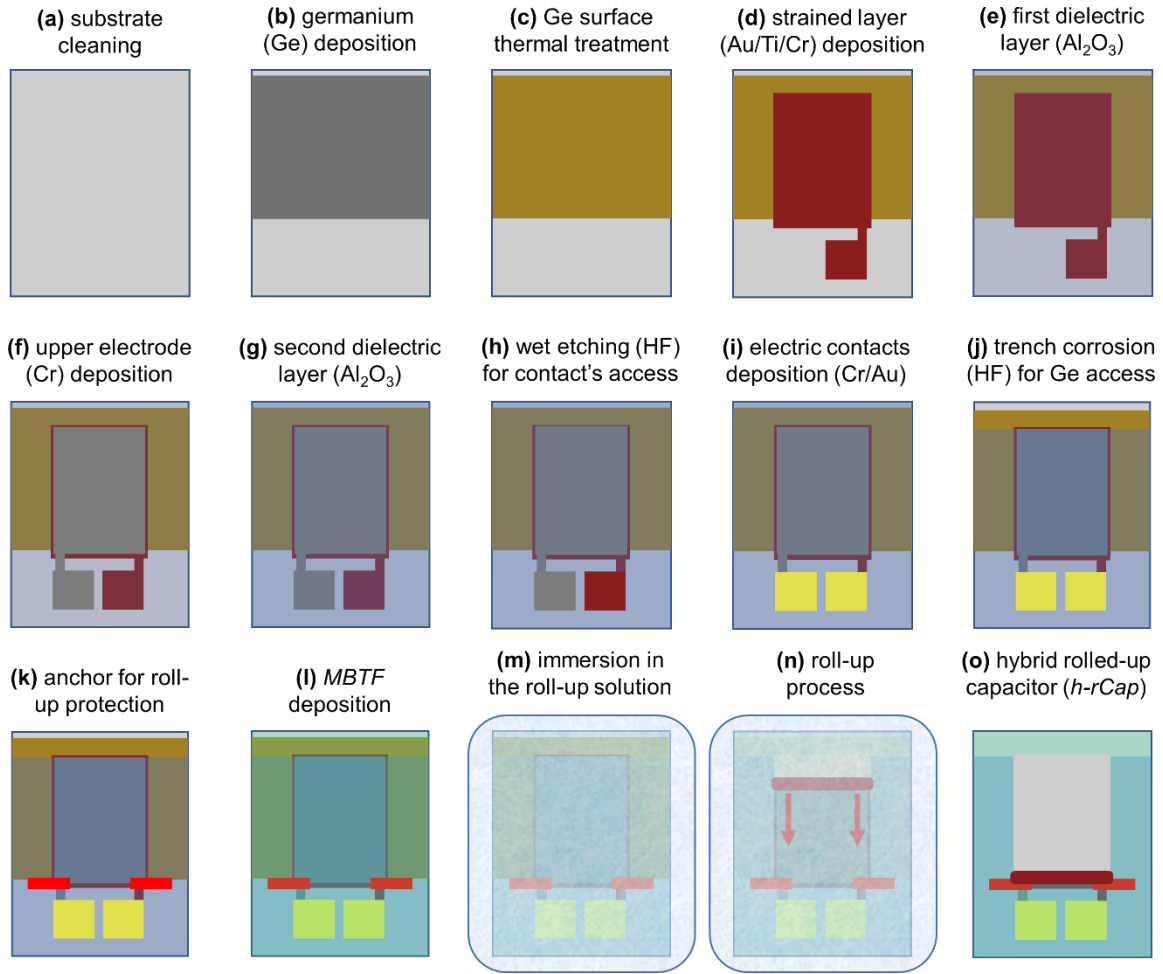


Figure 15: Fabrication processes for rolled-up capacitors. **(a)** Substrate cleaning; **(b)** patterning of the Ge layer; **(c)** thermal treatment for the Ge oxidation, forming the GeO_x sacrificial layer; **(d)** patterning of the stressed metallic NM consisting of Au/Ti/Cr (5/10/10 nm) onto the sacrificial layer; **(e)** deposition of Al_2O_3 (10 nm) onto the metallic NM; **(f)** patterning of the Cr (10 nm) layer on Al_2O_3 , configuring a conventional parallel-plate capacitor; **(g)** deposition of Al_2O_3 (10 nm) onto the parallel-plate capacitor; **(h)** patterning and wet etching (with HF) for accessing the electric contacts; **(i)** deposition of the electric contacts of Cr/Au; **(j)** patterning and wet etching of the trench for accessing the GeO_x layer, for the roll-up; **(k)** patterning of anchors for the tubes protection on the rolling of the NM; **(l)** deposition of the MBTF onto the capacitor (MPc evaporation or HKUST-1 SURMOF growth); **(m)** immersion of the sample in the roll-up solution; **(n)** dissolution of the GeO_x sacrificial layer, enabling the roll-up process; **(o)** *r*-NM-based capacitor (*h-rCap*) formed. **Source:** adapted from (SILVA; MERCES; BOF BUFON, 2020).

Three configurations of devices are proposed here to properly characterize MBTF materials as dielectric layers. The (i) inorganic planar “pre-rolled” capacitor (*i-pCap*) provides the dielectric constant spectroscopy of the bare Al_2O_3 layer between parallel plate electrodes. Using the dielectric information of the oxide provided by *i-pCap* measures, (ii) inorganic rolled-up capacitor (*i-rCap*) investigation makes available the contribution area of the rolled-up device, to the determination of the interface formed by the NM after the roll-up process. With the extracted data from both devices above described, (iii) the hybrid rolled-up capacitor with

the MPc or the HKUST-1 SURMOF layers (*h-rCap*), provides the dielectric properties of the investigated materials. The roll-up of the *NM*-based capacitors is described in sections 3.2.1 and 3.2.2.

3.1.3.3. Rolled nanomembrane-based junctions (*r-NM-junctions*)

These devices were also fabricated on conductive Si wafers <100> covered by 2- μm -thick SiO_2 . The first step was the creation of the finger-like (mesa) structure by patterning and etching 190 nm of the SiO_2 layer through a reactive ion etching (RIE) process using CF_4 gas, as shown in **Figure 16a**. Next, the bottom electrode (finger electrode) was formed by depositing Cr/Au (5/10 nm) on the mesa region, **Figure 16b**. Both metallic layers, Cr and Au, of the finger electrode were deposited at 0.5 $\text{\AA}/\text{s}$. In the sequence, a 20 nm thick germanium layer was deposited at 0.2 $\text{\AA}/\text{s}$ and patterned “in front” of the mesa region, as shown in **Figure 16c**. The GeO_x sacrificial layer was formed by the oxidation of the Ge layer using a homemade chamber under high RH (90%) for 16 h. Next, it was performed the formation of the strained metallic nanomembrane with lateral dimensions of 250 μm x 50 μm on the top of the GeO_x layer, **Figure 16d**. The strained metallic layer consists of a trimetallic Au/Ti/Cr nanomembrane (5/15/20 nm) deposited at 0.5, 1, and 5–6 $\text{\AA}/\text{s}$, respectively. Then, the contact-pads Cr/Au (20/60 nm) of the strained layer were deposited, both at 1 $\text{\AA}/\text{s}$, **Figure 16e**. The SURMOF growth was done following the quasi-LPE process. The SURMOF patterning was also performed using conventional photolithography. During the patterning, the region of interest was protected with a photoresist layer. After the O_2 plasma surface treatment (90 W, 3 mbar) for 10 min, the unprotected SURMOF region is removed. Then, the samples were immersed in acetone for photoresist dissolution, keeping the SURMOF patterned on the region of the finger electrode, **Figure 16f**. After the SURMOF patterning on the finger electrode, the devices were ready for the rolling-up process, **Figure 16g-h**. The fabrication description here is extracted from (ALBANO et al., 2020).

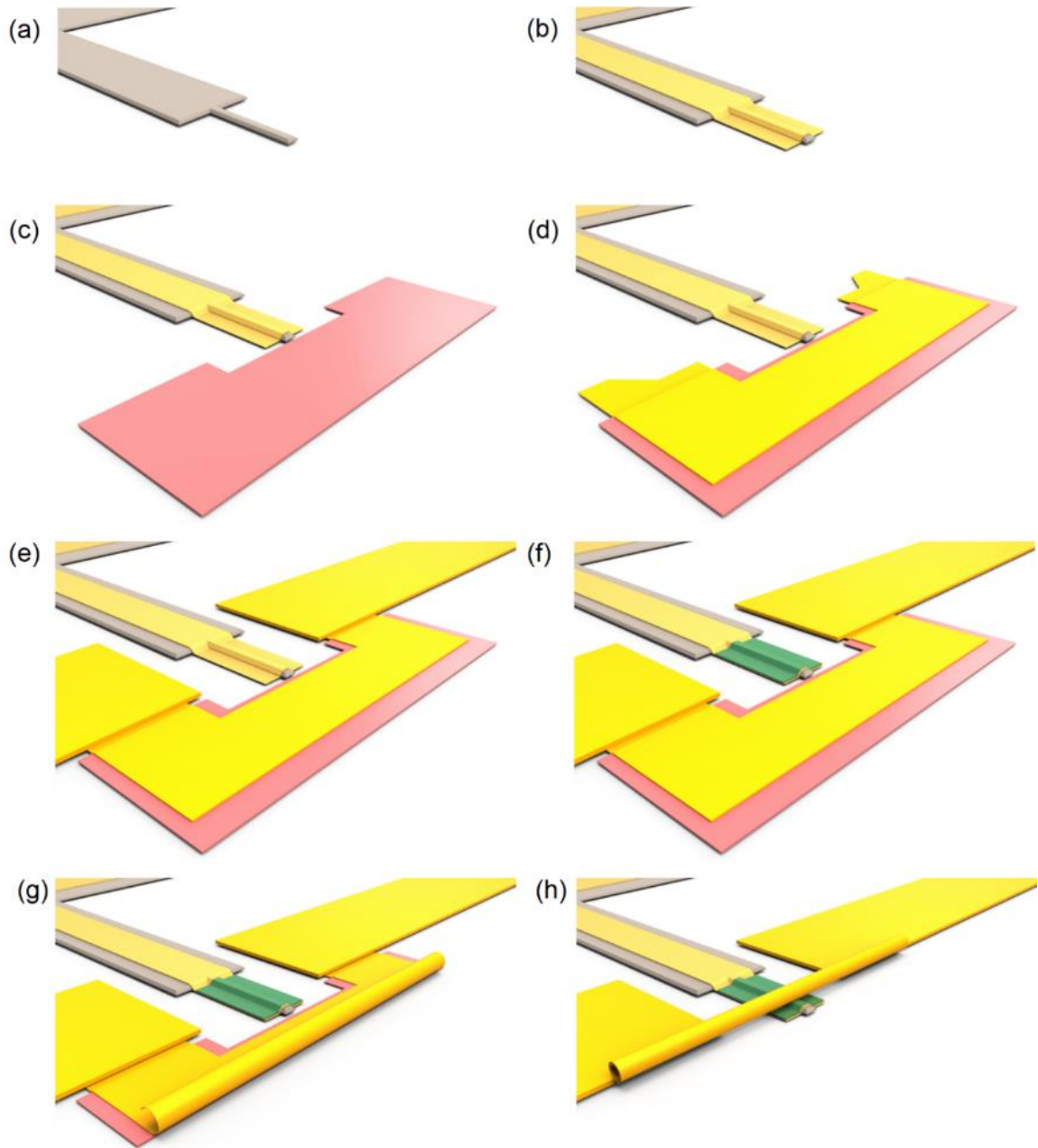


Figure 16: Fabrication of the *r*-NM-junction. The process comprises the determination of the: **(a)** dielectric mesa (by SiO₂ substrate corrosion) to elevate the bottom electrode; **(b)** Au bottom electrode (finger-shaped). **(c)** sacrificial layer (GeO_x); **(d)** strained metallic NM consisting of Au/Ti/Cr. **(e)** electric contacts. **(f)** HKUST-1 SURMOF (active area). **(g)** The roll-up process occurs by dissolving the sacrificial layer and releasing the NM. **(h)** Final configuration of the *r*-NM-junction, established with the tubular top contact. **Source:** adapted from (SILVA et al., 2022).

The parameters for the roll-up of the *r*-NM-junctions were even more differentiated than for the capacitor-like architectures and are described in Section 3.2.3 below.

3.2. *r*-NM-BASED FORMATION: NM RELEASING / ROLL-UP PROCESS

The roll-up of the *NM*-based devices is based on the controlled removal of the sacrificial layer, releasing the strained nanomembrane and promoting a directional roll-up of the device.

Figure 17 panel illustrates the process of *NM* releasing in the roll-up process.

Such a controlled strain releasing implies the planar structure to bend up, later compacting itself into a rolled-up cylindrical shell. Depending on (i) the metal deposition parameters and (ii) the *r*-*NM* geometrical features (thickness, width, and length), the diameter and the number of windings of the rolled-up structure can be adjusted (BOF BUFON et al., 2010; SHARMA et al., 2014). Depending on the uppermost *MBTF* layer, some of the fabrication parameters vary, such as the deposition rate of the strained layer and the composition of the roll-up solution. Therefore, a new calibration for the roll-up process must be determined for each composition of the device. Following, the specifics of the roll-up process for each kind of *MBTF* (i.e., MPc and HKUST-1 SURMOF) are described. The formation of the tubes for the hybrid *MBTF*-based devices is illustrated in **Figure 15m-o**.

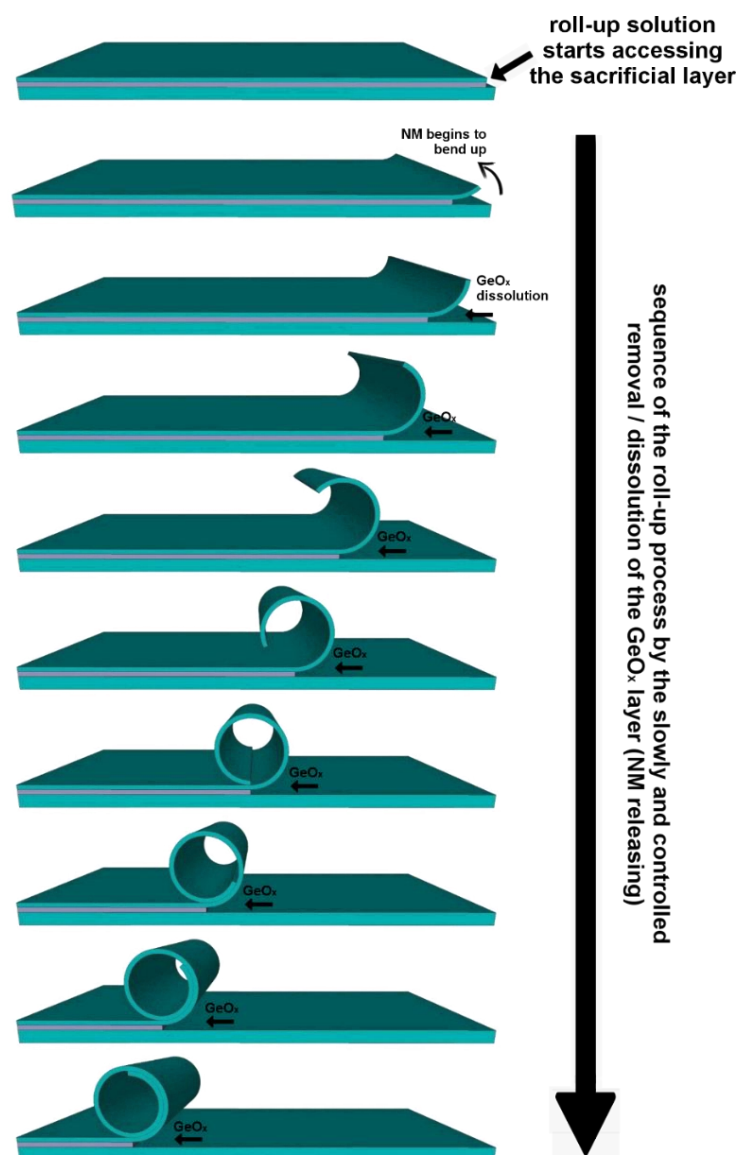


Figure 17: Scheme illustrating the process of roll-up – controlled removal of a sacrificial layer to the directional release of a stressed *NM*. The strained *NM* is liberated in a way that promotes a tubular-shaped structure. **Source:** adapted from Carlos C. B. Bufon courtesy animation.

3.2.1. Tubes Formation for the MPcs Capacitors

The *NM* roll-up process was carried out in a 1% v:v H₂O₂:H₂O solution. The samples composed of planar capacitors were immersed in solution to the GeO_x sacrificial layer removal. During this process (~20 min), the GeO_x etching starts from the Al₂O₃ trench and gradually releases the strain energy stored in the metallic layers of the planar device. It is worth mentioning that the parallel plate capacitor approximation (*i.e.*, $E = V/t$, where E and t are respectively the electric field and the dielectric thickness) remains valid as the diameter of the rolled-up devices is considerably higher than its thickness (μm vs. nm). The as-fabricated 84-device microchips have exhibited yield factors down to 20 – 25%, considering the *r-NM* devices. The yield factor for the planar devices was *ca.* 100%. Details of the fabrication until the roll-up process is shown in **Figure 15**.

3.2.2. Tubes Formation for the HKUST-1 SURMOF Capacitors

The rolled-up process was performed by immersing the devices into 80% (v/v) ethanolic aqueous solution at 50°C for approximately 60 min. The nanomembrane releasing and consequent tube formation transpires similarly as described in the immediately preceding Section. After, devices were left to dry for at least 24 h in room conditions, followed by 24 h in a desiccator vacuum before electrical characterization. The aforesaid in Section above, regarding the parallel plate capacitor approximation, also is valid here, as the diameter of the rolled-up devices is considerably higher than its thickness. Details on the step-by-step fabrication of the rolled-up hybrid devices with HKUST-1 SURMOF are shown in **Figure 15**.

3.2.3. Tubes Formation for HKUST-1 SURMOF *r-NM*-junctions

First, a trench region was defined through conventional photolithography to avoid rolling in different directions. Then, the samples were immersed in a 0.5% (v/v) H₂O₂ aqueous solution for 3 min, allowing the dissolution of the GeO_x layer without damaging the SURMOF layer (protected by the photoresist resin). Such a process enables the rolling of the strained metallic nanomembrane, which was limited by the trench. In the sequence, by immersing the samples in acetone, the photoresist-structured trench was removed through its dissolution, and the strained nanomembrane was released from the substrate toward the finger electrode to

establish the top mechanical contact on the SURMOF film. The roll-up process is demonstrated in **Figure 16g-h**. Next, the samples were placed in a vacuum for at least 24 h to dry. Notice that each substrate has an 81 mm² area with 32 devices, and the tube electrode exhibited a typical radius of ~4 μm.

CHAPTER IV: CHARACTERIZATION METHODS

4.1. MORPHOLOGICAL CHARACTERIZATION OF THE FILMS AND SAMPLES

The morphological characterizations for the thin films and devices were carried out using the LNLS and LNNano facilities, in CNPEM. For such, many microscopies and spectroscopies were performed. The specific characterization for each investigation is described below in this Section.

4.1.1. Optical microscopies of the films and devices

Conventional optical microscopy was performed using a Zeiss Axio Imager, with available lens magnifications of 5x, 10x, 20x, 50x, 100x, and 150x (see **Figure 18a**). Laser Scanning Confocal Microscopy (LSCM) from Keyence VK-X200 (shown in **Figure 18b**) provided multifocal 3D optical top images of the devices.



Figure 18: Instruments used for the optical microscopies performed in this work. **(a)** Conventional optical microscope Zeiss Axio Imager. **(b)** LSCM from Keyence VK-X200. **Source:** Images acquired and adapted from the official LNNano site¹, at 18/03/2023.

The conventional optical microscopy was vastly performed during the fabrication processes of the samples to attesting the quality and certify the standard of each step of the fabrication process, while the LSCM was used to assist the area determination of the device dimensions for the MSM and NM-based architectures, as to the radii determination for the tubes.

¹ <https://lnnano.cnpem.br/instalacoes-e-divisoas/divisao-de-nanomateriais/laboratorio-de-microscopia-eletronica-de-varredura-duplo-feixe/>

4.1.2. Atomic force microscopy (AFM)

The Al_2O_3 films were grown onto Cr thin films deposited on SiO_2 substrates for the surface topography investigation. At the devices, the Al_2O_3 layers are deposited as dielectrics onto electrodes of Cr films for the capacitor arrangement. For the Al_2O_3 films, the AFM images were obtained with a NaioAFM Nanosurf, operating in peak force tapping mode (**Figure 19a**).

The MPCs molecular ensembles were deposited from powder (CuPc - Alfa Aesar; CoPc - Alfa Aesar; F_{16}CuPc - Sigma Aldrich) on the top of Al_2O_3 dielectric layers for the surface topography investigation. After the Pcs films thermally evaporation, the surface roughness of each film on the substrate was explored. For the HKUST-1 SURMOF films, the smaller (10-cycles samples) and the bigger (40-cycles samples) thicknesses were here chosen for the AFM investigation, as dielectric layers integrated into the *r*-NM-based capacitors. The films were grown onto MHDA SAM functionalized Al_2O_3 substrates. The characterization of all the MBTFs films were performed with a NaioAFM Nanosurf, with similar operation specifications to those used for the Al_2O_3 investigation, and a Park Systems NX10 Microscope with an NX-AFM controller (**Figure 19b**), operating in peak force tapping mode, and using a Silicon tip coated by Aluminum (Al), from NanoWorld was used, also. The AFM tips used here have a nominal resonant frequency of 75 kHz and a nominal force constant of 2.8 N/m.

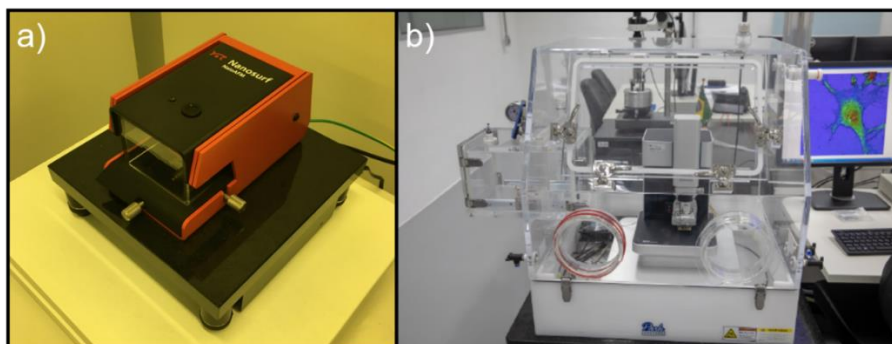


Figure 19: AFM equipment used for the topological exploration of the dielectric films. **(a)** NaioAFM Nanosurf. **(b)** Park Systems – NX10. **Source:** images acquired and adapted from the official LNNano site², at 18/03/2023.

The demonstration of more in-depth morphological analysis of the MPCs thin films fabricated here can be found in other works published by the group (BATISTA et al., 2022; SERGI LOPES et al., 2020; SILVA; MERCES; BOF BUFON, 2020).

² <https://lnnano.cnpem.br/instalacoes/microscopia-e-criomicroscopia/microscopia-de-forca-atmica/>

4.1.3. Electron Microscopies and Spectroscopy

Scanning electron microscopy (SEM), Focused Ion Beam (FIB), Energy-Dispersive X-ray Spectroscopy (EDS), and Scanning Transmission Electron Microscopy (STEM) techniques were performed using a (FEG-SEM) Inspect F50 from FEI (Japan), shown in **Figure 20**, to the



Figure 20: Scanning Electron Microscope (FEG-SEM) Inspect F50 from FEI (Japan). **Source:** the author.

assessment of more detailed structural information of the HKUST-1 SURMOF films. Such microscopy techniques were performed for the MSM device with HKUST-1 SURMOF as dielectric layer, mainly for both analyses: (i) the survey of the surface morphology formed on the growth of the SURMOF films; (ii) for assess the interface configuration

(dielectric-top electrode) created by a thermally deposited metallic layer onto the porous dielectric layer.

The structural analyses of the *i-pCap*, *i-rCap*, and *h-rCap* devices were performed using SEM and LSCM. Such characterizations revealed characteristics of the *NM*-based devices such as the external radii and the morphology of the nanomembrane at the inner part of the tubular structures.

4.2. ELECTRICAL CHARACTERIZATION OF THE SAMPLES

The electrical characterizations for the devices were also carried out using the LNLS and LNNano facilities, from CNPEM. For such, parameter analyzers were operated for performing current vs. potential and impedance spectroscopy (IE) measures, in different temperatures and atmospheric conditions. The main probe stations and parameter analyzers equipment used are illustrated in **Figure 21**.

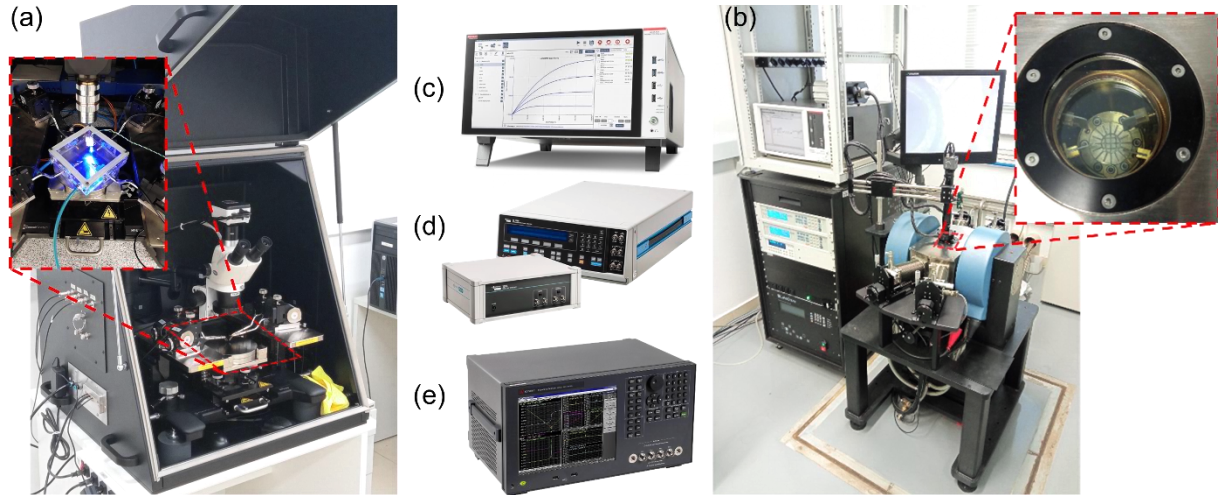


Figure 21: Demonstration of the electric characterization set-up and equipment used: **(a)** Probe station cascade (4-tip probes) with detail on the atmosphere-controlled box (**inset**); **(b)** LakeShore system for cryostat-support station (4-tip probes) with detail on the sample chuck (**inset**); **(c)** Keithley 4200 for I_xV measurements; **(d)** Solartron 1260A for impedance analysis; **(e)** Keysight E4980A for impedance analysis. **Source:** the author.

For the electrical access of the devices, an MPS150 Cascade Microtech probe station positioned into a Faraday cage was coupled to impedance (I_{AC} output measurement) and I_xV (I_{DC} output measurement) analyzers.

The main electrical measurements for all the samples are the IS, acquired by using the probe station equipped with micromanipulators and an optical microscope. The contact is performed through conventional tungsten tips connected to the micromanipulators, which have triaxial connectors plugged to a Solartron 1260A Impedance Analyzer or a Keysight E4980A impedance analyzer. The measurements were performed applying a sine-wave voltage of 100 mV amplitude and 0 V of offset with 10 points-per-decade. For the capacitor structures fabricated and investigated in this work, the dielectric films thickness is considered as the distance between the electrodes.

4.2.1. Electrical Characterization of the *h-rCap* Devices with MPCs

For the electrical characterization of the MPC-comprised devices, both impedance amplitude vs. frequency ($Z-f$) and impedance phase angle vs. frequency ($\theta-f$) were investigated as a function of reservoir temperature (T). The Cascade probe station positioned into a Faraday cage was coupled to a Keysight E4980A impedance analyzer to allow the characterization at environmental temperature. A Lakeshore EMPX-HF (cryogenic probe station) was employed

to evaluate the accumulation properties of the capacitors as a function of T . The Z - f - T and θ - f - T measurements were performed in the dark. We have evaluated an amount composed of 6 devices – planar/inorganic (*i-pCap*), rolled-up/inorganic (*i-rCap*), and rolled-up/hybrid (*h-rCap*) capacitors. Each fabricated *h-rCap* sample was formed by 5 nm-thick molecular ensembles of CuPc, CoPc, or F₁₆CuPc. Before the electrical characterization, the devices were stored in a vacuum of 10^{-2} Torr to remove solvents from the self-rolling process and preserve the as-fabricated properties. Sine-wave voltage stimuli – amplitude of 100 mV, frequencies ranging from 20 Hz to 10^7 Hz – were used for the electrical characterization.

4.2.2. Electrical Characterization of the MSM and *h-rCap* Devices with HKUST-1 SURMOF

The IE were performed using the above-mentioned (**Figure 21**) probe station equipped with micromanipulators and an optical microscope, with conventional probe tips of tungsten connected to micromanipulators, the latter ending triaxial connectors, which was plugged into a Solartron 1260A Impedance Analyzer. The measurements were performed applying a sine-wave-form voltage of 0.01 V (relatively low) amplitude (peak-to-peak), reducing the space-charge contribution, and approximating to the ohmic formalism for the impedance determination. A 0 V of offset, with 10 points-per-decade from 3×10^6 to 3×10^{-1} Hz. A homemade chamber (~ 50 cm³) was used to sustain the electric measurements in different atmosphere conditions (saturated of N₂, water vapor, ammonia, and acetone). The N₂ and high relative humidity (RH) desired levels were controlled by adjusting water vapor and N₂ gas inside the chamber. The ammonia (NH₃) expositions were performed by placing a recipient inside the chamber containing 20 mL of 5% (v/v) aqueous NH₃ ($\sim 28\%$, Sigma Aldrich), the same volume was established for the saturated solution of acetone. For the UV exposition, a UV light provided by a mercury lamp (USHIO UV lamp USH-508S) with a luminous flux of 35200 lm was used with a cumulative dose of 500 mJ/cm². All IS data acquisitions were performed immediately after each exposition.

The data resulting from the IS measures were treated according to the models (described afore), established for each capacitor architecture, in the software Z-view® (EIS data analysis) and hand-made calculations for comparison. The equivalent circuits were fitted according to the appropriated model for each device architecture. The values obtained for the electrical properties of each layer of the films were determined according to the fitted data. As a reminder,

one of the main goals of this work relies on the evidencing of the electrical response for supposedly similar films relative to their distinct behavior when incorporated as dielectrics into different architectures of microdevices, to the determination of a more appropriate structure for such investigation, which evidences the importance of high-quality fabricated samples for their reproducibility and reliability on the electrical responses, along with a coherent interpretation of the impedance-measured data, which places the IS as the most relevant characterization for this work.

4.3. FEM SIMULATIONS OF DIELECTRICS FOR INTERCONNECTIONS

To better elucidate the HKUST-1 performance as ILD, finite element method (FEM) simulations were performed, placing the material between 40-nm apart interconnections. The FEM simulations were performed using FeniCS (2019.1.0) library, *i.e.*, Python library, to solve Partial Differential Equations (PDEs) (LANGTANGEN; LOGG, 2016). The complete simulation was performed with the assistance of several applications, namely GMSH (3.6.0) for the geometry and mesh generation (GEUZAIN; REMACLE, 2009). The mesh was imported into FeniCS to solve the electrostatic problem, and Paraview 5.9.0 was used as a post-processing tool (AYACHIT; GEVECI; AVILA, 2015). The entire simulation was performed by using a modern laptop (i7 8750H processor, 16 Gb dd4 ram, and 500 Gb SSD).

A square domain representing the device cross-section was modeled, with dimensions $\Omega = [0,2] \times [0,2]$ ($\mu\text{m} \times \mu\text{m}$), $\Omega \in \mathbb{R}^n$, and Dirichlet boundary conditions prescribed (LANGTANGEN; LOGG, 2016). The domain was divided into two subdomains, $\Omega_0 = [0,2] \times [0,1]$ and $\Omega_1 = [0,2] \times [1,2]$. The values for static relative permittivity were $\varepsilon'_r(x,y) = \varepsilon_r^0$ in Ω_0 and $\varepsilon'_r(x,y) = \varepsilon_r^1$ in Ω_1 , where ε_r^0 and ε_r^1 were set to be constant for each medium. The relative permittivity of air was set to $\varepsilon_{air} = \varepsilon_r^0 = 1$, while ε_r^1 was set to be the static permittivity tensor ($\varepsilon_r^1_{xx} = \varepsilon_r^1_{yy}$) for HKUST-1, SiO_2 , and Al_2O_3 . The two gold electrodes were set as Dirichlet boundary conditions with electric potential $V = V_{bias} = 150$ mV on the left, and both floating and grounded on the right, respectively. The mesh was processed as a set of dozens of thousands of unstructured P1 Lagrange elements (LANGTANGEN; LOGG, 2016; LANGTANGEN; MARDAL, 2020; MULTIPHYSICS, 2016). The structure simulated is illustrated in **Figure 22a-e**.

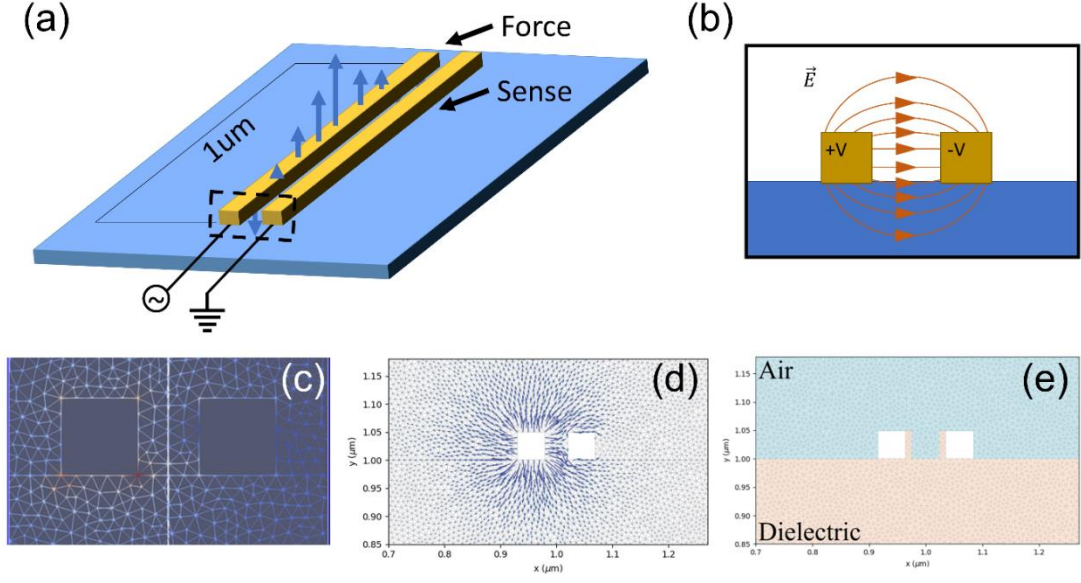


Figure 22: Illustrative representation of the domain for the FEM simulation performed. **(a)** 3D demonstration of the interconnections (out of scale) on the dielectric substrate. **(b)** Cross-section of the interconnections, with illustrative opposite-charged electric potential applied. **(c)** Mesh structure for the Lagrange elements. **(d)** Example of electric field distribution on the mesh after applied potentials. **(e)** Different structure created for the simulation, with the dielectric as a wall for the interconnections, besides their substrate. **Source:** the author.

The variational formulation was derived, and the weak formulation in the standard notation for bilinear $a(u,v)$ and $L(v)$ linear forms (LANGTANGEN; LOGG, 2016) are shown in Equations 67 and 68. Then, the value-boundary problem was solved in FeniCS (LANGTANGEN; LOGG, 2016).

$$a(u,v) = \int_{\Omega} \varepsilon(x,y) \cdot \nabla u \cdot \nabla v \cdot dx \quad (67)$$

$$L(v) = \int_{\Omega} f \cdot v \cdot dx \quad (68)$$

where $u(x)$ and $v(x)$ are the test (unknown) and the trial functions, respectively. Therefore, the statement of the variational problem is to find $u \in V$ such that $a(u,v) = L(v)$, $\forall \hat{V}$. The test space V is defined as Equations 69 and 70:

$$\hat{V} = \{v \in H^1(\Omega) : v = 0 \text{ on } \partial\Omega\} \quad (69)$$

$$V = \{v \in H^1(\Omega) : v = u_0 \text{ on } \partial\Omega\} \quad (70)$$

The test V and trial $\hat{V}$ function spaces are convenient Sobolev spaces. A complete description can be found in H. P. Langtangen and A. Logg (LANGTANGEN; LOGG, 2016; LANGTANGEN; MARDAL, 2020).

CHAPTER V: STRUCTURAL ANALYSIS FOR THIN FILMS OF THE DIELECTRIC MATERIALS

The morphological characterizations for the films and devices were carried out using the LNLs and LNNano facilities, from CNPEM. For such, many microscopies and spectroscopies were performed. The specific characterization for each investigation is described below in this Section.

5.1. Surface Topography Characterization of the Al₂O₃ films

The Al₂O₃ films were grown onto SiO₂ substrates and Cr thin layers for morphological investigation. At the devices, the Al₂O₃ layers are deposited as dielectrics onto electrodes of Cr

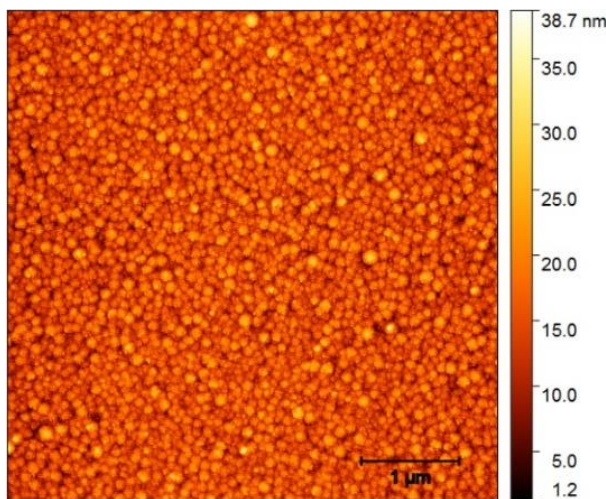


Figure 23: AFM image of a 400-nm-thick Al₂O₃ film, presenting an RMS value of ≈ 4.0 nm.

Source: extracted from (SILVA; MERCES; BOF BUFON, 2020).

films for the capacitor arrangement.

Figure 23 shows an AFM image of the topography of a 400 nm thick (250 cycles) film of Al₂O₃.

The Al₂O₃ films were grown by ALD at 1.6 nm/cycle, with a fast-valve time opening of 0.02 s for the TMA, as Al precursor, and a fast-valve time opening of 0.2 s for the D.I. H₂O_(v), as the O precursor.

This characterizes a thermal growth of the oxide. The pressure in the chamber varied from 120 to 260 mTorr. The characterization of the films exhibited a high uniformity and low roughness, revealing no need to a Plasma-Assisted ALD process for the film quality desired (PETRINI et al., 2018).

5.2. Surface Topography Characterization of the MPcs films

The AFM surface images for each MPc are shown in **Figure 24**. The deposition rate for each material was calibrated by the following process: deposition of the materials onto a pre-

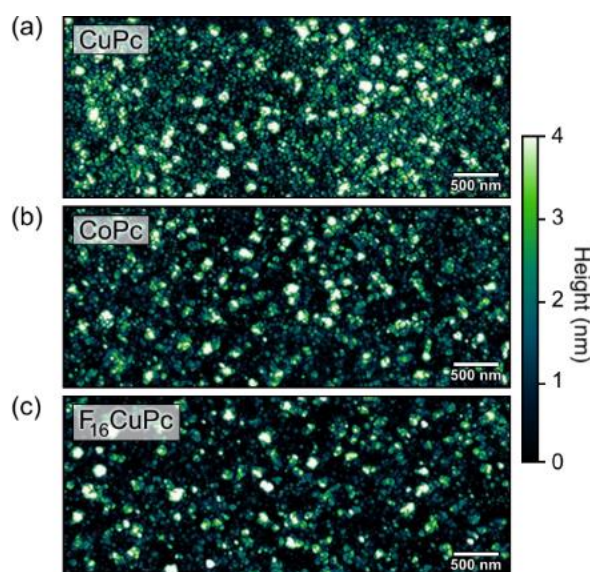


Figure 24: Atomic force microscopy (AFM) images of 10-nm-thick MPc films: **(a)** CuPc, **(b)** CoPc, and **(c)** F₁₆CuPc. **Source:** Reprinted with permission from (SILVA; MERCES; BOF BUFON, 2020).

determined lithography pattern on the substrate; a lift-off process promoting the reproduction of a pattern of the films, establishing steps with substrate-organic interfaces on the surface of the sample; AFM analysis of the steps formed for the determination of the thickness of the films in the deposition process.

From the results depicted in **Figure 24**, the *RMS* values were found as 1.4, 1.3, and 1.3 nm for the CuPc, CoPc, and F₁₆CuPc ensembles, respectively. One may note that such roughness values are close to each other for the MPcs, besides relatively higher than for the Al₂O₃. The demonstration of more in-depth

morphological analysis of the MPcs thin films fabricated here can be found in other works published by the group (BATISTA et al., 2022; SERGI LOPES et al., 2020; SILVA; MERCES; BOF BUFON, 2020).

5.3. Structural Characterization of the HKUST-1 SURMOF Films

As the novelty material fabricated and investigated in this work, the SURMOF HKUST-1 films required more in-depth morphological characterization. Therefore, a broader series of microscopy techniques (described below) was used for the material study.

5.3.1. Electrical Microscopies and Spectroscopy

The SEM, FIB, STEM, and EDS techniques were performed using a Field Emission Gun Scanning Electron Microscope (FEG-SEM) for the morphological investigation of a 100 cycles thick HKUST-1 SURMOF film incorporated as the dielectric layer into the MSM junction. The FIB process is required for the further STEM and EDS characterizations. However, such a technique reveals to be possibly aggressive to organic-based (“soft”) structures (BASSIM et al., 2012).

Figure 25 shows the SEM images of the FIB process steps performed for the preparation of a lamella detached from an arbitrarily selected region (relatively far from the electrode edges) of an arbitrarily selected electrode (positioned relatively far from the sample borders).

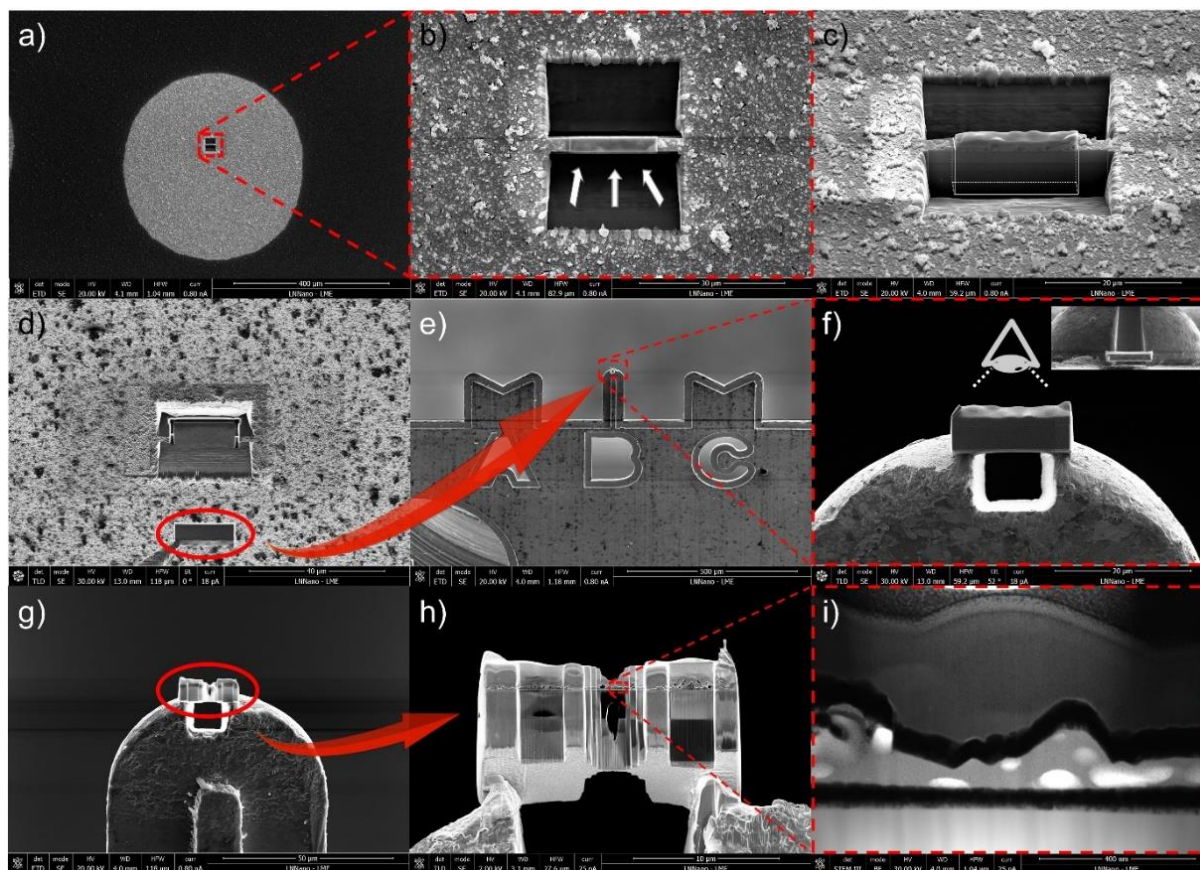


Figure 25: STEM images of the stages for the lamella preparation of an MSM device with a layer of 100 cycles of the HKUST-1 SURMOF between metallic electrodes using the FIB technique. **(a)** Image of one MSM device with the region etched by the ion beam. **(b)** Zoomed into the upper view of the etched region, with the arrows indicating the **(c)** angular perspective of the etched region. **(d)** Prepared lamella (highlighted) detached and soldered to a micromanipulator. **(e)** Lamella (highlighted) attached (soldered) to the grid for probing. **(f)** Zoomed in the (rough) lamella on the grid, with a respective top view (**inset**). **(g)** Lamella after ion beam polishing procedure for STEM and EDS characterization. **(h)** Zoom on the polished lamella. **(i)** Detail of the HKUST-1 SURMOF layer sandwiched by the electrodes in the MSM structure. **Source:** the author.

The analysis of the STEM characterization reveals the junction profile for a region of the HKUST-1 SURMOF dielectric layer (100 cycles) in between metallic electrodes, as emphasized in **Figure 26**.

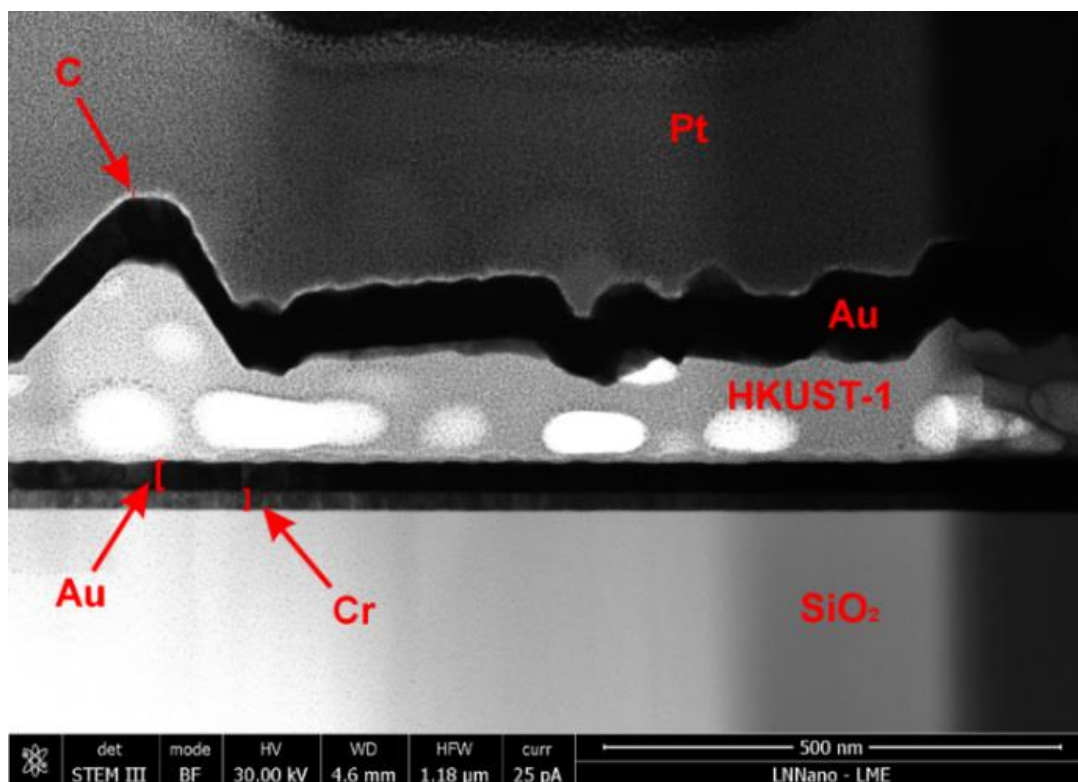


Figure 26: Bright Field STEM image of a 100 cycles film of the HKUST-1 SURMOF in MSM device, after the cut and preparation of a lamella of the sample by FIB technique. **Source:** the author.

From the STEM image of **Figure 26**, one may notice that, over the length of the junction, there is a substantial variation in the height of the (100 cycles height, the thicker film investigated here) HKUST-1 SURMOF dielectric layer into the MSM device. As well, it can be noticed some regions of color nuanced in the HKUST-1/top Au interface in **Figure 26**, indicating a possible permeation of metal particles thermally deposited as the top electrode in the porous dielectric, which may generate shortening regions between the electrodes that, despite of relatively short comparing to the thicker dielectric layer, may depict relevant thickness for the thinner films.

Unfortunately the data analysis of the EDS investigation reveals a significant contamination in the SURMOF layer into the MSM junction, probably generated by the ion beam conducted in the FIB process to produce the lamella, due to the porous nature of the HKUST-1. Also, the signal count for the elements composing such a porous film revealed not enough to their detection. Therefore, despite of mentioned here, the EDS results were “neglected” (not deeply explored) further in this work. Although, the primary treated data acquired from the EDS characterization is shown in **Figure 27**.

The EDS spectroscopy of the MSM junction (**Figure 27**) reveals a consistent result for the metallic electrode layers composition (bottom Cr/Au and top Au electrodes, in the darker regions).

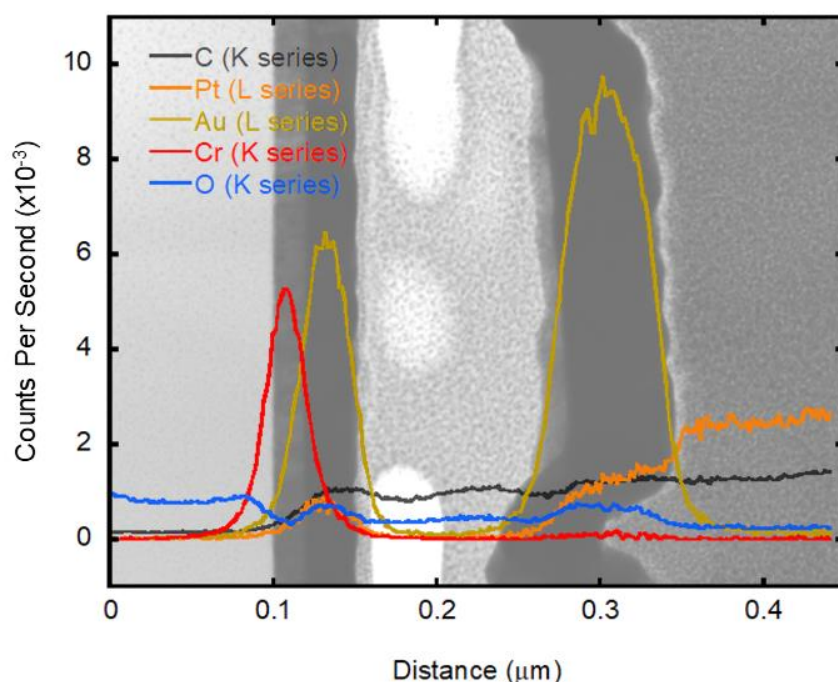


Figure 27: EDS for the MSM junction. **Source:** the author.

regions). However, despite representing the main composition of the SURMOF, the count of carbon atoms in the HKUST-1 layer region is negligible compared to its count in the electrode films (which is present probably due to contamination). The Cu was not detected and therefore is not represented. These

results indicate that the low density of the porous material, together with the contamination from the FIB, turns it as not enough for the technique detection.

5.4. Grazing Incidence X-Ray Diffraction (GIXRD)

Figure 28 shows the Grazing Incidence X-Ray Diffraction (GIXRD) patterns of the HKUST-1 SURMOF for different quasi-LPE deposition cycles. The HKUST-1 was grown on top of the 10-nm-thick Al_2O_3 film functionalized with a PHDA SAM (VELLO et al., 2017a, 2017b). The diffraction patterns were obtained using a synchrotron radiation source.

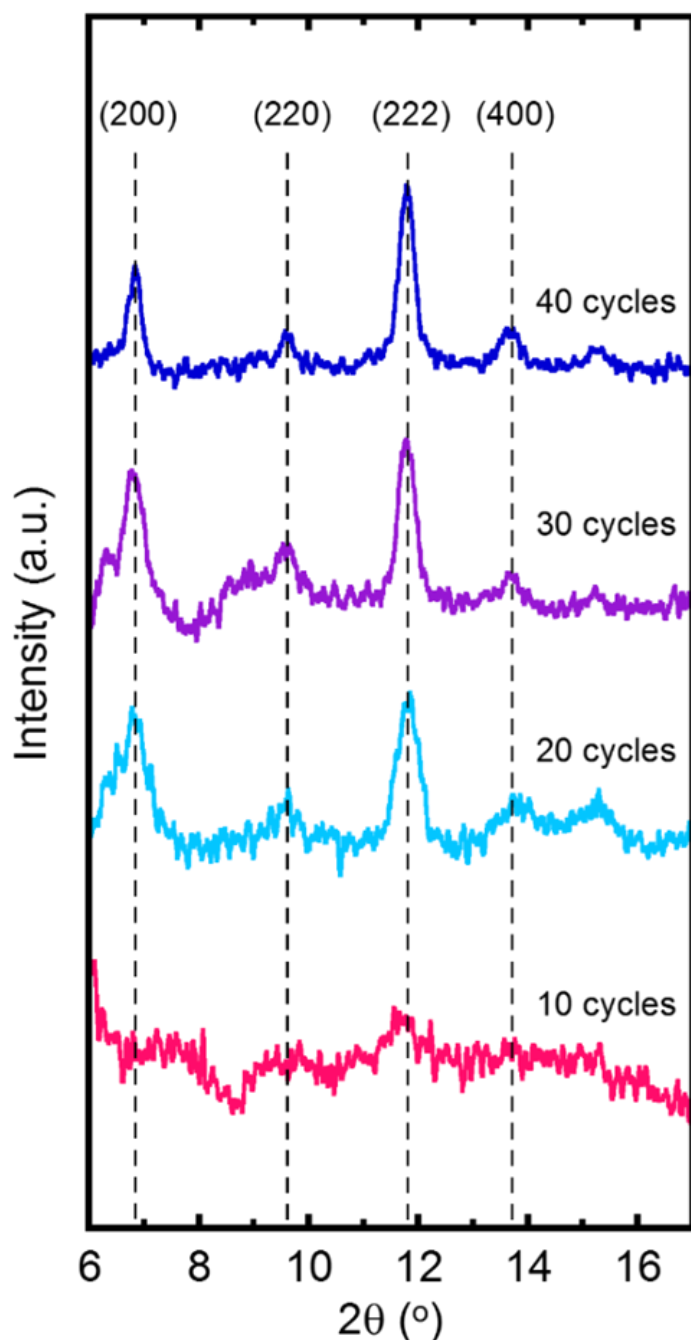


Figure 28: GIXRD pattern for different deposition cycles on functionalized Al_2O_3 surface. **Source:** Extracted from (SILVA et al., 2022).

SURMOF film. Therefore, tests were performed to follow the endurance of the SURMOF thin films after a certain time immersed in ethanolic-aqueous solutions. The tests included GIXRD characterization (see **Figure 29**) of the samples with 20 cycles of LbL grown HKUST-1

The principal (200) and (222) crystalline planes reflect a dynamic growth of the HKUST-1 SURMOF, with preferential orientation corresponding to [100] and [111] directions. As the SURMOF thicknesses increase, *i.e.*, the number of deposition cycles, the film crystallinity increases favoring the [111] direction. This behavior is consistent with those previously reported (VELLO et al., 2020), where the preferential orientation changes could be controlled by either increasing the film thickness or changing the SAM chain length. Furthermore, the reduction in peak intensity observed for the 10-cycles grown samples is mainly attributed to the low film thickness of ~ 20 nm, **Figure 30a-b**, which makes the diffraction patterning hard to be detected by GIXRD technique.

The manufacturing of *r*-NM-junctions (see Section 3.1.3.3) uses a process of photolithography performed over the HKUST-1

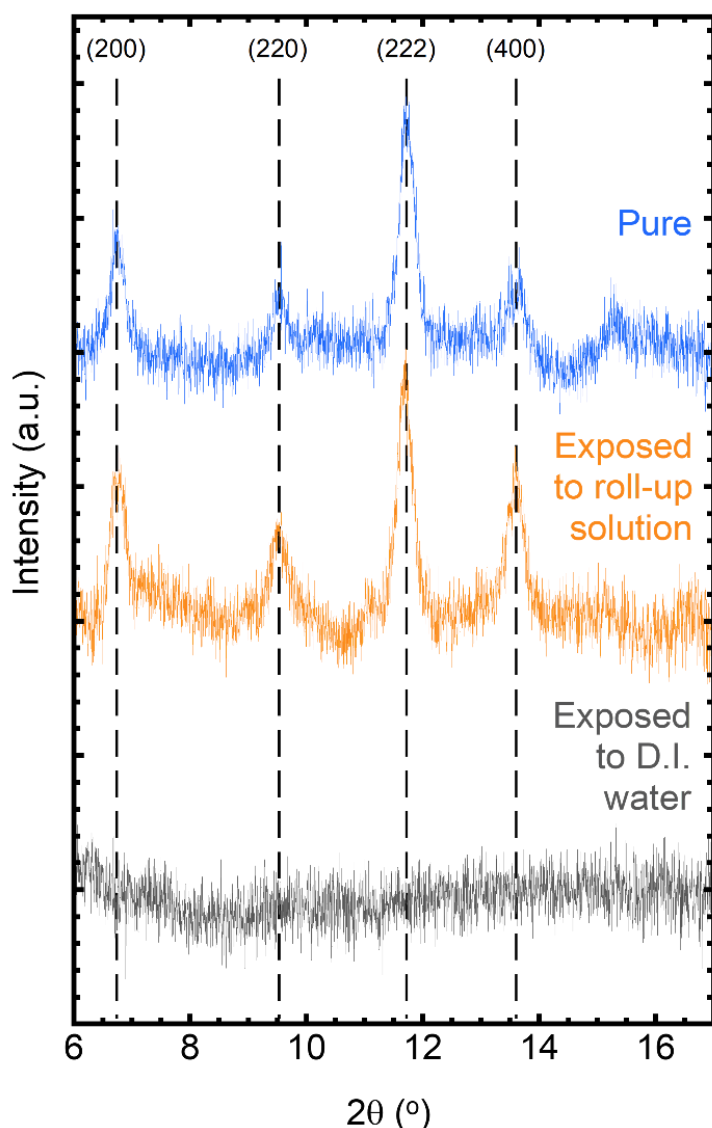


Figure 29: XRD patterns of 20 cycles of HKUST-1 SURMOF film grown onto Al_2O_3 substrates functionalized with PHDA SAM. The image depicts the comparison between diffractograms of the film: pure, immersed in 60% ethanol / 40% water v/v solution for 3 h, and immersed in DI water for 3 h. **Source:** the author.

SURMOF films on Al_2O_3 substrate, under three conditions: (i) pure, (ii) after immersion in 40% DI water / 60% ethanol (v/v) solution for 3 h and (iii) after immersion in 100% DI water for 3 h. The XRD patterns reveal no relevant differences in the peaks position and intensity for pure and solution-exposed films. On the other hand, the patterns of the samples exposed to DI water reveal no peak signs, indicating that the SURMOF films were degraded.

These results indicate that the HKUST-1 SURMOF thin-film endures the ethanolic-aqueous solution – 60% ethanol / 40% DI water (v/v) – for 3 h immersion. Thus, these films should resist the roll-up solution, which contains a lower water concentration – 80% ethanol / 20% DI water (v/v) – for the time

of formation of the tubes (≈ 60 min). The endurance of the HKUST-1 SURMOF to the photolithography process is also similarly asserted, which makes the full process of fabrication of the *r*-NM-junction valid, setting it as a viable platform for the investigation of HKUST-1 ultrathin films, preserving its integrity. It also allows further device configurations requiring photolithography onto the surface of HKUST-1 films, since the process is maintained as described.

5.4.1. Atomic Force Microscopy

Relative to the thicknesses chosen for the investigation as dielectrics in the *r*-NM-based capacitors, AFM measurements of the steps for the thinner (10-cycles samples) and the thicker (40-cycles samples) of the HKUST-1 SURMOF films are around 20 and 80 nm, respectively, as shown in **Figure 30a,c**.

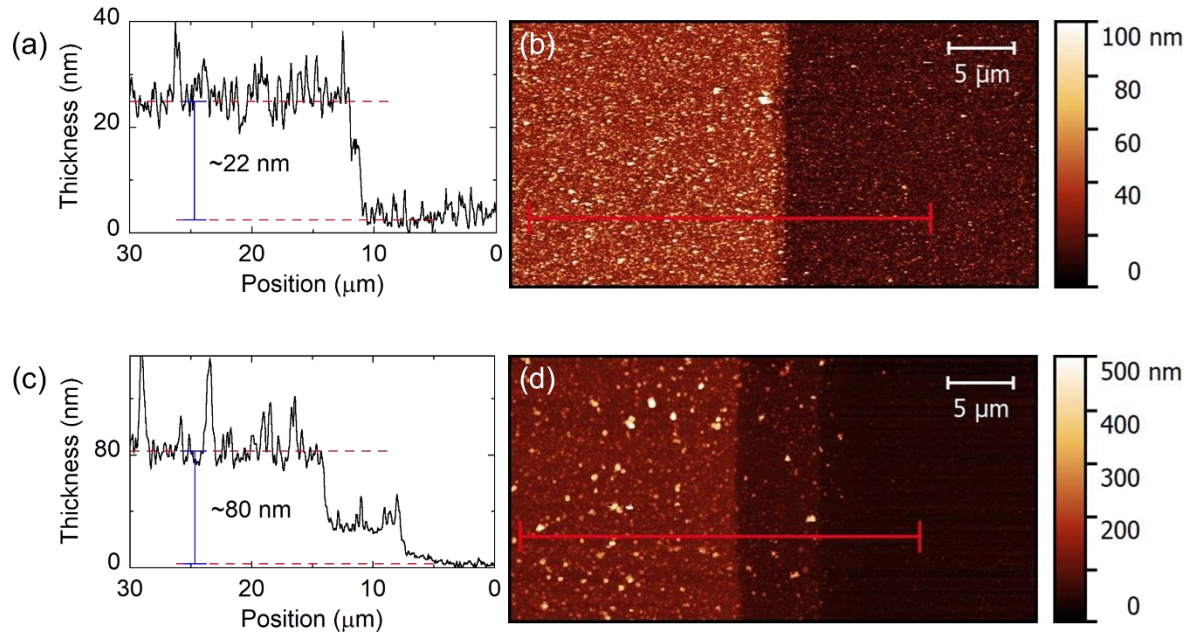


Figure 30: (a) Profile of the HKUST-1 SURMOF thickness for 10 deposition cycles obtained from the 20 μm x 40 μm AFM topography image shown in (b). (c) Profile HKUST-1 SURMOF thickness for 40 deposition cycles obtained from the 20 μm x 40 μm AFM topography image shown in (d). **Source:** extracted from (SILVA et al., 2022).

AFM images of the topographies for the respective thicknesses of the SURMOF are shown in **Figure 30b,d**. In both cases, the films have a homogenous surface without pinholes and significant agglomerates for a 5 μm x 5 μm area. The surface roughness, corresponding to the *RMS*, was found as 10.4 ± 0.3 nm and 41.2 ± 8.3 nm, respectively. These values are compatible with typical SURMOF films (VELLO et al., 2020).

Figure 31a (inset) shows the mean clusters size of 16.5 ± 5.2 nm for 10-nm-thick films, while for 40-nm-thick films, the mean size of 2.4 ± 0.8 was obtained, as demonstrated in **Figure 31c (inset)**. Both histograms were plotted using data extracted from the images in **Figure 31a-d**.

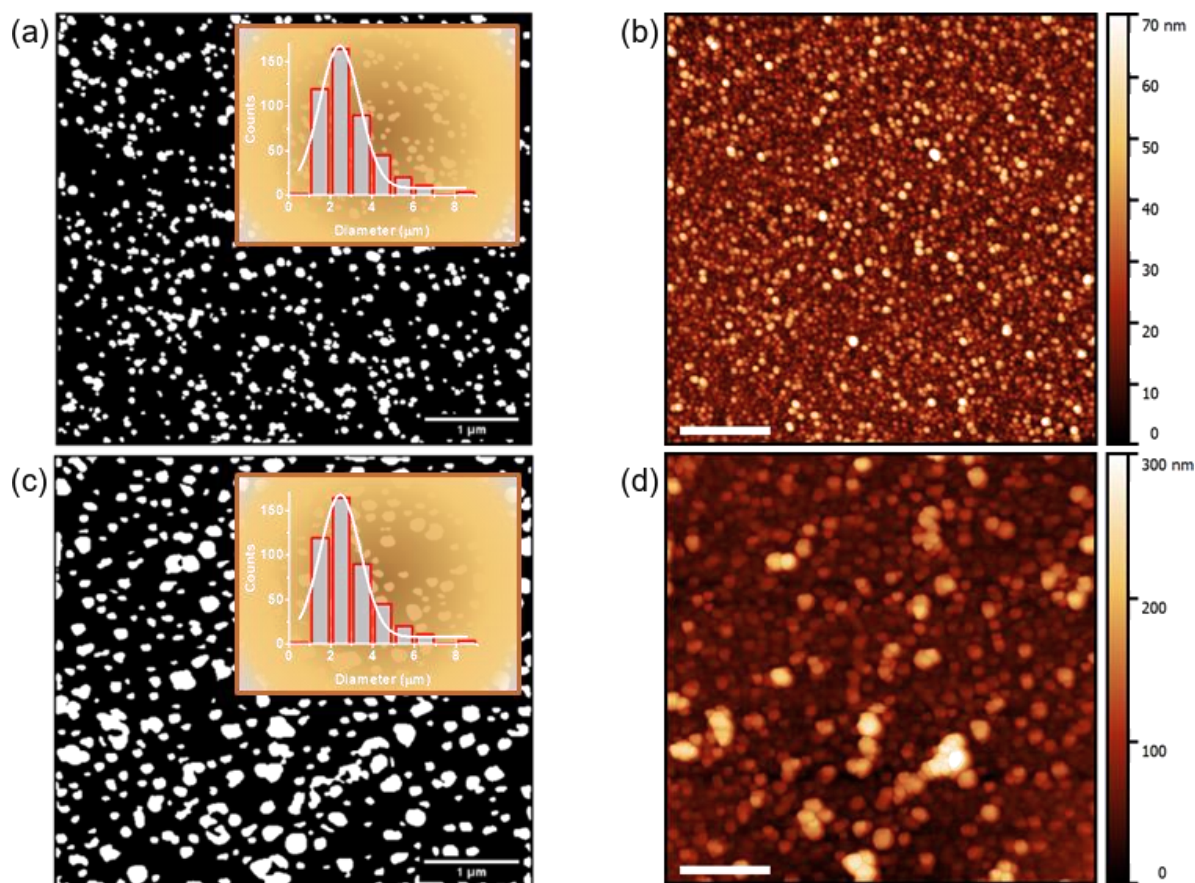


Figure 31: $5\ \mu\text{m} \times 5\ \mu\text{m}$ AFM topography images of the HKUST-1 SURMOF films for: (a) 10 deposition cycles of a black and white threshold-created treated image showing a cluster size of about 5 nm, with its respective (b) original AFM image; (c) 40 deposition cycles of a black and white threshold-created treated image showing a cluster size of about 0.5 μm , with its respective (d) original AFM image. **Source:** extracted from (SILVA et al., 2022).

The increase of *RMS* owing to the cluster size for thicker SURMOF films is coupled with the number of deposition cycles, as well as the preferential growth directions observed in **Figure 28**.

CHAPTER VI: MP_C THIN FILMS INTO ULTRACOMPACT CAPACITORS

6.1. ON THE MICRO / NANOSCALE CAPACITIVE DEVICES

The fundamentals holding up the dielectric response of nanoscale materials regard mainly the concepts that arise from mesoscopic chemical physics (VILAN; ASWAL; CAHEN, 2017). The characteristics arising from the “lightweight” structure of nanoscale organic materials, their small spin-orbit coupling, and the ability in providing nano-objects with biofunctional properties, have continuously been proposed to enhance the efficiency of the devices, power consumption, energy recovery, as well as biological and environmental compatibility (LIAO et al., 2015). For organic solar cells, for example, determining the dielectric properties of organic semiconductor (OSC) molecules at the nanoscale is extremely relevant. There, molecular engineering and dielectric polarization analyses have allowed the achievement of closer-to-ideal conditions for charge separation between active molecular layers and electrodes (ARMIN et al., 2017). Another example is related to the development of electro-mechanical logic gates for distributed multi-element smart systems, where the understanding of materials polarization has led to the improvement of the electric response of devices (CHORTOS et al., 2020; O'BRIEN et al., 2010). Furthermore, miniaturized pumps and valves for lab-on-a-chip applications also have benefitted from the research on the polarization effects in nanoscaled objects. In this case, the enhancement of mechanical response due to changings in the polarization of elastomers has improved the operation of actuators within microvalves systems (KUSSMAUL et al., 2011; RENARD et al., 2017).

However, when it comes to the incorporation of molecular nanomaterials into functional hybrid organic/inorganic devices, there is an important task still pending: how to guarantee the integrity of few-molecule active layers, thus preserving their envisioned function. In this scenario, the deposition of electrodes on top of the molecular layers has severe limitations (ARISTOV et al., 2005; SHEN; KAHN, 2001). Alternatively, some approaches consider using liquid-metal, or even employ stamp methodologies and lift-off assisted techniques, to place electrodes in close contact with molecules (HAICK; CAHEN, 2008). For such methods, the device integrability within hands-on electronics is usually compromised. Despite this, an

effective approach aligned with the simplicity of microfabrication techniques consists of using *r-NMs*. The *r-NMs* can provide an accurate and reliable contact between molecular ensembles and metal electrodes via the controlled releasing of surface-like structures (LEANDRO MERCES, 2018). For electronics, the *r-NM* technology also provides an inherent advantage of reducing the footprint of the devices, giving rise to ultracompact circuitry components (KARNAUSHENKO; KANG; SCHMIDT, 2019; WANG et al., 2019) such as energy storage units (BOF BUFON et al., 2010), sensors (MERCES; DE OLIVEIRA; BOF BUFON, 2018), inductors (KARNAUSHENKO; KANG; SCHMIDT, 2019), biosensors (HWANG et al., 2015), capacitors (PETRINI et al., 2018), transistors (GRIMM et al., 2013), memristors (ALBANO et al., 2020), and vertical heterojunctions (DE OLIVEIRA et al., 2018; MERCES et al., 2017a).

Here, the organic semiconductor-like MPcs are incorporated as dielectric layers into *rNM*-based devices. Thin films of 5 nm of CuPc, CoPc, and F₁₆CuPc were deposited on the capacitive devices, followed by the roll-up of the system. Each *h-rCap* formed contains a different thickness (on the nanoscale) of the MPc placed between electrodes, as the rolling-up of the *NM* establishes a mechanical contact between the organic ensembles and the strained layer.

6.2. DEVICES ENSEMBLE

The fabrication details of the devices are described in Section 3.1.3.2 The fabrication steps are also detailed in **Figure 15**. To create the hybrid structure, the molecular ensembles were deposited onto the *NM*-based structures from powder (CuPc - Alfa Aesar; CoPc - Alfa Aesar; F₁₆CuPc - Sigma Aldrich) on top of the upper Al₂O₃ dielectric layer. The hybrid organic/inorganic capacitors were obtained from the self-rolling of such planar devices. The *NM* releasing (self-rolling) of the devices is detailed in Section 3.2.1, and the electric characterization description can be found in Section 4.2.1.

6.3. PHTHALOCYANINES AS DIELECTRIC LAYERS

Thin films of metal MPcs (*viz.*, CuPc, CoPc, and F₁₆CuPc) as dielectric layers between electrodes, in a capacitor-like structure, were possible by the incorporation of the molecular

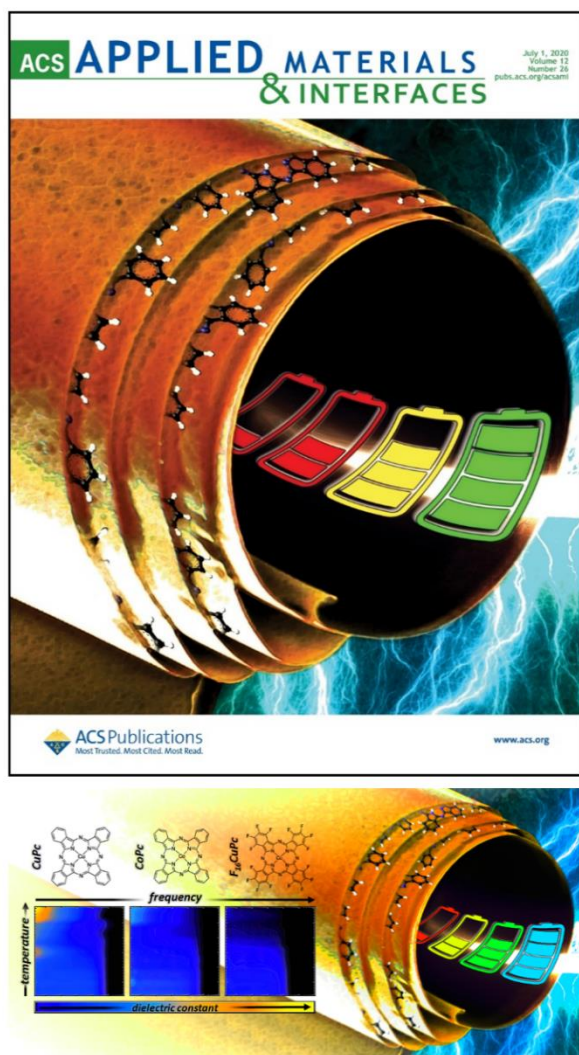


Figure 32: Cover page of *Applied Materials & Interfaces*, volume 12, number 26 (top panel), and article divulgation image (bottom panel) of the article entitled *Temperature-Independent Polarization of Ultrathin Phthalocyanine-Based Hybrid Organic/Inorganic Heterojunctions*. **Source:** adapted from (SILVA; MERCES; BOF BUFON, 2020).

layers into *NM*-based capacitors. The *roll-up* technique brought a new approach to the study and comparison of the polarization mechanisms relative to minor modifications to the Pc molecular structure. The results of such a study were published (SILVA; MERCES; BOF BUFON, 2020) and highlighted on the cover page of the scientific journal *Applied Materials & Interfaces*, volume 12, number 26, as reprinted in **Figure 32**.

6.3.1. Design of Each Capacitive Structure Assayed

The devices fabricated in planar, and tubular (self-rolled) configurations are shown in **Figure 33**. The planar heterojunction (*i-pCap*, **Figure 33a**) – regards a simple parallel-plate capacitor having an Al_2O_3 dielectric layer sandwiched by two Cr plates (10-nm-thick each). Also, the samples were designed to allow the manufacture of either inorganic *r-NM* heterojunctions (*i-rCap*, **Figure 33b**) or

hybrid organic/inorganic devices (*h-rCap*, **Figure 33c**). As organic materials, 5-nm-thick MPc ensembles (4-7 molecules stacked up) were used. The device cross-sectional views, as well as each equivalent-circuit expansion in terms of impedance, are presented in **Figure 33d-f**. Circuit terminals A and B stand for the top and bottom electrodes, respectively. A direct comparison between *i-rCap* and *h-rCap* may be done by considering each MPc layer grown at the top of the *i-pCap* as an impedance Z_m^r placed in series to Z_i^r – both in parallel to Z_i – to compose the total impedance of the *h-rCap*. The labels *i*, *h*, *m*, and *r* stand for “inorganic,” “hybrid,” “molecular” and “rolled-up”, respectively. Au was employed as the material of electrode

contacting the MPC ultrathin films to guarantee small contact resistance (DE OLIVEIRA et al., 2016; MERCES et al., 2017b). The contact regions of the *i-rCap* and *h-rCap* (i.e. the result from the roll-up process) are evidenced by (i) the orange double-arrow in **Figure 33e**, and (ii) the green double-arrow in **Figure 33f**. Such arrows represent the geometrical contact formed between the bottom electrode and the top active material as the NM rolls up. This contact has a mechanical nature, so the effective contacting region is expected to be smaller than the geometrical area due to the roughness of the materials (MERCES et al., 2017a; MERCES; DE OLIVEIRA; BOF BUFON, 2018).

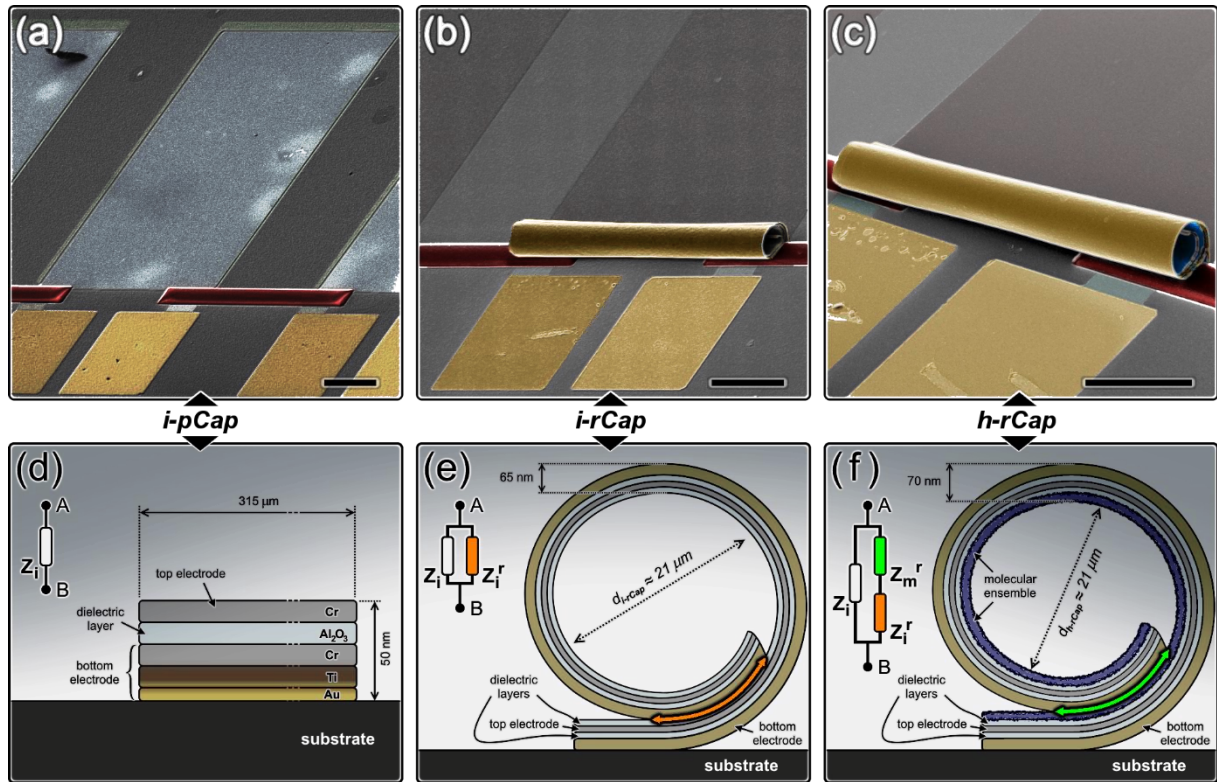


Figure 33: SEM images of the devices: (a) *i-pCap*, (b) *i-rCap*, and (c) *h-rCap*. The SEM images were artificially colored. The scale bars in panels (a-c) are 40 μm long. The cross-sectional view of each device is illustrated in panels (d-f) below the respective SEM image. Each dielectric layer is considered as an impedance (Z) in the system – see each equivalent-circuit expansion as **insets** in the panels (d-f). **Source:** extracted from (SILVA; MERCES; BOF BUFON, 2020).

In this scenario, both devices *i-pCap* and *i-rCap* were used to estimate the active area of the *h-rCap*. For this purpose, the Al_2O_3 dielectric properties were determined from the *i-pCap* and then employed to estimate the active area between the windings of the *i-rCap*. Notice that *i-pCap* and *i-rCap* are composed of similar dielectrics. As the 5-nm-thick MPC layers have not modified the diameter or the number of windings for the devices, it is assumed that the self-rolled active areas are similar to each other, either considering *i-rCap* or *h-rCap* (see the double-

arrows in **Figure 33e** and **Figure 33f**, respectively). Such an assumption is fulfilled by the surface roughness values obtained for each active material – *i.e.*, < 4 nm for Al_2O_3 films (400-nm-thick), and 1.4, 1.3, and 1.3 nm for CuPc, CoPc, and F_{16}CuPc films, respectively (10-nm-thick). The details on the topography of the as-grown active films by AFM images are presented in **Figure 24**, such as for the Al_2O_3 in **Figure 23**.

6.3.2. Impedance Spectroscopy vs. Temperature

The electrical measurements were performed at 25 different T -values, ranging from 6 to 300 K, for the three device configurations. To rule out the effects of T on the self-rolled active

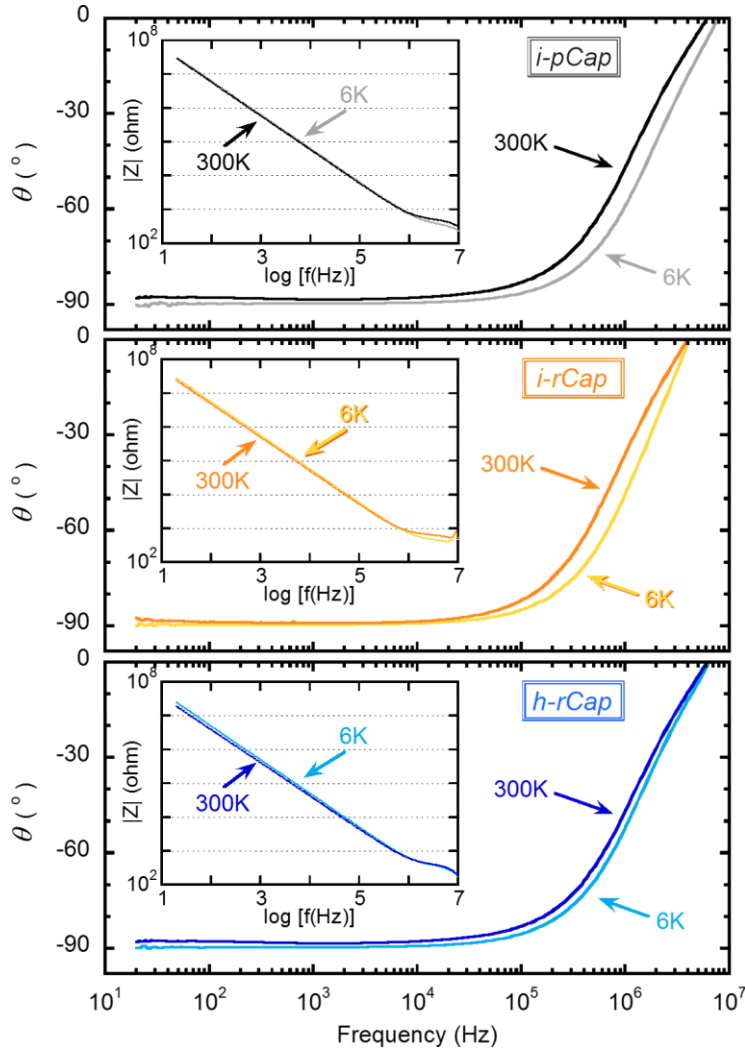


Figure 34: Impedance phase (θ) as a function of f at 6 K and 300 K for **(a) *i-pCap***, **(b) *i-rCap***, and **(c) *h-rCap***. **Inset:** Respective impedance modulus ($|Z|$) as a function of f at 6 K and 300 K. **Source:** extracted from (SILVA; MERCES; BOF BUFON, 2020)

areas, we have evaluated the impedance features of both *i-pCap* and *i-rCap* at each applied T . Hence, each inorganic component of the *h-rCap* was previously considered. **Figure 34** shows the direct influence of T on the impedance measured for the three device architectures.

In **Figure 34**, the devices preserved the capacitive behavior for $20 < f < 10^5$ Hz, as indicated by the impedance phase angles (θ) close to -90° (**Figure 34a-c**). Such a behavior has been found predominant at both 6 and 300 K. Notice, however, that θ has slightly shifted toward capacitive angles at low temperatures – the 6 K-traces (**Figure 34**) are closer to $\theta = -90^\circ$ than the 300 K-traces.

Along with θ measured for *iCap*, *i-rCap*, and *h-rCap*, each respective impedance modulus is shown as insets of **Figure 34a-c**. One may observe a soft increase of the impedance modulus of each device due to T lowering, indicating a drop of the leakage current – *i.e.*, the current through dielectric and semiconducting films, as suggests the plot in **Figure 35**.

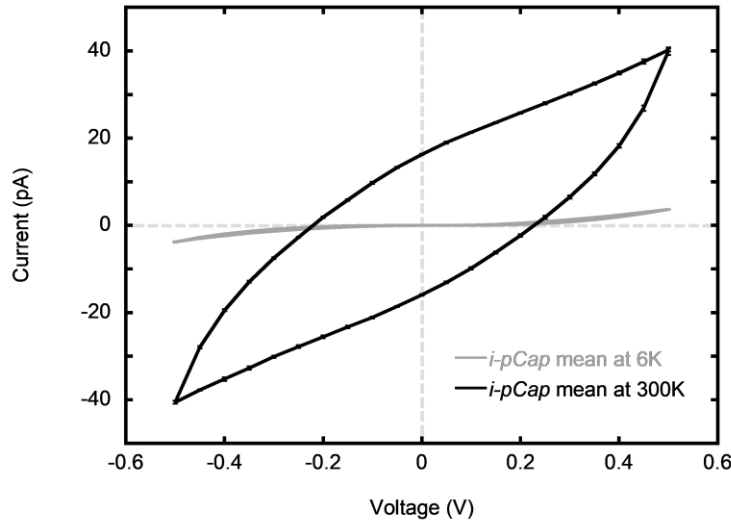


Figure 35: IxV plot graph for *i-pCap* with Al_2O_3 dielectric layer, showing the leakage current through the film at 6K and 300K. **Source:** the author.

However, it is worth mentioning that the increments of impedance moduli do not necessarily increase dielectric polarization. Both film polarization and leakage current (*i.e.*, by trapping/de-trapping of charges) may contribute to the measured impedance (HRAIBAT et al., 2013; MAGLIONE, 2016; WANG; ZHANG, 2007). By reducing T , the thermoactivated mechanisms

of transport and polarization are expected to decrease or even vanish (HRAIBAT et al., 2013; WANG; ZHANG, 2007). The increasing impedance modulus thus implies a decrease of free charge carrier density in the active materials. Consequently, the contribution of leakage current to the polarization of the system is reduced. Hence, the suppression of charge trapping/de-trapping events by decreasing T was found capable of restraining the resultant polarization in the materials to an intrinsic dielectric response.

6.3.3. Capacitive Response at Low- T

The device geometries and the impedance investigation allowed us to treat the active materials as effective dielectric layers in capacitive arrangements. The model used here thus considers the systems as ideal capacitors connected in parallel to resistive elements that are responsible for the small leakage currents. Such an assumption is known as $C_p - R_p$ approach. The measured impedances have provided profiles of capacitance spectroscopies as a function of T (from 6 K to 300 K). **Figure 36** shows the influence of T on the capacitance (C_p) measured

for *i-pCap*, *i-rCap*, and *h-rCap*, employing CuPc as the organic semiconducting layer (ca. 5-nm-thick).

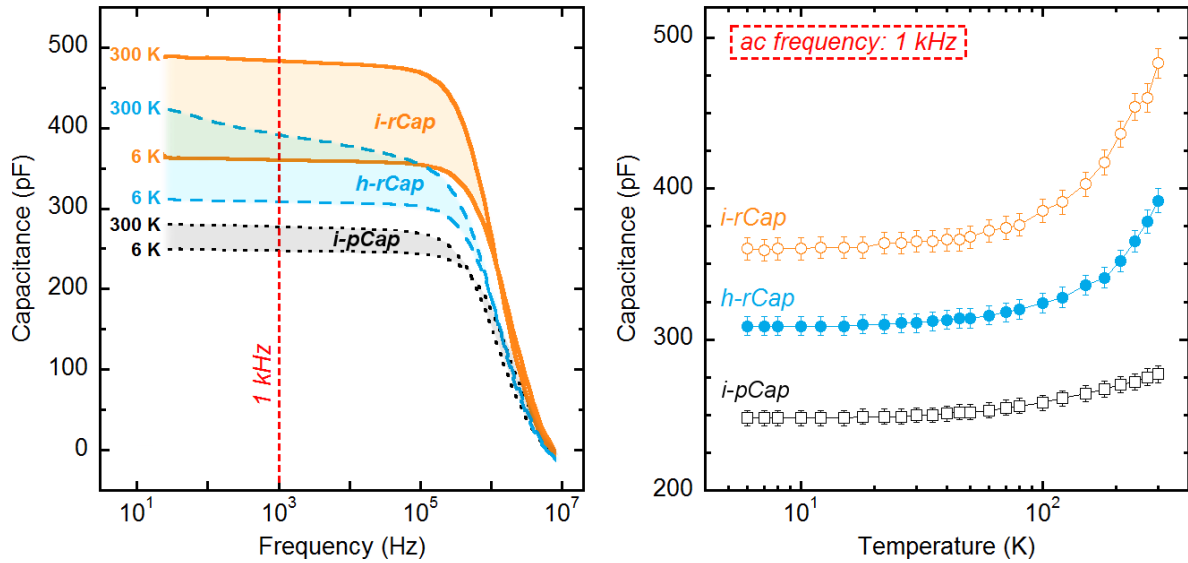


Figure 36: (a) Capacitance as a function of f for each device architecture at 6 and 300 K. (b) Capacitance as a function of T for $f = 10^3$ Hz. **Source:** extracted from (SILVA; MERCES; BOF BUFON, 2020).

In **Figure 36**, regardless of the distinct capacitor architectures, one may see that the decrease of T from 300 to 6 K implies an overall decrease in capacitance. As the capacitance decreases, the charge accumulation in a dielectric film is expected to decrease as well. For the Al_2O_3 films in *i-pCap* and *i-rCap*, as T drops, a reduction of the accumulation mechanisms is observed at the whole frequency-range, so that the capacitance-frequency curves (plateaus) are preserved. The plateaus extend from 20 to 10⁵ Hz, indicating that the active Al_2O_3 dielectrics are most likely homogeneous (AZAM et al., 2010; MACEDO; OLIVEIRA; HERNANDES, 2007). Acharya, J. *et al.* demonstrated that nanometer-thick Al_2O_3 dielectrics growth by ALD exhibits high structural quality as well as low leakage current (ACHARYA et al., 2018). Here, the dielectric uniformity is evaluated by measuring the topography of an as-grown Al_2O_3 layer (250 ALD cycles). An *RMS* of ca. 4.0 nm is found – see the atomic force microscopy image in **Figure 23**. Thus, the small number of defects in the as-grown Al_2O_3 films could provide the dielectric layers of *i-pCap* and *i-rCap* with charge accumulation intrinsically correlated to the presence of small structural dipoles.

On the other hand, the *h-rCap* measurements include the contribution of CuPc as a molecular counterpart (Z_m^r , see **Figure 33f**) forming the hybrid organic/inorganic heterojunction. The direct product of the CuPc incorporation within the system is the emerging

of transient currents composed of charge carriers that populate/de-populate the OSC trap centers as f changes. Depending on the material time constants, the transient currents are expected to change as the field frequency increase, resulting on the impedance variation measured (SCHNORR et al., 2016). At 300 K, the *h-rCap* capacitance profile (**Figure 36a**) was found f -dependent within the whole experimental range investigated ($20 < f < 10^5$ Hz). However, at low temperatures (viz, $T = 6$ K), the capacitance of the *h-rCap* is characterized by a well-established plateau for $f < 10^5$ Hz (**Figure 36a**).

To directly visualize the dependence on T of the capacitance in the devices, **Figure 36b** depicts C_p vs. T curves obtained at $f = 10^3$ Hz. Such a frequency is representative of the plateau characteristics observed, mainly considering the response of the devices at the lowest temperatures. For $T < 80$ K, the capacitances were found practically T -independent. Above $T \sim 120$ K the capacitance is strongly influenced by T . One may notice that *i-rCap* and *h-rCap* have exhibited the most prominent capacitance dependence on T , while the *i-pCap* has displayed smaller capacitance changes in similar conditions. Such a discrepancy probably arises from the distinct interface formed spontaneously during the self-rolling of the *NM*, since the roll-up process (for *i-rCap* and *h-rCap*) gives rise to mechanically made interfaces, distinct from the as-deposited ones (of *i-pCap*). Macedo, Z. S. et al. reported the occurrence of a similar T -dependence of capacitance when structure inhomogeneity provides devices with space-charge and thermally activated effects usually modeled by the Maxwell-Wagner approach (MACEDO; OLIVEIRA; HERNANDES, 2007). Accordingly, that inhomogeneity may arise from grain boundaries, porosity, and defects (AZAM et al., 2010). In the particular case presented in this work, defects such as interfacial voids are more expected to be found at the mechanical contact established by the *rNM*, as described in previous work from my group (PETRINI et al., 2018). Therefore, as the thermally activated effects were not observed to take place in any device for $T < 80$ K, here it is attributed to the decreasing of T the suppression of inhomogeneity-driven polarization mechanisms, such as those attributed to the mechanically formed interfaces.

6.3.4. Modeling the Electric Permittivity of the Active Materials

For temperatures in which the capacitance plateaus were observed, the active-materials permittivity was calculated for the full range of frequencies investigated (from 20 to 10^7 Hz).

The plateau characteristics have been successfully adjusted by the Havriliak-Negami formalism given by:

$$\varepsilon_r^* = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{[1 + (i \cdot \omega \cdot \tau)^\alpha]^\beta} \quad (71)$$

where ε_r^* is the complex relative permittivity, ε_∞ the relative permittivity at the high-frequency limit, ε_S the static (low-frequency) relative permittivity, ω the angular frequency of the applied electric field, and τ the relaxation time of the dielectric at a given T . The parameters α and β account for the frequency dispersion. The capacitance plateaus observed for low thermal activation energies were well-adjusted by a particular case of the Havriliak-Negami formalism in which $\alpha = \beta = 1$ – i.e., a situation equivalent to Debye's predictions on dielectric relaxation. The Debye relaxation accounts for the dielectric response of a population of dipoles submitted to an alternating external electric field but displaying reduced interactions with each other. Such a quasi-ideal condition of polarization has been achieved here by reducing the thermal activation of the systems. Accordingly, the real part (ε_r' , i.e.,) and imaginary part (ε_r'') of the relative permittivity of the material is given by:

$$\varepsilon_r' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + \omega^2 \cdot \tau^2} \quad \varepsilon_r'' = \frac{(\varepsilon_S - \varepsilon_\infty) \cdot \omega \cdot \tau}{1 + \omega^2 \cdot \tau^2} \quad (72)$$

Given equations 71 and 72, we proceed with evaluating the dielectric properties of both the Al_2O_3 layer and the MPc semiconducting films. The calculations of relaxation time (τ) and dielectric constant (ε_r') were made using the experimental data acquired at each T . **Figure 37** (top panel) exhibits the relative permittivity map – as a function of T and f – obtained for the 15-nm-thick Al_2O_3 films employed in the *i-pCap*. Such data analysis is important for the evaluation of the dielectric characteristics of the MPc ultrathin films since the *h-rCaps* have contributions from both *i-pCap* and *i-rCap*. One can note the slight recoil in the frequency for the relative permittivity decay at the temperature around 240 K, which derives from an artifact on that specific measurement, probably due to a bad probe contact. Such detail shall not jeopardize further analysis performed here, for it mostly does not minutely assess the results on this specific temperature. **Figure 37** (bottom panel) shows the Al_2O_3 relative permittivity as a function of f for $T = 6$ K and $T = 300$ K.

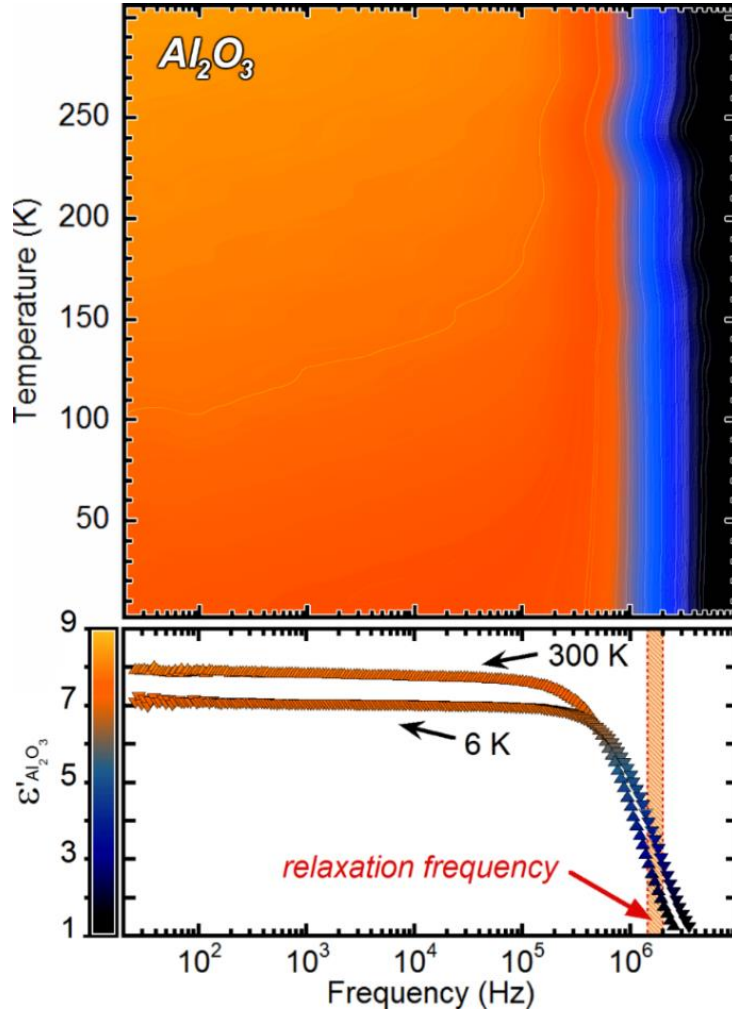


Figure 37: Relative permittivity for a 15-nm-thick Al_2O_3 film *i-pCap*. The top panel exhibits the diagram of permittivity as a function of f (abscissa axis) and T (ordinate axis). The color scale bar is shown in the bottom panel along with the permittivity-frequency plot obtained at 6 and 300 K. **Source:** extracted from (SILVA; MERCES; BOF BUFON, 2020).

permittivity within the plateau region occurred along with the f increments. This indicates that polarization mechanisms originating from space-charge (movement of charged particles related) phenomena, namely: (i) Maxwell-Wagner-Sillars interfacial effect (mostly present in multiphasic materials) and/or (ii) Hopping charge transport are both negligible (AZAM et al., 2010; MACEDO; OLIVEIRA; HERNANDES, 2007; YOU et al., 2006).

The respective fits to Equations 72 can be found in **Figure 38**, where the real and imaginary parts of the complex capacitance (C^*), relative to the geometrical capacitance ($C_0 = \epsilon_0 \cdot A/t$), are depicted. The capacitive reactance ($Z = j.X_C = -1/(j.\omega.C)$) from the *i-pCap* measured was used for the extraction of the C^* . The polarization mechanisms occurring in the Al_2O_3 film, as well as the *i-pCap* capacitance, were found slightly depending on T . Thus, $\epsilon'_{r\text{Al}_2\text{O}_3}$ exhibits a less pronounced decrease when the system is cooled down and the plateau characteristics found at $T = 300$ K are preserved as T decreases.

In **Figure 37** (bottom panel) and **Figure 38a**, for fixed T -values, no variation of the

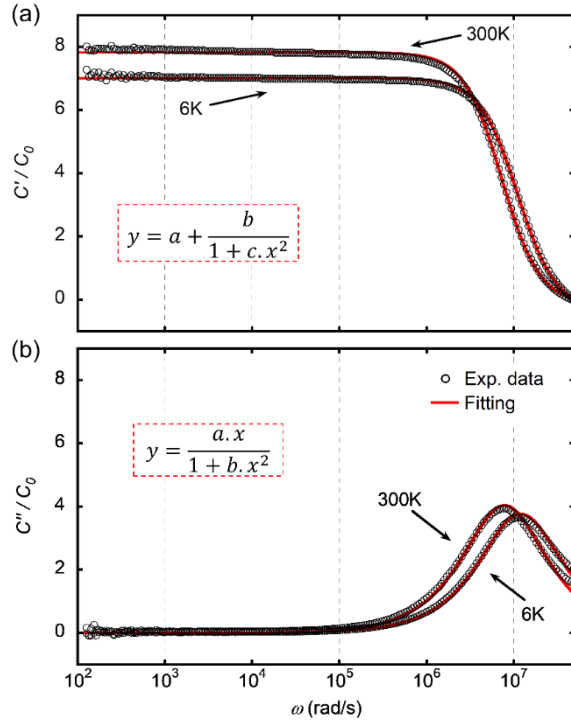


Figure 38: (a) Real and (b) imaginary part of the capacitance of the Al_2O_3 , relative to the geometric capacitance value of the parallel-plates device, both at 6 and 300 K. The lines are curves fitted by the respective Debye model, exhibited as **inset** panels. **Source:** extracted from (SILVA; MERCES; BOF BUFON, 2020).

As a result, $\varepsilon'_{r\text{Al}_2\text{O}_3} = 7.4 \pm 0.6$ was found for $20 < f < 2.0 \times 10^6$ Hz regardless of the T -values. Similar values have been reported previously in the literature for Al_2O_3 thin films employed as dielectric layers of capacitors (KHOSA et al., 2018; ROBERTSON, 2004; VANBESIEN et al., 2006). Details on the Al_2O_3 dielectric loss factor are also provided in **Figure 38b**. Furthermore, the plateau observed at $T = 6$ K indicates that the primary polarization mechanism of induced dipoles begins to relax at $f_{\text{rel}} \sim 1.5 - 2.0 \times 10^6$ Hz, similarly to the 300 K-plateau characteristics. Such a relaxation frequency f_{rel} stands for the maximum electric-field variation rate that the predominant polarization mechanism can follow. Hence, from the approximation of f_{rel}

it is possible to estimate a value of $\tau_{\text{Al}_2\text{O}_3} \sim 0.5\text{-}0.7$ μs . In fact, the measured data were fitted to Equation 72 (**Figure 38**, determination coefficient $R^2 > 0.99$) and allowed the calculation of $\tau_{\text{Al}_2\text{O}_3} = 1.0 \pm 0.1$ μs . One can note that the approximation of the dielectric behavior on the oxide films really fits to the presupposed mechanism for all the range investigated on this work, as demonstrate in **Figure 37** and later in **Figure 39**.

6.3.5. Dielectric Properties of the Ultrathin Semiconducting Molecular Ensembles

Here the role of ultrathin (~ 5 nm) MPC ensembles on the charge accumulation of the hybrid structures is discussed. The MPC molecules behave as organic semiconductors when forming thin and ultrathin films (MELVILLE; LESSARD; BENDER, 2015; SAGAR et al., 2006; ZHOU; SUN, 2011). Consequently, the MPC ensembles forming the upper dielectrics in $h\text{-rCap}$ (**Figure 33c,f**) are expected, at low- T , to preferentially accumulate charges instead of conducting them. **Figure 39** exhibits permittivity diagrams – color-scale bar in panel (d) – of the 5-nm-thick ensembles (CuPc, CoPc, and F_{16}CuPc) as a function of T and f . Each MPC

structure is depicted as an inset of the respective permittivity map of **Figure 39a-c**. Depending on the molecular structure and growth orientation, 5-nm-thick MPC ensembles are expected to form stacks of $\sim 4 - 7$ molecules (DE OLIVEIRA et al., 2018; PEISERT et al., 2009). As shown in **Figure 39**, each of the molecular-ensemble permittivity exhibit a dependence on T for $T > T'$ (see the dotted lines in **Figure 39a-c**). The value of T' was experimentally determined as the minimum temperature at which polarization could be thermally influenced.

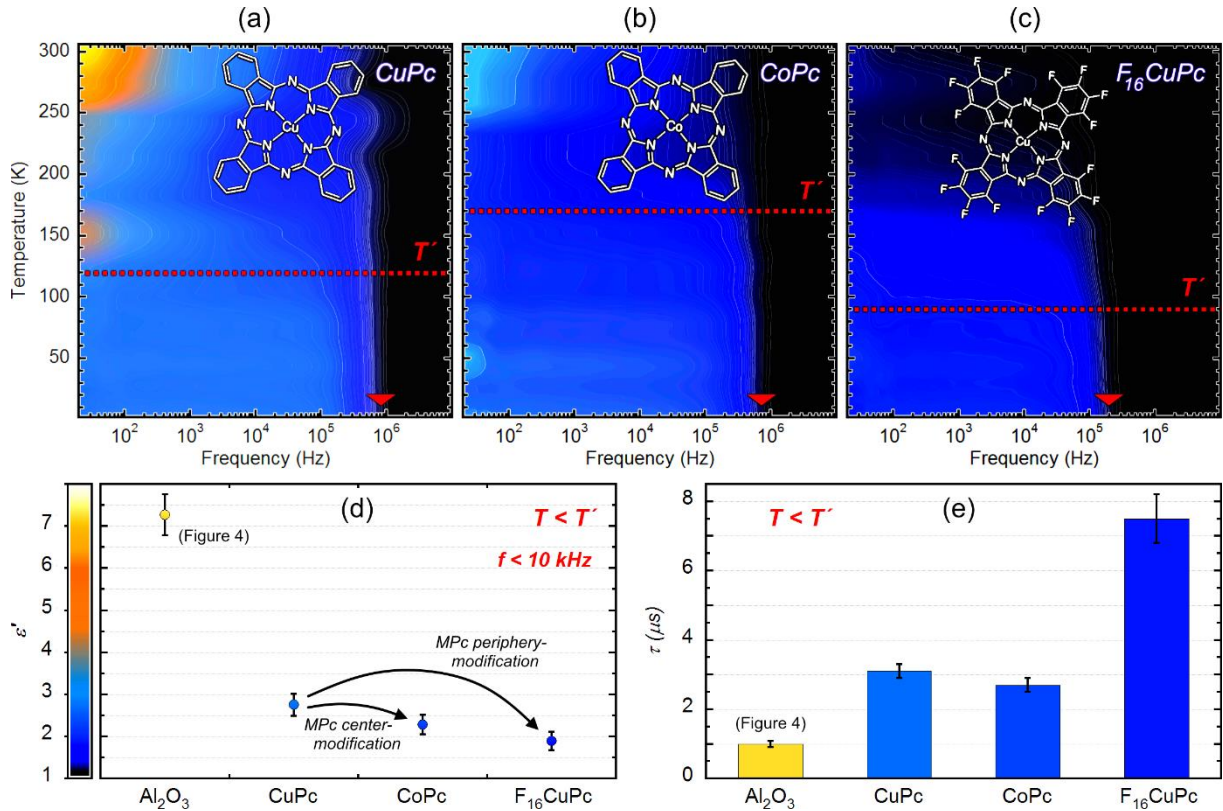


Figure 39: Relative permittivity diagrams of 5-nm-thick molecular ensembles of (a) CuPc, (b) CoPc, and (c) F_{16} CuPc, as a function of f and T . (d) Permittivity values calculated for $T < T'$ and $f < 10^4$ Hz and the color scale bar. The respective relaxation times are exhibited in panel (e). **Source:** extracted from (SILVA; MERCES; BOF BUFON, 2020).

For $T > T'$ (**Figure 39a-c**), the permittivity of each MPC decreases as f increases. Such behavior is observed for $f < 10^5$ Hz, indicating the presence of polarization mechanisms originating from the MPC films and respective interfaces (HRAIBAT et al., 2013; SALEH et al., 2012; SHIHUB; GOULD, 1995). According to literature, the charge transport across conjugated molecules (viz. MPC), as well as the presence of defects at the structure interfaces (viz. Al_2O_3 /MPC, MPC/Au) may result in charge accumulation along with the active transport channel in the device – giving rise to the f -dependent polarization observed at low- f (MAGLIONE, 2016; WANG; ZHANG, 2007). As f increases, the free-monopole effects, such

as leakage current and population/depopulation of traps, are likely to fade away since the moving charges become unable to follow the alternating field (WANG; ZHANG, 2007). At $T = 300$ K for example, we found $\varepsilon'_{r\text{ CuPc}}$ varying from *ca.* 6 to *ca.* 2 for $20\text{ Hz} < f < 10^5\text{ Hz}$. Concerning this measurement, we have found $\varepsilon'_{r\text{ CuPc}} \sim 4.2 \pm 0.4$ ($T = 300\text{ K}$, $f \sim 10^{2-3}\text{ Hz}$) which is in agreement with the value of the dielectric constant for CuPc ensembles as a function of film thickness, previously reported by our group (PETRINI et al., 2018). Furthermore, under similar experimental conditions (*i.e.*, $T = 300\text{ K}$, $f \sim 10^{2-3}\text{ Hz}$), here was found $\varepsilon'_{r\text{ CoPc}} \sim 2.8 \pm 0.1$ and $\varepsilon'_{r\text{ F16CuPc}} \sim 1.3 \pm 0.1$ (**Figure 39d**).

The permittivity measurements as a function of T and f have revealed that thermally activated polarization, which also involves the transit of electric monopoles, may be suppressed for $T < T'$. Within this temperature range, information about the intrinsic polarization mechanisms can be investigated as a function of (i) MPc structure (*i.e.*, central, and peripheral modifications), and (ii) MPc orientation at the inorganic interfaces (Al_2O_3 and Au). For $T < T'$, the plateaus of MPc permittivity were observed for $20\text{ Hz} < f < 10^5\text{ Hz}$ because of suppression of leakage current and low thermal activation energy of the MPc. The values of f_{rel} ($\sim 10^{5-6}\text{ Hz}$) are indicated by arrowheads on the x -axis of each permittivity plot in **Figure 39e**.

6.3.6. The Role of Pc Structure on Molecular-Ensemble Dielectric Properties

Figure 39d exhibits a direct comparison between the T -independent permittivity of the ensembles. The permittivity of Al_2O_3 employed as the inorganic dielectric layer in the hybrid device was plotted in addition. The values of MPc permittivity exhibited in **Figure 39d** were calculated considering $T < T'$ and $f < 10^4\text{ Hz}$ (lower than f_{rel}). The electronic structure and atomic polarizability of the metal atom in the molecule core are expected to influence the real part of MPc permittivity (HRAIBAT et al., 2013). In this scenario, considering the replacement of Cu by Co at the center of the MPc molecule, the permittivity of the 5-nm-thick ensembles was found to decrease from $\varepsilon'_{r\text{ CuPc}} = 2.8 \pm 0.3$ to $\varepsilon'_{r\text{ CoPc}} = 2.3 \pm 0.2$. According to literature, the center of CoPc is expected to provide the molecule with more electron affinity than Cu provides for CuPc (LIAO; SCHEINER, 2001). The Co atom has also displayed binding energies higher than those found for the Cu complex (BUIMAGA-IARINCA; MORARI, 2018; LIAO; SCHEINER, 2001). From combined- and inverse-photoemission investigations, CoPc molecules were found strongly interacting with both conductive and insulating substrates, while the CuPc molecules weakly interact with insulators (XIAO; DOWBEN, 2009). Consequently,

the CoPc is expected to lay down on insulating substrates while the CuPc is likely to be found anisotropically oriented (BUIMAGA-IARINCA; MORARI, 2018; XIAO; DOWBEN, 2009). Therefore, the *h-rCaps* prepared here may exhibit different polarization once CuPc and CoPc ensembles have been sublimated on top of the Al₂O₃ surface. The contact asymmetry, namely Al₂O₃/CuPc/Au in comparison with Al₂O₃/CoPc/Au, may justify the higher polarization found for the 5-nm-thick CuPc ensembles ($\epsilon'_{r\text{ CuPc}} > \epsilon'_{r\text{ CoPc}}$).

In addition, **Figure 39** shows that the replacement of the CuPc peripheral H atoms by fluorine causes a variation of permittivity from $\epsilon'_{r\text{ CuPc}} = 2.8 \pm 0.3$ to $\epsilon'_{r\text{ F}_{16}\text{CuPc}} = 1.9 \pm 0.2$. Such a variation can be attributed to the decreasing electronic density at the neighboring MPc benzene groups due to the high fluorine electronegativity (PEISERT; KNUPFER; FINK, 2002; SCHUSTER et al., 2009). X-ray photoelectron spectroscopy (XPS) investigations have demonstrated that the changes in electronic density upon MPc fluorination also result in a decrease of the MPc/Au interface dipole (PAASCH et al., 2003; PEISERT; KNUPFER; FINK, 2002). As lower is the interface dipole, lower is the polarization when considering similar systems – specifically, 5-nm-thick ensembles of CuPc and F₁₆CuPc in contact with Au ($\epsilon'_{r\text{ CuPc}} > \epsilon'_{r\text{ F}_{16}\text{CuPc}}$).

The ϵ'_r -plateau characteristics observed for the 5-nm-thick MPc ensembles at $T < T'$ (**Figure 39a-c**) agree with the simplified Havriliak-Negami formalism (Equation 71, with $\alpha = \beta = 1$). The data fitting was done considering $T' = 120, 170,$ and 90 K for the CuPc, CoPc, and F₁₆CuPc ensembles, respectively. The data fittings, which returned $R^2 > 0.96$, are presented in **Figure 40**.

Also, the T -independent relaxation time (τ) of each MPc incorporated in the heterostructures was calculated. **Figure 39e** exhibits the values of τ

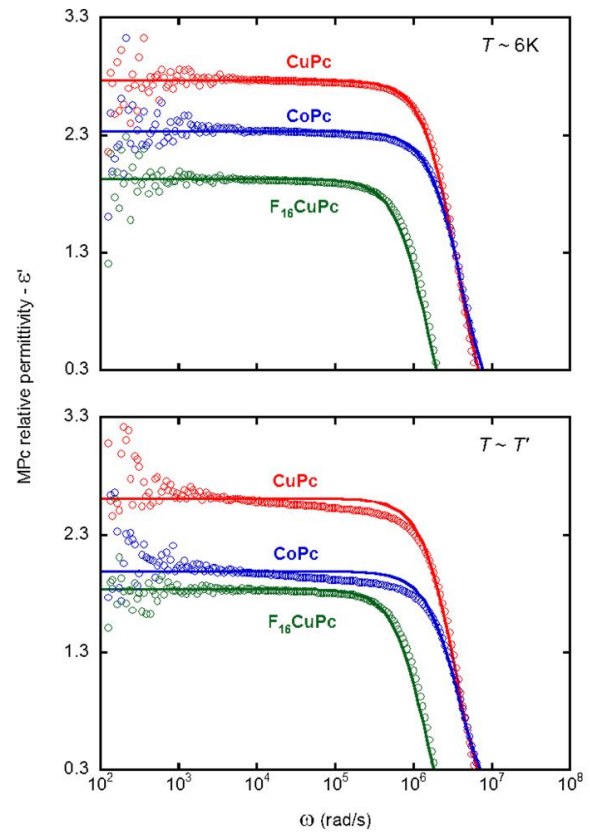


Figure 40: MPc relative permittivity at $T = T'$. The lines are curves fitted by the Havriliak-Negami model with $\alpha = \beta = 1$. **Source:** adapted from (SILVA; MERCES; BOF BUFON, 2020)

obtained for the MPc ensembles. The relaxation time of the Al_2O_3 dielectrics is also displayed for comparison. For CuPc, $\tau_{\text{CuPc}} = 3.0 \pm 0.2 \mu\text{s}$, while the CoPc ensemble exhibited a relaxation time of $\tau_{\text{CoPc}} = 2.7 \pm 0.2 \mu\text{s}$. In the literature, the dielectric relaxation times are in the order of $10^{-7} - 10^{-6} \text{ s}$ and are commonly attributed to dipolar effects such as induced polarization (WILSON et al., 2019). Here, the small differences between the relaxation time of the CoPc and CuPc may be related to the higher electronegativity of Co in comparison to Cu (LIAO; SCHEINER, 2001). This makes the electronic density in CoPc more center-concentrated than in CuPc. Such a gradient of electronegativity may be crucial to set how fast dielectric relaxation occurs. Therefore, while $\epsilon'_{r \text{ CoPc}} < \epsilon'_{r \text{ CuPc}}$ is a primer result of the distinct molecule-inorganics interfaces, $\tau_{\text{CoPc}} < \tau_{\text{CuPc}}$ indicates that the calculated relaxation seems to be more related to each single-molecule polarization along with the 5-nm-thick MPc films.

In **Figure 39e**, the molecular modification of CuPc by the fluorinated tail (F_{16}CuPc) is expected to impact the distribution of the MPc electronic density from the benzene groups to the peripheral fluorine (PEISERT; KNUPFER; FINK, 2002; SCHUSTER et al., 2009). Consequently, the electronegativity shifts from the metal center to the molecule periphery, which increases the relaxation time to $\tau_{\text{F}_{16}\text{CuPc}} = 7.5 \pm 0.6 \mu\text{s}$ ($> \tau_{\text{CuPc}}$). This means that the resultant dipoles established across the F_{16}CuPc ensembles require more time than the CuPc dipoles to complete relaxation, despite $\epsilon'_{r \text{ F}_{16}\text{CuPc}} < \epsilon'_{r \text{ CuPc}}$. The induced dipoles of F_{16}CuPc result from a molecular structure that is more intricate than the CuPc structure – *i.e.*, the fluorine atoms of F_{16}CuPc contribute with more constricted bonds, due to their high electronegativity (DONG et al., 2012; REICHENBÄCHER; SÜSS; HULLIGER, 2005; REN et al., 2011). Hence, the increase in the relaxation time due to CuPc fluorination (**Figure 39e**) confirms the hypothesis that the τ -differences are more likely related to the polarization of single molecules within the MPc ensembles, while the ϵ'_r -differences are more likely dependent on the close contact of the MPc ensembles with both Al_2O_3 dielectric and Au electrode.

CHAPTER VII: HKUST-1 SURMOF DIELECTRIC INVESTIGATION

7.1. INTRODUCING THE CHALLENGE

Establishing the *NM*-based capacitor structures for the exploitation of ultrathin films of organic materials has settled the basal background to the use of such architecture in the assessment of further (more “defiant”) materials. As the new promising class of materials for application in electronics, the hybrid HKUST-1 SURMOF was chosen to compose the *r-NM* structures for its dielectric investigation in ultrathin films. The unprecedented integration of ultrathin HKUST-1 SURMOF films into a 3D functional device architecture was the defiance here. Their dielectric properties are obtained by defining a soft electrical top contact using a freestanding nanomembrane that creates an ultracompact capacitor structure. The results of such a study were published in the scientific journal *Advanced Electronic Materials*, number 2200175 (SILVA et al., 2022), and the graphical abstract is reprinted in **Figure 41**.

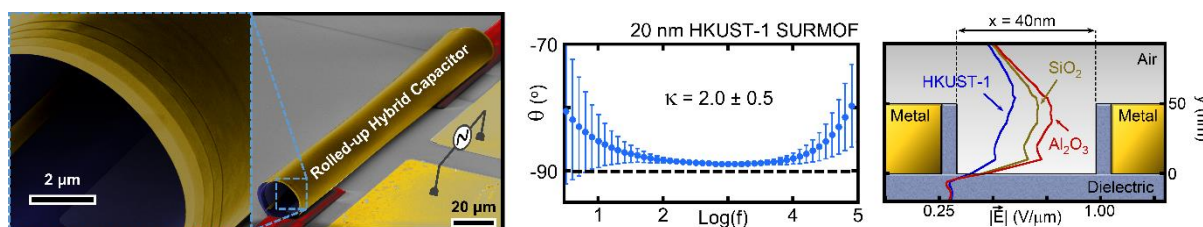


Figure 41: Graphical abstract of the work exploiting HKUST-1 ultrathin layers incorporated into *r-NM* capacitors. **Source:** extracted from (SILVA et al., 2022).

7.2. MORPHOLOGY OF THE HKUST-1 SURMOF THIN FILMS

The analysis of the thickness, topography, and structure of HKUST-1 SURMOF films grown onto Au substrates functionalized with the SAM MHDA, and onto Al₂O₃ functionalized with SAM PHDA, were determined by AFM, XRD, SEM, and FIB techniques. The details on the morphology characterization of the films are demonstrated in Section 5.3.

7.3. HKUST-1 SURMOF INTO DEVICES

The investigation of polarization properties of HKUST-1 is still poorly reported, primarily in sub-50 nm-thick layers incorporated in functional electronic devices. Thus, in this work thin films of HKUST-1 SURMOF layers of ~ 100 -20 nm-thick are incorporated into capacitive devices in MIM structures (here defined MSM, as metal-SURMOF-metal structures) and in *h-rCap* devices for comparison of its dielectric response.

7.3.1. Dielectric Layers in MIM (MSM) Structures

HKUST-1 SURMOF films with different thicknesses were used to form standard MSM structures, where the top electrode was made by thermal evaporation (see **Figure 42** and **Figure 14**). The MSM devices were investigated via IS in inert atmosphere conditions (N_2), and the HKUST-1 thicknesses were controlled by the number of LPE deposition cycles (from 20 to 100).

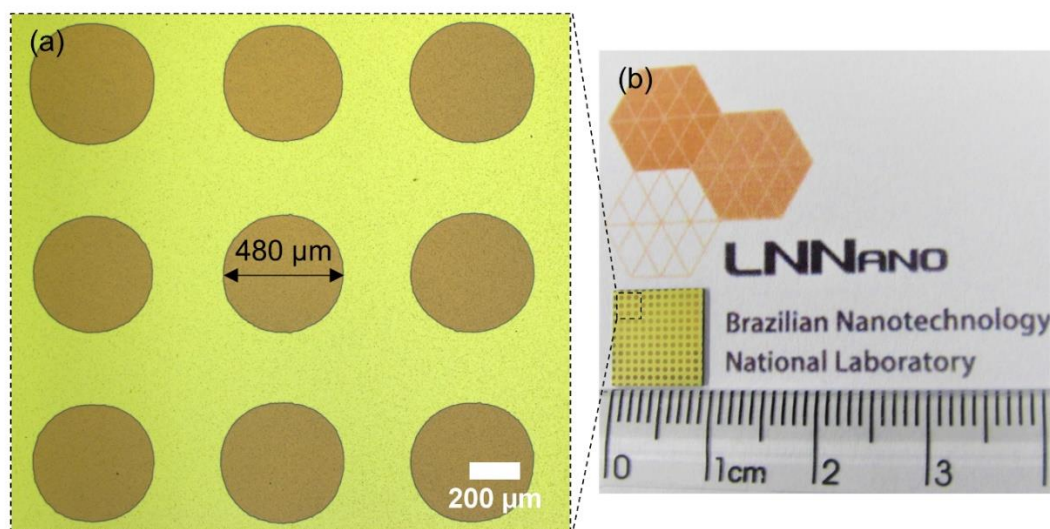


Figure 42: Parallel-plate capacitors-based HKUST-1 SURMOF in MIM structures. **(a)** Optical microscopy image showing an array of 9 devices on a chip. The active area of about 0.2 mm^2 is determined through the area of the circular top gold electrode. **(b)** Photography showing the entire $9 \times 9 \text{ mm}^2$ chip with 121 MSM devices fabricated. **Source:** extracted from (SILVA et al., 2022).

As expected, the impedance response revealed an increase in the number of short-circuited capacitors as the SURMOF film thickness reduces – see the impedance phase angle (θ) histograms in **Figure 43** and **Figure 44**. More than 80% of capacitors presented non-capacitive behavior, *i.e.*, $\theta \ll -90^\circ$, for 20-cycles films (**Figure 44**), limiting the dielectric

characterization of small HKUST-1 thicknesses in conventional MSM device configuration. This reinforces the *r*-NM-based capacitor structure as a powerful tool for determining the dielectric properties for SURMOFs.

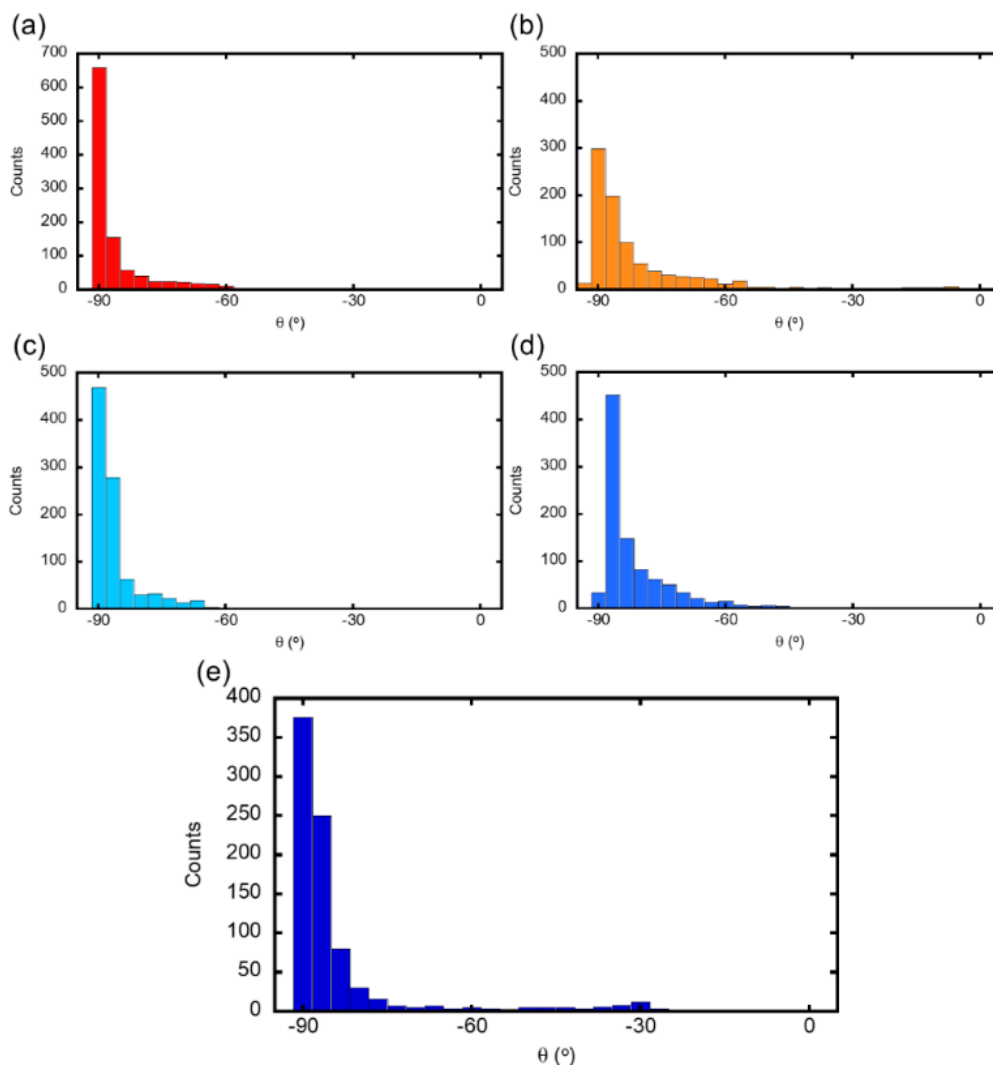


Figure 43: Histogram phase degree for different MSM devices with HKUST-1 SURMOF. **(a)** 30, **(b)** 40, **(c)** 50, **(d)** 75, and **(e)** 100 deposition cycles. The counts are the phase values of 22 different MSM devices for each SURMOF thickness, covering the frequency range from 1 kHz to 50 mHz (10 points/decade). **Source:** extracted from (SILVA et al., 2022).

Therefore, the thickness of HKUST-1 SURMOF measured as a dielectric layer into an MSM-like (MIM) structure has a lower limit, as **Figure 44** depicts. Something between a 20 to 30 cycles-thick layer (~ 40 -60 nm) splits the measurable from the unmeasurable layer of the SURMOF as a dielectric into a MIM capacitive (with thermally evaporated top electrode) configuration.

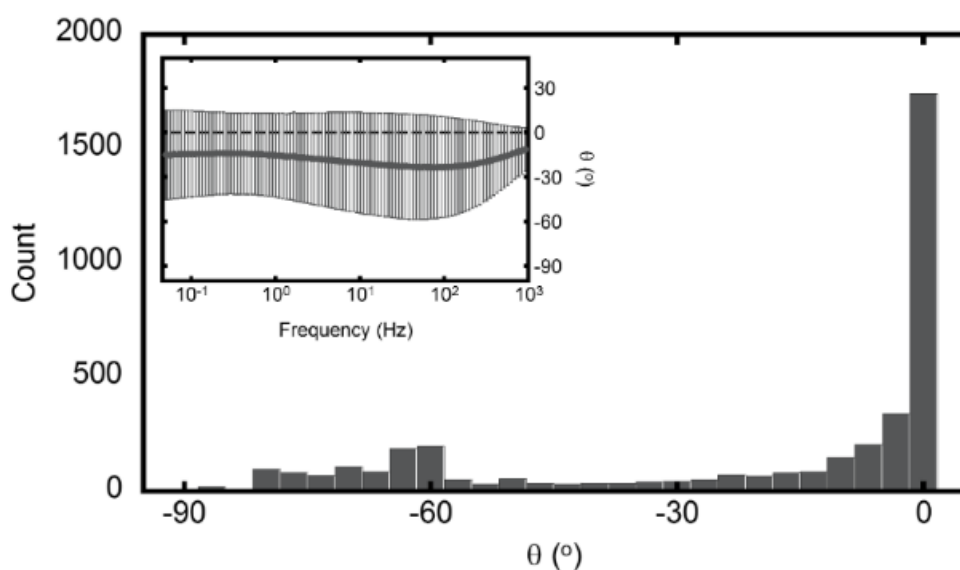


Figure 44: Histogram phase degree for different MSM devices with HKUST-1 SURMOF deposited for 20 cycles. **(inset)** Mean values and respective standard errors of impedance phase spectroscopies for the same structures. The counts were performed considering the phases of 20 different MSM devices covering the frequency range from 1 kHz to 50 mHz (24 points/decade). **Source:** extracted from (SILVA et al., 2022).

7.3.2. Dielectric Layers in *h-rCap* Devices

Figure 45a,b shows an illustration of the *h-rCap* devices with the HKUST-1 SURMOF layers used to investigate their dielectric properties. Before the rolling-up process, the equivalent circuit that better represents the architecture corresponds to a conventional parallel-plate capacitor (*i-pCap*), having top and bottom electrodes sandwiching a 10 nm-thick Al_2O_3 film. Through the selective removal of a sacrificial layer, based on germanium oxide (GeO_x), the whole thin-film capacitor structure curls, making the outermost layer of the strained tri-metallic layer touch the HKUST-1 SURMOF from the top, creating a hybrid *r-NM*-based capacitor (*h-rCap*), like the formation of the *h-rCap* for the MPc-based devices. **Figure 45c** shows the layer sequence for each architecture. A detailed illustration of device fabrication can be found in **Figure 15**. As mentioned, the ultra-compact architecture allows a damage-free, reliable, and soft electrical top contact between the *r-NM* and the SURMOF layer (BOF BUFON et al., 2010; PETRINI et al., 2018; SILVA; MERCES; BOF BUFON, 2020). Furthermore, as the number of windings increases through the roll-up process, the SURMOF layer is compacted into the tubular structure, enabling additional protection against hazardous agents that can eventually damage its integrity (TORIKAI et al., 2018). The number of windings

can be controlled by accessing the capacitor dimensions, the strain configuration during the thin film deposition, and the SURMOF thickness.

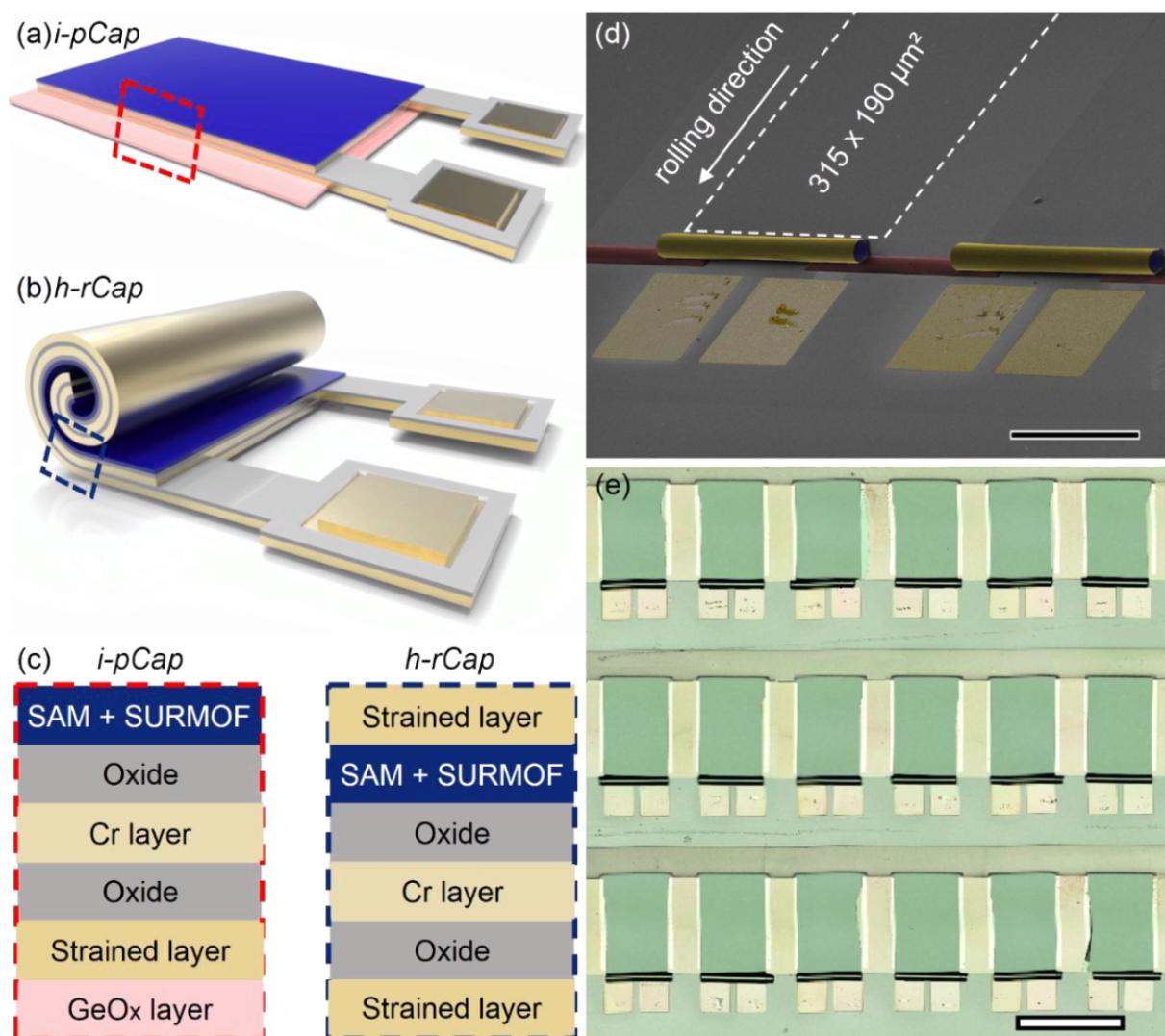


Figure 45: Layout and layer composition of the devices. **(a)-(b)** Illustration of the *i-pCap* and *h-rCap* device structures. The roll-up process starts after the GeO_x dissolution; the top electrical contact on the SURMOF is accomplished as the outermost surface of the strained tri-metallic layer curls. **(c)** Respective layer sequence for the regions indicated in the dotted rectangles for *i-pCap* and *h-rCap*. **(d)** SEM image of a couple of *h-rCap* devices, highlighting the reduction of the device footprint area. **(e)** LSCM image from an array of 18 devices shows the reproducibility and scalability of the fabrication process of the *h-rCap* structures. **Source:** reprinted from (SILVA et al., 2022).

Figure 45d shows the SEM image of two *h-rCaps*. The former device footprint area of $6 \times 10^{-8} \text{ m}^2$ is reduced to $4 \times 10^{-9} \text{ m}^2$ after five rolled windings. The external tubular diameter is $\sim 20 \text{ }\mu\text{m}$, a reduction of *ca.* 90% of the occupied area. These values are similar to the achieved for the semiconducting molecular ensembles integrated into *r-NM*-based capacitors, as reported elsewhere (PETRINI et al., 2018; SILVA; MERCES; BOF BUFON, 2020). Such a substantial

reduction of the footprint is particularly interesting for increasing the number of devices per area. In **Figure 45e**, LSCM image shows an array of 18 fabricated devices. As can be seen, all devices were successfully rolled-up, evidencing the reproducibility and scalability of the fabrication processes based on conventional photolithography methods. The high yield demonstrated here attests to a reliable and robust fabrication process, which allows profitable statistics of the obtained electrical data.

For a proper comparison, the IS results of MSM and *h-rCap* devices measurement are plotted and analyzed. **Figure 46a,b** shows the θ and the parallel-capacitance (C_p) values for MSM and *h-rCap* devices in N_2 atmosphere condition, considering structures with 20-cycles HKUST-1 SURMOF films. While θ exhibits a capacitive behavior ($\sim -90^\circ$) for *h-rCaps* (from 10^1 to 10^4 Hz), for MSM devices, the values of θ vary considerably. Also, the error bars are substantially higher for MSM devices than for *h-rCaps*, revealing a deficiency in reproducibility for MSM architecture. The corresponding C_p for both configurations (**Figure 46b**), follows the same tendency observed for θ in **Figure 46a**. As shown in **Figure 46c**, the *h-rCap* architecture allowed us to obtain excellent capacitive behavior at different SURMOF thicknesses from 10^1 to 10^4 Hz. The respective C_p , in the yellow region, is shown as an inset. **Figure 46d,e** presents the equivalent electric circuit for each employed architecture. This approach allows the determination of the dielectric properties of HKUST-1 SURMOF. The permittivity values were extracted from the angular coefficient of the linear regression from the plot Area/Capacitance versus thickness for both configurations, as shown in **Figure 46f**.

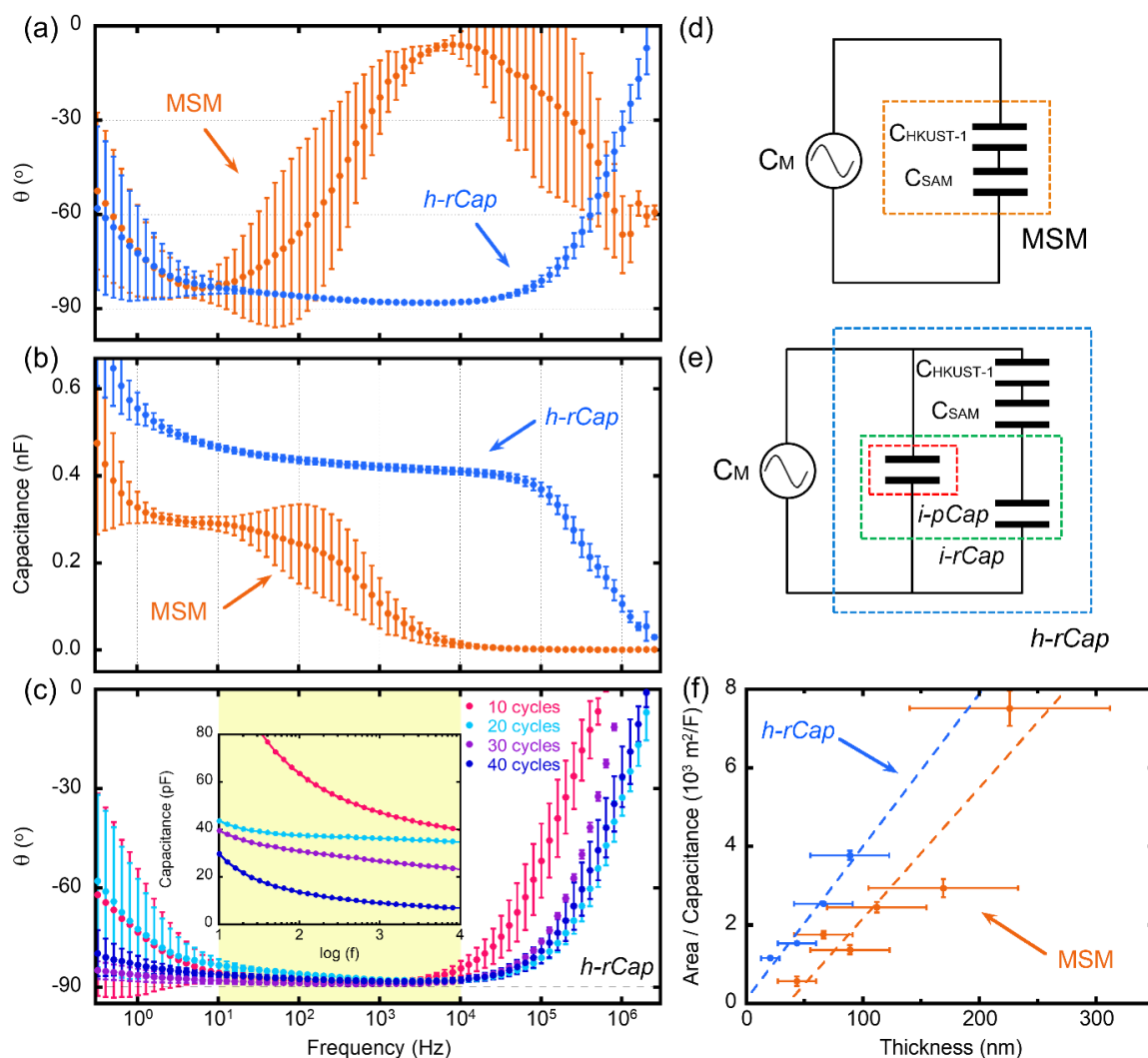


Figure 46: Impedance characteristics for MSM and *h-rCap* devices in N_2 atmosphere condition. **(a)** **(b)** Typical impedance θ and C_p as a function of frequency for devices comprising 20 LPE deposition cycles of HKUST-1. **(c)** θ as a function of frequency for *h-rCap* devices with different LPE deposition cycles. The highlighted region indicates the frequency range where the devices exhibit typical capacitor behavior; **(inset)** the measured C_p in this region. **(d)** **(e)** Equivalent circuit for MSM and *h-rCap* devices. **(f)** Area/Capacitance as a function of HKUST-1 SURMOF thickness. **Source:** extracted from (SILVA et al., 2022).

From now on, the ε'_r will be referred as κ , since they represent the same physical quantity, and such parameter for the SURMOF is explored for the application as a low- κ dielectric. The κ of HKUST-1 is calculated, considering that $\kappa = 1/(\alpha * \varepsilon_0)$, where α is the angular coefficient obtained from the data presented in **Figure 46f**. The linear regression coefficient (R^2) demonstrates a better agreement for the *h-rCap* devices (95%) than for MSM structures (86%). From the data fit $\kappa = 2.0 \pm 0.5$ for the *h-rCap* and 3.4 ± 0.7 for MSM. Both values agree with the results reported for bulk MOFs (BABAL et al., 2019, 2020; SCATENA; GUNTERN; MACCHI, 2019).

7.3.3. Self-Encapsulation of *r*-NM-based Capacitors Exposed to Diverse Atmospheres

One of the main characteristics of *r*-NM-based capacitor architecture is its self-encapsulation. Such a feature is applied here to ensure that the dielectric characteristics of HKUST-1 are preserved under exposure to different hazardous environments. **Figure 47a,b** illustrates a scheme of the scenario investigated in this work. Both device structures with 40-cycles HKUST-1 SURMOF films were exposed to different volatile compounds and UV ($\lambda = 365$ nm) irradiation. The laboratory condition (ambient - *amb*) involves a relative humidity of around 70% and a temperature of 25°C. In **Figure 47c**, θ remains -90° for the entire frequency range once the MSM is placed in the N_2 atmosphere. If the environment is modified, θ changes considerably since the HKUST-1 porous gets filled by the solvent molecules, and the UV irradiation may cause the eventual degradation of the organic linker. The degradation may also occur by water molecules and O_2 adsorption, leading to catalytic effects in the SURMOF structure (WANG et al., 2020).

The results presented in **Figure 47c** show that MSM architecture does not allow an effective SURMOF encapsulation. **Figure 47d** shows the impact of the self-encapsulation on the dielectric properties of the HKUST-1 incorporated into the *r*-NM-based capacitor architecture. By comparison, a substantial improvement in thin-film shielding is observed between 10^1 to 10^5 Hz. The respective C_p values are shown in **Figure 47e,f** where the effects caused by environmental changes on the HKUST-1 dielectric properties can be further correlated with θ for both scenarios. For better visualization, the inset in **Figure 47e** shows in detail the C_p at high frequencies after NH_3 exposition for the MSM device.

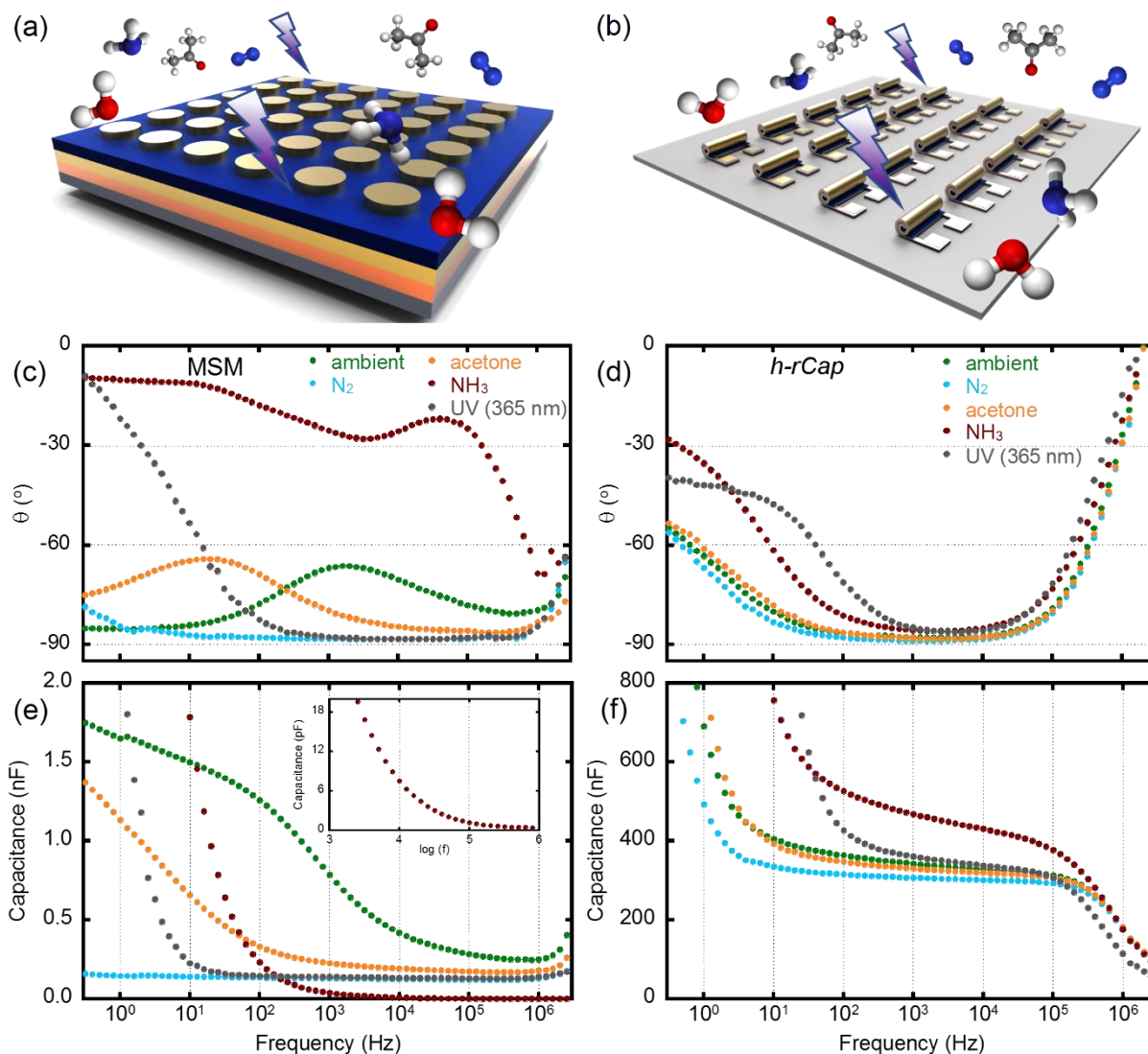


Figure 47: Influence of the environmental conditions on the dielectric properties of 40-cycles HKUST-1 SURMOF films. **(a)-(b)** Illustration of MSM and *h-rCap* devices exposed to different environments. **(c)-(d)** Respective θ and **(e)-(f)** C_p as a function of frequency for MSM and *h-rCap* devices. The **inset** in **(e)** shows the C_p at high frequencies after NH₃ exposition for the MSM device. The laboratory condition (*amb*) involves a relative humidity of around 70% and a temperature of 25°C. **Source:** extracted from (SILVA et al., 2022).

HKUST-1 is a porous framework structure with a high surface area (XUE et al., 2018), which allows the diffusion of different molecules from the atmosphere into their pores. The incorporation of these molecules may induce different polarization effects under the externally applied electric field, resulting in distinct impedance responses. Besides, the NH₃ atmosphere and UV exposition proportioned an irreversible effect on the impedance response for the SURMOF films. For the *h-rCap* architecture, access to the surface of the SURMOF is blocked due to the self-encapsulation feature, which is directly evidenced by the minor changes in the

dielectric response. This result was maintained even for a 20-nm-thick SURMOF film, as can be seen in **Figure 48**.

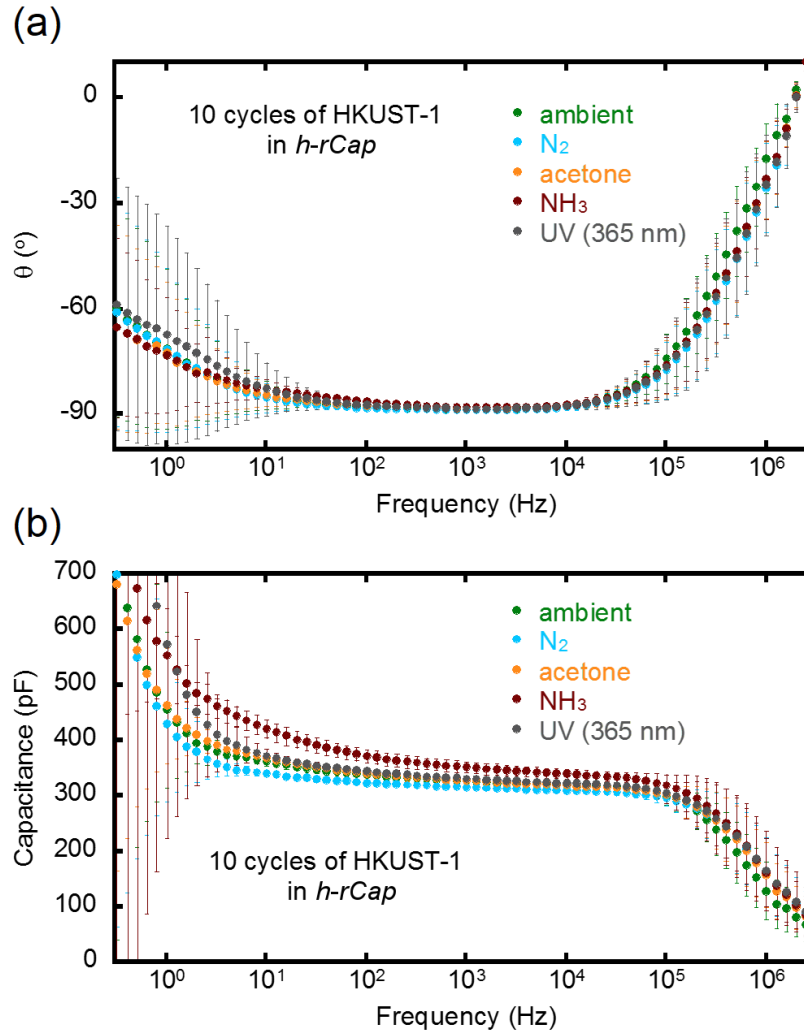


Figure 48: Dielectric response of the *h-rCap* devices with 10-deposition cycles of HKUST-1 SURMOF measured at different environmental conditions. **(a)-(b)** θ and capacitance as a function of frequency. The minor variation in the θ and capacitance response is related to the low SURMOF thickness (~ 20 nm) for 10-deposition cycles, which allows a better-compacted structure after the rolled-up process. **Source:** extracted from (SILVA et al., 2022).

Figure 49a shows the percentage changes of θ at 10 kHz for both architectures. These percentage variations were calculated considering the data obtained in the N_2 condition as a reference. For a frequency region where a capacitive behavior is expected, i.e., at 10 kHz, θ variations are higher for *amb* and NH_3 conditions for MSM devices. However, for *h-rCap* devices, this tendency is not followed, and the values are kept mostly stable in the different exposure conditions. These results confirm the effectiveness of the self-encapsulation process.

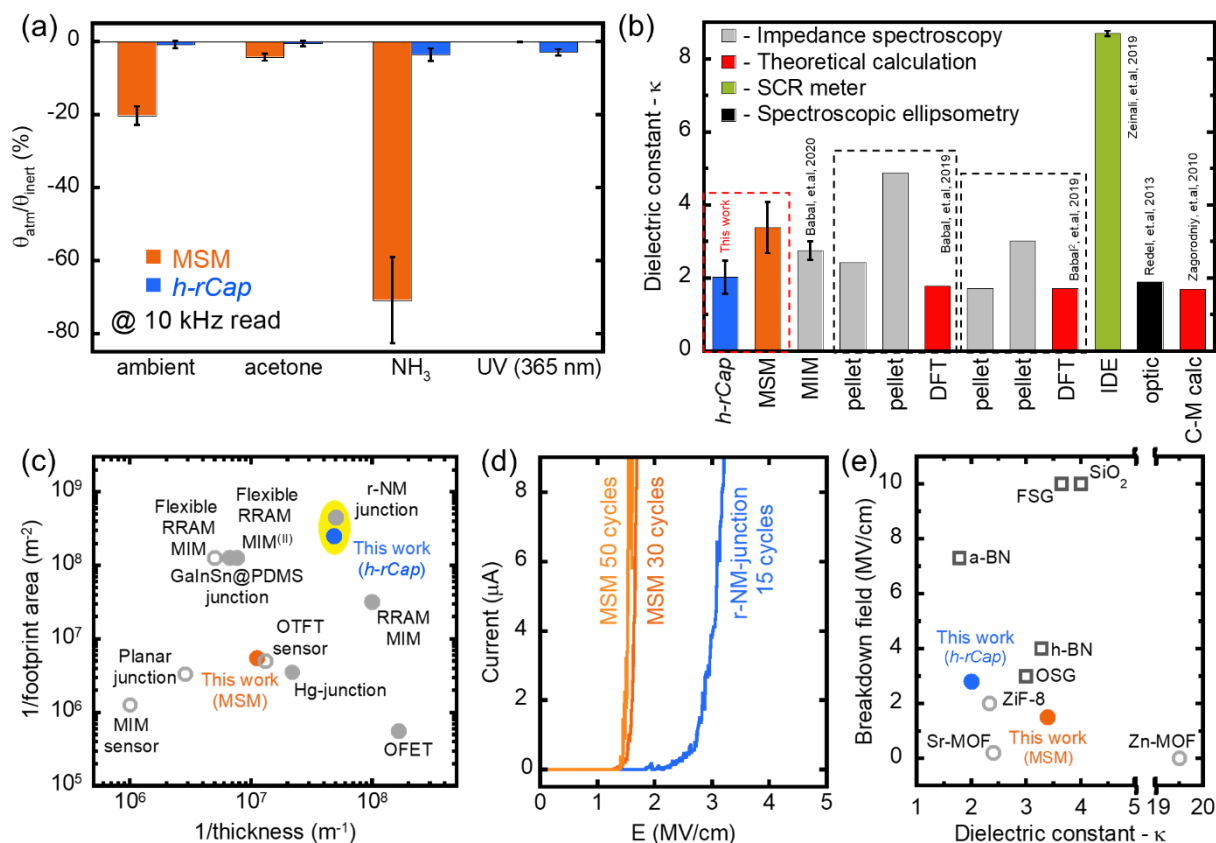


Figure 49: (a) Percentage changes of θ at 10 kHz for MSM and h -rCap devices relative to the N_2 atmosphere condition. (b) κ values for HKUST-1 obtained in this work compared to previously reported works. The error bars indicate the uncertainty of the data, which is not reported in most cases. (c) A survey of the inverse of footprint area versus the inverse of the thickness of the active layer, comparing the results from the devices in this work, and other device in the literature. (d) Typical current versus applied electric field for MSM and r -NM-junction. (e) Breakdown electric-field versus κ for this work compared with other low- κ materials reported in the literature. In (c) and (e) MOFs are open circles and SURMOFs are solid circles. **Source:** adapted from (SILVA et al., 2022).

For effective comparison, **Figure 49b** shows the κ values of HKUST-1 reported here and the data presented previously in the literature. As can be seen, both MSM and h -rCap values are in excellent agreement with the literature. As expected, the investigations performed by using theoretical calculations and spectroscopic ellipsometry result in lower κ values. Usually, these methods do not consider the orientational (dipolar) polarization caused by possible framework deformations. In particular, the Clausius-Mossotti relation, commonly used for the theoretical calculation of dielectric properties (ZAGORODNIY; SEIFERT; HERMANN, 2010), does not consider the contributions from orientational and vibrational polarizations, leading to underestimated dielectric permittivity values. For comparison, the results found here depict a polarization factor of $\alpha \sim 0.3$ not precedent from optical polarization effects. In the meanwhile, spectroscopy ellipsometry is usually employed by using ultra-high frequencies,

inducing electronic polarization effects, and detecting the optical response part only, from the effective permittivity alone (GU et al., 2015; REDEL et al., 2013). Furthermore, the SCR meter method allows obtaining the dielectric response restricted to a single frequency, resulting in tendentious κ values that depend on the chosen frequency.

For the reported cases of investigation on the HKUST-1 incorporated to devices, Zeinali *et al.* reported the use of an SCR meter to determine the κ of HKUST-1 using interdigitated electrodes (ZEINALI; HOMAYOONNIA; HOMAYOONNIA, 2019); however, they found a considerable contribution of edge effects, compromising the representativeness of the equivalent circuit used, which probably justifies such outlier value found for HKUST-1 dielectric constant, presented in **Figure 49b**. Babal et al. also described the fabrication of pellet structures with HKUST-1 powder as the dielectric by performing IS in different temperatures and pressure conditions (BABAL et al., 2019). The pressure applied to the pellet electrodes produced a considerable variation on the materials density and on the κ , the later varying from 2.42 at 0.5 t ($\sim 3.7 \times 10^7$ Pa) to 4.88 at 10 t ($\sim 7.4 \times 10^8$ Pa) pressure, evidencing that MOF powders are difficult to shape for device integration. In comparison, the estimated pressure created by the *r-NM* contact to the material below is of ~ 0.17 Pa (MERCES; DE OLIVEIRA; BOF BUFON, 2018), with a magnitude of 10^8 times lower than the reported for pellet incorporation, evidencing the soft contact promoted by the tube after the roll-up. As shown in **Figure 49b**, IS represents a reliable and complete method to investigate the dielectric properties of low- κ materials incorporated into *r-NM*-based devices, since both electronic and ionic contributions can be included by properly defining the frequency range.

The device dimensions are explored in **Figure 49c**, where they are compared with selected works based on different MOFs and SURMOFs used as active layers. As one may notice, the *NM*-based devices depict interesting features in terms of miniaturization for the SURMOF investigation in electronics. To better elucidate the potential of ultrathin HKUST-1 SURMOF heterojunctions as a low- κ dielectric material, the electrical breakdown strength was determined through the typical current versus the applied electric field, as can be seen in **Figure 49d**. For such, two different device architectures were employed: the MSM and *r-NM*-junction. The *r-NM*-junction was used to rule out any eventual effect of the metal diffusion into the SURMOF thin films, commonly observed in MSM architecture. Furthermore, the *r-NM*-junction does not need the Al_2O_3 layer to grow the SURMOF, which could have resulted in an erroneous electrical breakdown strength. Despite the typical small geometric area of the *r-NM*-junctions difficult the effective dielectric characterization, they are an excellent choice for the

establishment of the materials breakdown strength and charge transport investigation (MERCES et al., 2017a). Details regarding this vertical junction can be found in our previous work (ALBANO et al., 2020). The layout and fabrication steps of the device can be found in **Figure 16**. From the respective curves obtained in **Figure 49d**, a breakdown field of about 1.5 MV/cm was obtained for MSM architecture for SURMOF thicknesses. Interestingly, a superior breakdown field of 2.8 MV/cm is obtained for the *r-NM*-junction, indicating that metal evaporation has possibly affected the SURMOF films in MSM devices. **Figure 49e** shows an interesting benchmarking of the dielectric properties between the results obtained here with the state-of-the-art low- κ materials reported in the literature. As can be seen, the κ and breakdown field values obtained are in excellent agreement with the literature. The good aspect ratio is overcome only by the amorphous boron nitride (a-BN) (HONG et al., 2020), which has a 3 nm-thick film. Therefore, ultrathin SURMOF heterojunctions have great potential as low- κ dielectric materials when they are effectively integrated.

The *r-NM* presents itself as a functional platform that guarantees a small device footprint area and reliable top contacts on the nanoscale-thick films. As shown in **Figure 49c**, in addition to the high aspect ratio obtained for the *r-NM*-junction (ALBANO et al., 2020), the *h-rCap* device structure offers a larger soft contact area by enveloping the SURMOF layer and creating the self-encapsulation. Such a feature is observed to improve the charge accumulation of the HKUST-1 SURMOF interface, providing a detailed investigation of its dielectric properties.

7.3.4. FEM Simulations

After properly determining the dielectric properties of the HKUST-1 films, FEM simulations were performed considering two parallel interconnects separated by an inter distance of 40 nm – a scenario similar to the interconnect systems employed in CMOS technology (ADVANCING TECHNOLOGY FOR HUMANITY, 2018). Here, different substrates, such as well-known dielectrics (SiO_2 and Al_2O_3), are compared to HKUST-1 in electric field distribution for an applied electric potential. The simulations were performed considering the different κ for the respective dielectrics, namely 2 (HKUST-1), 3.9 (SiO_2), and 9 (Al_2O_3). The κ values for the oxides were taken from the literature (HONG; WANG; CHUNG, 2016; ROBERTSON, 2004). **Figure 50a** illustrates the two parallel interconnects on the HKUST-1 substrate; the electric potential of $V_{DC} = 150$ mV is applied to the left interconnect (force terminal) while the right one is kept grounded (GND, sense terminal). The

inset shows the distribution of representative electric field lines, where a significant difference in flow through the air and substrate (dielectric) is noted. The electric field distribution is obtained by solving Laplace and Poisson relations, shown in Equation 73.

$$\nabla^2 \varphi = \frac{-\rho}{\varepsilon'} \quad (73)$$

where ∇^2 is denoted as the Laplace operator, φ is the electric potential, ρ is the electric charge density, and ε' is the (real) electric permittivity. For the equilibrium case where $\rho = 0$, the boundary conditions turn the problem described by Laplace's equation.

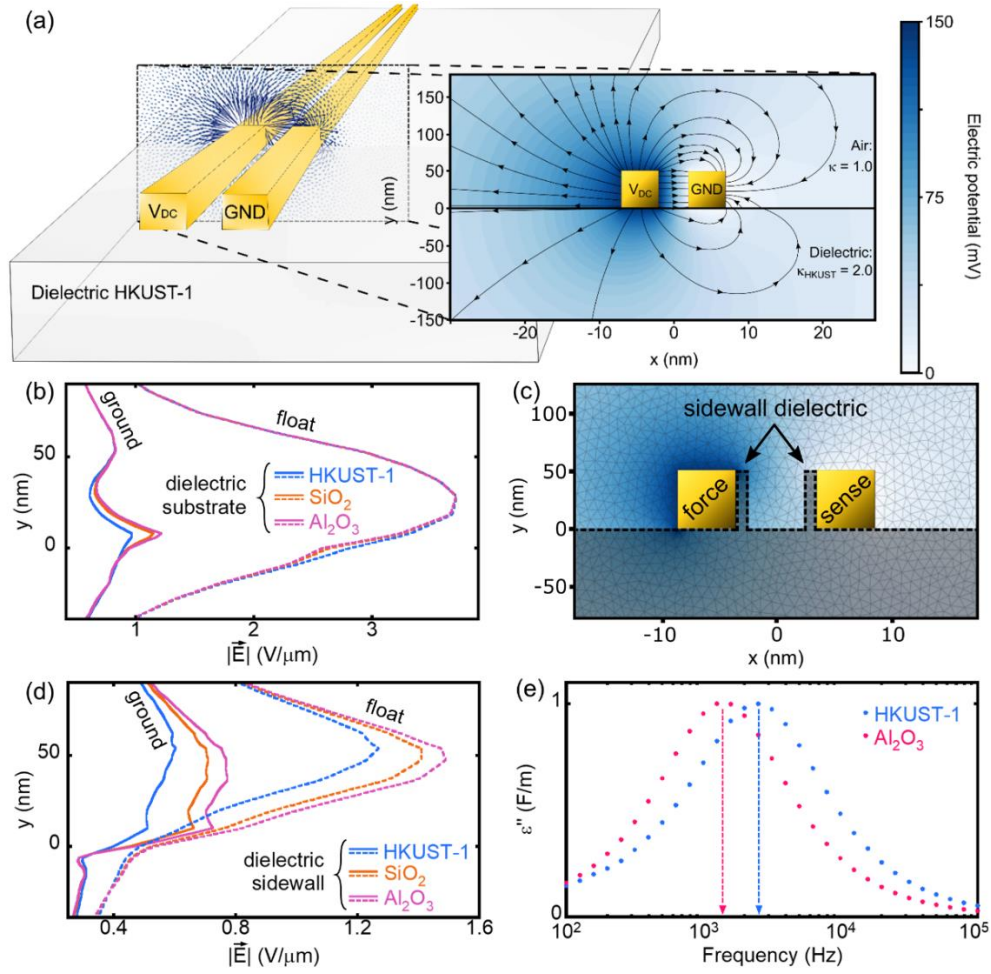


Figure 50: FEM simulations for HKUST-1, SiO₂, and Al₂O₃. **(a)** Illustration of two parallel interconnects on HKUST-1 as substrate. V_{DC} and GND correspond to the force and sense terminals for an applied DC electric potential. **(inset)** Respective electric field lines distribution for cross-section. **(b)** Electric field (in modulus) between the two parallel interconnects (vertical line, $x = 0$) for HKUST-1, SiO₂, and Al₂O₃ as substrate. **(c)** Representation of the setup for simulation, considering the respective dielectrics as sidewalls for both parallel interconnects. **(d)** Electric field (in modulus) between the two parallel interconnects (vertical line, $x = 0$) for different dielectrics as substrate and sidewalls. **(e)** Experimental dielectric loss spectroscopy for HKUST-1 and Al₂O₃ as the dielectric layer in a MIM configuration. In **(b)** and **(d)**, solid and dotted data lines represent grounded and float configurations for the sense electrode. **Source:** adapted from (SILVA et al., 2022).

Considering a vertical line at $x = 0$ in the inset of **Figure 50a**, the calculated electric field distribution can be obtained for the different dielectrics for both grounded and float sense terminal configurations (see **Figure 50b**). For the case with a floating sense terminal, the distribution is nearly the same for all dielectrics. Setting the sense terminal to the ground potential shows a significant difference for the HKUST-1 substrate. As shown in **Figure 51**, the simulated system evidences a more responsive electric field distribution at the substrate, *i.e.*, below its surface, with contributions in both axes of the plane.

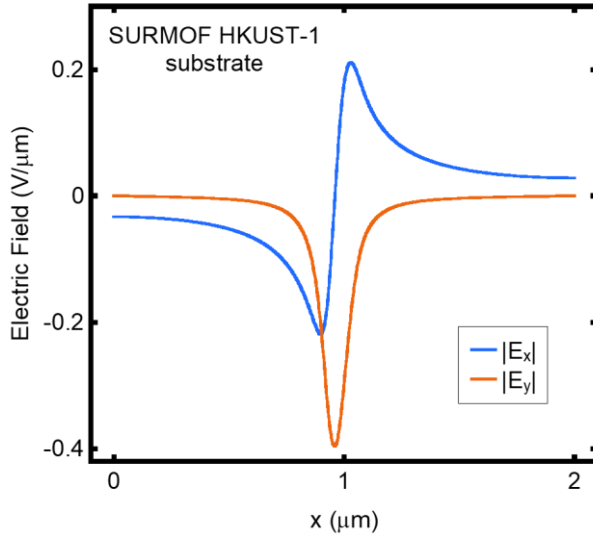


Figure 51: The electric field in the x-axis at 1 μm below the surface of the HKUST-1 substrate, for the simulated cross-section area of parallel interconnections, 40-nm-apart from each other. **Source:** adapted from (SILVA et al., 2022).

Next, we employ the sidewall dielectric approach to the parallel interconnects using the same dielectric material from the substrate (**Figure 50c**). This approach is widely known in CMOS-like configurations to reduce the inherent and undesired effects from R and C_p (resistance and parasitic capacitance of the conductor, respectively) that significantly compromise the overall performance (HUANG et al., 2008). Thus, we assume the net described in **Figure 50c** as a scenario considering the dielectrics as ILD-like to insulate the parallel interconnects. As shown

in **Figure 50d**, the respective electric field distribution exhibits a considerable reduction for both sense terminal configurations (ground and float) for HKUST-1, followed by SiO_2 and Al_2O_3 dielectrics. Furthermore, these results can be better explained by applying a classical approach, *i.e.*, determining a Gaussian surface (S) around the sense electrode according to Gauss's law, Equation 74.

$$\Phi_D = Q_{free} = \int_S \vec{D} \cdot d\vec{A} = \epsilon'_r \int_S \vec{E} \cdot d\vec{A} \quad (74)$$

where Φ_D is the electric flux through the gaussian surface, Q_{free} the free charge, $\vec{D}$ the displacement of the flux, $d\vec{A}$ an infinitesimal element related to S , ϵ'_r the electric constant, and $\vec{E}$ the electric field. The free charge induced at this terminal was calculated for both dielectric configurations, *i.e.*, with and without dielectric sidewall. Without a dielectric sidewall, the charge induced in the sense terminal for HKUST-1 as the substrate is smaller than for SiO_2 and

Al₂O₃ dielectrics (see **Table 3**). Notably, the charge induced for Al₂O₃ at this configuration is more than twice the value obtained for HKUST-1. The same tendency is observed for the calculated capacitance. The charge induced reduces substantially with dielectric sidewall for all dielectrics due to the lower electric field distribution observed in **Figure 50d**. Nevertheless, HKUST-1 still possesses smaller values compared with the other dielectric materials.

Table 3: Calculated charge induced and capacitance from the FEM simulations considering the sense terminal grounded. Extracted from (SILVA et al., 2022).

Dielectric configuration	Dielectric material	Charge induced in the sense (pC)	Capacitance – Q_{charge}/V_{force} (pF)
Substrate only	HKUST-1	-4.24	28.26
	SiO ₂	-5.88	39.24
	Al ₂ O ₃	-10.06	67.06
Substrate and sidewall	HKUST-1	-1.48	9.90
	SiO ₂	-1.96	13.08
	Al ₂ O ₃	-2.94	19.60

Figure 50e shows the experimental dielectric loss spectroscopy for HKUST-1 and Al₂O₃ as the dielectric layer in the MIM configuration. The thicknesses for both dielectric layers are about 80 nm – to mimic a scenario close to the situation exploited in FEM simulations. This thickness corresponds to 40 step-by-step deposition cycles of HKUST-1 SURMOF. It is worth mentioning that HKUST-1 films below this thickness have a reasonable probability of presenting a behavior different from a pure capacitor owing to the possible diffusion of metal atoms into the HKUST-1 pores during evaporation. The dielectric loss (ε_r'') for each data point obtained from impedance spectroscopy was calculated following Equation 75.

$$\varepsilon_r'' = \frac{G}{\omega} \quad (75)$$

The peak observable for both dielectric losses evidence the different relaxation time responses – meaning that the related charge accumulation mechanisms are not responding to the applied AC signal owing to the higher frequencies. The such effect occurs first for HKUST-1 (at ~2.54 kHz) followed by Al₂O₃ (at ~1.38 kHz) in the employed MIM configuration, considering that the data acquisition begins at higher frequencies. The peak frequencies

obtained indicate that HKUST-1 could provide, in principle, better switching performances than Al_2O_3 .

Comparing to the well-established dielectrics used in electronics (SiO_2 and Al_2O_3), the HKUST-1 provides a better response as ILD for electronic devices, according to the experimental and simulation investigations. Therefore, the results place this hybrid structure as a promising candidate for the new generation of low- κ materials.

CHAPTER VIII: FINAL CONSIDERATIONS

8.1. CONCLUSIONS

In this work, well-known MPc molecules were investigated as thin-film dielectrics in *r*-NM-based devices, and their polarization-related properties were determined by impedance spectroscopy in the function of the temperature. The exploitation of the organic semiconductors confirmed the viability of the rolled-up capacitors as a functional and reliable platform for the study of the dielectric properties of ultrathin films. This perception provided the basis for the incorporation of more complex material into the rolled capacitors, such as HKUST-1 SURMOF. The study of the porous hybrid material as dielectric layers in the devices was performed, and the dielectric properties of the SURMOF were extracted in a similar electric characterization, exposing not only to ambient, but also other atmospheric compositions. Simulations were performed for comparison of the HKUST-1 with other insulators as ILD, in neighbor conducting lines, and the superior performance of the HKUST-1 ultrathin layer is evidenced for such application. The specific achievements for each material explored here are described below.

8.1.1. MPcs in *h*-*r*Cap Devices

Hybrid organic/inorganic functional devices (*h*-*r*Caps) were developed, characterized, and applied to investigate the dielectric properties of ultrathin (*ca.* 5 nm) MPc films. Each active component of the *h*-*r*Cap was investigated as a function of both f and T , using impedance spectroscopy. The impedance spectra obtained from 20 to 10^7 Hz have demonstrated that the *h*-*r*Caps exhibited a capacitive behavior. The inorganic component of the *h*-*r*Cap (15-nm-thick Al_2O_3 film) revealed dielectric polarization weakly dependent on T for the full range studied ($6 < T < 300$ K). Consequently, the permittivity and relaxation time of Al_2O_3 were found as $\varepsilon'_{\text{r Al}_2\text{O}_3} = 7.4 \pm 0.6$ and $\tau_{\text{Al}_2\text{O}_3} = 1.0 \pm 0.1$ μs , respectively. Concerning the organic components of the *h*-*r*Caps (*viz.* 5-nm-thick CuPc, CoPc, or F_{16}CuPc ensembles), it was observed a minimum critical temperature T' , above which dielectric polarization exhibits dependence on T . Below T' , the capacitive response of the semiconducting molecular ensembles was found T -independent. In this scenario, capacitance plateaus manifested for $f < 10^5$ Hz. The T -

independent permittivity of each ultrathin molecular ensemble was found as $\varepsilon'_{r\text{CuPc}} = 2.8 \pm 0.3$, $\varepsilon'_{r\text{CoPc}} = 2.3 \pm 0.2$, and $\varepsilon'_{r\text{F16CuPc}} = 1.9 \pm 0.2$. The MPc relaxation times were also determined as $\tau_{\text{CuPc}} = 3.0 \pm 0.2 \mu\text{s}$, $\tau_{\text{CoPc}} = 2.7 \pm 0.2 \mu\text{s}$, and $\tau_{\text{F16CuPc}} = 7.5 \pm 0.6 \mu\text{s}$. A critical analysis of the findings considering the literature has indicated that: (i) the permittivity of ultrathin molecular ensembles may be influenced by the close contact with dielectric and conductive films (*viz.* Al_2O_3 and Au); and (ii) the ensemble relaxation times are more-likely related to each single-molecule polarization within each ultrathin MPc ensemble. Our findings contribute to the development of a reliable heterojunction platform to investigate the polarization properties of hybrid organic/inorganic nanomaterials as a function of external parameters (*e.g.*, the temperature). Such advances support the development of novel device architectures for applications in solar cells, miniaturized pumps to perform lab-on-a-chip, and electro-mechanical logic gates for multi-element smart systems.

8.1.2. HKUST-1 SURMOF in *h-rCap* Devices

By modeling the characteristic impedance data of thin films of HKUST-1 SURMOF in *h-rCap* devices through equivalent circuits, a low- κ value of 2.0 ± 0.5 was obtained, in good agreement with the literature. The low- κ value and the breakdown field of 2.8 MVcm^{-1} provide one of the best aspect ratios reported so far, demonstrating the great potential of HKUST-1 SURMOF as the low- κ dielectric material. Besides, the device structure has good compactness in tubular form. This feature enabled a reduction of 90% from the original device footprint area and considerable protection of the SURMOF dielectric properties against hazardous agents. The experimental findings are correlated using FEM simulations, considering the HKUST-1 as substrate and sidewalls for two parallel interconnects separated by nanometric inter distances. The results provide a consistent benchmarking on the dielectric properties of HKUST-1, compared with the well-established dielectrics used in electronics (SiO_2 and Al_2O_3), projecting this hybrid structure as a promising candidate for the new generation of low- κ materials. Furthermore, the dielectric properties of ultrathin SURMOFs are effectively accessed at the nanoscale solid-state device, using a 3D functional device architecture fully compatible with standard microfabrication processes. Also, these devices are appealing to exploit exciting quantum-electrodynamical effects, where the tube-shaped capacitors could operate as integrated optical microcavities to develop novel and advanced technologies in the context of optical sensors.

8.2. SCIENTIFIC CONTRIBUTIONS

This project regarding the incorporation of *MBTF* into *NM*-based capacitors has rendered contributions to the scientific community, generally in form of publications. Some of them are described here below.

8.2.1. Periodical Peer-Reviewed Publications

The productions arising from this project were published in very relevant scientific journals, such as *Advanced Electronic Materials* - Wiley (I.F. 2021: 7.633), *Nano Letters* - ACS (IF 2021: 12.262), *Applied Materials and Interfaces* - ACS (IF 2021: 10.383), and *Nanotechnology* - IOP (I.F. 2021: 3.953). The graphical abstract from each publication is, respectively, shown in **Figure 52a-d**.

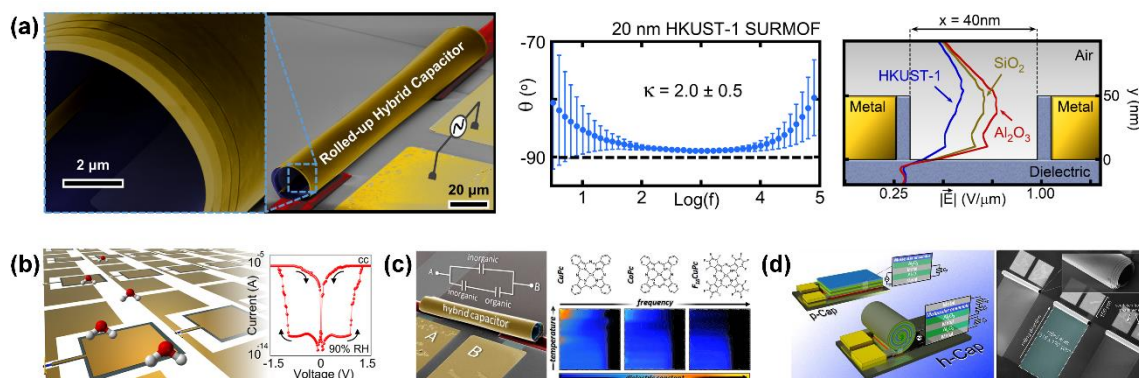


Figure 52: Graphical abstracts of the scientific contributions to the literature from this author and project. The titles of the papers are: **(a)** *Surface-Supported Metal-Organic Framework as Low-Dielectric-Constant Thin Films for Novel Hybrid Electronics* (SILVA et al., 2022); **(b)** *Ambipolar Resistive Switching in an Ultrathin Surface-Supported Metal–Organic Framework Vertical Heterojunction* (ALBANO et al., 2020); **(c)** *Temperature-Independent Polarization of Ultrathin Phthalocyanine-Based Hybrid Organic/Inorganic Heterojunctions* (SILVA; MERCES; BOF BUFON, 2020); **(d)** *Hybrid nanomembrane-based capacitors for the determination of the dielectric constant of semiconducting molecular ensembles* (PETRINI et al., 2018).

The detailed references of the publications in the literature periodicals are described following:

- I. *Surface-Supported Metal-Organic Framework as Low-Dielectric-Constant Thin Films for Novel Hybrid Electronics*. **R. M. L. da Silva**, L. G. S. Albano, T. P. Vello, W. W. R. de Araújo, D. H. S. de Camargo, L. D. Palermo, C. C. Corrêa, C. Wöll, C. C. B. Bufon. *Advanced Electronic Materials*. 2022, p. 2200175.

- II. *Ambipolar Resistive Switching in an Ultrathin Surface-Supported Metal-Organic Framework Vertical Heterojunction*. L. G. S. Albano, T. P. Vello, D. H. S. de Camargo, **R. M. L. da Silva**, A. C. M. Padilha, A. Fazzio, C. C. B. Bufon. *Nano Letters*. 2020, v. 20 (2), p. 1080-1088.
- III. *Temperature-Independent Polarization of Ultrathin Phthalocyanine-Based Hybrid Organic/Inorganic Heterojunctions*. **R. M. L. da Silva**, L. Mercês, C. C. B. Bufon. *Applied Materials and Interfaces*. 2020, v. 12, p. 29556-29565.
- IV. *Hybrid Nanomembrane-Based Capacitors for the Determination of the Dielectric Constant of Semiconducting Molecular Ensembles*. P. A. Petrini, **R. M. L. da Silva**, R. F. de Oliveira, L. Mercês, C. C. B. Bufon. *Nanotechnology*. 2018, v. 29, p. 265201.

In the above referencing, the name of this author (**Ricardo Magno Lopes da Silva**) is highlighted to facilitate the spotting of the authorship and relative contribution to each work.

8.2.2. Event and Congress Participations

Besides the contribution in form of scientific periodic journal publications, the works from this project were also displayed and spread through congresses and other events. The specifics of such displays are the detailed following:

- I. *Fabricação e Caracterização de Estruturas Metal-Orgânicas de Superfície (SURMOFs) Incorporadas a Microcapacitores*. VIII Workshop de Pesquisa e Tecnologia em Ciência dos Materiais (workshop). 2021.
- II. *Estruturas Metal-Orgânicas de Superfície (SURMOFs) Integradas a Microcapacitores Baseados em Nanomembranas (NMs)*. 1ª Reunião Técnica Virtual do Programa de Pós-Graduação em Ciência e Tecnologia de Materiais (congress). 2020.
- III. *Self-rolled Microcapacitors Based on Nanomembranes for Evaluating the Dielectric Properties of Organic Thin Films*. PanNano (congress). 2020.
- IV. *Surface-Supported Metal-Organic Frameworks (SURMOFs) Incorporated in Ultra-Compact Energy Storage Devices*. PanNano (congress). 2020.

- V. *Filmes Finos de Estruturas Metal-Orgânicas de Superfície (SURMOF) para Dispositivos Armazenadores de Energia Baseados em Nanomembrana*. Congresso dos Estudantes do CNPEM – CEC (congress). 2019.
- VI. *Filmes Finos de Estruturas Metal-Orgânicas de Superfície (SURMOF) para Armazenamento de Energia em Dispositivos Baseados em Nanomembranas*. Nanopesquisa II (congress). 2019.
- VII. *Fabricação e Caracterização de Microdispositivos Capacitivos para Análise de Estruturas Metal-Orgânicas de Superfície*. VII Workshop de Pesquisa e Tecnologia em Ciência dos Materiais (workshop). 2019.
- VIII. *Rolled-up Nanomembrane-based Capacitors for Evaluating the Dielectric Properties of Organic and Hybrid Thin Films*. Brazil MRS Meeting – SBPMat (congress). 2018.
- IX. *Capacitores Ultracompactos para Caracterização Elétrica de Filmes Finos de Materiais Híbridos e Orgânicos*. VI Workshop de Pesquisa e Tecnologia em Ciência dos Materiais (workshop). 2018.

The above-mentioned works were presented in the events by this author.

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APPENDIX

APPENDIX A: HKUST-1 IN COLLAPSED TUBE CAPACITORS

Thin films of HKUST-1 SURMOF were also incorporated into *r*-NM-junctions-like structures, but with some modifications to their architecture. The modifications aimed to optimize the dielectric area explored between finger-tube electrodes. For such, the finger area (bottom electrode) was redesigned. Also, after the roll-up process of the *NM*, the new tubular architecture undergoes a collapsing process at the drying, forming a planar top electrode on the finger-supported SURMOF layer. This way, the MIM capacitor-like structures (here denominated collapsed-tube *r*-NM-based vertical-heterojunctions, or CTVJ) allow easy extraction of its geometrical area. Also, this architecture favors the exploitation of the constant, relaxation time, and breakdown dielectrics properties. The mask with the new design for CTVJ-structures formation comprises four finger different areas, seven devices with each area. The different fingers present the same length, but four distinct widths (*i.e.*, 30, 60, 90, and 120 nm broad). **Figure A1** illustrates the masks for the CTVJ samples fabrication.

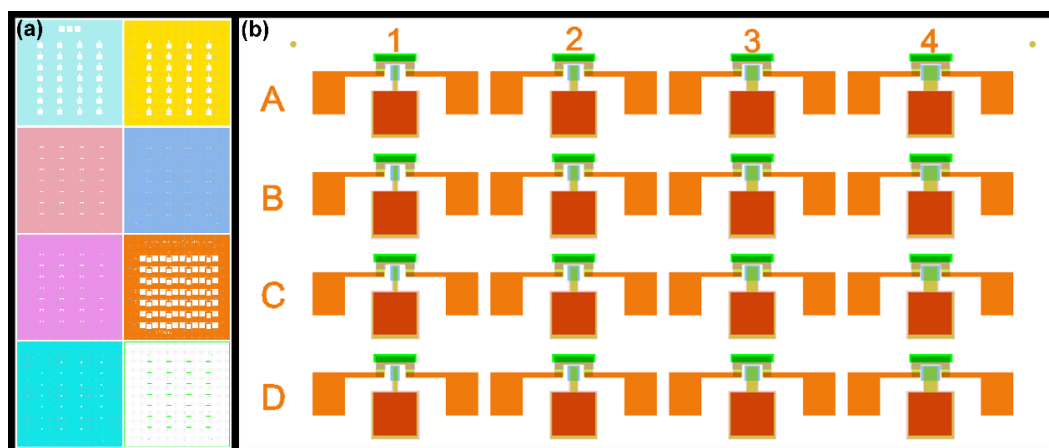


Figure A1: Virtual mask for CTVJ patterning. **(a)** Separated masks used for each of the eight patterning steps for the fabrication of the samples. **(b)** Superposition of the virtual masks (upper part) used for the fabrication of the CTVJ. Samples on each column have a finger-width: column 1 has 30 nm; column 2 has 60 nm; column 3 has 90 nm; column 4 has 120 nm.

The new CTVJ structures were fabricated by the above-described microfabrication techniques. The masks displayed in **Figure A1,a** were used for each of the eight steps for the

patterning of the devices, and **Figure A1,b** depicts the superposition of the upper parts of the masks.

Optical microscopies show the HKUST-1 SURMOF successfully grown onto the finger structures of the CTVJ devices, as demonstrated in **Figure A2**.

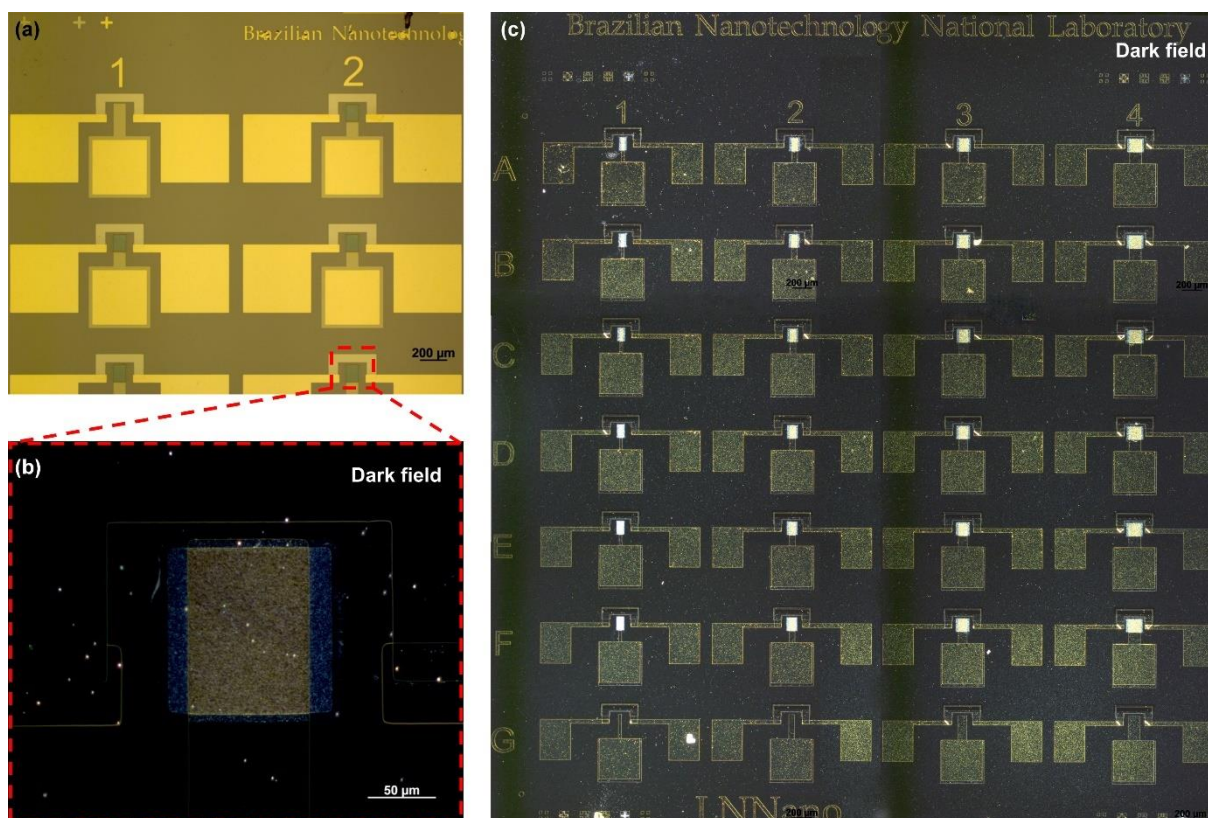


Figure A2: Optical microscopies of a CTVJ sample. **(a)** Six devices showed in bright field microscopy, with the HKUST-1 SURMOF grown onto the finger structures on five of them, and the first device left without the SURMOF layer for the electric considerations of the set-up. **(b)** Darkfield microscopy of the HKUST-1 film onto one zoomed-in finger structure. **(c)** Darkfield microscopy of a sample highlighting the HKUST-1 SURMOF films onto the fingers of CTVJ devices.

The devices were formed and then rolled up. The tube composition was projected to not endure the drying of the sample, so after the roll-up process, while the roll-up solution naturally evaporated from the surface of the sample, the formed tubes collapsed and formed planar membranes softly landed onto the SURMOF layer.

The extraction of the geometrical area in between electrodes of the CTVJ structures was performed using conventional microscopy and, for more precise determination, LCSM. The starter samples still depict a non-uniform tube-collapsing process, resulting in a not reproducible active area for each device. Therefore, each succeeded formed-device area was

extracted using LSCM and the software *VK Analyzer*. The optical microscopy and respective LCSM for one example of each width-finger device are shown in **Figure A3**.

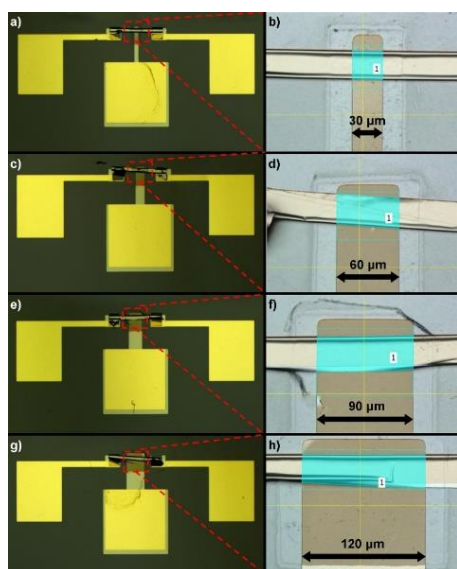


Figure A3: Optical microscopy and LCSM for in-between electrodes of the CTVJ devices area determination (highlighted blue area) for the, respectively: 30 μm wide (a),(b); 60 μm wide (c),(d); 90 μm wide (e),(f); 120 μm wide (g),(h).

After the area estimation of the devices, the samples were placed in an $\text{N}_{2(g)}$ atmosphere for impedance spectroscopy analysis. The electric set-up was modeled for parasitic capacitance removal from the measured data. The direct results of area determination and parallel capacitance (C_p) from the impedance spectroscopy are displayed in **Table A1**. The mean C_p is calculated with the capacitance values from 10^0 - 10^6 Hz.

Table A1: Estimation of the individual between-electrodes area for the CTVJ devices, and their respective C_p measured by impedance spectroscopy.

Device denomination	Area (m^2)	Mean C_p (F)
1B	8.044×10^{-10}	2.01×10^{-12}
1C	8.810×10^{-10}	2.01×10^{-12}
1D	7.960×10^{-10}	2.01×10^{-12}
1E	7.842×10^{-10}	1.99×10^{-12}
1F	9.495×10^{-10}	2.00×10^{-12}
1G	8.234×10^{-10}	1.99×10^{-12}
2D	1.701×10^{-10}	2.09×10^{-12}
3C	2.710×10^{-10}	2.26×10^{-12}
3D	2.890×10^{-10}	2.29×10^{-12}
4A	3.552×10^{-10}	2.28×10^{-12}
4C	3.734×10^{-10}	2.36×10^{-12}
4D	3.532×10^{-10}	2.35×10^{-12}
4F	3.853×10^{-10}	2.48×10^{-12}

The information on the capacitance of the system, besides the between-electrodes area, and the film thickness, allows the determination of values for the HKUST-1 dielectric properties.

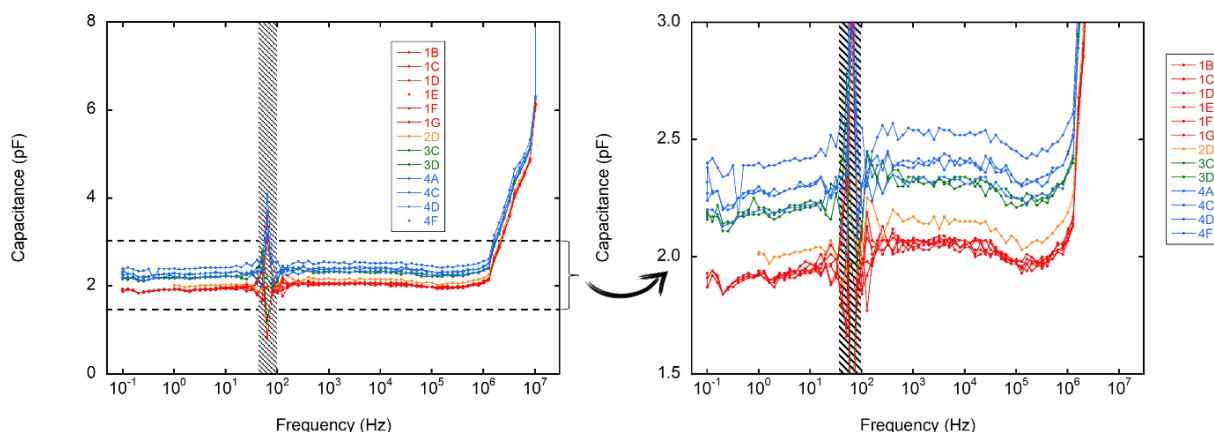


Figure A4: Capacitance (C_p) in the function of frequency for the CTVJ devices, color-discerned according to their column on the samples (different finger lengths).

The characterization of the devices was performed under high ($\approx 80.0\%$) and low ($\approx 0.1\%$) relative humidity (RH) atmospheres. The linear regression of the mean values for C_p vs. A was performed for the calculation of dielectric properties of the HKUST-1 SURMOF 40 cycles-thick film.

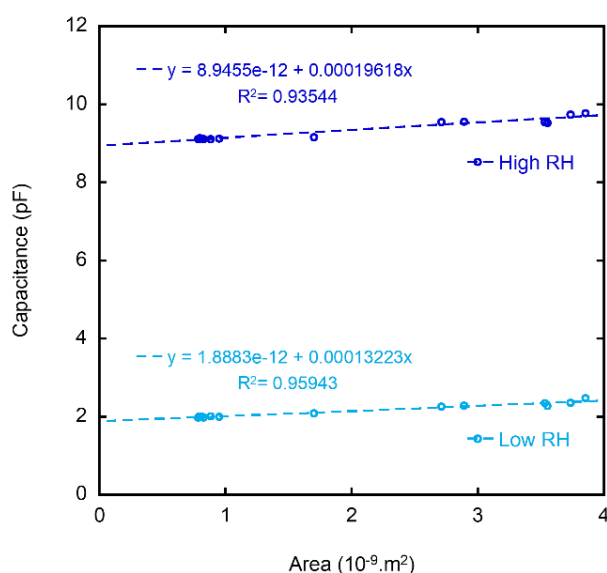


Figure A5: Mean values of the C_p in the function of the CTVJ devices area, for low and high RH atmospheres. The linear fitting of the values is displayed for each case.

The fitted linear curve returns an angular coefficient, enabling the extraction of a value of $\kappa \approx 0.9$, and $\kappa \approx 1.3$ in the low and high RH atmosphere, respectively, for the HKUST-1 film. The values achieved are not acceptable, physically wise (specifically, the 0.9). Therefore, further

investigation and analysis are necessary. Air humidity plays an important role in the dielectric response, but the establishment of such a role needs a more detailed study, beginning with the accounting of the data error values, and then the investigation and fit of the model that better

describes the polarization on the material in each case (the modeling of the system is not adequate yet).

Furthermore, I vs. V measures were performed and the results are plotted in **Figure A6**. The electric characterization for different devices with a similar area (1B with 1D, and 2C with 2D) is shown in **Figure A6,a**, while **Figures A6,b-d** display the I responses for the same devices measured in high and low air humidity.

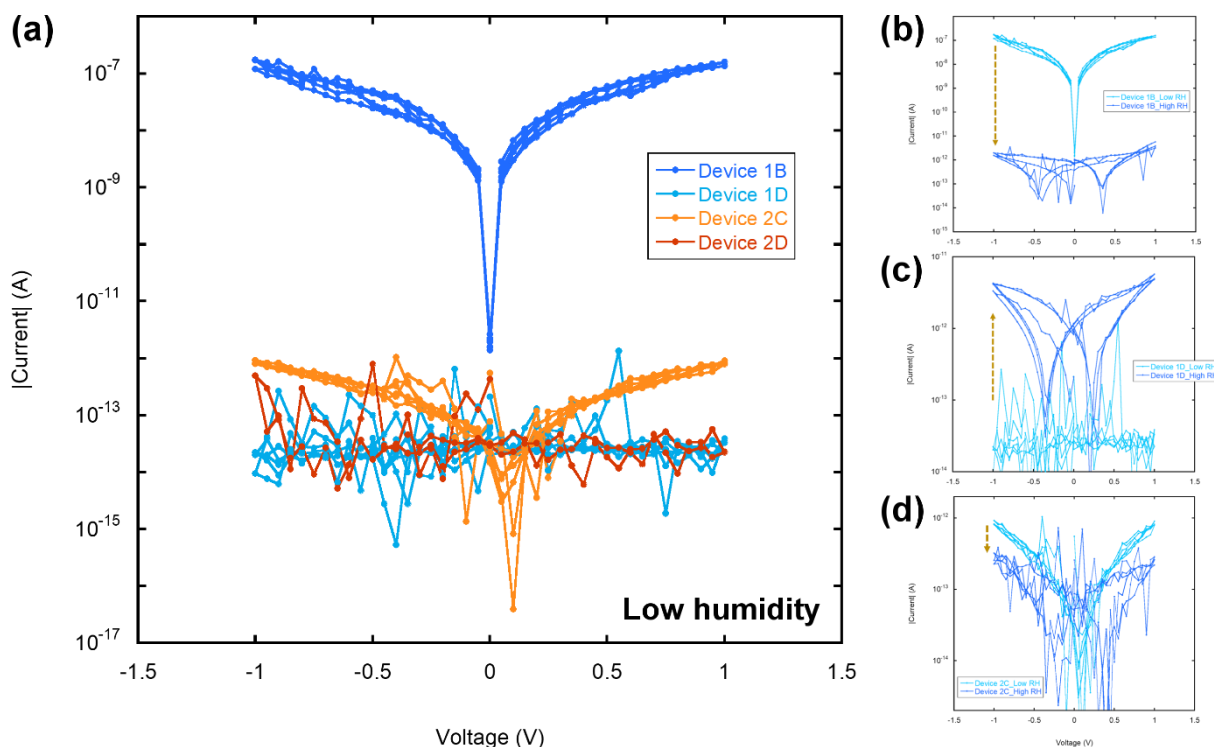


Figure A6: I vs. V plots of the electric measures for the CTVJ devices. **(a)** Electric current response for different devices with a similar area (1B with 1D, and 2C with 2D). **(b)-(d)** Electric current response for the same devices in high and low air humidity conditions.

As one may note, the measures of similar area devices do not demonstrate a reproduction of the current response. Neither the measures in high and low humidity for the same devices (**Figure A6,b-d**). This may represent the different charge injection areas on each device due to the mechanical contact established by the tube collapse. To attest to such an assumption, one may compare the I vs. V data with the impedance spectroscopy, since the Z' partially corresponds to the current response on the device, and Z'' does not directly relate to the charge injection area of the top electrode.

The design of the CTVJ comprises a promising device architecture for the investigation of charge accumulation and transport through dielectric ultrathin films, placed between

electrodes with soft-established top contact. Further study is necessary for the continuation of the projects regarding the CTVJ device.

APPENDIX B: HKUST-1 IN ANTENNAS

High-performance low- κ dielectrics can also be of benefit by their application in micro-scaled antennas. Miniaturization of antennas represents an obstacle since their resonance responses happen in wavelengths of the same magnitude orders as their sizes (half or quarter-wave dipole antennas, for instance). In a simplified way, the smaller the size of the antenna, the higher the generated signal frequency must be. A dielectric media around the antenna may shift the signal resonance frequency without significant power loss. In this scenario, dielectrics such as the HKUST-1, SiO₂, and Al₂O₃ were simulated-tested and further deposited onto micro-scaled antennas (in planar and rolled-up systems), for the study of the signal response of such irradiating structures.

The electric investigation of such structures is performed in high-frequency V_{AC} generators ($\approx$ GHz). For this kind of high-frequency measurement, power, and energy are considered easier to quantify than currents and voltages. Therefore, the use of the scattering parameter (S) is commonly employed. The scattering term directly regards what happens to a potential or current signal inside a network. When the traveling signal meets a different impedance, it acts like a barrier to the signal, which will be “scattered” (partly pass through the barrier, partly reflect, partly irradiate, partly dissipate/store, among other interactions). In a network with N ports (where a port is a pair of terminals, with the same entering and exiting current) S is represented as a matrix of dimensions $N \times N$ (with N^2 elements), each one a complex number. In a many-impedance system (many components/devices in a circuit), all these scattered signals will mix up, which results in a complex interaction for the response in each of the network ports. Each term of the $S_{N \times N}$ matrix represents part of the interferences of the signal.

An antenna represents a simple one-port network (two-terminal device). In this case, the scattering parameter is denominated Γ (or S_{11}) and is defined as follows:

$$\Gamma = S_{11} = \frac{V_{reflected}}{V_{incident}} = \frac{Z_{load} - Z_0}{Z_{load} + Z_0} \quad (76)$$

where Z_{load} is the impedance of the device under test (DUT), and the Z_0 is the impedance of the setup. We consider the set-up a purely real impedance, so $Z_0 = Re_{Z_0} = Z'_0$. Hence, we can relate:

$$\Gamma = Re_{(S_{11})} + j.Im_{(S_{11})} \quad S_{11} = \frac{Z_{load} - Z_0}{Z_{load} + Z_0} \quad (76)$$

$$Re_{(S_{11})} + j.Im_{(S_{11})} = \frac{(Re_{Z_{load}} + j.Im_{Z_{load}}) - Re_{Z_0}}{(Re_{Z_{load}} + j.Im_{Z_{load}}) + Re_{Z_0}} = \quad (77)$$

$$= S'_{11} + j.S''_{11} = \frac{Z'_{load} + j.Z''_{load} - Z'_0}{Z'_{load} + j.Z''_{load} + Z'_0} \quad (78)$$

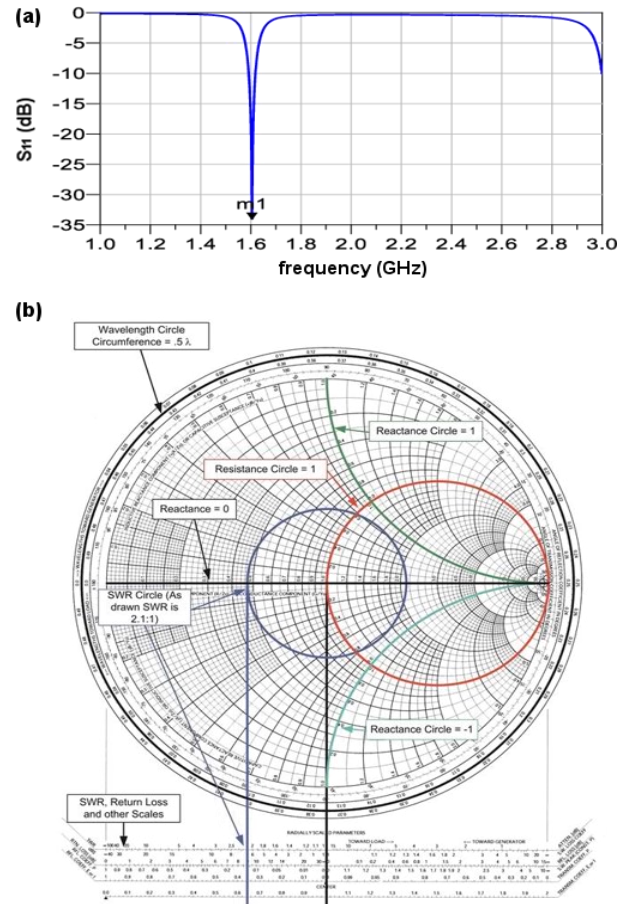
$$S'_{11} = \frac{Z'^2_{load} + Z''^2_{load} - Z'^2_0}{(Z'_{load} + Z'_0)^2 + Z''^2_{load}} \quad S''_{11} = \frac{2.Z'_{load}.Z'_0}{(Z'_{load} + Z'_0)^2 + Z''^2_{load}} \quad (79)$$

$$Z'_{load} = \frac{Z'_0.(1 - S'^2_{11} - S''^2_{11})}{(1 - S'_{11})^2 + S''^2_{11}} \quad Z''_{load} = \frac{2.Z'_0.S''_{11}}{(1 - S'_{11})^2 + S''^2_{11}} \quad (80)$$

$$RL = -20.log\left(\left|\frac{V_{ref}}{V_{inc}}\right|\right) = -20.log(|\Gamma|) = -20.log(|S_{11}|) \quad (81)$$

In the equations, RL is the resistance loss, V_{ref} is the reflected potential and V_{inc} is the incident potential. To impedance matching of the electronic systems, it is universally defined as a value of $Z_0 = 50 \Omega$ for ICs. Therefore, the set-ups destined for S-parameters characterization usually have a purely resistive (negligible imaginary part) impedance equal to 50Ω . The most common plot representations of the S_{11} values usually depict (i) a frequency dependency/variation in a cartesian chart, or (ii) the real and imaginary parts of the parameter in a polar chart (Smith Chart). Both representations are shown in **Figure A7**.

Figure A7: Illustration of the charts representation for the S-parameters data. **(a)** S_{11} in a function of the applied frequency with one resonant peak, depict in a frequency of ≈ 1.6 GHz. **(b)** Smith chart representation of the S_{11} , where the horizontal axis represents the S' (resistance) values, the external circular axis represents the S'' (reactance) values, and the rulers below indicate



the power losses. The web-like tangled dashes are guidelines for the relationship between the data and its respective values on the axes.

The micro-scaled antennas were designed for fabrication. **Figure A8** shows the architectures used here. The antenna designs depicted in **Figures A8,a-b** are references, for comparison matters. The smaller reference antenna (**Figure A8,b**) has one-quarter of the area of the bigger reference antenna (**Figure A8,a**). The four antenna designs in **Figures A8,c-d** are the architectures developed for the roll-up process. The antennas in **Figure A8,d** are similar to their respective ones in **Figure A8,c**, only presenting longer wires (with more cycle patterns) and different designs for rolling-up direction. The longer antennas are supposed to reveal lower values of the resonant frequency.

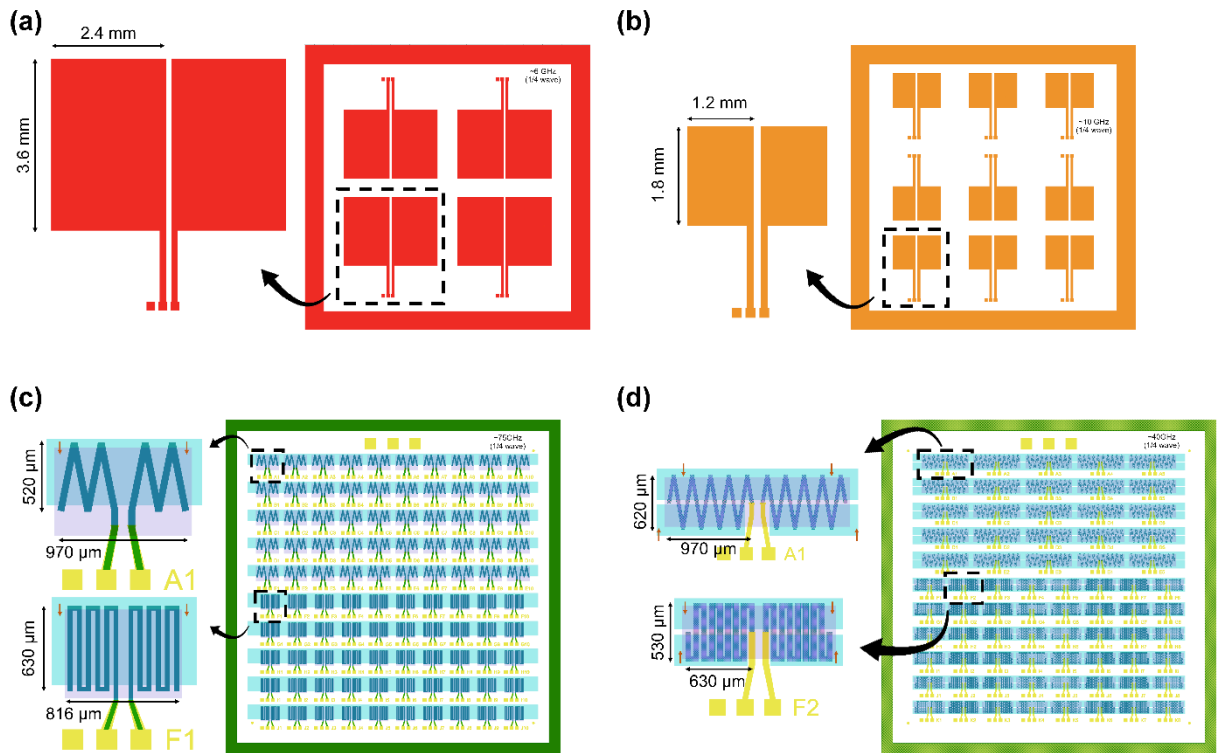


Figure A8: Macro and micro-scaled architectures of antennas used here. (a)-(b) Reference antennas developed in the millimetric scale, for later comparison matters. (c)-(d) Antennas in the micrometric scale, designed for the roll-up process.

The architectures of the antenna were used in simulations for the determination of the irradiation response of such systems (**Figure A9**) and later turned into masks for the fabrication of the devices (**Figure A10**). All the simulations –the early results are illustrated in **Figure A9** – were performed in the Software ANSYS (from *ANSYS Inc.*). Further simulations also revealed that, for the indicated structures in **Figure A9**, the variation in the performance was

representative, so those were chosen for reproduction by the microfabrication techniques already described in this work, and later for the roll-up process. After the first results, better models were raised and calculated for the determination of the final structures fabricated and measured (**Figure A9** illustrates only the results for the early simulations).

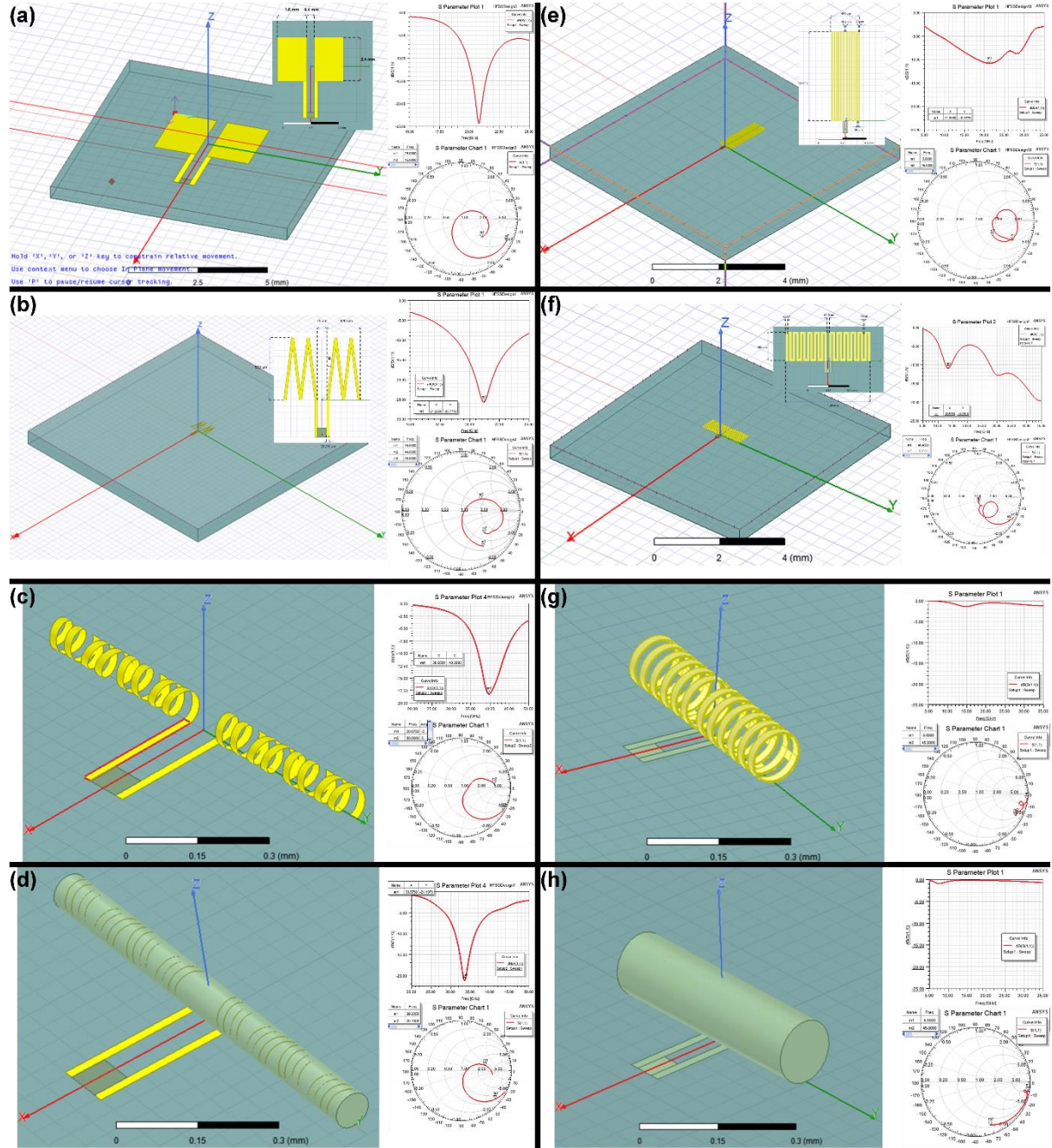


Figure A9: Illustration of the antenna structures used so far, as well as their respective high-frequency simulation results plotted in S_{11} vs. f and Smith Chart. The structures are: (a) reference planar; (b) shorter triangular-shaped planar; (c) longer triangular-shaped rolled-up; (d) longer triangular-shaped embedded in dielectric and rolled-up; (e) shorter rectangular-shaped planar; (f) longer rectangular-shaped planar; (g) longer rectangular-shaped rolled-up; (h) longer rectangular-shaped embedded in dielectric and rolled-up.

The simulations demonstrated better performance of the rolled-up system (left-shifting the resonant frequency) and an improvement in the magnitude of the signal for the structures embedded into dielectrics. Some of the fabricated structures are represented in **Figure A10** (the equivalent to those in **Figure A8c**). The roll-up process was again calibrated for the new *NM* releasing devices, and the structures represented in **Figure A10** were the only ones successfully fabricated and rolled up, up until now.

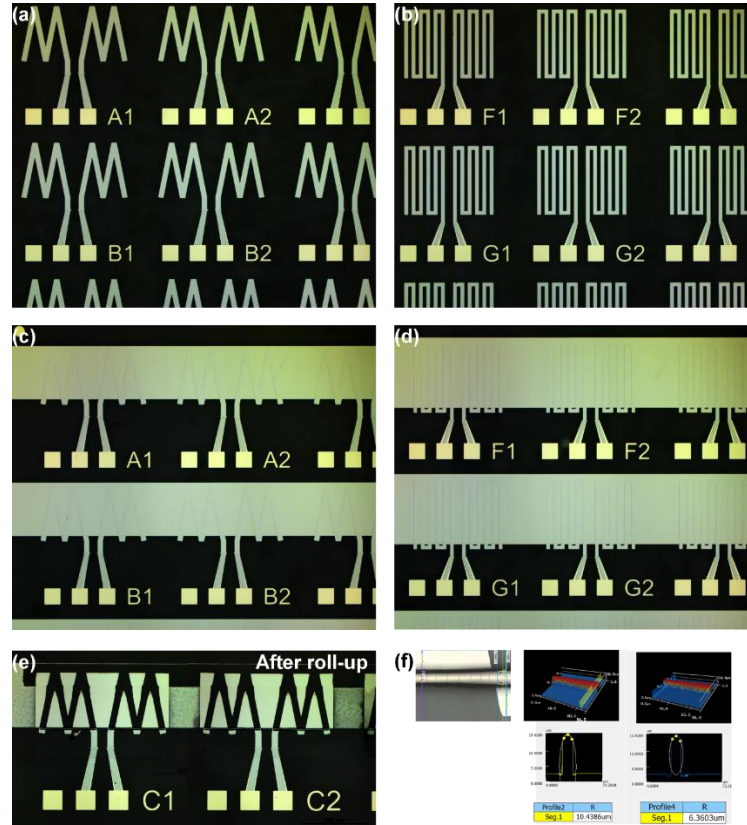


Figure A10: Optic microscopy of the fabricated antennas with the architectures defined after simulation tests. **(a)** Shorter triangular-shaped planar; **(b)** shorter rectangular-shaped planar; **(c)** shorter triangular-shaped for roll-up; **(d)** shorter rectangular-shaped for roll-up; **(e)** shorter triangular-shaped embedded in dielectric and rolled-up; **(f)** LSCM for the determination of the dimensions of the antenna tubes.

As demonstrated in **Figure A10,e** the shorter triangular-shaped dielectric-embedded (Al_2O_3) antennas were successfully rolled-up and are the only antenna design presenting suitable devices for electric measurement, up to now. **Figure A10,f** shows LSCM for dimensions characterization of the tubular-shaped antennas, revealing tubes of $\approx 10.4 \mu\text{m}$ in the wider parts and $\approx 6.4 \mu\text{m}$ in the narrower parts (the tubes present different widths, naturally from the triangular-shape rolling-up).

The succeeded antennas were taken to the Brazilian Center for Research in Physics (in Portuguese *Centro Brasileiro de Pesquisas Físicas, CBPF*) for the high-frequency electric measurements, performed in a Vector Network Analyzer (VNA). The measured antennas, such as their VNA measurement results, are displayed in **Figure A11**.

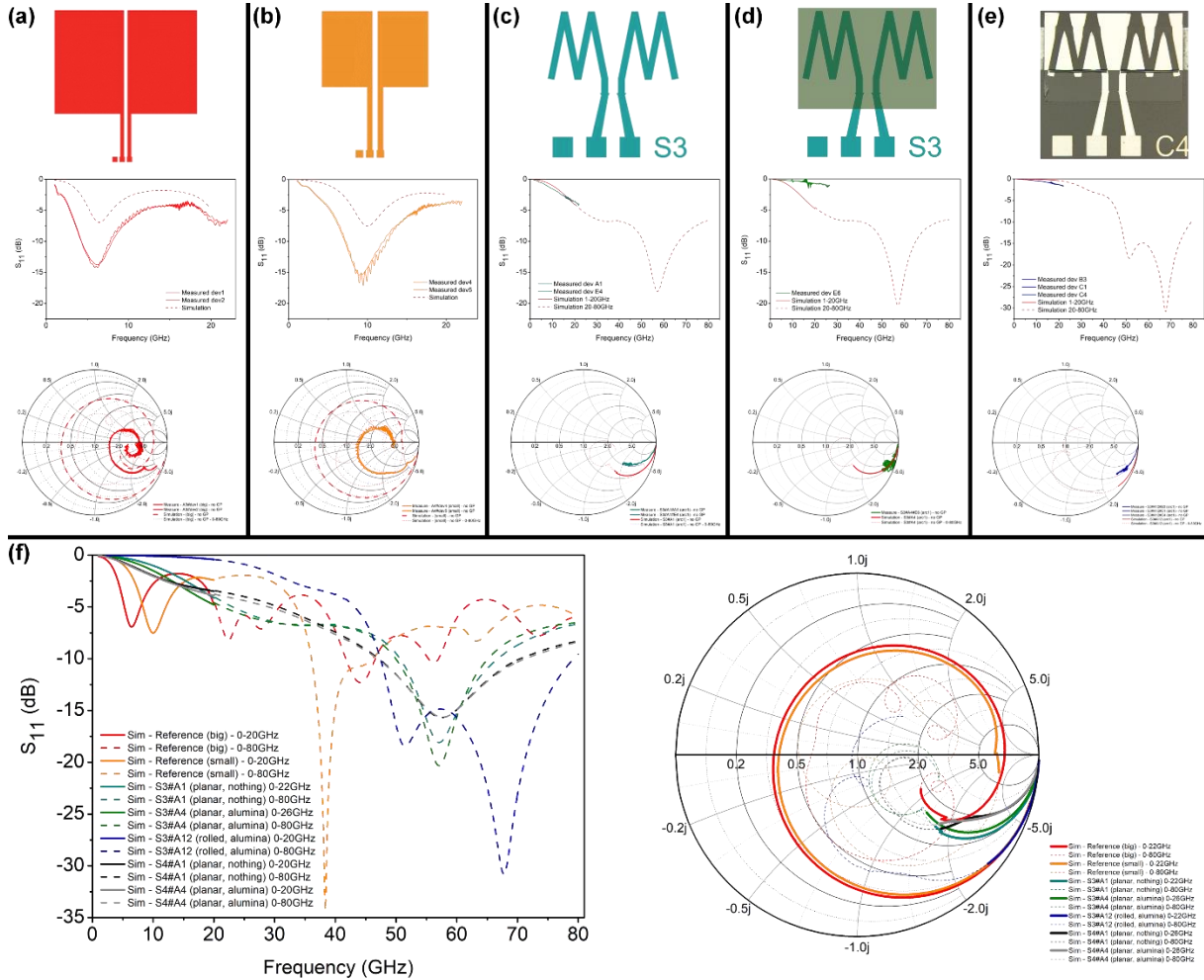
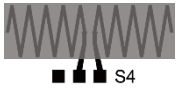


Figure A11: Antenna architectures taken to *CBPF* for VNA measurements and respective results. Representation of the devices measured: **(a)** bigger reference planar; **(b)** shorter reference planar; **(c)** shorter triangular-shaped planar; **(d)** shorter triangular-shaped embedded in (Al_2O_3) dielectric; **(e)** shorter triangular-shaped embedded in (Al_2O_3) dielectric and rolled-up. **(a)-(e)** displays the device architectures in the upper panel, S_{11} vs. f results in the middle panel, and the Smith Chart in the bottom panel. **(f)** S_{11} vs. f results for all the measured architectures. **(g)** The Smith Chart of all the measured architectures.

The measurements on the VNA for the antennas revealed partially expected results for the last simulations taken before the fabrication of the devices. However, the limitations of such electric measurements are found in the high-frequency restrictions. The maximum value achieved for the VNA and cables on the set-up was ≈ 18 GHz, for reliable results. One may note that the experiment data only take a small part of the whole simulated profiles on the plots.

Another point to raise is that, according to the last simulated data, the resonance peaks for the rolled structures are yet too high for a realistic application of such devices. The highlighted results of the VNA measurements are demonstrated in **Table A2**.

Table A2: Main results on the VNA measures for the micro-scaled antennas.

Antennas architecture	Antennas illustration	First peak frequency (GHz)	First peak intensity (dB)	Higher peak frequency (GHz)	Higher peak intensity (dB)
Bigger reference		6.46	-6.93	44.10	-12.31
Smaller reference		9.98	-7.51	38.35	-34.30
Planar smaller triangular antenna – nothing over it		57.09	-18.10	57.09*	-18.10*
Planar smaller triangular antenna – Al ₂ O ₃ over it		57.09	-20.33	57.09*	-20.33*
Rolled smaller triangular antenna – Al ₂ O ₃ over it		51.48	-18.43	67.73	-30.81
Planar bigger triangular antenna – nothing over it		57.54	-15.67	57.54*	-15.67*
Planar bigger triangular antenna – Al ₂ O ₃ over it		57.64	-15.64	57.64*	-15.64*

*Higher peak is the first and only relevant peak in the frequency range explored.

The results of the measurements on the VNA reveal that, for the more complex structures, even the newer simulations considered here did not properly describe the behavior of the devices, despite approaching the electric results for the reference antennas. Parameters such as ground plane and structural composition of the tri-metallic *NM* (Au/Ti/Cr) were raised, but for a more appropriate simulation, other parameters need to be considered. The skin effect presented in conductor-thin films is an example. Also, the structuration of the tubular form in the simulation software must be better analyzed and determined.

Besides that, a better model for simulations allows further exploitation of new architectures of antennas, to a better approximation of a resonant peak for the devices. Finally, the antenna *NM* structures and roll-up parameters must be better calibrated. To sum up, this project reveals promising expectations but still has many steps before achieving the exciting, expected results.

APPENDIX C: ORGANIC-HYBRID INTERFACE: NM-BASED HETEROJUNCTION

For a possible next step of the project, after the development of an investigation of the MPcs and HKUST-1 SURMOF layers as dielectrics, the necessity of the study of an MPc / HKUST-1 interface comes almost naturally. For such, the first step is to incorporate such heterojunction into the *r-NM*-junction device, as its process is by far better calibrated. After that, to solve the problem of the area determination of the *r-NM*-junction, the heterojunction would be incorporated into the CTVJ structures, and its charge accumulation and transport would be better explored in a more precise area determination device. The well-explored properties of the CuPc (organic semiconductor) can be used for the extraction of the mechanisms responding in the HKUST-1 interface as an insulator, such as the charges behavior and deep-trapped accumulation.

The first attempts already resulted in an interesting response of the heterojunction (on the finger, with the *NM*-based tubular top electrode). **Figure A12** shows the *I* vs. *V* plot for an *r-NM*-junction with the heterojunction SURMOF HKUST-1 / CuPc between the finger and tube electrodes.

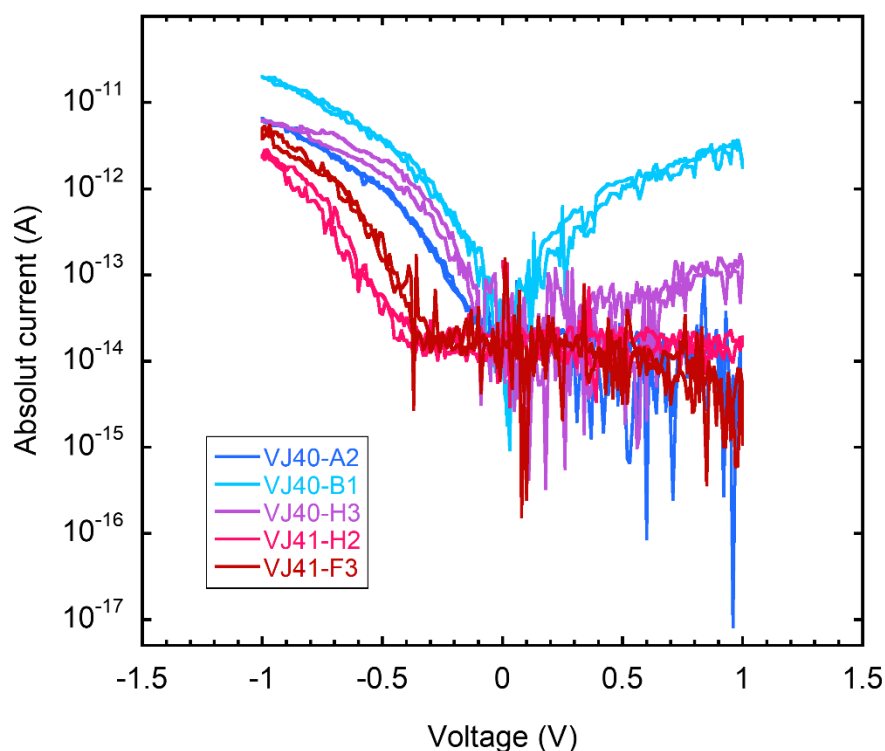


Figure A12: Plotted results of the electric measurements (I vs. V) of five r -NM-junction devices containing a SURMOF HKUST-1 / CuPc heterojunction.

In this case, a principle of rectification is observed for the negative biases. Regarding the structure of the devices, the LbL-deposition was performed onto a SAM MHDA on the finger, and a very slow deposition rate ($\approx 0.15 \text{ \AA/s}$) of the CuPc was performed on the HKUST-1. The measure was made by applying a potential in the tube while grounding the finger electrode. A first analysis indicates that the CuPc is acting as an n-type semiconductor (transporting negative charge carriers), despite being a p-type organic semiconductor. More investigation is necessary.

Also, the main difficulty finds up to now is the establishment of a proper interface between MPc and the SURMOF HKUST-1. A possible solution to circumvent the interface formation problem relies on the inversion of the layers: the growth of HKUST-1 films onto the CuPc layer indicates a viable alternative, once the Cu core of the later molecule provides nucleation sites for the chemical reaction required for the kick-off of the MOF growth. Such an approach was explored, and the bi-layer CuPc/HKUST-1@TCNQ (dopant molecule for the MOF) was placed into the r -NM-junction. First I vs V results of such structures revealed some rectification expected for the junction (**Figure A13**).

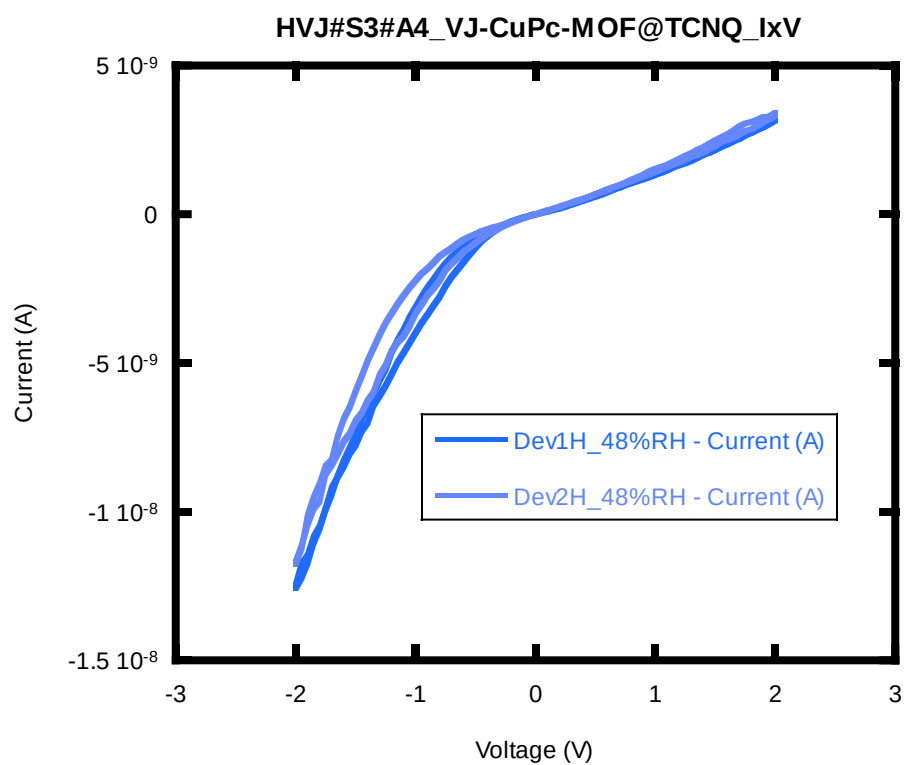


Figure A13: Plotted results of the electric measurements (I vs. V) of five r -NM-junction devices containing a CuPc / HKUST-1@TCNQ heterojunction.

The ongoing work reveals exciting results to urge further investigation.