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CARO LEITOR NÃO
RISQUE O LIVRO

PLASMA O MEIO, MACROMOLÉCULAS E POLÍMEROS OS
PRODUTOS.

Texto Sistemático Crítico Apresentado à Faculdade de
Engenharia da Universidade Estadual Paulista - Campus de
Guaratinguetá para o Concurso de Livre - Docência.

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DEDICATÓRIA

Á minha família e a todos
que de várias formas buscam
sempre o caminho da felicidade.

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Rogério Pinto Mota

Texto Sistemático Crítico

**Apresentado à Faculdade de Engenharia da Universidade
Estadual Paulista - Campus de Guaratinguetá para o Concurso de
Livre - Docência.**

APRESENTAÇÃO

Guaratinguetá, novembro de 1996



Texto Sistemático Sobre Nossas
Contribuições no Estudo de
“Plasma o Meio, Macromoléculas e
Polímeros os Produtos”

Elaborado por

Rogério Pinto Mota

APRESENTAÇÃO

Resolvi por esta forma de apresentação, que trata de uma análise crítica de alguns trabalhos que desenvolvi após a conclusão do doutorado no Instituto de Física da Universidade Estadual de Campinas em 1992, em substituição à tradicional tese de Livre - Docência elaborada por vários pesquisadores. Trabalhos estes desenvolvidos na UNESP e alguns deles em parceria com a UNICAMP de 1992 até o presente momento.



Optei por esta sistemática, salientando em primeira instância que procuro apresentar uma visão crítica da importância de nossos trabalhos referentes ao estudo de Plasmas reativos e os produtos neles gerados.

Portanto, com esta análise crítica, procuro não competir com os estudantes de iniciação científica e pós - graduação, assim como com meus colegas e amigos de profissão que trabalham nesta área junto comigo, sobretudo busco ressaltar aqui algumas entre várias contribuições que temos dado na área interdisciplinar de Plasmas e suas aplicações.

1.1 Primeiro Trabalho de submissão aos Arquivos Lattes

1- Primeira Parte - Considerações Gerais

Não abordamos de forma direta como surge o plasma de um Plasma de baixa temperatura, e sim, como este plasma de baixa temperatura surge a partir da ionização do Plasma e algumas propriedades físicas e químicas, assim como a sua aplicação em diversas áreas da física.

2- Segunda Parte

Utilização do plasma como meio de síntese e preservação

3- Terceira Parte

Utilização do plasma na síntese de materiais - síntese de materiais



VISÃO GERAL DO TEXTO

No presente texto discutimos criticamente nossos trabalhos de cunho experimental, relacionados com estudos espectroscópico-ópticos e elétricos de Plasmas derivados de hidrocarbonetos e organometálicos como siloxanos e silazanos, assim como os subprodutos sólidos provenientes destes Plasmas, procurando enfatizar suas morfologias e propriedades físicas como tensão mecânica, adesão e difusividade térmica.

O Presente Trabalho se subdivide nas Seguintes Partes:

1- Primeira Parte - Considerações gerais.

São abordados de forma sumária nesta etapa noções gerais de um Plasma de baixa temperatura, o polímero nele produzido, as técnicas utilizadas para a caracterização do Plasma e algumas propriedades termo-mecânicas dos polímeros, essenciais para a compreensão do texto.

2- Segunda Parte

Utilização do plasma como simulador de atmosfera planetária.

3- Terceira Parte

Utilização do plasma na síntese de materiais compostos chamados "CERMETS"



4- Quarta Parte

O plasma empregado na deposição de polímeros fluorados

5- Quinta Parte

Estabilidade e propriedades termo-mecânicas de polímeros depositados a plasmas

A fim de facilitar a compreensão, os trabalhos foram agrupados no texto seguindo os tópicos acima. Primeiramente é feita a abordagem crítica em cada tópico e em seguida apresentado o trabalho no formato em que ele foi publicado ou se encontra em vias de publicação.

No texto crítico como um todo, não foram levantadas as referências bibliográficas, pois consideramos que as mesmas estão contidas nos próprios artigos.



PRIMEIRA PARTE

Considerações Gerais

- O Plasma e o Polímero
- Espectroscopia Óptica do Plasma Usando Actinometria
- Medidas Elétricas no Interior do Plasma Utilizando Sonda de Langmuir
- Tensão Mecânica Residual Interna
- Adesão Filme / Substrato



O Plasma e o Polímero

Em vários locais no Universo, seja em laboratório ou não, é sempre possível se encontrar partículas neutras. Em especial, pode-se em vários casos perceber a presença de elétrons e de íons negativos e positivos e cujas populações tanto podem estar acima quanto abaixo daquelas constituídas pelas partículas neutras. Estamos comentando aqui o Campo da Ciência que abrange o PLASMA.

Desde a estrela mais próxima, um ponto longínquo no universo, uma lâmpada fluorescente ou mesmo ainda um diminuto reator em um laboratório, pode se sentir os efeitos do plasma se considerarmos que íons positivos e elétrons participam em igual número em qualquer destes meios. A luz gerada destes plasmas apresentará maior ou menor intensidade, mediante maiores ou menores níveis de excitação dos estados energéticos que compõem estes meios.

Portanto, reações internas e externas a um sistema, principalmente processos colisionais, sejam eles eletromagnéticos ou não, são em princípio fontes geradoras de um plasma qualquer.

Alguns caminhos estão diretamente relacionados com o estudo que contempla este ramo da ciência, dentre eles, aqueles que buscam o entendimento e o controle da fusão, como os que tratam do processamento de materiais de interesse tecnológico como os polímeros e dos constituintes pré-bióticos da matéria.

Em nosso caso especial, os plasmas frios, isto é, aqueles que apresentam baixa temperatura eletrônica, assim como baixa densidade de elétrons quando comparado ao



total de partículas neutras, são no momento fontes importantes no desenvolvimento de novos materiais.

Quando um plasma desta natureza é criado através de excitação de tensão contínua ou de frequência variável como áudio, rádio e microondas entre outras, sobre atmosferas de baixas pressões, provenientes de vapores e / ou gases orgânicos ou misturas de inorgânicos / orgânicos, dá-se origem a intensos processos de fragmentações moleculares.

Dentre estes processos temos: Fragmentação por radiações eletromagnéticas, impactos provenientes de transferência de momentum entre partículas de maior massa, decaimento e em especial colisões por impacto energético de elétrons. Uma vez iniciada a fragmentação molecular, mecanismos complexos de recombinações envolvendo íons, elétrons, radicais livres, partículas neutras, etc, tomam lugar no ambiente onde esteja ocorrendo estas reações. Como produto resultante, temos a formação de macromoléculas e polímeros na forma sólida, que podem coexistir na fase de vapor em suspensão na descarga, constituindo elementos no formato de pó, ou ainda na forma de filme fino, quando as reações ocorrem ao contato com algumas superfície interna ao reator.

Após recombinação, quando as moléculas se tornam muito grandes, contendo um número de átomos encadeados superior a uma centena e podendo atingir valor ilimitado, as propriedades destes novos grupamentos ganham características próprias, gerais, muito mais dominantes que as características que decorrem da natureza química dos átomos que as constituem ou dos grupos funcionais presentes.



Estas propriedades físicas e químicas decorrem de interações envolvendo segmentos da mesma macromolécula ou de outras, cuja forma e o comprimento das ramificações presentes no elemento final desempenham um papel extremamente importante.

Quase sempre, estes polímeros, como estes elementos usualmente são conhecidos, apresentam cadeias bastantes ramificadas e entrelaçadas. Em decorrência deste fato as moléculas são fortemente unidas fazendo com que estes tipos poliméricos sejam de baixa solubilidade e bastante inertes a ácidos e bases fortes, além de serem bem aderentes aos mais diversos tipos de substratos. Aliado às características anteriores, o processo de deposição a plasma apresenta a característica peculiar de produzir polímeros cuja estrutura está livre de “Pinholes”, isto é; de buracos minúsculos. Razões estas, que fazem estes materiais promissores no desenvolvimento tecnológico.



Espectroscopia Óptica do Plasma Usando Actinometria.

A técnica espectroscopia óptica de emissão actinométrica, ou simplesmente ACTINOMETRIA é um método para diagnosticar a evolução de espécies químicas em um plasma reativo, de forma não intrusiva, isto é, o comportamento das espécies químicas está intimamente relacionado com a luz emitida pelo plasma e analisada por um espectrômetro monocromador, sem a necessidade de se inserir nenhum tipo de sonda na região do plasma.

Por este método, uma pequena proporção de um gás não reativo, o “actinômetro”, é adicionada ao ou aos gases que compõem o plasma. A intensidade de emissão óptica de uma linha do actinômetro é dada por:

$$I_a = n_a \eta_a k_a \quad (1)$$

onde n_a é a densidade de moléculas do actinômetro no estado fundamental, η_a é a eficiência de excitação do estado fundamental para levar as espécies do estado fundamental ao estado excitado responsável pela emissão óptica, k_a é uma constante. Deve-se lembrar que η_a depende da função distribuição de energia dos elétrons do plasma e aumenta com o aumento da atividade do plasma.

O parâmetro atividade do plasma é definido como $A = \bar{\rho} \bar{E}$ onde $\bar{\rho}$ e $\bar{E}$ são respectivamente a densidade de elétrons e a energia média destes elétrons. Se n_a é



mantido constante, pode ser visto na expressão (1) que trocas na intensidade de emissão do actinômetro, refletem modificações na atividade do plasma.

Combinando medidas de emissão óptica da espécie reativa x com as do actinômetro, segue que a determinação das trocas relativas das espécies em estudo, tomadas em função dos parâmetros do plasma, como pressão, potência, composição, etc, podem ser efetuadas.

Seja I_x a intensidade de uma emissão da espécie x , então:

$$I_x = n_x \eta_x k_x \quad (2)$$

onde η_x e n_x são respectivamente a eficiência de excitação para levar as espécies x do estado fundamental ao estado excitado e a densidade da espécie x no estado fundamental, k_x é uma constante.

Combinando as equações (1) e (2) podemos escrever:

$$n_x = n_a \left[\frac{k_a I_x \eta_a}{k_x I_a \eta_x} \right] \quad (3)$$

Como o método presume que os limiares de excitação do actinômetro e da espécie de interesse sejam próximos, e tomando n_a como constante, temos:

$$n_x = k' \frac{I_x}{I_a} \quad (4)$$

onde k' é uma constante e I_x e I_a linhas de emissão medidas com o espectrômetro.

Medidas Elétricas no Interior do Plasma Utilizando Sonda de Langmuir.

Medidas de densidade e temperaturas eletrônicas são comumente feitas em um reator na região onde está presente um plasma, quando se introduz uma sonda eletrostática, constituída por uma ponta metálica isolada externamente, no interior do plasma. Este tipo de configuração é conhecido como sonda de Langmuir. A técnica em si, consiste em introduzir a sonda no plasma e observar a corrente coletada da sonda em função da diferença de potencial estabelecida entre o eletrodo e uma referência. A sonda é então bombardeada por íons e elétrons. Os elétrons se acumulam nas vizinhanças dela dependendo de sua menor massa ou maior mobilidade ao se comparar com a massa dos íons.

Um campo elétrico é então originado, próximo a sonda, sendo ele responsável pela desaceleração dos elétrons e aceleração dos íons até que o fluxo final de cargas na sonda seja nulo. A sonda passará a ter um potencial flutuante V_F . Ao se aplicar um potencial V_S na sonda, menor que V_F , aparecerá uma corrente I_S representativa dos íons positivos se a sonda for polarizada negativamente. À medida que a tensão V_S é aumentada, os elétrons mais energéticos vencem a barreira de potencial e atingem a sonda igualando o fluxo de íons e elétrons. Deste ponto em diante o número de elétrons que alcançam a sonda passam a ter uma distribuição exponencial entre os potenciais V_P e V_S , onde V_P representa o potencial do plasma. Para $V_S > V_P$, os elétrons são acelerados e os íons repelidos, até que haja uma saturação dos elétrons.



A corrente $I(V)$ de elétrons na direção x que colidem com a sonda, quando esta é colocada no plano yz é dada por:

$$I(V) = n_e e A \int_{v_{\min}}^{\infty} dv_x v_x \left(\frac{2\pi k T_e}{m_e} \right)^{-1/2} \exp\left(\frac{-m_e v_x^2}{2k T_e} \right) \quad (5)$$

onde:

m_e = massa do elétron

e = carga do elétron

k = constante de Boltzman

T_e = temperatura eletrônica

A = área total da sonda

v_x = velocidade na direção x

n_e = número de elétrons

Tensão Mecânica Residual Interna

A grande maioria dos filmes finos, independente do processo de deposição, apresentam tensões mecânicas residuais internas σ . Esta tensão mecânica está relacionada com diversos fatores tais como a variação na microestrutura do filme, a densidade de defeitos inerentes ao processo de crescimento e a incorporação de gases residuais presentes no reator, bem como as reações químicas entre as espécies depositadas. Todos estes fatores contribuem para que ocorram rearranjos atômicos durante e após o processo de crescimento, contribuindo para o surgimento de tensões localizadas que com o passar do tempo podem comprometer de forma definitiva a estabilidade do filme.

Se durante ou após a deposição, o filme tender a contrair-se (diminuir seu volume), surgirá no mesmo uma tensão de tração, porque o vínculo com o substrato impede parcialmente a relaxação do mesmo, i. é., o filme não pode se deslocar livremente em relação ao substrato. Desta forma, o substrato curvar-se-á ficando o filme acomodado na parte côncava. Por outro lado, se o filme tender a dilatar-se (aumentar o seu volume) durante ou após a deposição, surgirá no mesmo uma tensão de compressão, resultando na curvatura do substrato, ficando o filme acomodado na região convexa. Logo, a tensão mecânica está relacionada com o raio de curvatura do substrato, provocado pelo filme.



Considera-se inicialmente a lei de Hooke na forma generalizada que relaciona tensões e deformações no interior de um material elástico e isotrópico, dada pela relação:

$$\sigma = \frac{E}{1-\mu} \varepsilon \quad (6)$$

onde ε e σ são respectivamente a deformação relativa e a tensão, e E e μ são os respectivos módulo de Young e a razão de Poisson.

Considerando o substrato como sendo uma barra retangular, de largura L e espessura t_s , após alguma álgebra a tensão mecânica será dada pela relação:

$$\sigma = \frac{E}{1-\mu} \frac{Z}{R} \quad (7)$$

A expressão para a tensão média armazenada no filme definida como a força média resultante na seção reta do filme, sobre a área desta seção será:

$$\sigma = \frac{F_f}{L t_f} = \frac{E_s t_s^2}{6(1-\mu) t_f} \left[\frac{1}{R_b} - \frac{1}{R_a} \right] \quad (8)$$

onde;

F_f = força no filme

L = largura do substrato

t_f = espessura do filme

E_s = Módulo de Young do substrato



t_s = espessura do substrato

R_b = raio de curvatura do substrato após o filme ter sido depositado

R_b = raio de curvatura do substrato antes do filme ter sido depositado

Os raios de curvatura antes e após a deposição do filme, são medidos pela reflexão da luz de um feixe de laser HeNe incidindo sobre o substrato e sobre o substrato/filme.



Adesão Filme-Substrato

Embora seja bastante importante do ponto de vista tecnológico, o estudo da adesão envolvendo filmes finos e superfícies sólidas não se encontra tão avançado. O motivo é a dificuldade dos ensaios experimentais e principalmente a abordagem do assunto.

Os métodos experimentais de medidas de adesão se classificam em mecânicos e não mecânicos, ambos apresentando ora natureza quantitativa ora qualitativa.

Entende-se a adesão como sendo a intensidade de ligação entre duas superfícies. Estas ligações que são atômicas ou moleculares podem ser do tipo Van der Waals, eletrostáticas ou ligações químicas, e ocorrem através de uma camada interfacial geralmente muito fina, formada entre o filme e o substrato. Uma medida correta da adesão é feita quando a separação entre as superfícies ocorre na camada interfacial e não na região do filme ou do substrato.

Os parâmetros envolvendo a camada interfacial, tais como: ligações atômicas formadas, a tensão mecânica residual, as constantes elásticas e a resistência à fratura, são imprescindíveis na determinação da intensidade da adesão. Logo, quaisquer alterações provenientes destes parâmetros podem acarretar modificações no valor da adesão e com isto explicar possíveis espalhamentos de resultados obtidos em filmes supostamente iguais, pois o seu controle é difícil.

Muitos fatores influenciam os mecanismos de adesão filme/substrato, em particular, a natureza dos materiais pares substrato/filme, a qual determinará o tipo de ligação e a natureza da superfície a ser formada. Por outro lado, são igualmente



importantes , os tratamentos de limpeza dados ao substrato antes do processo de deposição do filme, pois uma camada artificial pode ser criada entre o substrato e o filme, dependendo do processo de limpeza.

As condições e técnicas de deposição do filme ao substrato também alteram as características da interface e com isto da adesão. Normalmente, os filme depositados utilizando a técnica “sputtering” a baixas pressões do plasma, apresenta uma melhor aderência que técnicas de evaporação, pois as energias dos átomos que incidem sobre o substrato são maiores para a técnica “sputtering”, o que entre outros fatores é capaz de provocar uma limpeza adicional no substrato. por último, a temperatura envolvendo filme/substrato durante a deposição, é também fator importante na adesão, pois ela pode promover modificações na mobilidade, na difusão e na reatividade dos átomos do filme com a superfície do substrato.



SEGUNDA PARTE

Utilização do plasma como simulador de atmosfera planetária

No artigo “LABORATORY SIMULATIONS OF TITAN’S ATMOSPHERE: A POSSIBLE PATHWAY FOR PREBIOTIC CHEMICAL COMPOUNDS SYNTHESIS”, submetido à revista *Planetary and Space Science* em 1996, abordamos dois aspectos; um deles é a própria atmosfera e o segundo é o produto sólido formado que é a tolina.



A astronomia e astrofísica são ramos da ciência extremamente fascinantes, uma vez que elas tratam entre outros fatores da busca de nossa origem. E não é de hoje, a astronomia é uma ciência milenar. No entanto, as informações a cerca do universo são observacionais e nos presentes dias mais especificamente através de sondas enviadas ao espaço. Assim é uma procura constante reconhecer e mapear os astros celestes, desde cometas, planetas, estrelas e outros e seus elementos químicos constituintes.

O professor C. Sagan, da Universidade (de Cornell), mundialmente conhecido por ser o autor da “SÉRIE COSMOS” escrita e televisada, vem trabalhando por mais de duas décadas em simulações a nível de laboratório de atmosferas planetárias. Dentre estas atmosferas se situa o estudo de Titan, um importante satélite de Saturno rico em nitrogênio e metano. Seus trabalhos mais recentes sobre este asteróide datam de 1992 para cá.

Não obstante a nossa curiosidade na área, passamos a fazer parte do grupo de investigadores em simulações atmosféricas de astros celestes a nível experimental em laboratório. Em virtude da presença de nitrogênio e hidrocarbonetos, elementos essenciais a uma condição PRÉ-BIÓTICA, procuramos também estudar a atmosfera de “Titan”.

O primeiro passo foi a definição da atmosfera, baseado em dados de sondas espaciais. Nos trabalhos experimentais correntes na literatura os percentuais de nitrogênio abrangem valores de 80 a 99%, metano de 0,2 a 6,0%, argônio de 0 a 10%. Optamos em nosso trabalho por uma mistura Nitrogênio/Metano/Água nas proporções de 95/4,8/0,2%, onde acreditamos que a água possa ser produto de colisões provenientes de meteoros e planetesimais, com o satélite Titan, composição



atmosférica esta, não proposta até então. No entanto, estamos bastante eufóricos com nossa proposição, já que neste ano de 1996, sondas mostraram indícios de água na forma de gelo, próximo ao mar de metano na superfície de Titan. Saliento aqui que obtivemos esta informação, com nosso trabalho praticamente concluído.

Após definida a atmosfera, utilizamos um mini reator de vidro pyrex, evacuado a pressões de fundo da ordem de 10^{-3} Torr para o início da simulação. Trabalhamos numa faixa de pressão que correspondeu a uma altitude planetária do quilômetro 130 ao quilômetro 190 relativos à superfície de Titan. Portanto cobrindo uma camada significativa e não uma mera análise entre duas altitudes, como na quase totalidade dos trabalhos correntes. Não tivemos oportunidade de simular uma camada que abrangesse a superfície do asteróide, devido a limitações inerentes ao tipo de experimento a que propusemos. Todavia, esperamos fazê-lo em breve.

Consideramos a partir daqui a importância dos conhecimentos de plasma, no estudo da evolução planetária, em particular os plasmas de baixas densidades e temperaturas.

Presentes nas atmosferas dos astros em geral, os processo colisionais, podem ser uma fonte de pequenas, médias ou altas energias que portanto podem ser responsáveis por fragmentações atômicas e/ou moleculares que desencadeiam processos de recombinações que podem gerar substâncias sólidas ao longo do tempo se o meio onde esteja ocorrendo estas colisões for um meio que contenha entre outros elementos aqueles de natureza carbono-hidrogenados. Normalmente estas colisões ocorrem por radiações cósmicas, descargas elétricas e impactos eletrônicos.



O nosso trabalho descreve a ação de uma descarga elétrica contínua de até 1KV atuando na atmosfera de $N_2/CH_4/H_2O$, para pressões variando num intervalo de 0,8 a 3.0 Torr. Proveniente desta descarga, obtivemos um sub-produto sólido decorrente da fragmentação de $N_2/CH_4/H_2O$ seguida de uma concomitante recombinação das espécies fragmentadas, em especial da recombinação de radicais livres, característicos deste tipo de plasma. A taxa de formação deste material é rápida, quando comparamos as escalas de tempo para uma descarga elétrica contínua em um reator e este mesmo material quando processado na própria atmosfera do asteróide ao longo do tempo. No entanto, consideramos que elétrons energéticos sejam a principal fonte de fragmentação molecular em nosso reator, particularmente pela alta mobilidade destes elétrons.

Enfatizamos mais uma vez nesta crítica, uma nova abordagem na simulação planetária em laboratório, quando apresentamos no presente trabalho os comportamentos das densidades e temperaturas dos elétrons ao longo do intervalo de pressão em estudo, o que pouco se observa dentro dos trabalhos na área. Não estamos discutindo aqui as temperaturas físicas locais, mas os valores médios associados aos elétrons, os quais são responsáveis pelos processos de fragmentação no interior do reator, isto é: discutimos energias mínimas que estão associadas ao mecanismo de formação do sub-produto sólido.

Por outro lado, empregamos uma técnica espectroscópico-óptica para investigar o comportamento evolutivo das principais espécies químicas no interior da descarga. Contudo talvez seja este o primeiro trabalho na área, comparado ao mesmo tipo de estudo daqueles que tratam de investigar atmosferas planetárias, utilizando



espectroscopia-óptica. Ressaltamos que nossa inovação provém da aplicação da técnica actinométrica desenvolvida por Cobourn e Chen em 1981 e largamente aplicada em plasmas de baixa temperatura utilizados no processamento de novos materiais, dentre eles os polímeros a plasma.

A actinometria, acima de qualquer fato, procura corrigir possíveis erros provenientes de um mero acompanhamento da intensidade de emissão óptica de uma determinada espécie química em função de algum parâmetro de operação do reator, no presente trabalho, a pressão do sistema.

O artigo mostra a intensidade relativa de emissão, correspondendo a uma excitação do argônio tomada em função da pressão. O argônio serviu para parametrizar a tendência dos comportamentos das espécies químicas fundamentais à produção do sub-produto sólido. Neste ponto em particular, tivemos oportunidade de mostrar a viabilidade e confiabilidade da técnica, pois a curva representativa da intensidade relativa de emissão do actinômetro em função da pressão, apresentou o mesmo comportamento da possível curva representativa do produto densidade e temperatura eletrônica, obtida por outra técnica, a chamada sonda de Langmuir, que por sinal é intrusa ao sistema, diferentemente da espectroscopia-óptica-actinométrica. Por este resultado, nossos dados mostram que os elétrons são elementos fundamentais no próprio processo da descarga, bem como no mecanismo de crescimento do sub-produto sólido.

Outra vertente igualmente importante a ser considerada neste artigo é o estudo da composição química e estrutura molecular do produto sólido obtido da descarga elétrica em $N_2/CH_4/H_2O$.



Uma das grandes preocupações do homem, não se trata apenas em investigar uma atmosfera de um corpo celeste qualquer, porém a existência da possibilidade de no mínimo haver uma condição pré-biótica em algum ou vários locais do Universo.

Há mais de uma década, o próprio C. Sagan, quando estudava descargas elétricas em atmosferas da mistura N_2/CH_4 a baixa pressão, obteve como produto sólido do plasma atuando sobre N_2/CH_4 , um material de cor marrom escuro alaranjado. A este material ele denominou de “tolina”, que em outras palavras, representa aspecto barrento. De lá para cá novas experiências foram realizadas por outros investigadores, na mesma mistura, todavia em composições diferenciadas, porém apresentando um material sólido proveniente destas descargas, com características iguais ou semelhantes ao material obtido por Sagan. No entanto, houveram discordâncias com respeito ao nome, que poderiam ser desde heteropolímeros à macromoléculas.

Embora em nossa composição atmosférica proposta tenhamos água, a coloração do material obtido não fugiu à regra daqueles sintetizados por Sagan e outros.

Em nosso reator foi possível depositar um produto sólido tanto na forma de pó, na fase gasoso, quanto na forma de filme fino quando as reações ocorreram em contato com as superfícies internas do reator, e nos substratos de vidro nele contidos.

As ligações químicas inerentes ao nosso material, não foram diferentes daquelas presentes nas tolinas e/ou macromoléculas, como queira que o produto seja denominado. Todavia, parte considerável de grupos hidroxila no material por nós obtido, se deve ao fato do mesmo apresentar em sua estrutura uma grande quantidade de radicais livres, os quais são fontes captadoras de oxigênio residual ao fim do processo de deposição interno ao reator ou mesmo ao contato com o meio ambiente,



onde OH pode ser proveniente de vapor d'água além da água contida na própria mistura $N_2/CH_4/H_2O$.

Por outro lado, é importante salientar aqui um outro ponto de vista. No início dos anos que compreenderam à década de 1960, Goodman desenvolveu algumas experiências de descargas elétricas em hidrocarbonetos, obtendo a partir destes, materiais sólidos altamente dielétricos, os quais despertaram grande interesse tecnológico. A estrutura molecular do material obtido por Goodman ou mais recentemente por pesquisadores trabalhando na síntese de hidrocarbonetos a plasma objetivando a produção de novos materiais aplicáveis às indústrias eletro-eletrônica, mecânica e ótica não difere substancialmente da estrutura molecular do produto obtido de uma simulação atmosférica planetária. Trata-se pois de uma questão de objetivos, de um lado a procura de novos materiais para o uso no dia a dia e por outro, a síntese de algo com características pré-bióticas.

Quão importante seria para a Ciência se as comunidades que pesquisam nestas distintas áreas do conhecimento, já estivessem se interagindo há mais de duas décadas!

Temos trabalhado com descargas elétricas a baixa pressão em hidrocarbonetos há mais de 10 anos. Em várias das experiências foram feitos estudos de estrutura molecular em produtos sólidos obtidos de descargas de corrente contínua e/ou frequência variável como rádio-frequência e áudio-frequência em benzeno, etano, propano, acetileno, etc. Os sólidos ali sintetizados chamamos de polímeros, onde mantivemos interesse restrito à propriedades físicas e químicas destes materiais. Em alguns casos estudamos a composição química, procurando identificar as proporções de carbono, hidrogênio e mesmo oxigênio neste tipo de polímero. Contudo, neste



artigo em que trata da simulação de uma atmosfera planetária por nós investigado, fez-se necessário uma análise da composição do sólido utilizando espectrometria de massa.

Observamos a presença de moléculas cujos pesos atômicos puderam atingir valores próximos de 300. Elas constituem a classe de aldeídos, açúcares, amino-ácidos, nitrilas, álcoois, purinas, pirimidinas, ácidos e nucleosídeos, que entre outros fatores são elementos fundamentais na constituição pré-biótica.



LABORATORY SIMULATIONS OF TITAN'S ATMOSPHERE:

A POSSIBLE PATHWAY FOR PREBIOTIC CHEMICAL COMPOUNDS SYNTHESIS

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Abstract

In this paper is presented the optical and electrical measurements on plasmas generated by DC excited glow discharges in mixtures composed by 95 %N₂:4.8%CH₄:0.2% H₂O at pressures varying from 800 mTorr (1.064 mbar) to 3000 mTorr (4.0 mbar). These discharges were performed in order to simulate the chemical reactions that may occur in Titan's atmosphere in the presence of meteorites and ice debris coming from Saturn system, assisted by cosmic rays and high energy charged particles. The results obtained from actinometric optical emission spectroscopy, combined with the results from pulsed Langmuir probe, shown that the chemical species CH, CN, NH and OH are important precursors in the final solid product's synthesis and that their chemical kinetics are essentially driven by electronic collision processes. It is shown that the presence of water is enough to produce complex solid products whose components are extremely important in prebiotic compounds synthesis.



1. Introduction

Laboratory simulations of planetary atmospheres is an important issue in current scientific literature since many years ago (Sagan and Miller 1960, Sagan and Khare 1979), being subject of recent reviews (Cabane and Chassefière 1995).

The main reason for that is its inherent importance for the understanding of the processes that created the basic conditions for synthesis of prebiological organic compounds (Sagan et al 1992, Raulin et al 1989).

Among the systems studied up to now, Titan, the largest moon of Saturn is one the most fascinating because it presents several characteristics that make it the natural candidate for reproducing the conditions of the primitive Earth's atmosphere.

The Stratosphere of Titan is composed mainly by Nitrogen (varying from 86 % up to 99 %), Methane (varying from 0.5 % up to 3.4 %), Argon (varying from 0 to 10 %), and Hydrogen (varying from 0.2 % up to 0.6 %) (Coustenis et al, 1989, 1991). It also have been pointed out in literature that water based chemistry could be taken into account for events concerning the entrance of meteorites and ice debris from the Saturn system, in Titan's atmosphere (Owen 1987, Yung 1987). It should be stressed here that the mole fraction of water in Titan's atmosphere is rather negligible.

The importance of Titan for the understanding of the mechanisms of the planetary atmosphere evolution was recognised soon after the in situ analyses performed by Voyager missions in 1980 and 1981 (Hanel et al 1981, Krimigis et al 1981, 1982, Vogt et al 1981, 1982). According the observations and the



models adopted for explaining the results (Sagan and Thompson 1984), the main mechanisms for energy deposition on Titan's atmosphere are the UV photons from the solar irradiation, the cosmic rays and the high energy charged particles classified as Saturn's magnetosphere electrons and protons, and interplanetary electrons (Sagan and Thompson 1984).

The effects of such mechanisms on the Titan's atmosphere chemical kinetics may be simulated in laboratory using different techniques (Cabane and Chassefière 1995).

The interaction of solar UV photons may be simulated using spark sources and common UV light sources like hollow cathode lamps. In spite of its occurrence at very high altitude, the photodissociation of Nitrogen molecule by solar UV is rather negligible at relative low altitude because the triple bonds are very stable requiring the absorption of high energy photons ($\lambda < 1000 \text{ \AA}$), to be broken.

Laser induced plasmas, spark discharges and high field electric discharges may simulate the lightning conditions, in spite of the fact that the occurrence of lightning on Titan is rather unlikely (Thompson et al 1991).

Plasmas generated on radio-frequency (RF) or on direct current (DC) excited glow discharges are able to reproduce quite well the effects of cosmic rays and charged particles on Titan's atmosphere (Cabane and Chassefière 1995). The energy transfer occurring in these processes are much more effective in driving the atomic Nitrogen based chemistry, which is responsible for the production of many different chemical species within the atmospheric environment.



The main feature of the plasmas created in these glow discharges is that the electrons and the other chemical species within the discharge are not in thermal equilibrium. In fact, for such low pressure glow discharges, electrons may acquire energy enough to cause molecular fragmentation through inelastic collisions (Yasuda 1985). Therefore these cold plasmas are extremely reactive allowing the formation of chemical species that would not be produced under a thermal equilibrium condition. From this point of view the study of the chemical kinetics of such discharges is fundamental for the understanding of the possible pathways followed in the synthesis of the complex compounds produced within the glow discharges. These complex chemical structures, named Tholins, were observed to be present among the final products of the reactions, even in the early laboratory simulations of Titan's atmosphere (Sagan and Khare 1979).

In this paper are presented the results obtained from plasmas generated in DC glow discharges on mixtures of 95 % Nitrogen, 4.8 % Methane, and 0.2 % Water for pressures varying from 4 mbar (3 Torr) to 1 mbar (0.75 Torr). The purpose of such experiment was simulate the chemistry occurring on Titan's atmosphere altitudes between 130 km and 180 km, in the presence of meteorites and ice debris, assisted by cosmic rays and high energy charged particles.

It was performed simultaneously optical and electrical diagnostics of the discharges, for different values of pressure and power coupled to the plasma reactor. These measurements allowed one to determine the relative concentration of the different chemical species and the electronic density and temperature.



These data are extremely important for characterisation of the chemical kinetics developed within the plasma environment.

The solid final products, obtained from our atmosphere simulations for different values of gas pressure and electric power coupled to the reactor, were removed from the electrodes and the reactor's walls, being subsequently submitted to pyrolysis for identification of its chemical composition.

2. Experimental Set up

The schematic diagram of the experimental set up used in our simulations of Titan's atmosphere is shown in figure 1. It was constituted by a cylindrical Pyrex chamber with 15 cm of length and 5 cm of internal diameter. The plasma was created between two parallel disk shaped stainless steel electrodes with 2.5 cm of diameter, whose separation could be controlled in order to keep the homogeneity of the discharge. The Pyrex chamber has two cylindrical lateral entrances, placed in opposite sides, whose symmetry axis is contained in the middle plane between the electrodes. These entrances were used for fixing optical windows and the Langmuir electrical probe.

The discharges were excited by a DC power supply operating in the voltage range from 0 to 2 kV. The pressure inside the plasma reactor was kept by a common rotatory mechanical vacuum pump with a pumping speed of 22 m³/h being able to reach the ultimate pressure of 10⁻³ Torr (1.33 μbar). The reactor was purged several times with Ar, for cleanness purposes. The gas mixture of 95% N₂:4.8%CH₄:0.2%H₂ was introduced inside the plasma reactor through needle valves. The gas pressure was varied from 1 to 4 mbar (0.75 to 3.0 Torr).



The optical analysis of the discharge was performed using a monochromator Zeiss model PGS-2 with 2 m of focal distance and optical dispersion of 3.7 Å/mm. The signals, measured through a photomultiplier Hamamatsu, were stored in a PC-486 for posterior analysis.

Electron temperature and density were determined from the current $\times$ voltage characteristic of a cylindrical Langmuir probe, operating in pulsed regime (Cherrington 1982, Sudit and Woods 1993, Neumann et al 1993).

The use of the pulsed technique, for which the probe was biased by a ramp wave form varying from -100 V to +100 V in 1 ms, was necessary to ensure one that the probe's tip was not contaminated by the solid product produced within the plasma. The data were stored in a digital oscilloscope Tektronix model TDS 310 with a bandwidth of 100 MHz, being subsequently transferred to a PC-486.

The molecular structures of the solid chemical compounds, obtained from the simulations of Titan's atmosphere, were studied using a Perkin Elmer infrared Fourier transform spectrometer operating in the spectral region between 5000 cm^{-1} to 400 cm^{-1} . For this kind of analysis the samples were collected over appropriate KBr substrates placed over the reactor's electrodes.

The chemical analysis of the solid product's components was performed through mass spectroscopy of the gas products obtained from their pyrolysis using a gas chromatograph/mass spectrometer HP model 5988A.



3. Actinometric Optical Emission Spectroscopy

The determination of the chemical composition of a reactive low pressure glow discharge is a very difficult task. The problem is that the number of channels opened for energy redistribution is very high. This essentially occurs because many chemical species are created within the discharge, resulting from the molecular fragmentation produced by the inelastic collisions. Among the inelastic processes that occur within such environments, those one involving high energy electrons are the most profitable in molecular fragmentation. This occurs because in such low pressure glow discharges electrons may acquire much more energy from the field due to its low mass in comparison to the other species present in the plasma. Therefore the relative population of a chemical specie within the discharge may vary abruptly depending on how the electron energy distribution function changes with the plasma parameters, like pressure and power. The same occurs for the population of a chemical specie in an excited state whose excitation was caused by electronic impact. In this context the monitoring of the light emitted by a chemical specie does not give any information about its relative concentration inside a reactive plasma.

A method proposed by Coburn and Chen in 1980, named Actinometry, have been used for determining the relative concentration of reactive chemical species within plasma environment (Coburn and Chen 1980, D'Agostino et al 1981, 1985).

The method consists in adding a small amount (no more than 2 %) of a noble gas, named actinometer, and monitoring simultaneously the light



emission of the noble gas and the chemical specie whose concentration is to be determined. Since the actinometer density is known, the excitation efficiency of its levels may be determined simply by dividing the emission intensity related to that level by the noble gas density. If the excited state responsible for the gas noble optical emission matches closely in energy with the energy level responsible for the emission of the chemical specie one may consider that the same group of electrons will be responsible for the excitation of the both levels. Therefore the excitation efficiency of these levels will have the similar dependence on plasma parameters. Thus the relative concentration of the reactive chemical specie may be determined by combining its emission intensity with the excitation efficiency of the noble gas. The use of the method may be illustrated more easily through the following equations. The intensity emitted by the chemical specie whose concentration is unknown is:

$$I_X \propto N_X \eta_X \quad (1)$$

where N_X is the density of the chemical and η_X is the excitation efficiency of the discharge to promote the transition of the specie X from the ground state to the electronically excited state responsible for the optical emission. The excitation efficiency may be written as:

$$\eta_X = N_e \sqrt{\frac{2e_0}{m}} \int_{\epsilon_{th}}^{\infty} \sigma_{X^*}(\epsilon) f(\epsilon) d\epsilon = N_e Z_X \quad (2)$$

Here e_0 and m denotes the electron charge and mass, respectively, $\sigma_{X^*}(\epsilon)$ is the cross section for the excitation processes and $f(\epsilon)$ is the electron energy distribution function and Z_X is the excitation rate coefficient. The equations (1) and (2) are valid for both the actinometer and the chemical specie. Combining

these equations one may obtain the actinometric equation (Coburn and Chen 1980, D'Agostino et al 1981, 1985):

$$\frac{I_X}{I_{act}} \propto \frac{N_X}{N_{act}} \frac{\eta_X}{\eta_{act}} = \frac{N_X}{N_{act}} \frac{Z_X}{Z_{act}} \quad (3)$$

If the ratio of the excitation efficiencies or rate coefficient of the emitting species and the actinometer does not depend on the discharge parameters subject to variation, the equation (3) may be written simply as:

$$\frac{I_X}{I_{act}} \propto \frac{N_X}{N_{act}} \quad (4)$$

This equation allows one to determine the concentration trends of the chemical specie X from the variation of the intensity ratio I_X / I_{act} when the concentration of the actinometer is known or is kept constant. It should be stressed here that the validity of the actinometry depends on the constancy of the ratio Z_X / Z_{act} which can vary with the differences in the shape of the cross-section profiles $\sigma(\varepsilon)$, and on the differences in the values of the energy threshold ε_{th} for excitation. While differences in the cross-section shapes have not been found to introduce large deviations from equation (4), the matching of the energy threshold between the actinometer and the chemical specie is essential for the use of actinometry for monitoring the trends of the reactive chemical species within the plasma (D'Agostino et al 1985).

4. Results and Discussion

In this paper was performed Actinometric Optical Emission Spectroscopy (AOES) in plasmas of $N_2/CH_4/H_2O$ excited by DC discharges in order to

follow the trends of the different chemical species within the plasma environment for pressures varying from 0.8 Torr (1.0 mbar) to 3.0 Torr (4.0 mbar). It is shown in table 1 the main products obtained from the fragmentation of the components of the mixture 95 % N_2 : 4.8 % CH_4 : 0.2 % H_2O , using Ar as actinometer (concentration kept constant in 2 % of the total pressure).

INSERT TABLE 1 HERE

The variation of the relative light intensity emitted by Ar with pressure inside the plasma chamber is shown in figure 2. It may be appreciated that the intensity increases up to a maximum, around 2000 mTorr (2.66 mbar), and decreases for higher values of pressure. This may be attributed to inelastic electronic collisions that are much more effective in the low pressure regime. In the high pressure condition the electronic mean free path within the discharge is not enough for Ar excitation by inelastic collisions. Therefore figure 1 essentially shows the behaviour of the excitation efficiency η_{act} with pressure, that depends directly on the electron energy distribution function. It may be pointed out here that the above mentioned result it is an indicative that the plasma activity, defined as a product of the mean electronic density by the mean electronic energy (Durrant et al 1992) also increases with pressure.

It is shown in figures 3 and 4 the variation of the relative concentration with pressure of the chemical species CH, NH and CN, OH respectively.

INSERT FIGURES 3 AND 4 HERE

The importance of studying the kinetics of these species in the discharge is related to their role in the formation of the solid products within the plasma. In fact these species are the elementary blocks in the synthesis of solids products obtained in glow discharges performed in mixtures containing hydrocarbons (Yasuda 1985).

The increase of the relative concentration of the chemical species CH and NH with pressure may be attributed to the increase of the plasma activity up to 2000 mTorr (2.66 mbar). After this value the concentrations fall down indicating that, for a fixed value of the power, the plasma efficiency in molecular fragmentation presents a maximum. The existence of this maximum may be explained in terms of inelastic and elastic collisions. The decreasing of the CN specie up to 1000 mTorr (1.33 mbar) may be attributed to the significant increasing of the NH specie in the discharge. This occurs because the recombination processes of atomic Nitrogen with Hydrogen is much more effective than the recombination processes of Nitrogen with Carbon and Hydrogen with Carbon. The decrease of the relative concentrations of all chemical species for higher values of pressure is an indicative that the molecular fragmentation by electronic impact is not so effective. This is in close agreement with the plasma activity behaviour mentioned above.

In figure 5 is shown the dependence of the mean electronic temperature and density with pressure.

INSERT FIGURE 5 HERE

It can be appreciated that the electron temperature increases up to a maximum around 2000 mTorr (2.66 mbar) due the predominance of elastic processes.

After reaching a maximum the electron temperature falls down indicating the predominance of inelastic processes. It is observed that the mean electronic density remains almost constant with the gas pressure up to 2000 mTorr (2.66 mbar). This may be attributed to the fact that processes for which free electrons are liberated and captured are occurring almost simultaneously within the discharge. For higher values of pressure is observed that the number of chemical species responsible for electronic capture decreases causing the increasing of the electronic density. This behaviour is in agreement with the decreasing of the relative concentration of the different chemical species observed for pressures higher than 2000 mTorr. It should be noted here that the electron density behaviour is also in agreement with the dependence of the emission of Ar with pressure, shown in figure 2.

The results obtained from these optical and electrical measurements allow one to conclude that the chemical reactions originating the elementary blocks responsible for the synthesis of the solid products are driven essentially by the electrons within the plasma. This reinforces the importance of using glow discharges for simulating the processes involving high energy charged particles in planetary atmospheres.

The processes that occur inside a low pressure plasma generated by a DC glow discharge in organic atmospheres are very complicated involving the fragmentation and recombination of many chemical species. Such recombination most of the time follow very complicated pathways. An additional difficulty for modelling these discharges is the lack of data about cross-sections for most of the processes. In spite of these difficulties it is described in literature three basic mechanisms for explaining, in a semi qualitative way, the



solid products formation within the plasma (Yasuda 1985), namely, "Molecular Solid Plasma Deposition", "Solid State Plasma Deposition-Atomic State" and "Ablation". These three mechanisms may happen together and their effective contribution for the product's growth is strongly dependent on plasma parameters.

In the molecular solid plasma deposition the chains are formed due to the joiment of the molecular units from the monomer that is fragmented under discharge's action. In this processes the polymer formation within the discharge is quite similar to the conventional polymerization processes using chemical catalysers. Thefore the structure of the solid, obtained in a processes where molecular solid plasma deposition is predominant resembles the structure of the original monomer.

In the solid state plasma deposition the monomer's molecules are fragmented by electronic inelastic collisions, ion collisions, free radical colisions, and so on. The recombination processes of the different chemical species within the discharge gives origin to new molecules or intermediate solids. These new chemical species may be fragmented under the action of the discharge or may be deposited on the reactor's walls. The structure of these solid products are extremely irregular due to the great number chemical species contributing to its formation. Its structure resembles the "intractable polymers" or "Tholins" that have been studied in literature since many years ago (Sagan and Khare 1979, Sagan et al 1992).

These Tholins may be formed in a gas phase or in a surface assisted processes. In the former, the macromolecules resulted from the aggregation of several different chemical species, precipitate over the surfaces and in the



later, the chemical species are gradually aggregated to the thin solid film formed over the surface. Tholins formed in the gas phase are composed by irregular grains with low adhesion to the surfaces while tholins formed in a surface assisted processes present a very high adhesion.

In the ablation processes may occur etching or sputtering of the tholins deposited over the surfaces. The etching is characterised by the removal of the deposited solid film due to the action of very reactive atoms in the discharge. This is particularly important in a atomic-oxygen assisted processes. The sputtering is characterised by the removal of the deposited solid film due to momentum transfer of the high energy heavy particles present in the plasma. Both processes were not so important in our Titan's atmosphere simulations.

The tholin's structures are highly crosslinked being inert to the attack of mild acids and bases. These structures may also present a great amount of free radicals.

The tholins deposited over quartz substrates presented different colours varying from orange to brown depending on the plasma conditions. It was performed an absorption spectra using a spectrophotometer Perkin Elmer Lambda 9 running from 53000 cm^{-1} to 3000 cm^{-1} (UV-Visible). These measurements allowed one to determine that the Tholin's refractive index changed from 1.65 (orange) to 1.76 (brown) and the optical gap changed from 3.1 eV to 2.5 eV.

It is presented in figure 6 the infrared absorption spectra of a tholin obtained from a DC discharge in 95 % N_2 : 4.8 % CH_4 : 0.2 % H_2O , at 2000 mTorr (2.66 mbar), that corresponds to the Titan's atmosphere at 148 km of altitude.



INSERT FIGURE 6 HERE

It may be appreciated that the absorption at 3350 cm^{-1} and 3240 cm^{-1} correspond to N-H stretching of primary amine. It must be emphasised here that this band is superimposed to the hydroxyl band in 3400 cm^{-1} . It is observed anti-symmetric and symmetric C-H stretching in functional groups CH_2 and CH_3 in 2929 cm^{-1} and 2872 cm^{-1} , respectively. It is observed a peak in 2200 cm^{-1} corresponding to $\text{C}\equiv\text{N}$ vibration associated to nitrile groups, and a peak in 2100 cm^{-1} corresponding to $\text{C}\equiv\text{C}$ stretching. The functional group $\text{C}=\text{O}$ associated to carbonyl presents a peak in 1650 cm^{-1} superimposed by a strong absorption band in 1640 cm^{-1} corresponding to N-H stretching in primary amine. This band is superimposed to the $\text{C}=\text{C}$ stretching in 1650 cm^{-1} and C-C vibrations associated to aromatic groups in 1500 cm^{-1} and 1600 cm^{-1} . It should be stressed here that in spite of the relative low concentration of oxygen in the discharge, the tholin's infrared spectra shown strong absorption bands corresponding to hydroxyl and carbonyl groups indicating an expressive amount of oxygen incorporated in tholin's structure. This is a strong indicative that the processes occurring in the presence of meteorites and ice debris, assisted by high energy particle and cosmic rays in Titan's atmosphere were effective in producing oxygen-contained complex compounds. In spite of these differences the infrared spectra of our tholin is quite similar to the spectra presented recently in literature for a mixture of 90 % N_2 : 10 % CH_4 (MacDonald et al 1994).



The tholins synthesised in our atmospheric simulations were removed from the plasma chamber electrodes and walls being subsequently submitted to pyrolysis in a gas chromatograph-mass spectrometer. The method allowed us to identify the presence of several aldehydes, (formic, acetic, glyoxal, glyceraldehydes), purine and pyrimidine bases including xantine, guanine and adenine, alcohols (methanol, glycerol, benzeneethanol), sugars (fructose and ribose), nitriles (hydrogencyanide, acetonitrile, propanenitrile, benzenedicarbonitrile, pyridenecarbonitrile), amino-acids (alanine, aspartic acid, valine, leucine, lysine and hydroxylysine), acids (formic, acetic, propanoic, anthranilic, benzeneacetic), nucleoside as cytidinenucleoside, cyclic hydrocarbons (cyclopropane, cyclobutane, cyclopentane, benzene, toluene, cycloheptatriene) and polycyclic aromatic hydrocarbons as benzeneanthracene.

These results present a series of aminoacids like leucine, lysine and hydroxylysine that were not observed in literature (Khare 1986). This is explained by the presence of water in our composition that provides oxygen to the discharge. It must be stressed here that these chemical compounds fulfil almost completely the diagram proposed by Chang (Chang 1991). These compounds represents the synthesis of the most simples biomolecules. The completeness of the Chang's diagram might be verified with the advent of Cassini-Hygens mission to the Saturnian system in 2004 (Raulin et al 1992).



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Figure Captions

Fig. 1. Schematic block diagram of the experimental set up used in Titan's atmosphere simulations

Fig. 2. Pressure dependence of the light emitted by Argon ($\lambda = 4300 \text{ \AA}$) for pressures varying from 800 to 3000 mTorr. The power coupled to the discharge was kept constant in 25 watts.

Fig. 3. Pressure dependence of the relative concentration of NH and CH determined by actinometric optical emission spectroscopy. The wavelength used was $\lambda = 4314 \text{ \AA}$ for CH and $\lambda = 3360 \text{ \AA}$ for NH. The power coupled to the discharge was kept constant in 25 watts.

Fig. 4. Pressure dependence of the relative concentration of CN and OH determined by actinometric optical emission spectroscopy. The wavelength used was $\lambda = 3883 \text{ \AA}$ for CN and $\lambda = 3428.1 \text{ \AA}$ for OH. The power coupled to the discharge was kept constant in 25 watts.

Fig. 5. Pressure dependence of the electronic temperature and density determined by Langmuir pulsed probe technique. The power coupled to the discharge was kept constant.

Fig. 6. The characteristic Fourier-transform infrared spectrum of the solid product generated in simulations of Titan's atmosphere.

Table 1. Main chemical species resulted from the fragmentation of the mixture 95%N₂:4.8 %CH₄:0.2 %H₂O within the plasma environment. The wavelengths in the right column were used for the actinometric optical emission spectroscopy of the discharge.

CHEMICAL SPECIES	WAVELENGTH (Å)
CO	4500.5
CO ₂	3562.2
OH	3428.1
OH ⁺	3565
NO	3572.4
NH	3370
O ₂	3369.6
O ₂ ⁺	4082.5
CN	3883
N ₂	3371.3
CH	4314
C	4771.7
H	4861.3
H ₂	4863.6
Ar	4300

FIGURE 1

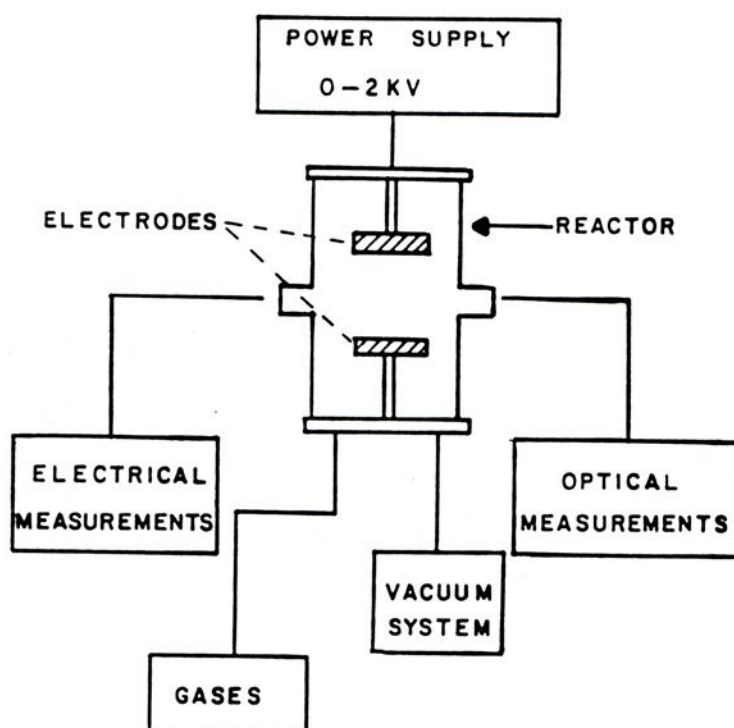


FIGURE 2

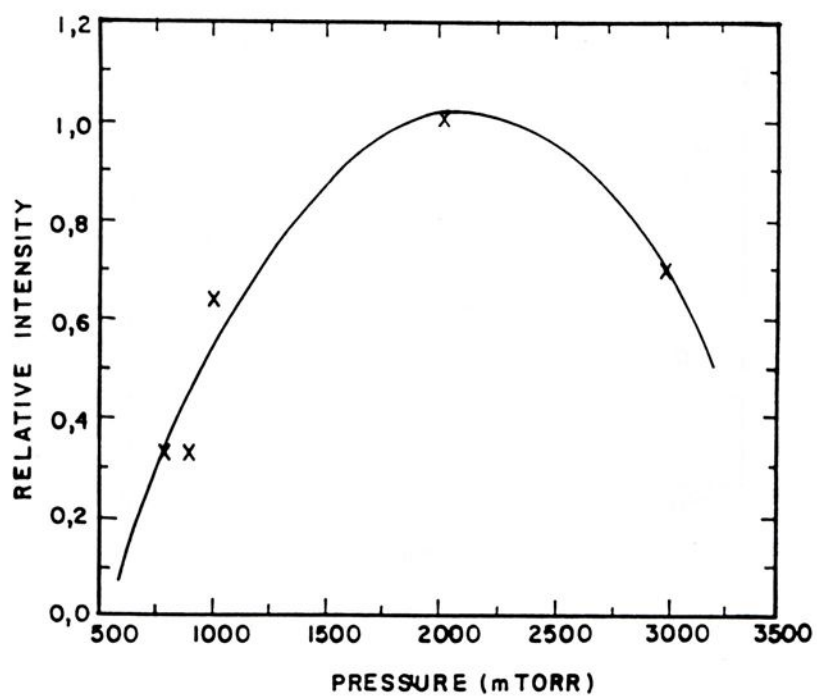


FIGURE 3

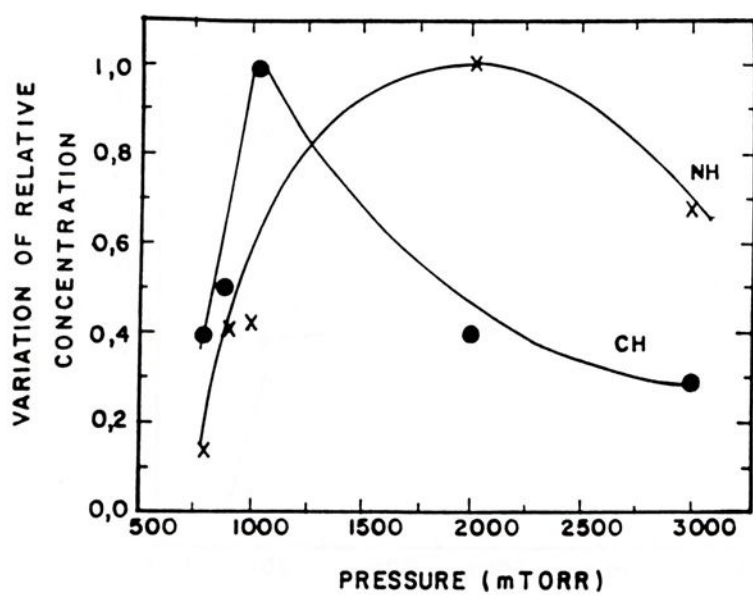


FIGURE 4

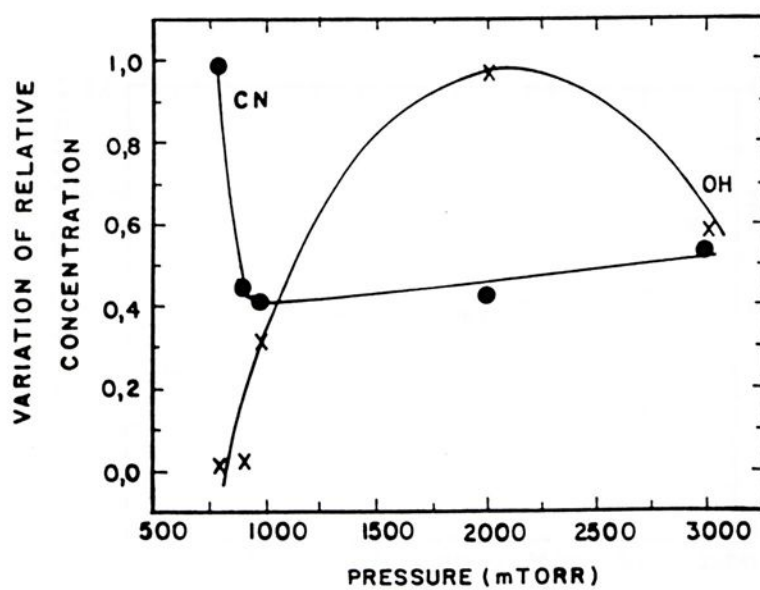


FIGURE 5

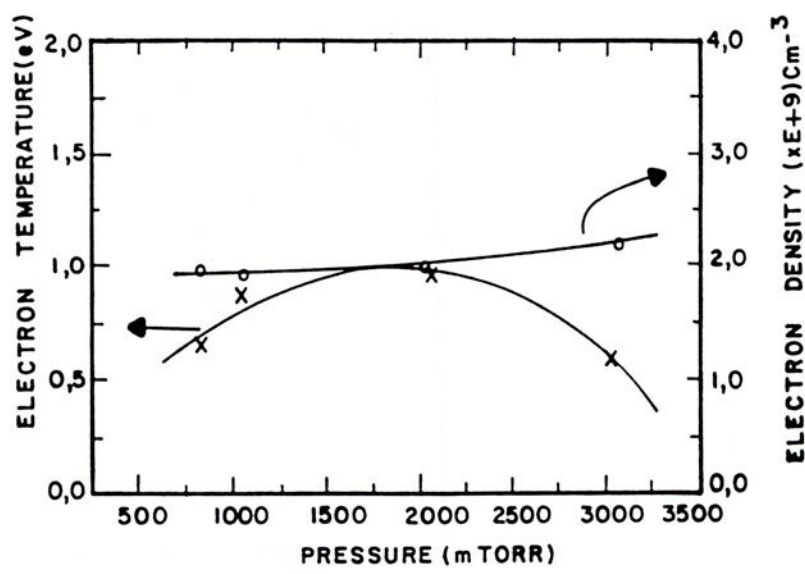
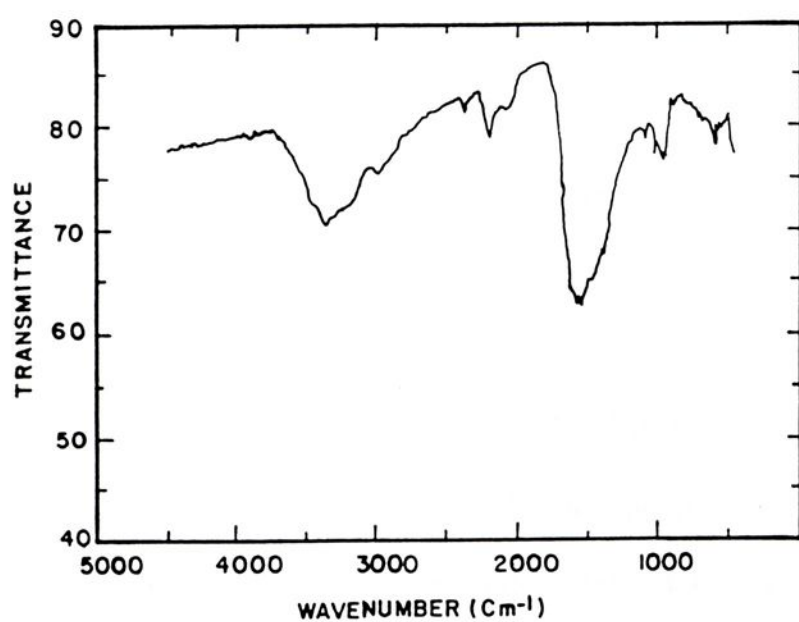


FIGURE 6



TERCEIRA PARTE

Utilização do plasma na síntese de materiais compostos chamados “CERMETS”

Nos artigos “PLASMA POLYMERIZED HEXAMETHYLDISILOXANE: DISCHARGE AND FILM STUDIES”, publicado em *Vacuum*, 47, 187(1996) e “PLASMA POLYMERIZATION IN HEXAMETHYLDISILOXANE-ARGON DISCHARGES PRODUCED IN A MAGNETRON SYSTEM WITH A COPPER CATHODE”, publicado na *Rev. Bras. Apl. Vac.*, 11, 26(1992), discutimos a utilização do plasma como fonte de síntese de filmes finos compostos de metal/polímeros orgânicos, co-depositados a vácuo.



Materiais compostos têm sido estudados há bastante tempo em virtude de suas inúmeras aplicações tecnológicas, em especial na mecânica e na metalurgia. O termo material composto não carrega consigo, rigorosamente uma definição própria. No entanto, como uma primeira idéia, ele pode ser a composição de dois ou mais materiais cujas características não são aquelas pertencentes a cada um dos constituintes, mas sim do coletivo formado. Os compostos na sua grande maioria são produzidos por processos químicos e mecânicos, isto depende da aplicabilidade dos mesmos. Pode-se ressaltar aqui as fibras resinadas, as cerâmicas metálicas e outros.

Não obstante os meios de produção acima citados, os compostos também podem ser sintetizados usando tecnologia de plasma. Os primeiros materiais produzidos por esta técnica adviram a partir de 1970, quando utilizou-se ciência e tecnologia de filmes finos para produzir uma mistura óxido de níquel/ouro a partir de um meio físico envolvendo descargas elétricas de argônio em alvos metálicos e não-metálicos. Desta mistura objetivou-se estudar o comportamento dos processos de condução elétrica. Embora nem o ouro nem o óxido de níquel fossem cerâmicos, o conjunto foi denominado de “CERMET”- CERamic METals.

Nos primeiros anos da década de 1980, utilizou-se polimerização a plasma juntamente com evaporação metálica, de forma simultânea ou ainda, “*sputtering*” de metais concomitante ao processo polimerizante, para produzir os primeiros cermets, considerados cermets orgânicos. A parte não metálica, isto é, o polímero, adveio da polimerização de hidrocarbonetos simples e hidrocarbonetos fluorados. Nesta categoria de materiais tivemos a oportunidade de trabalhar desde 1984, primeiramente crescendo uma mistura de cobre e acetileno polimerizado a plasma, a partir da qual estudamos o



mecanismo de condução elétrica. Posteriormente os nossos compostos foram paládio, níquel e ouro, independentes um do outro, co-depositados junto ao acetileno polimerizado.

No início de 1992, passamos a trabalhar com misturas polímero-metal, contudo, não apenas procurando estudar as propriedades dos cermets orgânicos, mas também a própria descarga elétrica e/ou plasma, onde eram crescidos estes filmes finos.

Passamos agora à análise crítica dos trabalhos “PLASMA POLYMERIZATION IN HEXAMETHYLDISILOXANE-ARGON DISCHARGES PRODUCED IN A MAGNETRON SYSTEM WITH A COPPER CATHODE”, publicado na Revista Brasileira de Aplicações de Vácuo/1992 e “PLASMA POLYMERIZED HEXAMETILDISILOXANE DISCHARGE AND FILM STUDIES”, publicado na revista Vacuum/1995.

Um primeiro ponto a ser discutido nestes dois artigos é o plasma como meio, isto é, a própria caracterização da descarga utilizando a técnica actinométrica, em segunda instância, o produto final, que é o *Cermet* orgânico produzido.

Embora os sistemas experimentais utilizados para a produção dos cermets fossem diferentes, um deles sujeito a um campo elétrico e o outro a um campo eletromagnético, o princípio de produção do plasma foi o mesmo, ocorrendo entre dois eletrodos de placas paralelas. Portanto, os constituintes da descarga foram analisados na região entre os eletrodos.

Em um dos reatores, o eletrodo negativo era de cobre, razão pela qual o *Cermet* era polímero/cobre. No outro, o eletrodo negativo era de ouro, o que gerou um *Cermet*



polímero/ouro. Em ambas as descargas, o polímero adveio da polimerização do hexametildisiloxano (HMDS).

Para que se tornasse possível obter a mistura HMDS polimerizado/cobre e HMDS polimerizado/ouro, foi utilizado o argônio como elemento que através de seus íons positivos sob a ação do plasma, e dos campos elétrico e eletromagnético, viabilizassem a transferência de momentum entre estes íons de argônio e os eletrodos de cobre e de ouro, afim de que os Cermets tivessem condições de serem depositados. Desta forma, para tornar exeqüível o método actinométrico afim de caracterizar estas descargas, o gás de prova utilizado não foi o argônio, mas hélio ou mesmo nitrogênio, em proporções menores que 2%, para não interferir no plasma, que por sí, era um plasma de argônio/HMDS.

Uma análise da estrutura molecular destes Cermets não revelou a presença de nitrogênio nos filmes. Há de se considerar também o fato de que o nitrogênio vem sendo utilizado em actinometria em hidrocarbonetos fluorados.

Na crítica destes artigos, temos a realçar que, estamos utilizando o método actinométrico não para analisar o comportamento de espécies químicas no plasma como CH, H, SiH, O, etc., mas acompanhar o crescimento dos filmes produzidos, através dos sinais de cobre para a mistura polímer/cobre e ouro para a mistura polímero/ouro. Em ambos os casos, a proporção de metal no filme depositado é função das proporções de HMDS/argônio no plasma. Para baixos níveis de HMDS, o filme pode apresentar características mais predominantes de metal, ao passo que para maiores concentrações de HMDS na mistura HMDS/argônio, a característica do filme é mais isolante, portanto, polimérica.



Não obstante estes Cermets possam ser utilizados como resistores elétricos, há a possibilidade deles servirem como filtros ópticos e em especial, construir-se a partir deles, superfícies decorativas. Pois, embora em princípio o HMDS apresente transparência à luz visível, dependendo do metal a ser utilizado na mistura, jogos de cores podem ser formados. Razões estas que nos fizeram escolher o HMDS como fonte formadora do polímero nestas misturas, para compor os Cermets, visto que esta linha de pesquisa voltada nesta direção apresenta promissoras aplicações tecnológicas.





Plasma polymerized hexamethyldisiloxane: discharge and film studies

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Films were grown in hexamethyldisiloxane (HMDS)-argon mixtures in a diode sputtering system with a gold cathode. Quantitative optical emission spectroscopy (OES)-actinometry revealed that the electron density or mean electron energy (or both) increased with increasing Ar concentrations in the gas feed. Increasing concentrations of Ar produced greater sputtering of the cathode and hence greater plasma Au concentrations. Fragmentation of the HMDS molecule resulted in species such as CH, H, and Si which were detected by OES. Film deposition rate, as determined by optical interferometry, was found to be increased by the inclusion of Ar in the gas feed. Transmission electron microscopy revealed particles, probably of Au, embedded in the polymer films. Actinometric measurements of Au in the discharge and electron probe microscopy of the deposited material showed that film Au concentrations increase with increasing concentrations of Au in the plasma. A relatively low fragmentation of HMDS molecules in the dc plasma was revealed by the very small Si-H IR absorption band which is usually prominent in spectra of plasma polymerized HMDS films.

1. Introduction

Metal-dielectric composite films have been studied for several decades.^{1,2} Most of the work in this area has been concerned with the structural,² electrical^{2,3} and optical^{4,5} properties of inorganic films, but metal-containing polymer films have also been studied.⁶⁻⁸ Plasma polymerization of an organic monomer combined with sputtering or evaporation of a metal is often used to prepare metal-polymer films.

The deposition process is complex because fragmentation of monomer and comonomer molecules by free electrons in the discharge produces a variety of chemical species,⁹ which together with particles sputtered from the cathode, combine to form the film. Understanding of this process is currently incomplete.

The plasma polymerization of organosilicons such as methyltrimethoxysilane,¹⁰ tetramethylsilane,¹¹ hexamethyldisilazane^{12,13} and tetramethyldisiloxane¹⁴ is well known. Either silicon oxide or organosilicon films may be produced, depending on the monomer, comonomer and plasma conditions, such as flow rates and applied power. Hexamethyldisiloxane (HMDS) is of particular interest because it possesses a number of desirable properties: good adherence to glass substrates; relatively high deposition rate even in dc discharges; high transparency to visible radiation (unlike most other plasma polymers). Almost a quarter of a century ago, the plasma polymerization of HMDS-argon mixtures was investigated by Vasile and Smolinsky,¹⁵ who deposited films in a bell-jar reactor supplied with power at 13.56 MHz. In the same year, Thompson and Smolinsky¹⁶ studied the influence

of substrate material on plasma polymerized films from tetramethylsilane, vinyltrimethylsilane and HMDS, finding that substrates of silicon or tungsten gave particle-free films. The application of plasma polymerized HMDS as a protective coating for metallic substrates was suggested by Schreiber *et al.*¹⁷ in 1980.

Other studies of plasma polymerized HMDS have concentrated on the determination of the following parameters: internal stress;¹⁸ water contact angle;¹⁹ and chemical structure, as revealed by ESCA and NMR.^{20,21} Such studies are of contemporary interest,^{22,23} and applications of the deposited films, such as in the separation of gaseous mixtures (O₂/N₂),²⁴ have also been conducted. Interest in the use of HMDS as a monomer for the deposition of silicon oxide-like films also remains high.²⁵⁻²⁸

As noted above, metals may also be incorporated into plasma polymerized films; thus Cu, Co, Ni, Ag and Au have been so introduced into the deposited material,²⁹ altering its electrical, mechanical and optical properties. More specifically, in a preliminary study, a group at Batelle Columbus Laboratories produced red and pink coatings by co-depositing gold with HMDS.^{30,31}

Optical emission spectroscopy (OES) is a very powerful tool for the analysis of plasmas of organic gases³²⁻³⁴ and has been used successfully to control the deposition of polymer-metal films.^{35,36} Identification of the chemical species present in the plasma by OES is usually simple and there are various ways to measure the densities of such species.³⁷ Coburn and Chen³⁸ have reported a method for determining relative changes in the concentration of species of interest as a function of the plasma



parameters. Their procedure now widely called the *actinometric method* consists of adding a small amount of a non-reactive gas (actinometer) to a reactive plasma and measuring the emission intensities of some chosen lines from the non-reactive gas and the species of interest, X . The number density of the species X , n_X , is then given by the simple equation

$$n_X/n_A = k \cdot I_X/I_A \quad (1)$$

where n_A is the concentration of the actinometer, I_X and I_A are, respectively, the emission intensities from the species X and the actinometer, and k is a constant. However, eqn (1) may only be applied under certain conditions,³⁷ one of which is that the excitation efficiencies of the levels responsible for the optical emission in both the actinometer and the species X have a similar dependence on the plasma parameters. This condition has generally been considered to be fulfilled when the energy of the excited state level responsible for the emission from the actinometer closely matches that responsible for emission in the species X .

Here, we report a study of the deposition process and the properties of plasma polymerized hexamethyldisiloxane (HMDS)-gold films prepared in dc discharges of HMDS and argon in a diode sputtering system with a gold-covered cathode. Codeposition of gold, sputtered from the cathode, and polymer from the polymerization of HMDS, took place on substrates located on the anode. Actinometric OES, using N_2 and He as actinometers, was used to characterize the plasma. To correlate plasma and film properties, the rate of deposition, structure, and chemical composition of the films were studied at various argon concentrations. Thus our study differs from previous work principally because both discharge and film studies were undertaken to yield information on the polymerization process.

2. Experimental

The discharges were produced in a stainless-steel vacuum chamber containing two horizontal, water-cooled electrodes of 10 cm diameter mounted in a diode configuration (Figure 1). A negative dc power supply (0–4 kV) was connected to the upper electrode (cathode) which was covered with a sheet of gold (of purity >99.9%). Substrates were placed on the grounded lower electrode. Argon, N_2 , and He were admitted to the chamber via leak

valves. The purities of these gases were better than 99.99%. Hexamethyldisiloxane (99.8% purity) was admitted to the chamber from an evaporation cell consisting of a glass bulb half-filled with liquid HMDS and connected to the chamber via a leak valve. A total pressure of 80 mTorr was maintained prior to ignition of the plasma in each of the experiments. When the proportion of HMDS was increased, the proportion of Ar was correspondingly decreased. Measurements of the pressure in the chamber were made using a thermocouple gauge previously calibrated against a capacitance manometer (Datametrics, Barocel type 600). Prior to the depositions, the chamber was evacuated by a diffusion pump to about 10^{-5} Torr as indicated by the Penning gauge; the diffusion pump was then left pumping for 5 min. During depositions the chamber was pumped by a $13 \text{ m}^3 \text{ h}^{-1}$ two-stage rotary pump. A cathode voltage of 1600 V was employed.

A 10 cm diameter circular quartz window located in the chamber wall, between the electrodes, allowed optical measurements of the plasma by a scanning 1 m focal length monochromator (Spex, model 14300) with photo-multiplier detection (Burle, IP28A). For a given set of pressures, the emission intensities vary after the ignition of the plasma but soon reach a constant level. Unless otherwise stated, measurements were made under these equilibrium conditions.

Deposition rates were calculated from the thicknesses of films grown for known periods of time. For thickness determination, a mask was used to produce a well-defined step whose height was measured by a multiple-beam interferometer (Varian, A-scope).

For film microstructure studies, a transmission electron microscope was used (Zeiss, model EM 902). Parlodium-covered microscope grids, coated with a thin layer of carbon were used as substrates.

Using an electron microanalysis spectrometer the relative density of gold was determined in films having thicknesses of less than 100 nm, deposited onto graphite substrates. Graphite has a very low secondary electron yield and was used to minimize the contribution to the X-ray fluorescence line intensities from electrons backscattered from the substrate. For all measurements a square of side 0.1 cm on the film surface was scanned by the electron probe during a time t . The intensities I_f of the fluorescence lines were then determined by dividing the total number of counts registered by the X-ray detector by t . Measurements of the relative gold concentration were then made by dividing I_f by the film thickness d .

Analysis of the chemical structure of the films was performed from transmission spectra obtained by an infrared spectrophotometer (Jasco, model IR 700). Single crystals of KBr were used as substrates.

3. Results and discussion

3.1. Glow discharge analysis. Optical emissions from argon, gold and from some fragments of HMDS such as CH, H and Si were detected in the HMDS-Ar plasmas. Details of the particular wavelengths measured are given in Table 1, where the threshold energies for transition from the ground state to the state responsible for emission are also given. Figure 2 shows the relative emission intensities of Ar and the actinometers N_2 and He as a function of the concentration of HMDS in the HMDS-Ar plasma. In the case of argon it was necessary to divide the emission intensity by the partial pressure of Ar since the latter was not constant. The Ar intensity curve also stops at 75% HMDS

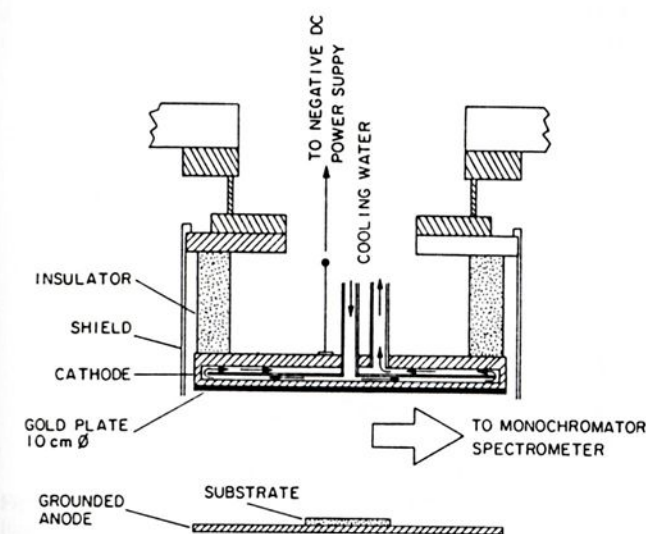


Figure 1. Electrodes of Diode Sputtering System.

Table 1. Spectral data of species of interest

Species	(nm)	Threshold energy (eV)
Au	267.6	4.6
Si	251.6	5.0
H	656.3	12.1
CH	431.4	< 11
N ₂	337.1	11.2
Ar	750.3	13.5
He	388.9	23.0

(no Ar was present at 100% HMDS). In contrast, the actinometers were always present at a concentration of a few percent of the total. Only one actinometer was used in any one experiment. The intensities of N₂, He and Ar can be related to some of the plasma parameters by the well-known equation³⁸

$$I_a = k_a n_a h_a \quad (2)$$

where I_a , n_a and h_a are the intensity of emission, the density of particles in the ground state and the excitation efficiency to the state responsible for the emission, respectively, and k_a is a constant. Thus, for N₂ and He, whose concentrations in the discharge were kept constant, I_a is proportional to h_a ; for Ar, the ratio I_a/n_a is proportional to h_a . Consequently the plots of Figure 2 may be taken as illustrating the excitation efficiencies of N₂, He and Ar as a function of the proportions of HMDS in the discharge. The implied decline in the values of h_a for the three gases leads to the conclusion that the plasma electron density or electron mean energy (or both) falls with increasing HMDS concentration. As shown in Table 1, N₂, He and Ar have widely different excitation thresholds. Nevertheless, the dependence of their excitation efficiencies on the proportion of HMDS in the feed is very similar. This may be taken to indicate that the excitation efficiencies of the chemical species of interest in the discharge, such as Au, Si, H and CH, whose excitation thresholds lie between or close to those of N₂ and He, have a similar dependence. Therefore we have applied the basic equation of actinometry, eqn (1), to Au, Si, H and CH to measure the relative changes in the densities of these species as a function of the discharge parameters. The equation has also been applied by d'Agostino and coworkers³⁹ to discharges fed with C₂F₆-H₂ and C₂F₆-O₂ mixtures to measure changes in concentrations of species

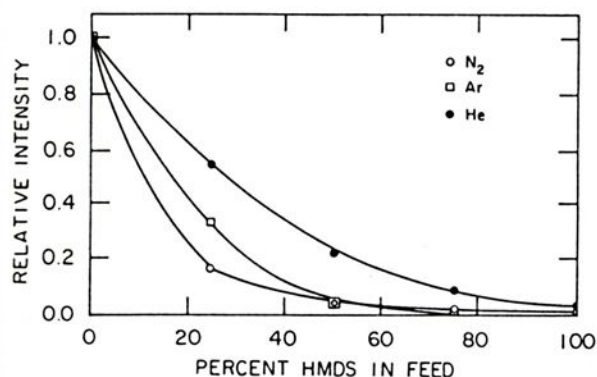


Figure 2. Relative intensity of Ar and the actinometers N₂ and He as a function of the percent HMDS in the feed. Cathode voltage = 1600 V; Total pressure = 80 mTorr.

whose excitation thresholds are far from those of the actinometers.

The relative intensity of Au in the plasma as a function of time is shown in Figure 3(a) for various partial pressures of HMDS. In each case the discharge was turned on at $t = 0$. The decay of the Au density with time reflects the effect of cathode poisoning: organic material from the discharge is deposited on the cathode surface, gradually decreasing the flux of outgoing sputtered Au atoms. As shown in the figure, while the sputtering of Au can be completely prevented at high HMDS concentrations, for relatively low concentrations such as 20%-a constant flux of sputtered Au atoms can be maintained. Such a steady state flux probably arises from an equilibrium between the deposition rate of polymeric material on the cathode surface and the rate of removal by sputtering, resulting in a constant cathode coverage.

Figure 3(b) shows the relative plasma gold concentration as a function of time following ignition of an all-argon plasma when the cathode is covered by a film of plasma polymerized HMDS. Clearly, sputtering of the cathode by argon gradually removes the protective polymer layer and more gold is sputtered into the discharge until a steady-state is reached. This is a "reversed case" of that illustrated in Figure 3(a).

The steady-state concentrations of Au, Si and H as a function of the proportion of HMDS in the feed are given in Figure 4. It can be seen that gold is present in the discharge only for percentages of HMDS in the feed of less than about 37%. The steady-state Au concentration produced, depends not only on

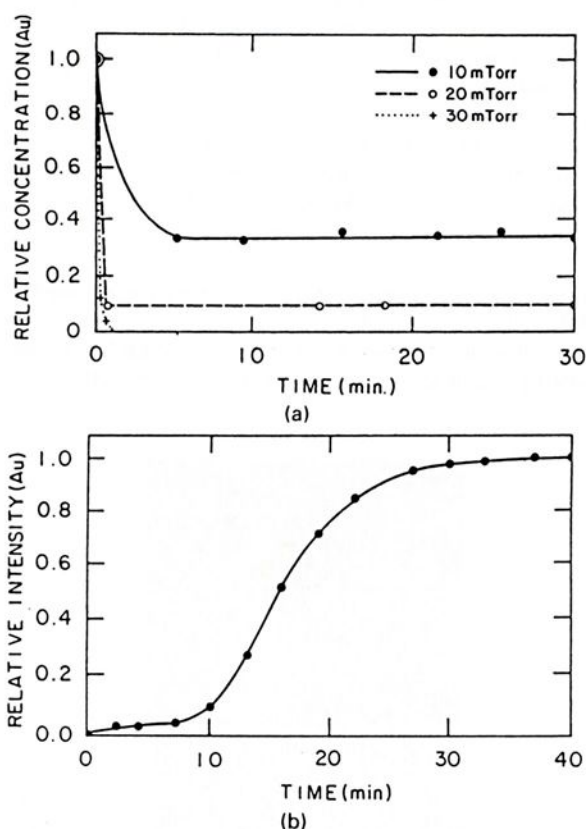


Figure 3. (a) Relative concentration of gold as a function of time for three HMDS feed pressures: 10, 20 and 30 mTorr. Cathode voltage = 1600 V; Total pressure = 80 mTorr. (b) Relative concentration of gold as a function of time in an argon plasma (Cathode voltage = 1600 V; Total pressure = 80 mTorr). Cathode initially contaminated with a film of HMDS (deposition conditions 10 mTorr HMDS and 70 mTorr Ar for 10 min).

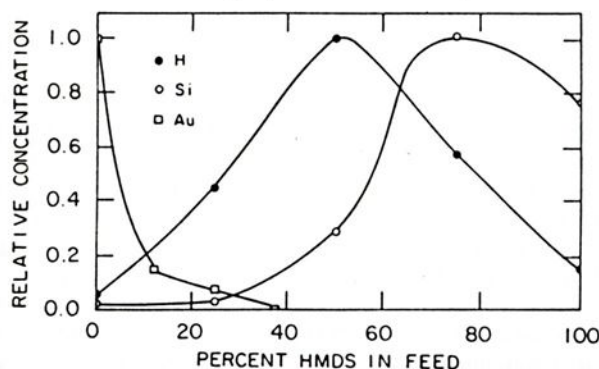


Figure 4. Relative concentration of Au, H and Si as a function of the percent HMDS in the feed. Cathode voltage = 1600 V; Total pressure = 80 mTorr.

the proportion of HMDS in the feed but also on the initial condition of the cathode. For example, a highly contaminated cathode may yield no sputtered gold atoms, even in plasmas of pure argon.

The relative concentrations of Si and H also show a strong dependence on the proportion of HMDS in the feed. Similarly, Figure 5 shows that the relative plasma CH concentration is also strongly dependent on the feed composition. Since the electron energy distribution function (EEDF) decreases rapidly with increasing percentages of HMDS in the feed, the Si, H and CH concentrations decrease at relatively high proportions of HMDS despite the greater supply of HMDS molecules.

Since the cathode is continuously bombarded with high energy Ar ions and other relatively heavy charged particles from the discharge, it seems reasonable to assume that sputtering of the polymeric material deposited on the cathode also contributes to the density of species such as Si, H and CH in the plasma. The non-zero concentration of Si shown in Figure 4 for the discharge of 100% Ar demonstrates that sputtering contributes to the density of Si in the plasma. Figures 4 and 5 also show that, with a pure argon plasma, the flux of sputtered CH is insufficient to produce significant concentrations. It should be stressed, however, that these conclusions hold only for discharges without HMDS. The composition of the polymeric material on the cathode probably varies according to the concentration of HMDS in the plasma. Furthermore, the number of Ar ions available for sputtering also varies with the discharge parameters. Therefore, the contribution of sputtering to the concentration of particles present in the plasma may depend strongly on the composition of the discharge.

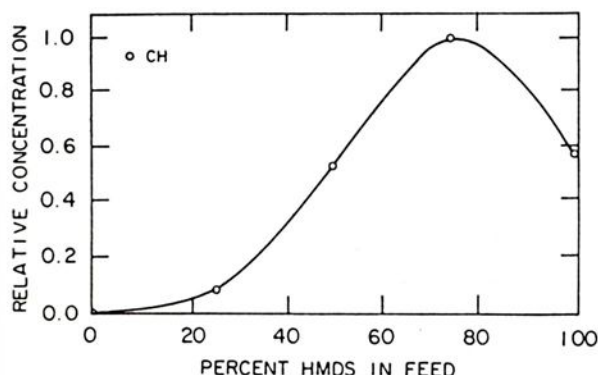


Figure 5. Relative CH concentration as a function of the percent HMDS in the feed. Cathode voltage = 1600 V; Total pressure = 80 mTorr.

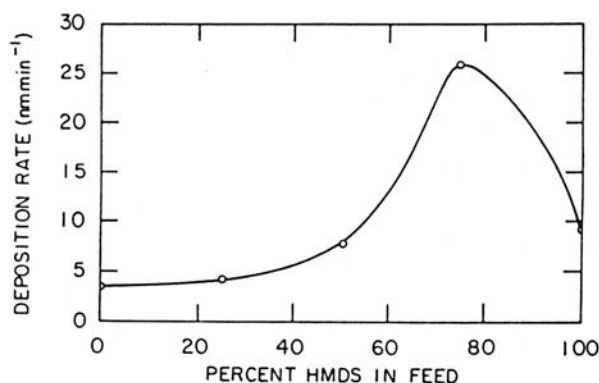


Figure 6. Deposition rate as a function of the percent HMDS in the feed. Cathode voltage = 1600 V; Total pressure = 80 mTorr.

3.2. Film deposition rate. The film deposition rate, R , is plotted in Figure 6, as a function of the proportion of HMDS in the feed. R exhibits values between 3 and 26 nm min⁻¹ depending on the feed composition. Increasing the proportion of Ar increases the deposition rate from 9 nm min⁻¹ (0% Ar in the feed) to a maximum of 26 nm min⁻¹ (25% Ar in the feed). As previously noted, the presence of Ar in the discharge increases the degree of fragmentation of the HMDS molecules, thus increasing the density of reactive species that will form the film.

In the formation of a polymer film in a plasma environment it is generally accepted that film growth is the result of the activation of surface sites by bombardment of electrons from the plasma, combined with adsorption of reactive species on the polymer surface.^{40,41} However, as previously discussed, the maximum density of reactive species in the plasma occurs in the range of 25–50% Ar in the feed (75–50% HMDS). As the maximum deposition rate occurs at this proportion of Ar, this strongly suggests that adsorption of reactive particles, rather than activation of surface sites, is the major contributor to film formation.

3.3. Film microstructure. A transmission electron micrograph of a film prepared in a discharge of HMDS–Ar with 15% HMDS is shown in Figure 7. Apparently, metallic particles may be dispersed in the polymeric matrix. This discontinuous structure is

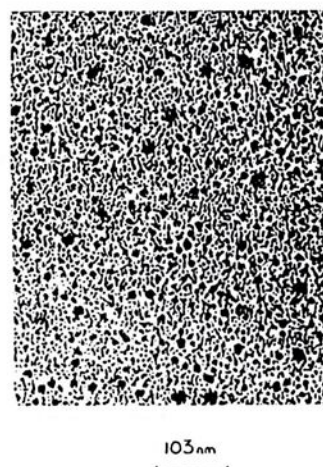


Figure 7. Transmission electron micrograph of a film prepared from a discharge of HMDS (15%)-Ar (85%). Cathode voltage = 1600 V; Total pressure = 80 mTorr.

typical of dielectric films, either inorganic² or organic,⁶ codeposited with metals. Typically, the dielectric phase of a dielectric-metal film shows high transparency to the microscope electron beam thereby allowing the taking of high-contrast micrographs.

As both Au and Si may be present in the discharge as atoms, the question arises as to the elemental composition of the metal particles shown in the micrograph of Figure 7. As our data show (Figure 4), for the proportions of HMDS used in the preparation of the film of Figure 7, the concentration of atomic Si in the discharge was rather low. Furthermore, TEM micrographs of samples prepared with 75% HMDS in the feed (maximum Si concentration in Figure 4) do not show a discontinuous structure. This may be taken as a strong indication that gold is the only constituent of the metal particles.

3.4. Gold concentrations in the discharge and film. In a separate series of experiments a pressure of HMDS of 5 mTorr was used and films deposited from HMDS-Ar plasmas at various pressures of Ar in the range 36 to 72 mTorr. Figure 8 shows the gold concentration in the plasma as a function of the gold concentration in the films. The former is a reasonable indicator of the latter and therefore might be used as a control parameter.

3.5. Infrared analysis. Figure 9 shows a transmission IR spectrum of a film deposited in a HMDS-Ar plasma with 15% HMDS. Several absorption bands can be seen. The weaker bands at 2960 and 2900 cm^{-1} are assigned, respectively to stretching vibrations of the C-H bond in CH_3 and CH_2 groups; stronger absorptions also present are related to groups containing Si bonds. These stronger bands include those due to SiH stretch in SiH_x at about 2100 cm^{-1} , Si-CH₃ at about 1250 cm^{-1} , SiO-CH₃ (in the range 1000–1100 cm^{-1}), Si-O-C and Si-O-Si in the same region and Si-CH₂ (at about 800 cm^{-1}).

In IR spectra of plasma-polymerized HMDS prepared in RF discharges, a strong band associated with the Si-H bond, is usually observed at 2130 cm^{-1} .⁴² Because the Si-H bond does not exist in the HMDS molecule, it must appear in the polymer as a result of reactions between molecular fragments containing Si and H. As the Si-H band is hardly visible in the spectrum of Figure 9, the degree of fragmentation of the HMDS molecules

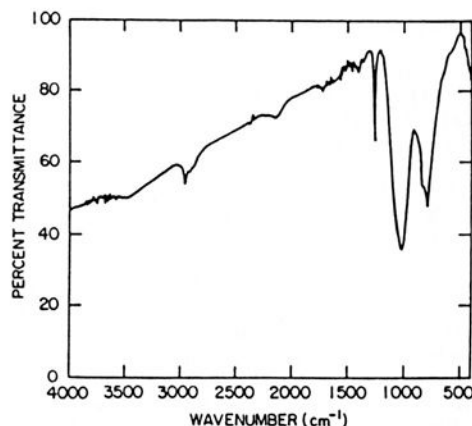


Figure 9. Infrared spectrum of a film deposited from a discharge of HMDS (15%)-Ar (85%). Cathode voltage = 1600 V; Total pressure = 80 mTorr.

in our dc discharges is probably less than that usually observed in rf discharges. Thus dc plasmas may be advantageous in the preparation of polymers in which one needs to preserve some of the chemical properties of the monomer.

4. Conclusions

In this work, new findings concerning HMDS-Ar discharges containing gold sputtered from the cathode are related primarily to the actinometric optical emission spectroscopy measurements. One interesting finding was that argon increases the plasma electron distribution function and consequently enhances the degree of fragmentation of the HMDS molecules, as is indicated by changes in the concentrations of atomic hydrogen and the species CH in the discharge. The plasma concentration of silicon rises with the supply of HMDS but, as a result of the lower plasma activity, falls at high proportions of HMDS in the feed.

The maximum plasma concentration of film-forming species occurs in the range of 25–50% argon in the feed, where the deposition rate is also a maximum. This suggests that absorption of reactive particles, rather than, as suggested elsewhere, the

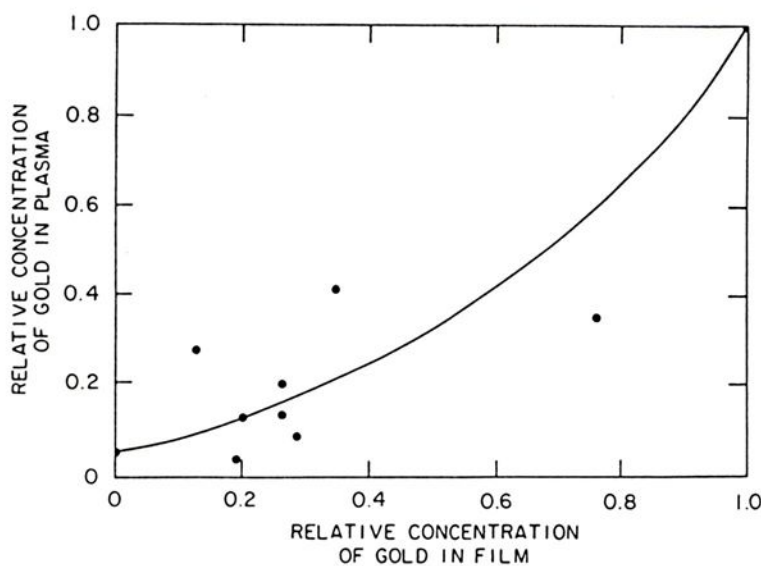


Figure 8. Relative concentration of gold in the discharge (determined by actinometry) as a function of the relative concentration of gold in the film (determined by electron probe microanalysis). Cathode voltage = 1600 V; Total pressure = 80 mTorr.

activation of surface sites,^{40,41} is the major contributor to film formation.

Control of the gold content of the films is possible since a strong correlation was observed between the plasma density of gold measured by actinometry and the gold content of the films determined by EPMA.

Transmission electron microscopy revealed, in some of our films, a two-phase structure of gold particles embedded in a well-defined plasma polymerized HMDS matrix. The latter was characterized by infrared spectroscopy. The gold content of the films depended strongly on the HMDS fraction in the discharge and also, as is to be expected, on the degree of poisoning of the cathode by the polymeric material which may severely inhibit the sputtering of gold. At argon proportions below about 70%, gold is not detected in the films. The poisoned cathode can be cleaned by sputtering if an argon plasma is present for sufficient time (say 30 min, see Figure 3(b)).

Acknowledgements

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PLASMA POLYMERIZATION IN HEXAMETHYLDISILOXANE-ARGON
DISCHARGES PRODUCED IN A MAGNETRON SYSTEM WITH A COPPER CATHODE

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ABSTRACT

Polymer-metal composite films have been deposited in glow discharge plasmas of hexamethyldisiloxane (HMDS) and argon in a planar magnetron system with a copper cathode. Actinometric optical emission spectroscopy was used to identify the chemical species in the discharge and the trends in their concentrations as a function of the discharge parameters (total pressure of the mixture HMDS-Ar, proportion of HMDS and Ar in the gas feed and cathode voltage). The relative contributions of gas-phase reactions and cathode sputtering to the plasma composition are discussed. The structure of the films was investigated by transmission electron microscopy. Residual stress measurements were also performed in the films using the bending beam method. The correlation between the discharge parameters and the film microstructure and composition is examined.

1. INTRODUCTION

Plasma polymerization is a well established technique for the production of dielectric thin films presenting remarkable physical and chemical properties. Integrated circuit lithography [1], integrated optics [2], ultrafiltration membranes [3] and protective coatings [4] are examples of technological applications of plasma polymers.

In the last decade, plasma polymers incorporated with metals began to be studied [5]. These composite materials are prepared by a combination of the techniques of plasma polymerization and sputtering [6] or thermal evaporation [7]. Their structure is similar to that of the cermet films [8], i.e., consists of a dispersion of microscopic metallic particles embedded in the polymer matrix. This type of structure is responsible for the peculiar optical [9], electrical [10] and mechanical [11] properties of the films. Wide variations in the optical constants and electrical conductivity can be attained by varying the metal

proportion in the film. Thus, control of the process of deposition is crucial in the preparation of films with predetermined properties.

One of the successful techniques which have been used in monitoring the process of deposition of polymer-metal films is actinometric optical emission spectroscopy (AOES). This method has the advantage of being non-intrusive and is very useful in the analysis of reactive plasmas, allowing measurements on the relative changes of density of gas-phase species which contribute to film formation.

In this paper we study polymer-metal composite films produced by the codeposition of plasma polymerized hexamethyldisiloxane [HMDS, chemical formula $(CH_3)_2SiO$] and sputtered copper. Plasma polymerized HMDS presents two interesting properties which are very important in technological applications: (i) high transparency in the visible range of the spectrum, and (ii) strong adhesion to metal and dielectric substrates. The AOES technique was used to characterize the discharge while the microstructure of the films were determined by transmission electron microscopy (TEM). Residual stress measurements were also performed in order to investigate the role of intrinsic stress in the film mechanical stability.

2. BACKGROUND: ACTINOMETRY

The technique of actinometric optical emission spectroscopy, or actinometry has been proposed by Coburn and Chen [12] as a method of diagnosis of reactive plasmas. In this procedure, a small proportion of a non-reactive gas - the actinometer - is added to the feed gas in order to probe the plasma. The intensity of an optical emission line of the actinometer is given by

$$I_a = n_a \eta_a \quad (1)$$

where n_a is the density of ground state actinometer molecules and η_a is the



excitation efficiency from ground state to the state responsible for the emission. It should be remembered that η depends on the electron energy distribution function (EEDF) of the plasma and increases as the activity of the plasma is increased. The parameter "activity", A , has been defined in an earlier paper [13] as

$$A = \rho E \quad (2)$$

where ρ and E are respectively the electron density and the electron mean energy. If n is constant, which is usually the case in actinometric measurements, we can see from Eq. (1) that changes in the intensity of the actinometer emission reflect changes in the plasma activity.

Combined optical emission measurements of a reactive species, x , and that of the actinometer allows the determination of the relative changes in the density of the former as the deposition parameters (composition of the feed gases, pressure in the chamber and applied power to the plasma) are varied. Let I_x be the intensity of an emission line of species x . Then

$$I_x = n_x \eta_x \quad (3)$$

where n and η are respectively the density of the ground state reactive species and the excitation efficiency. Combining Eqs. (1) and (3) we may write

$$n_x = n_a \frac{I_x \eta_a}{I_a \eta_x} \quad (4)$$

choosing excited states of the actinometer and reactive species such that η_a is approximately equal or proportional to η_x , we will have, for constant n_a :

$$n_x \approx k \frac{I_x}{I_a} \quad (5)$$

where k is a constant.

3. EXPERIMENTAL

The discharges in the HMDS and Ar mixtures were generated by a homemade planar magnetron electrode connected to a negative DC power source, as represented schematically in Fig. 1. The magnetic

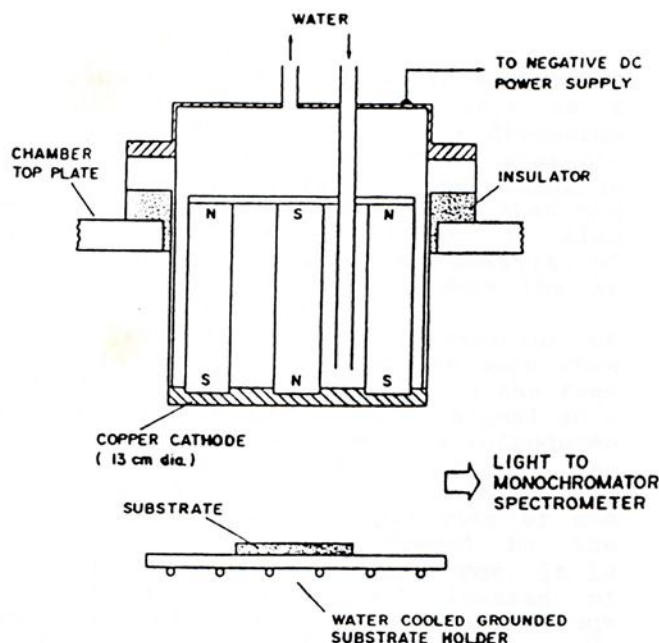


Fig. 1. Schematic diagram of the electrodes.

field in the discharge is supplied by the magnet shown in the figure, which is formed by a stack of circular loudspeaker magnets of 9 cm diameter. The electrodes were assembled inside a 30 cm diameter x 35 cm height aluminium vacuum chamber evacuated independently by a 12 m³ h⁻¹ two-stage rotary vane pump or a 150 l s⁻¹ diffusion pump. Pressure in the chamber is measured by a capacitance manometer (Datametrics Barocel type 600) and by a Penning gauge (Edwards model CP-25S). Pressures during film deposition were typically in the 0.05 - 0.1 mbar range. Prior to gas admission, the chamber was pumped out to the 10⁻⁵ mbar range by the diffusion pump during approximately 10 minutes.

Argon, nitrogen and HMDS vapor were admitted to the chamber through mass flow controllers (Datametrics, model 825). An evaporation cell was used to produce the HMDS vapor. It consists of a 10 cm³ glass bulb half-filled with liquid HMDS and connected to the mass flow controller through a leak valve (Edwards, model LV-5). Both gases and HMDS are of chemical purity better than 99.9%.

A quartz glass window in the chamber allows observation of light emitted by the plasma by a 1 m focal length optical monochromator (Spex, model 14300) equipped with a photomultiplier tube (Burle, 1P20A). Optical emission spectra were recorded by a strip chart recorder (Hewlett-Packard, 7100BM). Table I lists

Table I. Emission wavelengths of species of interest.

Species	λ (Å)
C	2479
Si	2516
Cu	3247
CH	4314
Ar	4072
N ₂	3371

the species of interest and their emission wavelengths.

Film thicknesses were measured by an interferometer microscope (Varian, λ -Scope). A transmission electron microscope (Zeiss, EM-902) was used to investigate the film structure. The residual stress measurements were performed by the bending beam method [14] using the apparatus described in a previous publication [15].

4. RESULTS

4.1 Optical Emission Spectroscopy of the Discharge

Typical emission spectra of the HMDS-Ar discharge are shown in Fig.2 in various wavelength ranges. Including Ar and N₂, which is used as an actinometer, emissions from Cu, C, CH and Si species are prominent in the discharge. While Cu arises from sputtering of the cathode, two mechanisms may account for the appearance of the C, CH and Si species: fragmentation of the HMDS molecules by the free electrons of the plasma and sputtering of the polymeric material

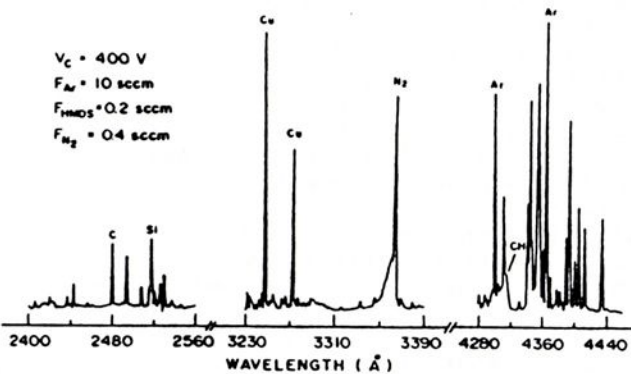


Fig. 2. Optical emission spectra of a HMDS-Ar discharge in several wavelength ranges. Nitrogen is added to the gas feed as an actinometer. The cathode voltage and the flows of Ar, HMDS and N₂ admitted to the chamber are illustrated above.

deposited on the cathode.

Figure 3 shows the intensity of emission of the actinometer (N₂) as a function of the Ar flow in a discharge without HMDS. Since the partial pressure of N₂ is nearly constant in the discharge we may conclude from the figure that the excitation efficiency for N₂ is also constant and consequently the activity of the plasma is not changed when the Ar flow varies from 10 to 14 sccm.

An entirely different behavior of the emission of N₂ is observed even when a small flow of HMDS is added to the feed gas. The dependence of the N₂ signal as a function of time, when HMDS is introduced in the discharge, is shown in Fig. 4. The steep rise in the intensity of the N₂ emission shows that the activity of the plasma is strongly increased by the presence of HMDS in the discharge. It is interesting to note that instead of levelling-off, the N₂ signal goes through a maximum and then decreases. We interpret this apparently odd behavior as due to the deposition of an insulating polymer coating on the electrodes thus reducing the discharge current. It should be mentioned however that the nature of the coating deposited on the cathode is different from that of the anode. As observed by several investigators [16] in plasma deposition in mixtures of organic gases and Ar, the polymer deposited on the cathode is a hydrogen-deficient material whose structure is deeply modified by the intensive bombardment of Ar ions.

This cathode coating also affects the flux of sputtered Cu atoms. Figure 5 shows the decays of the Cu emission lines

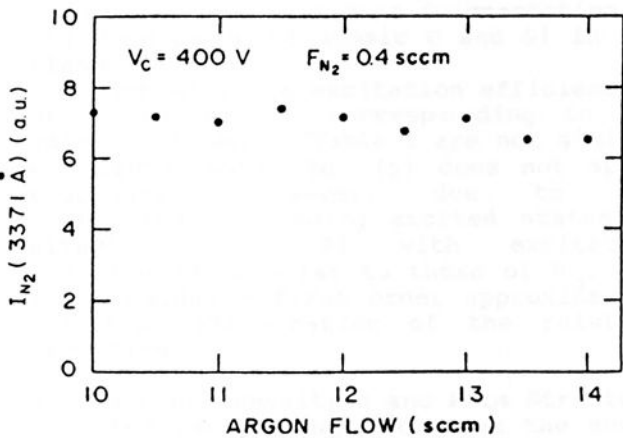


Fig. 3. Intensity of emission of N₂ as a function of the Ar flow in a discharge without HMDS.



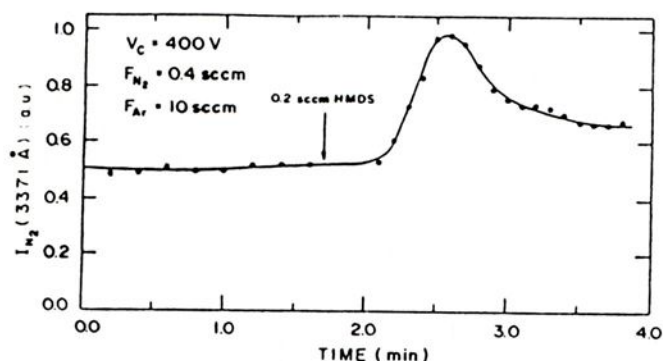


Fig. 4. Intensity of emission of N_2 as a function of time. The arrow indicates the time at which HMDS is introduced in the discharge.

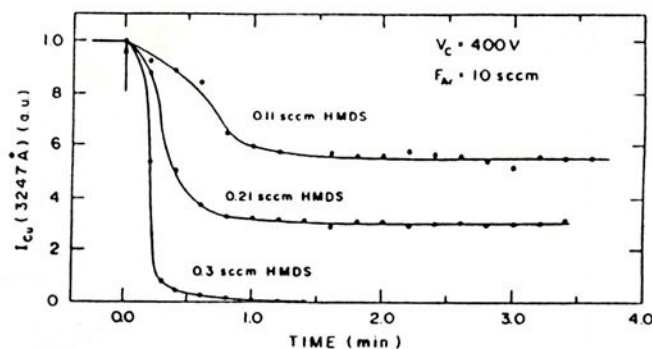


Fig. 5. Decay of the Cu emission line as a function of time for various HMDS flows. The arrow indicates the time at which HMDS is introduced in the discharge.

with time for three different flows of HMDS. The data of each decay was taken after a thorough cathode cleaning. The intensities of the Cu signals before introducing HMDS in the discharge are normalized to unity. For the HMDS flow of 0.3 sccm, the coating is formed very rapidly on the cathode and sputtering of Cu is totally inhibited at 1.5 minutes after HMDS is introduced in the gas feed. For HMDS flows of 0.11 and 0.21 sccm the rate of formation of the coating is smaller and the emission of sputtered Cu atoms from the cathode is only partially inhibited.

The growth rate of the polymeric coating on the cathode is the difference between the rate of polymer formation and the rate of etching by Ar and other massive positive ions of the discharge. The fact that steady-state fluxes of sputtered Cu atoms are attained for the HMDS flows of 0.11 and 0.21 sccm implies that the level of contamination of the cathode surface by the polymeric layer remains constant. This means that the rates of polymer formation and etching are equal. Since the preparation of films in the anode with uniform Cu density depend on a constant Cu gas-phase concentration, the plots of Fig. 5 illustrate the usefulness of optical emission spectroscopy in monitoring the process of deposition. It should be noted also that for HMDS flows smaller than 0.3 sccm, polymer films without Cu can be formed on the anode.

Since, as shown in the spectra of Fig. 2, atomic C and atomic Si are present in the discharge, it seems interesting to investigate the mechanisms of formation of these species. As pointed out earlier, fragmentation and sputtering effects may contribute to the formation of C and Si species. In order to investigate the relative importance of

these two effects, we have measured the emission intensities of C and Si in Ar discharges with and without HMDS. Figure 6 shows several emission spectra of the discharge in the wavelength region between 2400 and 2560 Å. The spectrum of Fig. 6(a) was taken with HMDS in the discharge while those of Figs. 6(b) and 6(c) were taken without HMDS. The latter were taken 5 and 10 minutes after that of Fig. 6(a). As seen in the figure, the C and Si signals are clearly present in the discharge as well as the peaks at 2443 and 2492 Å and the band at 2470 Å, not yet identified. Table II lists the relative concentrations of C and Si in the discharges, calculated from the data of Fig. 6, using Eq. (5) and taking N_2 as the actinometer. From the small changes in the densities of C and Si species in discharges with and without HMDS we conclude that sputtering plays a much more important role than fragmentation in the appearance of atomic C and Si in the plasma.

Actually the excitation efficiencies of C, Si and N_2 corresponding to the emission lines of Table I are not similar and consequently Eq. (5) does not apply rigorously. However, due to the difficulty of finding excited states in either C or Si with excitation efficiencies similar to those of N_2 , Eq. (5) provides a first order approximation for the determination of the relative densities.

4.2 Rate of Deposition and Film Structure

The rate of deposition on the anode and the proportion of copper to polymer in the films vary widely according to the discharge parameters. Figure 7 shows the deposition rate as a function of the Ar

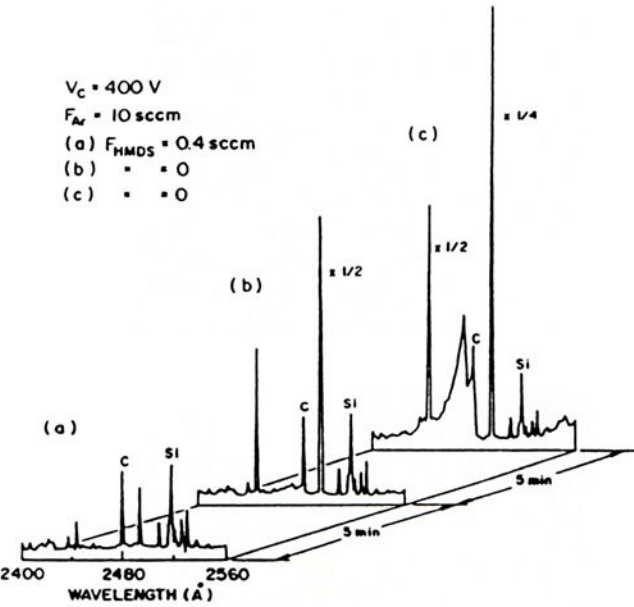


Fig. 6. Emission spectra of the discharge taken sequentially in 5 min intervals. (a) HMDS-Ar discharge. (b) and (c) Ar discharge.

flow for a constant cathode voltage and HMDS flow. The discharge parameters for the data point indicated by an arrow in the figure are the same as for the data of the uppermost curve of Fig. 5. This implies that Cu must be present in the discharge and consequently incorporated in the film. Since a rise in the Ar flow increases the flux of sputtered Cu from the cathode, films with increasing Cu content are expected to be deposited as the Ar flow changes from 10 to 14 sccm.

Transmission electron micrograph pictures of two films prepared under different conditions are shown in Fig. 8. The Ar flow varies from one sample to another while the cathode voltage and the HMDS flow are kept constant. As seen in the pictures, microscopic metallic particles (dark regions) are dispersed in the bulk of the polymer matrix. The density of metal increases from sample A to B as a consequence of the increase in

Table II. Relative densities of C and Si species in the discharge as a function of time.

Species	0 min	5 min	10 min
C	1.0	1.0	1.2
Si	1.0	0.96	0.80

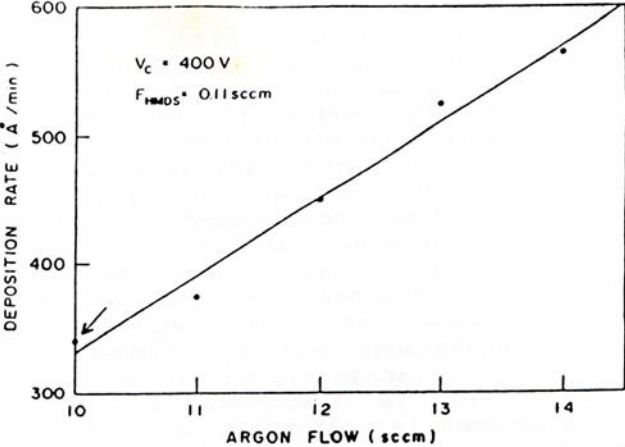


Fig. 7. Deposition rate in a HMDS-Ar discharge as a function of the Ar flow.

the Ar flow. These structures are consistent with previous observations in polymer-metal [17] and oxide-metal [18] composite films.

It should be pointed out that since atomic C and Si are present in the discharge, thus it is possible that the particles in the film are not constituted only by Cu but also contain C and Si either in metallic or combined forms such as carbides and silicides. In preliminary experiments using transmission electron diffraction we have observed that the films show well-defined diffraction rings even in samples with small Cu concentrations. It is thus expected that this technique will provide useful information on the crystalline structure of the particles.

4.3 Residual Stress Measurements

All the measurements in the films have shown that the stresses are compressive with values in the $10^8 - 10^9$ dyne cm^{-2} range. Table III lists the residual stresses of three films: a Cu-free, a polymer-Cu composite film and a polymer-free film. As previously observed [15, 19, 20], the residual stress depends on the film composition, structure and thickness. Since the thicknesses of the films listed in the table are similar, differences in stress due to thickness differences are eliminated. The all-metal film is that with the lowest stress while the composite film presents the highest stress.

Our results are different from those of Yasuda et al. [21] who report zero stress for plasma polymerized tetramethylsiloxane, a chemical compound

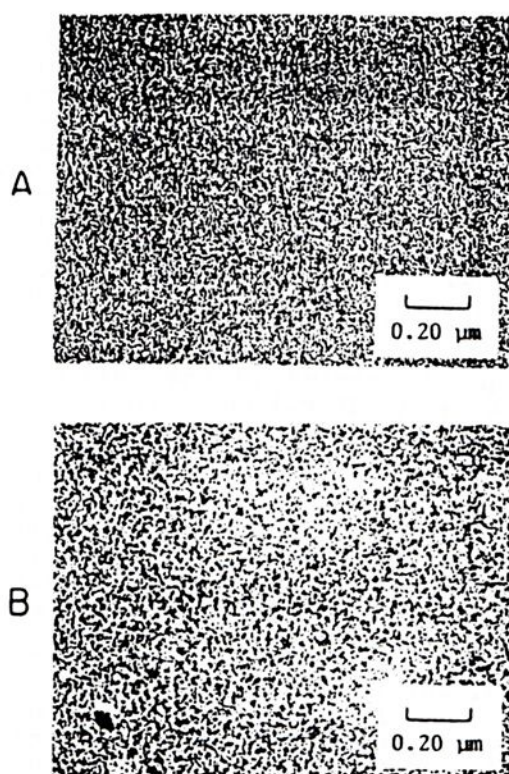


Fig. 8. TEM micrographs of two polymer-metal composite films prepared with $V = 400$ V and $F_{HMDS} = 0.15$ sccm. A: $F_{Ar} = 7.0$ sccm. B: $F_{Ar} = 10$ sccm.

very similar to HMDS.

The residual stress plays an important role in the mechanical stability of coatings. If the internal stress is too high, the internal forces in the film may overcome the adhesion forces to the substrate causing film cracking or peeling. As pointed out earlier, plasma polymerized HMDS show very good adhesion to substrates. Since our films are highly stressed, we interpret their long-term mechanical stability as a consequence of large adhesion forces between film and substrate.

Table III. Residual stress of films prepared at various HMDS and Ar flows.

Film thickness (Å)	F_{HMDS} (sccm)	F_{Ar} (sccm)	σ (dyne.cm ⁻²)
1510	0.4	0.0	1.5×10^9
1410	0.4	6.0	5.9×10^9
1580	0.0	6.0	5.0×10^8

5. CONCLUSIONS

We have studied the process of deposition, the structure and the residual stress of plasma polymerized HMDS films with copper incorporation.

Analysis of the discharge by OES has shown that the polymeric layer deposited on the electrodes strongly affects the plasma composition and the plasma current. From the behavior of the C and Si emission lines in Ar and HMDS-Ar discharges we conclude that cathode sputtering is the most important "channel" for the appearance of these species in the gas phase.

The structure of the films is typical of polymer-metal composites. The size of the metal particles increases with increasing proportions of Ar in the gas feed. Due to the presence of C and Si species in the discharge, it is possible that metallic C and Si and their compounds (carbides and silicides) are also present in the metal particles.

The long-term mechanical stability of our films, in spite of being highly stressed, strongly indicates high adhesion forces between film and substrate.

ACKNOWLEDGMENTS

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QUARTA PARTE

O plasma empregado na deposição de polímeros fluorados

Nos artigos “FLUORINATED POLYMER FILMS FROM RF PLASMAS CONTAINING BENZENE AND SULFUR HEXAFLUORINE” , publicado em Thin Solid Films, 220, 295 (1992), e “DEPOSITION AND ETCHING OF HMDSO/SF₆ PLASMA POLYMERIZED THIN FILMS” submetido à revista Polymer Preprints em 1996, discutimos a taxa de deposição e o mecanismo competitivo polimerização/corrosão, assim como a modificação estrutural em polímeros preparados a plasma .



Os estudos de descargas elétricas a baixa pressão, envolvendo misturas que contêm gases e/ou vapores orgânicos juntamente com gases fluorados, têm despertado grande interesse nesta última década. Este interesse se associa ao fato de que tais misturas podem ser responsáveis por mecanismos de polimerização e “etching”, dependendo da proporção do gás fluorado na mistura. Ou ainda o processo de remoção seletiva a plasma, denominado “etching”, pode agir por si só, caso se tenha por objetivo corroer um polímero num ambiente de plasma, na presença apenas de uma atmosfera fluorada.

Nesta seção apresentamos uma análise crítica dos artigos “FLUORINATED POLYMER FILMS FROM RF PLASMAS CONTAINING BENZENE AND SULFUR HEXAFLUORINE” E “DEPOSITION AND ETCHING OF HMDSO/SF₆ PLASMA POLYMERIZED THIN FILMS”. No primeiro, o plasma foi composto por uma mistura benzeno/hexafluoreto de enxofre, e no segundo, por uma mistura de hexametildisiloxano (HMDSO)/ hexafluoreto de enxofre.

Os polímeros fluorados podem ser largamente utilizados como coberturas protetoras de superfícies, uma vez que apesar de terem radicais livres em suas estruturas, eles são facilmente neutralizados e os polímeros apresentam boa adesão a substratos orgânicos e não orgânicos.

Nestes trabalhos, consideramos como fundamental a discussão das espécies ativas existentes no plasma, provenientes principalmente da fragmentação de SF₆, que são responsáveis pelos efeitos de “etching” e polimerização. A nossa crítica é feita



essencialmente sobre a taxa de deposição destes polímeros, que está associada aos mecanismos competitivos de polimerização e corrosão simultâneos. Apresentamos ainda uma análise crítica da modificação estrutural destes polímeros sujeitos a ambientes mais ou menos fluorados durante a descarga .

Embora os monômeros benzeno ($C_6 H_6$) e hexametildisiloxano ($(CH_3)_6 Si_2 O$) apresentem grupos funcionais completamente diferentes, os resultados representativos das taxas de deposição dos polímeros obtidos a partir das misturas destes monômeros com SF_6 , indicam mecanismos competitivos de polimerização e “etching”, governados pelo mesmo princípio, que são as espécies ativas .

É importante lembrar que a taxa de deposição de um filme polimérico é o saldo positivo entre os mecanismos competitivos de polimerização e ablação, onde a ablação é a soma de todas as contribuições responsáveis pela corrosão do polímero. Nas descargas de $C_6 H_6 / SF_6$ e HMDSO/ SF_6 , o mecanismo “etching” é particularmente ativo, devido a presença de flúor atômico .

A fim de poder comentar a elevação das taxas de deposições, mesmo aumentando os níveis de SF_6 nas misturas com $C_6 H_6$ com HMDSO, e após certos valores, se observar uma brusca queda nas taxas de deposição destes polímeros, deve-se enfatizar que os elétrons no plasma são fontes importantes na produção dos blocos formadores dos filmes poliméricos e ainda da espécies corrosivas, através de processos colisionais na fase gasosa. Eles são também responsáveis pela produção de sítios ativos por intermédio de colisões com a superfície do polímero durante o seu crescimento, o



que pode ser explicado em termos dos crescimentos ativados. Aqui levamos em consideração a interação da descarga com o crescimento do filme, através de um contínuo bombardeamento de partículas energéticas da descarga sobre a superfície do filme polimérico, gerando sítios ativos conjuntamente com modificações estruturais no filme. Podemos associar este bombardeamento as partículas energéticas, tais como os elétrons e íons. Os sítios ativos criados nas superfícies dos polímeros são provenientes das quebras de ligações e/ou através de átomos ligados as superfícies dos filmes .

Assim, os polímeros podem crescer mediante as reações destes sítios ativos com as espécies químicas existentes nas descargas .

Para níveis baixos de SF_6 , os efeitos de ablação são pequenos e os aumentos nas taxas de deposições podem ser atribuídos aos acréscimos nas concentrações dos blocos elementares formadores dos filmes poliméricos e/ou aos aumentos na ativação dos filmes, provocados por possíveis aumentos de energia cinética média dos elétrons, quando os plasmas apresentam maiores proporções de SF_6 nas misturas $\text{C}_6\text{H}_6 / \text{SF}_6$ e $\text{HMDSO} / \text{SF}_6$.

Por outro lado, os decréscimos nestas taxas de deposições estão provavelmente associadas aos decréscimos no número de elétrons com energias suficientemente grande para promover as ativações dos sítios nos polímeros, e ainda aos efeitos de “etching”, por parte dos átomos de flúor .



Em qualquer destas descargas, as estruturas moleculares dos polímeros resultantes foram profundamente modificadas, a medida que a concentração de SF_6 nestas misturas era aumentada .

Para os plasmas de Benzeno/ SF_6 , a característica hidrogenada do polímero obtido exclusivamente a partir de benzeno, cai de modo progressivo até que a quase totalidade das ligações químicas desapareçam, em contraposição ao surgimento de ligações químicas entre átomos de flúor, principalmente com carbono . Portanto, de uma natureza hidrogenada, ele passa a assumir uma característica fluorada .

Nos plasmas de HMDSO/ SF_6 , para maiores concentrações de SF_6 na mistura, os polímeros vão substituindo as ligações de hidrogênio entre os elementos por ligações flúor, não obstante o desaparecimento de ligações de silício.



Fluorinated polymer films from r.f. plasmas containing benzene and sulfur hexafluorine

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Abstract

Mixtures of C_6H_6 and SF_6 were polymerized in an r.f. discharge. Actinometry (quantitative optical emission spectroscopy) was used to determine trends in the plasma concentrations of the species F, H and CH as a function of the proportion of SF_6 in the feed. Infrared spectroscopy and electron spectroscopy for chemical analysis were employed to characterize the deposited material. Increasing proportions of SF_6 in the feed produced increased fragmentation of the benzene molecules and greater fluorination of the deposited material. The deposition rate, as determined by optical interferometry, was found to be enhanced about 4 times by the presence of 10–20% SF_6 in the feed. At 50% SF_6 in the feed, deposition rates were greater than in pure C_6H_6 plasmas despite the (probably large) etching effect of atomic fluorine from the discharge. Relationships between the plasma composition, electron density and temperature, film composition and growth rate are discussed.

1. Introduction

Both etching and polymerization may occur in glow discharges containing organic, or mixtures of organic and inorganic, gases [1]. The former process is of importance in microchip fabrication [2]; the latter for the production of films and coatings [3]. In discharges of mixtures of gases, at least one being the polymer-forming gas, chemical elements from both gases can be incorporated into the deposited film. Consequently, the chemical and physical properties of the film may be determined by a suitable choice of the gases used, combined with other deposition parameters such as applied power and system pressure.

Fluorinated films can be produced by plasma polymerization in a number of ways. Single fluorocarbons such as C_2F_6 [4], C_6F_6 [5], or mixtures such as CF_4 – C_2F_4 [6] have been polymerized in r.f. discharges. Alternatively, fluorine may be grafted onto the surface of a polymeric substrate by subjecting the specimen to a plasma containing a fluorinated gas. Fluorinated polymers have been produced, for example, by exposing substrates of polyethylene to an SF_6 plasma [7]. Another approach is to plasma-polymerize a mixture of organic and fluorinated inorganic gases [8].

This last alternative has been employed in this work to deposit fluorinated organic films. Mixtures of benzene and sulfur hexafluoride were polymerized in an r.f. system possessing external electrodes. The key system parameter was the proportion of SF_6 in the feed, which

was found to control the degree of fluorination of the deposited material.

The polymerization process, which despite widespread use is still poorly understood, was examined from several aspects. Optical emission spectroscopy was used to probe the discharge environment. In particular, the actinometric technique was utilized to find trends in the concentrations of species present in the plasma which may play a role in the polymerization process.

The actinometric technique, which uses the emissions from an inert probe gas (actinometer) to obtain relative concentrations of species of interest, is well established [9–11]. Its successful application depends upon the fact that the excitation mechanisms for the transitions of interest, of species x and actinometer α , are predominantly by direct electron impact. In addition, the excited states thus formed should decay only by photon emission. Finally, the threshold energies for the two transitions should be the same.

Actinometry relies on the fundamental relation

$$I_x = k_x n_x \eta_x \quad (1)$$

where α refers to the actinometer and I , n , and η are the intensity of emission, the concentration of the species in the ground state, and the excitation efficiency respectively; k_x is a constant. Thus, at a constant actinometer concentration, trends in the emission intensity indicate the functional form of the excitation efficiency. An increase in the excitation efficiency is itself usually related to an increase in the electron density or electron

mean energy (or both). Thus we propose the use of a parameter A , defined by

$$A = \bar{\rho} \bar{E} \quad (2)$$

where $\bar{\rho}$ is the mean electron density and $\bar{E}$ the mean electron energy. The parameter A therefore gives a rough indication of the "activity" of the plasma. Thus, by referring to the parameter A it is possible to avoid constant reference to an increase in the electron density or the electron mean energy (or both). We have used this shorthand in the subsequent text.

Material was deposited from feeds of different proportions of SF_6 . The structure of the films produced was studied using infrared (IR) spectroscopy and electron spectroscopy for chemical analysis (ESCA). The latter was also used in the investigation of the elemental composition of the films. Deposition rates were also measured. Inter-relationships between these parameters are highlighted.

2. Experimental details

The deposition system used was essentially that described previously [8]. Briefly, it consists of a vertical barrel-type reactor of diameter 7.5 cm made of Pyrex, terminating in a bell jar chamber of diameter 20 cm. The total volume of the reactor is $9.2 \times 10^3 \text{ cm}^3$ and it was pumped by a $12 \text{ m}^3 \text{ h}^{-1}$ two-stage rotary vane pump. Gases were fed to the reactor via needle valves and flowmeters (Datametrics type 831). The plasma was maintained by a homemade r.f. supply (120 MHz, 80 W maximum power output) which feeds two external aluminum ring electrodes 7.5 cm apart, embracing the glass tube. Power was measured by a through-line wattmeter. An impedance matching network was used to optimize power transfer to the plasma.

Sulfur hexafluoride and the actinometers (nitrogen, argon or helium) were supplied from cylinders. These gases were of 99.5% minimum purity. Benzene (purity 98%) was admitted to the reactor from an evaporation cell consisting of a glass bulb (5 cm^3) half-filled with liquid C_6H_6 and connected to a flowmeter via a needle valve. A Pirani gauge, previously calibrated for nitrogen against a capacitance manometer (Datametrics Barocel type 600) was used for pressure indication.

For actinometry, small percentages (about 1–3%) of N_2 , Ar or He were added to the gas feed. Characteristic peaks of particular species of interest were detected using a monochromator spectrometer (Spex Industries, model 14300). The UV–VIS photomultiplier (Burle IP28A) output was fed to an electrometer (Keithley Instruments, model 610CR) and monitored on a Hewlett–Packard chart recorder (model 17501A). A scan rate of 0.4 Å s^{-1} , allowing good definition of the

TABLE 1. Spectral data of species of interest

Species	λ (nm)	Threshold energy (eV)
CF	207.6	~6
CF_2	276.0	~4.5
CH	431.4	<11
H	656.3	12.09
F	703.7	14.74
N_2	337.1	11.2
Ar	750.3	13.47
He	388.9	23.01

peaks, was typically used. Peaks or bandheads of interest are listed in Table 1, together with their emission wavelengths and excitation thresholds.

Prior to each film deposition or optical measurement in the plasma, the reactor was pumped down to $2 \times 10^{-1} \text{ Pa}$. All the experiments were made at an applied r.f. power of 13 W and at a constant total flow of $1.35 \times 10^{-2} \text{ Pa m}^3 \text{ s}^{-1}$ ($1 \text{ Pa m}^3 \text{ s}^{-1} = 592 \text{ sccm}$) corresponding to an indicated pressure of approximately 20 Pa. For these conditions, the volume of the plasma region was typically some 20% larger than the volume in the reactor between the two electrodes (330 cm^3).

Since, under the conditions used, the polymer film deposition rate for benzene–sulfur hexafluoride mixtures is relatively high (typically 10 nm s^{-1}), deposition times of only 2 min were needed. A glass slide, partially covered with a second smaller glass slip, was used to obtain a well-defined step height. The film was then coated with a very thin evaporated aluminum layer (*ca.* 30 nm), using a vacuum deposition system. Thereafter it was possible to measure the film thickness by means of an optical interferometer (Varian, Å-scope).

Films for analysis by IRS were prepared on substrates of KCl. The analyses were performed using a Jasco IR 700 IR spectrophotometer.

ESCA data of the polymer films were taken with a VSW model HA100 spectrometer using the Al $K\alpha$ X-ray line (1487 eV) for photoelectron excitation, operating at a pressure of $2 \times 10^{-6} \text{ Pa}$. The atomic ratios were computed from the integrated areas of the peaks in the spectra, corrected for electron escape depth, spectrometer transmittance, and the photoelectron cross-sections for the photon energy of 1487 eV [12], according to the procedure described in the handbook of Wagner *et al.* [13]. In order to investigate the various binding states of the carbon atoms in the films, the carbon 1s spectra have been decomposed into various gaussian peaks via a least-squares fitting computer program developed by the Surface Science Group of the University of Campinas.

The main sources of error in the measurements were the instability of the plasma and the non-uniformity of the polymer coatings. The former affected the measurements of the intensities of the emission lines; the latter the determination of the film thicknesses. The instability of the plasma increased with increasing proportions of SF_6 in the plasma. Deviations in the intensity measurements were in the range 5–15% for a variation in the SF_6 percentage in the feed 0–40%. Owing to the non-uniformity of the film thicknesses, an average thickness was determined from measurements in at least five positions of the substrates. The error in this determination was estimated to be approximately 15%.

3. Results and discussion

3.1. Actinometry

Figure 1 shows the relative emission intensities of the actinometers N_2 , Ar and He as a function of the percentage of SF_6 in the feed. The three intensities exhibit a fairly similar dependence on this parameter, although at low SF_6 concentrations the He curve lies well below the others. Since variations in the emissions from the actinometers reflect changes in the activity of the plasma, A , the curves of Fig. 1 show that A depends strongly on the proportion of SF_6 . In the region between 10% and 25% SF_6 the activity reaches a maximum, then declines.

The curves of Fig. 1 provide further useful information on the behavior of the plasma electrons as a function of the proportion of SF_6 in the feed. The monitored helium emission corresponds to an energy threshold of 23 eV, considerably higher than either Ar or N_2 (cf. Table 1). Consequently, the trend in helium emission is an indicator of the behavior of relatively high-energy electrons, and illustrates that their density does not rise as rapidly as lower-energy electrons at low

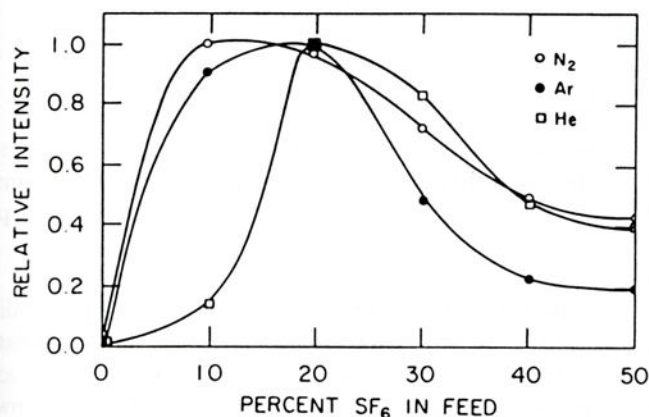


Fig. 1. Relative intensity of the actinometers (N_2 , Ar, and He) as a function of the percentage of SF_6 in the feed.

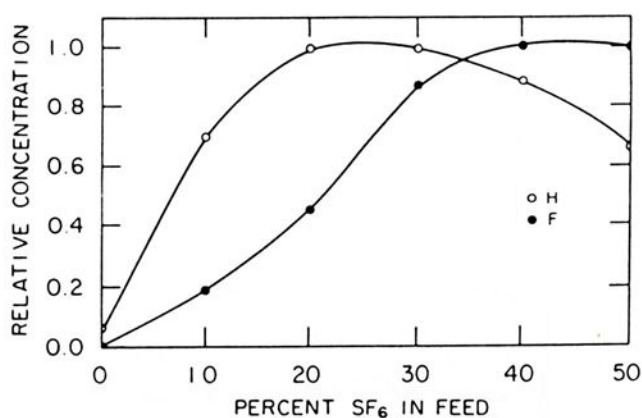


Fig. 2. Relative concentration as a function of the percentage of SF_6 in the feed for atomic F and H. Argon was used as actinometer at 1–3%.

SF_6 feed percentages. However, allowing for uncertainties in the measurements of the emission intensities, we may say that above about 20% SF_6 in the feed the three actinometer intensities exhibit a similar dependence. In these conditions actinometry may be applied, even to species whose threshold energies are far from those of the pool of the actinometers [14]. Thus the choice of an actinometer for the calculation of the relative concentrations of different species is relatively arbitrary.

To obtain the relative concentrations of the species H and F we have normalized their optical emission intensities to that of Ar. Similarly, the intensity of the species CH was normalized using the N_2 emission line. As indicated above, in this particular case these choices are not very critical, but were made on the basis of the closeness of the energy thresholds of the species and the actinometer.

Figure 2 shows the concentration of atomic F and atomic H as a function of the percentage of SF_6 in the feed. The fluorine concentration increases nearly monotonically with increasing SF_6 in the feed, only levelling-out at SF_6 percentages beyond about 40%. At such levels the increase in the supply of SF_6 may be offset by the falling activity of the plasma. The hydrogen concentration is seen to increase by more than one order of magnitude when the feed SF_6 concentration is raised from 0% to 10%. This probably reflects the ease of formation of atomic H relative to F in the active plasma obtained under such conditions. Hydrogen concentrations begin to fall only beyond a feed- SF_6 percentage of 30%. This is consistent both with the declining supply of benzene (and hence H) and the subsequent fall in the activity of the plasma.

The species CF and CF_2 exhibit various optical emissions in the ranges 197–220 nm and 220–280 nm, respectively. Relatively strong emissions might be expected at 207.6 nm (CF) and 276.0 nm (CF_2). How-

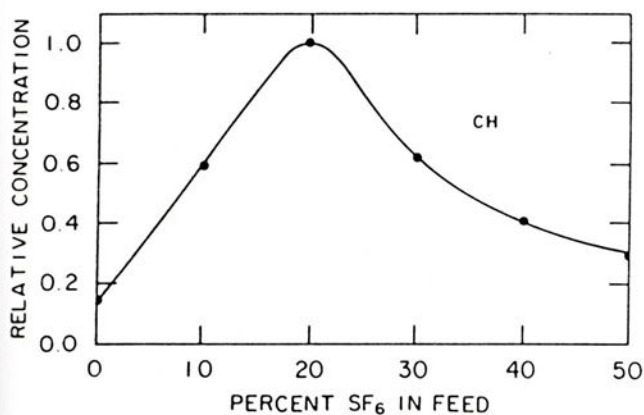
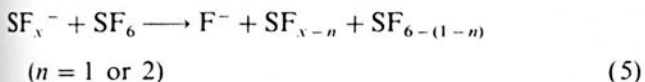
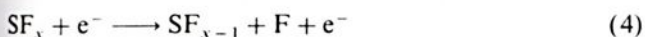
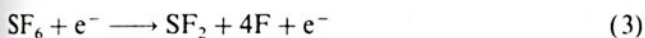


Fig. 3. Relative CH concentration as a function of the percentage of SF₆ in the feed. Nitrogen was used as actinometer at 1–3%.

ever, only the former was detected, at extreme sensitivity and with 50% SF₆ in the feed. Despite this, it seems possible that CF₂ and other species such as CF₃ and SF_x ($x = 1-6$) were also present, as well as benzene fragments.

Figure 3 shows the relative plasma CH concentration as a function of the percentage of SF₆ in the feed. Fragmentation of the benzene molecules present in the discharge probably accounts for the higher relative concentrations of CH found at greater proportions of SF₆. Beyond about 20% SF₆ in the feed, CH levels begin to decline due to the fall in the activity of the plasma and the decline in the supply of benzene (and hence the supply of CH units).

While the polymerization of benzene occurs readily under the conditions used, pure SF₆ does not polymerize, regardless of feed pressure or applied power [7]. However, SF₆ can be expected to fragment in the plasma [15] and react by routes such as [16]



where M is a third body. Thus the overall reaction scheme in a C₆H₆-SF₆ plasma must be extraordinarily complex.

3.2. IR studies

Films were grown at the same SF₆ feed percentages as used for the optical measurements. Figure 4 illustrates the transmission IR spectra obtained. Films grown in pure benzene plasmas (spectrum a) show the following main absorptions: (i) C-H stretching in the aromatic ring at about 3100 cm⁻¹; (ii) symmetric and

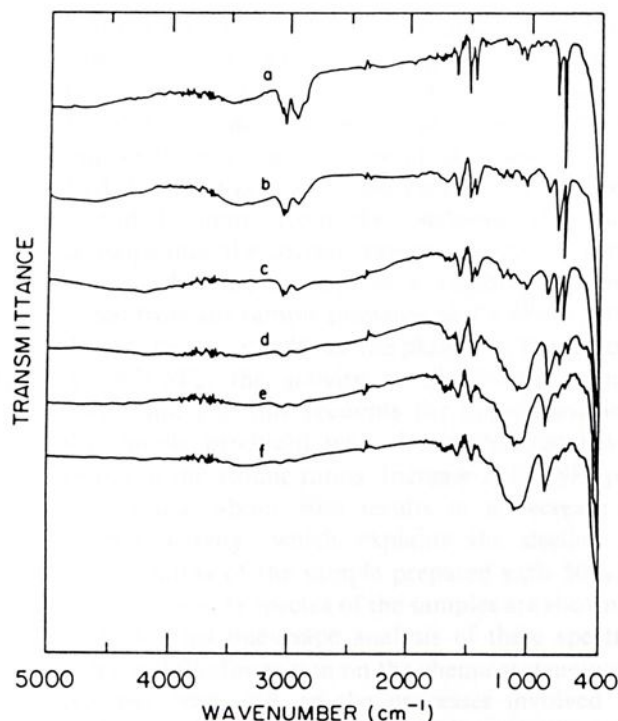


Fig. 4. IR spectra of polymers grown at 0% (spectrum a), 10% (spectrum b), 20% (spectrum c), 30% (spectrum d), 40% (spectrum e), and 50% (spectrum f) of SF₆ in the feed.

antisymmetric C-H stretching in CH₂ and CH₃ groups at 2930 cm⁻¹; (iii) vibrations of the phenyl ring at about 1500–1700 cm⁻¹; (iv) CH₂ and CH₃ bending at about 1400 cm⁻¹ (absorption for CH₃ umbrella at about 1380 cm⁻¹ is either very weak or non-existent); (v) in-plane hydrogen wag at about 1000 cm⁻¹; (vi) C-C stretching between 800 and 900 cm⁻¹; (vii) vibrations due to *meta*-, *para*- and *ortho*-substituted phenyl rings between 700 and 800 cm⁻¹.

The feature at 3500 cm⁻¹ is due to hydroxyl groups and it appears in the spectra as a consequence of oxygen contamination. The incorporation of oxygen could result from reactions with oxygen, water vapor or other oxygen-containing molecules still found in the reactor during film formation. It should be noted that plasma polymers may contain a high concentration of free radicals, trapped from the plasma [17]. Thus, the hydroxyl group could also arise from reactions between the free radicals and ambient oxygen [18].

Notably weak in the spectra are the characteristic absorptions at 1625 cm⁻¹ due to the presence of C=C bonds. Presumably, a high percentage of such bonds, present in the pure benzene, are saturated by F or H attachment. The detection of CH₂ and CH₃ groups indicates that either gas-phase reactions involving CH and H, or hydrogen attachment processes at the surface of the polymer, or both, must occur. Another feature of

the series of spectra is the clear emergence of the band at $900\text{--}1500\text{ cm}^{-1}$ at 30% SF_6 in the feed, indicating the presence of C–F bonds in the deposited material. Simple inspection of the CF band at $900\text{--}1500\text{ cm}^{-1}$ and the CH band at 2930 cm^{-1} shows that the C–F and C–H bonds coexist in the polymer films. As the feed percentage of SF_6 is raised, the CF absorption increases as the CH absorption decreases. At 50% SF_6 (spectrum f), the latter is almost entirely absent in the spectrum. Since at this feed percentage there are as many F atoms as H atoms in the discharge, spectrum f reflects the fact that C–F bonds are formed preferentially to C–H bonds in the polymer films.

3.3. ESCA studies

ESCA analysis was carried out on samples prepared with various proportions of SF_6 in the gas feed. Nitrogen, which has been used as an actinometer in the experiments previously reported, was also added to the discharge at a proportion of 3% of the total flow with the purpose of investigating its possible incorporation into the polymer films.

Fluorine, sulfur and nitrogen were detected in the samples prepared in the discharges containing SF_6 , while oxygen due to contamination was detected in all the samples. The atomic ratios of the elements detected in each sample are listed in Table 2.

The fact that nitrogen is detected in most of the samples means that nitrogen may react in the discharge and become incorporated in the film. However, for the amount of N_2 we have used in the gas feed, nitrogen incorporation could be considered as small. As Table 2 shows, at most about 4 N atoms are detected for each 100 C atoms.

Consistently with the IR results in the last section, fluorine is detected in the samples in various F:C ratios, depending on the percentage of SF_6 in the feed. Sulfur is also incorporated in the films at relatively high atomic ratios. From Table 2 it can readily be seen that, for the films prepared with SF_6 in the discharge, the S:F ratio varies from one sample to another in the range 0.37–0.64. Since the S:F ratio in the SF_6 molecule is 0.17, we conclude that S atoms are incorporated more effectively than F atoms in the polymer films.

TABLE 2. Relative atomic ratios in the polymer films

Sample	Percentage of SF_6 in the total flow	N:C	O:C	F:C	S:C
1	0	—	0.077	—	—
2	15	0.017	0.110	0.184	0.118
3	30	0.043	0.152	0.910	0.336
4	50	0.021	0.120	0.630	0.313

Inspection of Table 2 shows that all the atomic ratios vary in a similar manner as the proportion of SF_6 in the feed increases. Clearly, we expect the atomic ratios in the films to depend on the activity and on the composition of the plasma. For low percentages of SF_6 in the feed, both the activity of the plasma and the supply of S and F atoms from the discharge are small and consequently the atomic ratios are low. It should be noticed that the absence of a detectable nitrogen 1s signal from the sample prepared at 0% SF_6 is very likely due to the low activity of the plasma at this percentage. At 30% SF_6 , the activity of the plasma is near its maximum, and this accounts for the observation that the sample produced with this percentage has larger values of the atomic ratios. Increase in the SF_6 percentage beyond about 30% results in a decrease in the plasma activity, which explains the decline in the atomic ratios of the sample prepared with 50% SF_6 .

The carbon 1s spectra of the samples are shown in Fig. 5. A detailed line-shape analysis of these spectra provides useful information on the chemical structure of the polymer films and on the processes involved in film formation. With this purpose we have decomposed the spectra into several peaks assigned to C atoms in various functional groups in which the binding energy (BE) of the C 1s electron is well known [19]. Table 3 summarizes the functional groups, the BE at which the peaks are centered, and the percentage contribution of each peak to the total C 1s profile. As shown in Table 3, several functionals are assigned to the peak at 287.3 eV. For the peak at 285 eV, photoelectrons from both carbon atoms bonded to other carbons and to hydrogen contribute. However, according to the IR data of the last section, the C–H bond density in the polymer films decreases with increasing proportions of SF_6 in the discharge. Thus at high percentages of SF_6 in the feed, the photoelectron contribution to the 285 eV peak is predominantly from carbon bonded mainly to other carbons.

As we can see in Fig. 5, as the percentage of SF_6 in the feed increases, the C 1s spectrum broadens because of the increase in the intensity of the peaks with BE values higher than 285 eV. In the range 0–30% SF_6 , this increase is interpreted as a consequence of the rise of both the proportion of SF_6 in the discharge and the plasma activity. Consistently with the behavior of the plasma activity, these peaks decrease as the percentage of SF_6 changes from 30% to 50%.

It is interesting to compare our results with those from plasma polymerization of fluorocarbons. In films prepared in the glow region of C_6F_6 plasmas, for example, Clark and Abraham [5] found F:C ratios ranging from 0.9 to 1.1. Since the F:C ratio of the sample prepared with 30% SF_6 lies within this range, we conclude that reactions leading to the formation of C–F bonds take place at relatively high rates in the $\text{C}_6\text{H}_6\text{--SF}_6$ plasmas.

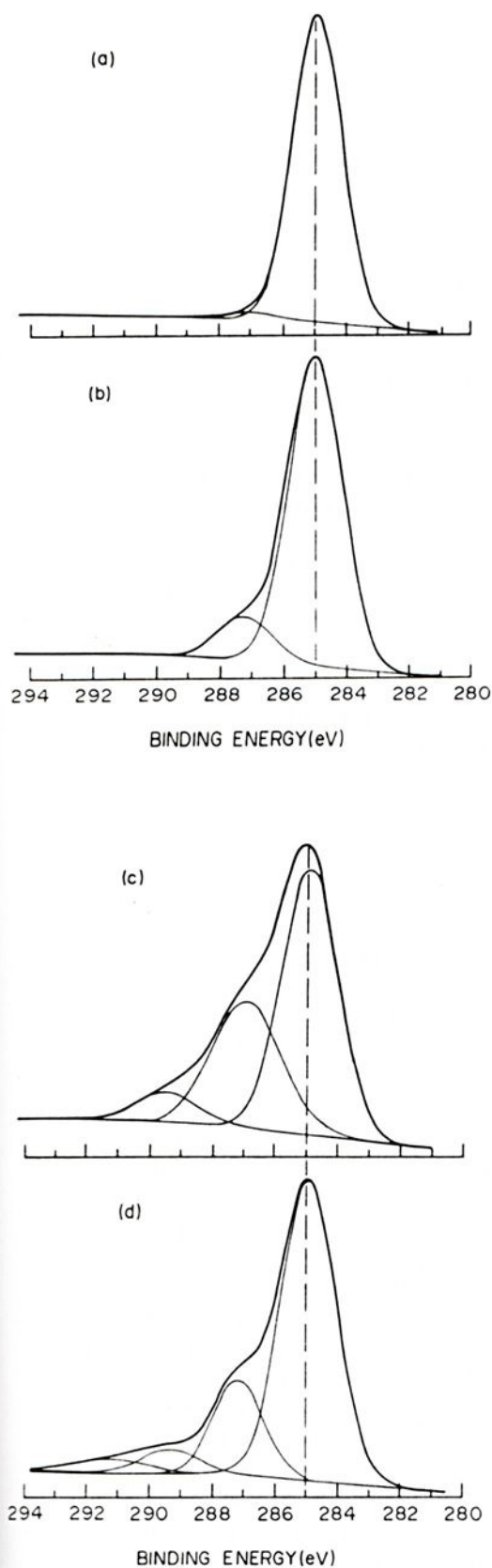


Fig. 5. Carbon 1s spectra of films prepared at (a) 0%, (b) 15%, (c) 30% and (d) 50% SF_6 in the feed. The percentage of N_2 in the total flow was 3%.

TABLE 3. Percentage contribution of each peak to the total C 1s spectrum

Functional group	Binding energy (ev)	Sample ^c			
		1	2	3	4
Hydrocarbon	285.0	100	88	59	70
β -shifted C ^a					
CO	287.3		12	34	20
CS					
CN					
CF	289.5			7	6
CF ₂	291.5				4

^aCarbon bonded directly to carbon and hydrogen but with one or two β -fluorine substituents.

The carbon 1s spectra from polymers produced in fluorocarbon plasmas [5, 20, 21] or from fluorinated polymer surfaces [7, 22, 23] usually contain the feature assigned to the CF_3 functional group at a BE value in the range 293–294 eV. In the spectra of Fig. 5 however, no significant peak can be assigned to this group. One possible explanation for this apparently odd behavior is based on the differences between the polymer films prepared in C_6H_6 – SF_6 discharges and those produced in fluorocarbon plasmas. As we have shown, the former films contain, besides C, F and H, also S and O in non-negligible proportions. The S, O and H atoms present in the discharge will compete with the F atoms for the formation of bonds with the C atoms, thus reducing the rate of formation of C–F bonds. Furthermore, because of this competition, the probability of formation of a CF_n functional group decreases with increasing n . This would then explain the absence of the feature assigned to CF_3 in the spectra of Fig. 5.

3.4. Deposition rate

The deposition rate is plotted in Fig. 6 as a function of the percentage of SF_6 in the feed. Greatly enhanced deposition rates are observed for relatively low proportions of SF_6 (10–20%). As discussed earlier, the concentrations of the H and CH species in the discharge are relatively large under these conditions, as a consequence of the high activity of the plasma. On the other hand, as shown by our ESCA data, CF and CF_2 groups are present in the films. Thus it is likely that the plasma concentrations of CF and CF_2 species are similarly enhanced. Concentrations of the latter species, together with the radical CH, have been considered as one of the key parameters in the deposition process [6, 24]. As can be seen in Fig. 6, the deposition rate decreases markedly for SF_6 percentages beyond 25%. This is interpreted as a consequence of both the decline in the supply of CH and CF_n “building blocks” and the increase in the polymer etch rate due to atomic fluorine.

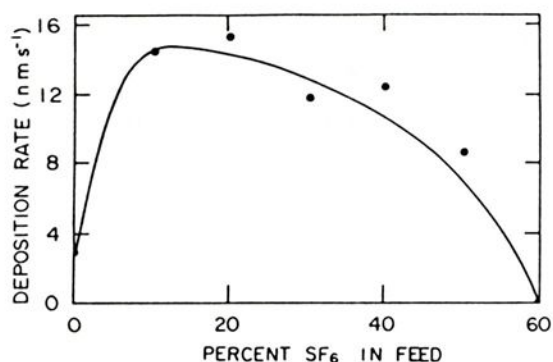


Fig. 6. Deposition rate as a function of the percentage of SF₆ in the feed.

It is interesting to note that at 60% SF₆, when the atomic F concentration is expected to be very high, no polymer is formed.

Another important factor that affects film growth is bombardment of the polymer surface by energetic electrons from the plasma. Collisions of the electrons with the film surface may produce active sites, thereby enhancing polymer growth [4, 6, 20]. Therefore, the activity of the plasma contributes to polymer film growth by generation of CH and CF_n species, which are the building blocks for film formation, and by the activation of sites in the polymer surface.

4. Conclusions

Fluorinated polymer films have been grown from C₆H₆-SF₆ mixtures in an r.f. plasma-polymerization system. Actinometry revealed the trends in the plasma concentrations of the species H, F, and CH as a function of the proportion of SF₆ in the feed. Our data strongly suggest that the species CH and CF_n act as building blocks for polymer growth; thus their plasma concentration is positively correlated with the deposition rate.

Plasmas produced with SF₆ percentages in the feed up to about 50% give much higher deposition rates than pure C₆H₆ plasmas even though atomic F, which is an etchant, is present in the former. It is the greater activity of the plasma when SF₆ is present in the discharge, that accounts for the higher growth rates observed. Greater plasma activity produces both more molecular fragmentation and greater activation of sites on the growing polymer surface.

IR spectroscopy showed that the films grown at progressively higher proportions of SF₆ in the feed contain progressively more fluorine. An aromatic structure was observed in films grown in pure C₆H₆ plasmas, but it diminished rapidly as SF₆ was introduced into the gas feed.

By ESCA analysis, the elemental composition of the films was studied and further details on the chemical structure of the films were investigated. The atomic ratios of N:C, O:C, F:C and S:F varied from one sample to another, consistently with the activity of the plasma. Bonding of the H, N, O, F and S atoms with the C atoms is revealed by the broadening of the C 1s peak profiles at higher SF₆ percentages. The notable absence of the peak corresponding to the CF₃ functional group in the C 1s profiles is explained based on the fact that in our plasmas, S, O and H atoms compete with the F atoms for the formation of bonds with carbon.

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DEPOSITION AND ETCHING OF HMDSO/SF₆ PLASMA POLYMERIZED THIN FILMS

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Introduction

Many organic compounds and their mixtures with inorganic compounds do not polymerize by conventional methods because the energy threshold involved is much above of the values attained in such processes. Plasma polymerization is in this case the most profitable technique because the products obtained are stable, pin-hole free and inert to almost organic solvents and mild acids. In this class of polymers we may cite the silicon-contained polymers obtained from DC and RF excited glow discharges. These polymers have been used in many applications encompassing biomaterials, permoselective membranes, photosensors devices and so on [1-4]. In many applications of such polymers is important to characterise their behaviour under action of etching processes. In this paper we present the results of deposition and etching of a mixture of Hexamethyldisiloxane (HMDSO) and Sulphur Hexafluorine (SF₆) in different proportions in order to study the changes in molecular structure of the polymers as function of SF₆ concentration within the discharge. It is also presented the results of etching of plasma polymerized HMDSO under action of a SF₆ DC excited plasma.

Experimental Set-up

It was used in this experiment a small cylindrical Pyrex plasma reactor with 15 cm long and 5 cm of diameter. The discharges were excited between two disk shaped stainless steel electrodes with 2 cm of diameter, whose separation could be controlled in order to keep the plasma homogeneity. The voltage applied to the discharge could be varied between 0 to 2 kV. The plasmas were created under a constant voltage value of 800 V at pressures of 0.6 mbar in atmospheres of HMDSO/ SF₆ at different concentrations of SF₆, varying from 0 to 50%. The polymeric films were deposited over KBr substrates and their structures were investigated using FTIR spectroscopy. The films thickness were investigated using an alpha step Tencor 100 apparatus.



Results and Discussion

It is shown in figure 1 the infrared spectra for plasma polymerized HMDSO/SF₆ for different concentrations of SF₆. The vibrational modes of the HMDSO are listed in table 1. The chemical units SiH, Si-CH₂-Si, and CH₃-Si-CH₃ play an important role in the polymerization mechanism establishing chemical bonds with other structures given origin to highly three dimensional cross-linked polymeric chains. In spite of the absence of oxygen in the mixture composition, it is observed the presence of hydroxyl in polymeric structure through the absorption in 3600 cm⁻¹ and

Tab.1. Vibrational modes of HMDSO. ν, δ, ρ denotes stretching, bending-wag, and bending, respectively.

λ (cm ⁻¹)	specie vibrational mode	λ (cm ⁻¹)	specie vibrational mode
CH ₃		Si-CH ₃	
2960	$\nu^a \text{CH}_3$	1410	$\delta^a \text{CH}_3$
2900	$\nu^s \text{CH}_3$	1260	$\nu^s \text{CH}_3$
2925	$\nu^a \text{CH}_2$	845	$\rho \text{CH}_3, \nu \text{SiC}$
2855	$\nu^s \text{CH}_2$	760	$\rho \text{CH}_3, \nu \text{SiC}$
1460	$\delta^a \text{CH}_2$	885	$\rho \text{CH}_3, \nu \text{SiC}$
Si-CH ₂		805	$\rho \text{CH}_3, \nu \text{SiC}$
1360		775	$\rho \text{CH}_3, \nu \text{SiC}$
1400		OH	
Si-H		3650	νOH
2140	νSiH	3400	νOH
SiOSi		CF ₂	
$\nu^a \text{SiOSi}$		740	amorphous band
1050		520	amorphous band

3400 cm⁻¹. This occurs due the incorporation of oxygen from leaking or water vapour, during the polymerization processes, or during the exposition of the film to the atmospheric environment [5-7]. It is observed in fig.1.b that the introduction of 10% of SF₆ reduces all the absorption associated to plasma polymerized HMDSO. This reduction is accentuated with the increasing of SF₆ concentration, as can be appreciated in figs. 1.c,d,e,f. It is also observed the appearance of a peak in 740 cm⁻¹ associated to CF stretching. This band becomes more intense with the increasing of SF₆. Figure 2 illustrates the competition between the polymerization and etching of HMDSO/SF₆,

during the polymerization processes. It is observed that HMDSO polymerization rate is approximately 90 Å/min. For concentrations above 30% of SF₆, the polymerization practically does not occur. This happens due the high concentration of atomic fluorine within the discharge. It should be stressed here that the deposition rate is higher for SF₆ concentration around 25% than for pure HMDSO plasma. This may be attributed to an increasing in the number of active sites [7,8] due to the presence of energetic particles colliding with the film structure. For a further increasing in SF₆ concentration the etching processes is predominant. In figure 3 is shown the etching rate for HMDSO films exposed to SF₆ DC excited plasmas, kept at 0.6 mbar. It is observed that the etching rate is strongly dependent on the time that the film remains under the action of the plasma. It is clear that the etching processes is predominant at the beginning, due to the recombination of atomic fluorine with H, C, O, and S, for instance. Many of these products may be removed by the vacuum system. Nevertheless many volatile products formed due to atomic fluorine's action may recombine with the film structure producing changes on it and reducing the etching rate.

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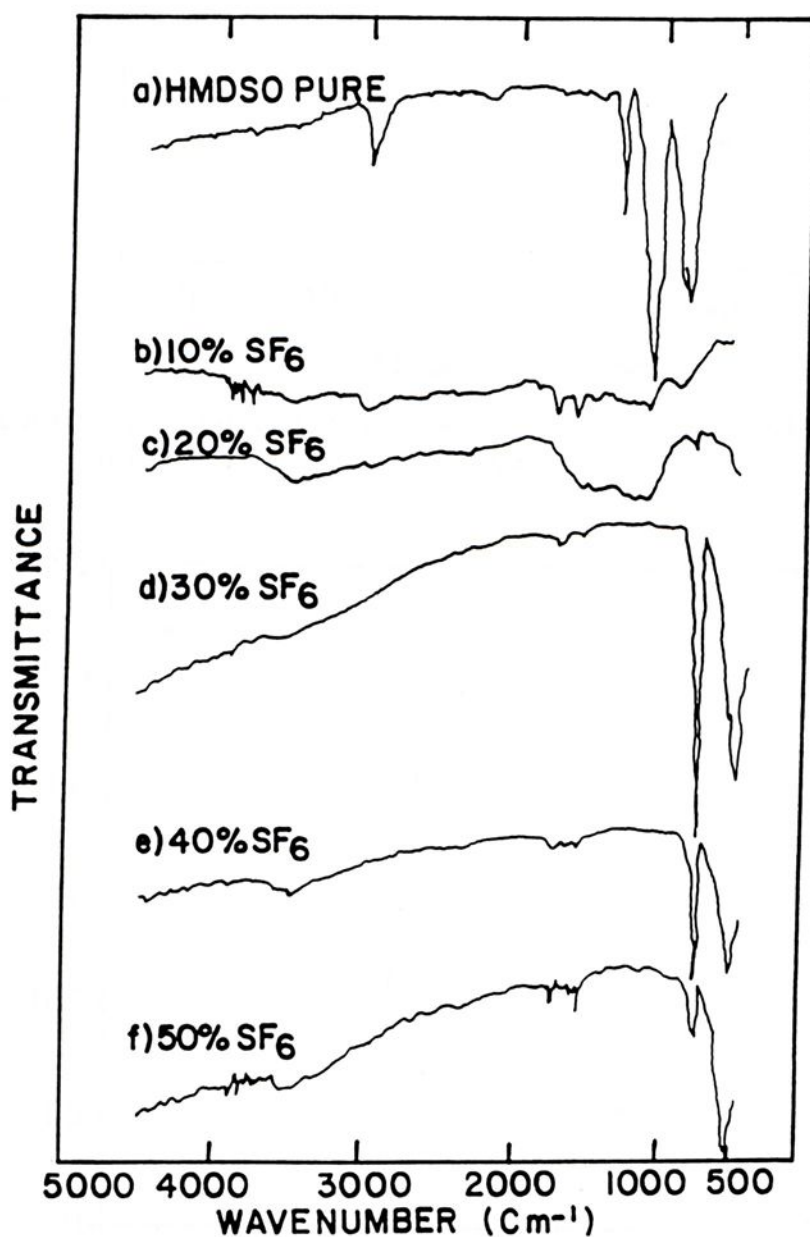


Figure 1. Absorption spectra of plasma polymerized HMDSO/SF₆, for different concentrations of SF₆.

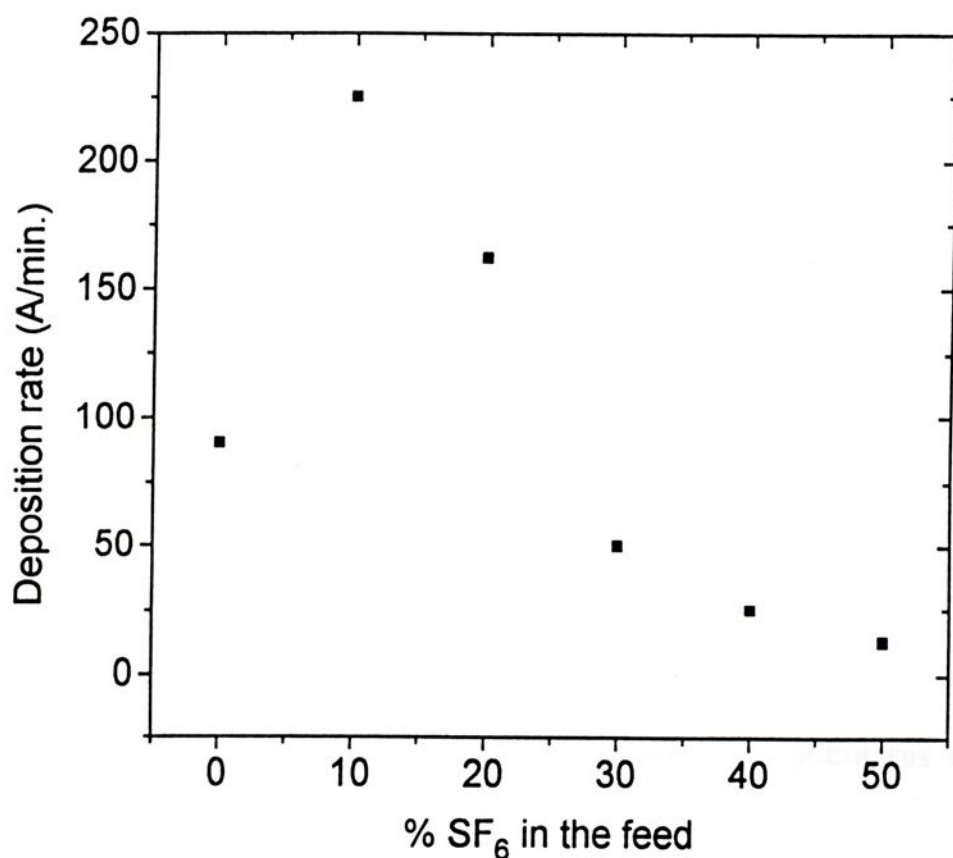


Figure 2. Deposition rate of plasma polymerized HMDSO/SF₆, for different concentrations of SF₆.

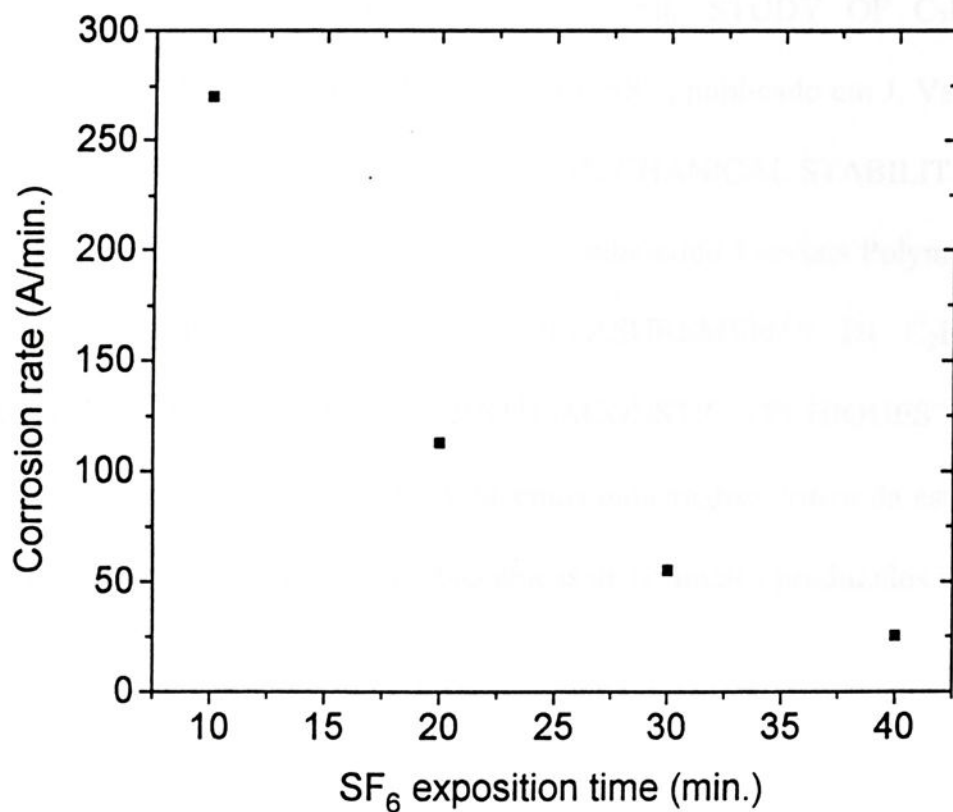


Figure 3. Corrosion rate of plasma polymerized HMDSO films, for different residence time within the SF₆ DC excited plasma.

QUINTA PARTE

Estabilidade e propriedades termo-mecânicas de polímeros depositados a plasmas.

Nos artigos “AN ACTINOMETRIC STUDY OF C_2H_2 PLASMA POLYMERIZATION AND FILM PROPERTIES”, publicado em J. Vac. Sci. Techol., 13 (6), 2747 (1995); “STUDY OF THE MECHANICAL STABILITY OF HMDSN PLASMA POLYMERIZED THIN FILMS”, submetido à revista Polymer Preprints em 1996 e “THERMAL DIFFUSIVITY MEASUREMENTS IN C_2H_2 PLASMA POLYMERIZED FILMS USING PHOTOACOUSTIC TECHIQUES” ,publicado em J. Mat. Sci. Lett. , 15, 590 (1996), fazemos uma análise critica da estabilidade e sua relação com as propriedades termomecânicas de polímeros produzidos via plasma .



O estudo de propriedades mecânicas e térmicas em filmes finos polimerizados a plasma, diferentemente daqueles obtidos por técnicas químicas convencionais, vem se tornando objeto importante na pesquisa do desenvolvimento de materiais .

Uma das questões fundamentais em discussão é a adesão de um filme polimérico a um substrato qualquer. Certamente, objetiva-se obter um polímero a plasma cuja característica básica é que o mesmo possa apresentar um bom nível de adesão ao ser depositado em alguma superfície.

Não obstante a isto, deve-se reconhecer o nível e a importância da aplicabilidade a que se deseja para o polímero. A partir deste ponto, define-se o tipo de material a ser polimerizado. Muitas das vezes, é comum observar, dependendo das condições de preparação do substrato e dos parâmetros de operação do sistema, a presença de deslocamentos e trincas no polímero a plasma. Mesmo que o substrato seja cuidadosamente limpo antes do processo de deposição.

No artigo “STUDY OF THE MECHANICAL STABILITY OF HMDSN PLASMA POLYMERIZED THIN FILMS” , o plasma é utilizado como um meio para a obtenção do polímero, a partir de uma descarga elétrica de tensão contínua no vapor de hexametildisilazano (HMDSN) .

Optamos pela escolha de um polímero derivado de silazano, pois a priori ele pode apresentar uma melhor estabilidade quando comparado a polímeros obtidos de hidrocarbonetos; já que elementos reativos como Nitrogênio fazem parte da estrutura



do material a ser polimerizado. O mesmo ocorreria para algum siloxano, caso este material fosse utilizado, no qual o elemento reativo é o Oxigênio.

A razão de se discutir a presença de elementos reativos nos monômeros, isto é, elementos usados para a deposição dos polímeros, advém do fato dos polímeros a plasma, sem que haja exceção serem constituídos de radicais livres. Estes radicais fazem parte da estrutura do polímero obtido de hidrocarboneto, siloxano, fluocarbono e outros. No entanto, para os elementos que contém átomos reativos, a quantidade de radicais livres é menor, o que pode ser um dos fatos responsáveis por uma melhor estabilidade do filme polimérico.

Para verificar a estabilidade do HMDSN polimerizado, submetemos estes polímeros depositados sobre substratos de vidro, a meios extremamente agressivos, como foi o caso da água do mar em estado de ebulição. Ao fim de oito horas de exposição quase nada foi arrancado do substrato, a menos de ligeiras regiões de corrosão. O resultado foi ainda melhor, quando o mesmo tipo de material foi exposto à água destilada, também em ponto de ebulição pelo mesmo intervalo de tempo. Portanto, de acordo com as normas técnicas americanas, a adesão HMDSN polimerizado/substrato pode ser considerada excelente.

Uma crítica importante a ser feita é que na literatura não constatamos medidas de adesão no polímero a plasma obtido do HMDSN, utilizando o método da submersão. No entanto, nossos resultados são compatíveis com os de outros



investigadores quando eles usaram técnicas qualitativas com o teste de riscagem e fitas adesivas em polímeros com estruturas similares aos nossos.

Uma outra abordagem a ser considerada aqui é o estudo de tensões mecânicas em polímeros a plasma. Para tanto, analisamos o trabalho “STUDY OF THE MECHANICAL STABILITY OF HMDSN PLASMA POLYMERIZED THIN FILMS” , assim como a seção que trata de tensão mecânica no acetileno polimerizado a plasma, descrito no artigo “AN ACTINOMETRIC STUDY OF C₂ H₂ PLASMA POLYMERIZATION AND FILM PROPERTIES” .

Apesar do grande número de estudos sobre tensões mecânicas em filmes finos, o estudo destas tensões em filmes poliméricos processados a plasma não está tão avançado assim.

No entanto, em ambos artigos, isto é, para o HMDSN polimerizado bem como para o acetileno polimerizado, a natureza compressiva da tensão pode ser interpretada como sendo devido a incorporação no filme de espécies reativas geradas no plasma como íons, moléculas excitadas e radicais livres que se interpõem nas cadeias poliméricas produzindo um efeito expansivo chamado efeito cunha. Por outro lado, a variação no volume destes polímeros também se deve a reações após o processo de deposição envolvendo as espécies reativas armazenadas nos filmes poliméricos. Pois como já foi dito anteriormente, os polímeros a plasma, dependendo dos parâmetros em que foram depositados e dos tipos do monômeros, podem conter uma grande quantidade de radicais livres. Portanto, reações que envolvem estes radicais podem



resultar em modificações na estrutura molecular do polímero, o que provoca alterações no volume do filme e desta forma na variação da tensão mecânica do mesmo.

Nestes dois artigos aqui discutidos, considerando as espessuras dos polímeros próximas, isto é, o acetileno e o HMDSN polimerizados apresentando variações na espessura menor que 10%, a tensão mecânica residual interna apresentou valores entre duas a três ordens de grandeza superior do acetileno polimerizado, na faixa de GPa, quando comparada ao HMDSN polimerizado, correspondendo a valores da ordem de MPa .

Os valores de tensão, menores no HMDSN polimerizado, podem estar associados a uma menor concentração de radicais livres neste tipo de polímero e essencialmente sua maior estabilidade se comparado ao polímero proveniente do acetileno.

Pode-se ressaltar ainda nesta análise crítica que os mecanismos responsáveis pela geração da tensão mecânica, estão intimamente relacionados com o nível de adesão polímero/substrato. E, para menores valores da tensão mecânica, melhor é a aderência entre o substrato e o filme polimérico. Portanto, é mais fácil o acetileno polimerizado descolar-se do substrato que o filme obtido de um plasma de HMDSN.

A última análise crítica a ser feita nesta seção se refere ao transporte de calor no acetileno polimerizado a plasma, como está mostrado no artigo "THERMAL DIFFUSIVITY MEASUREMENTS IN C_2H_2 PLASMA POLYMERIZED FILMS USING PHOTOACOUSTIC TECHNIQUES" .



A difusividade térmica é um parâmetro o qual mede a velocidade com que o calor se espalha em uma amostra e descreve ainda os processos transientes ou periódicos de transmissão de calor. Ela é pois uma característica do material, assim como a condutividade ou a resistividade elétrica, podendo ser utilizada para identificá-lo.

O processo microscópico do transporte de calor em polímeros amorfos e semicristalinos sintetizadas por meios químicos convencionais que não os via plasma, ainda não é bem compreendido.

Porém a difusão de calor nestes materiais pode ser explicada qualitativamente, onde o transporte de energia depende do tipo de ligações químicas intra e inter moleculares ao longo das cadeias. Podemos citar aqui que por mais que seja ordenado um polímero a plasma, seu grau de desordem é maior que o grau de um polímero convencional amplamente desordenado. A razão para este fato é a alta ramificação e o entrelaçamento característicos nos polímeros produzidos a plasma. Desta forma, é bastante difícil explicar o mecanismo da difusão de calor no polímero a plasma, no entanto, acreditamos que o mesmo possa estar próximo de um polímero convencional com certo grau de desordem, pois nossas medidas de difusividade térmica estão em boa concordância com valores apresentados na literatura para polímeros convencionais. Por último, salientamos aqui a importância deste tipo de caracterização, independentemente de uma possível explicação para o mecanismo de condução térmica, uma vez que até onde sabemos talvez seja esta a primeira medida neste tipo de polímero e portanto mais uma forma de caracterizá-lo.



An actinometric study of C₂H₂ plasma polymerization and film properties

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Thin polymer films were grown in radio frequency discharges containing C₂H₂. Actinometry revealed the trend in the plasma concentration of the CH species as a function of the operating pressure. The C-H bond density in the films, revealed by infrared analysis, was found to increase with the pressure of C₂H₂ in a similar way to that of the concentration of the CH species in the discharge. From transmission ultraviolet-visible spectroscopy data, optical parameters of the polymers, namely, the refractive index and the optical gap, were calculated. For the range of pressure studied, the refractive index decreased from 1.73 to 1.63 and the optical gap increased from 2.4 to 3.3 eV. Finally, measurements of the residual stress of the polymer films were carried out by the bending beam method, using a He-Ne laser, yielding values from 0.05 to 0.3 GPa. © 1995 American Vacuum Society.

I. INTRODUCTION

The plasma polymerization process began to attract academic and technological interest after some experiments were developed by Goodman,¹ who synthesized solid dielectric compounds using glow discharges of organic gases. At the present time, this type of process is of interest in the synthesis of new materials, particularly thin films exhibiting remarkable characteristics such as high uniformity, good adhesion to different substrates, and a lack of pinholes, as well as exhibiting singular optical, electrical, and mechanical properties. Such films have many promising applications as perm-selective membranes,²⁻⁵ anticorrosive surfaces,⁶⁻⁸ humidity sensors,⁹ temperature sensors,¹⁰ electrical resistors, and use in integrated circuit lithography,¹¹⁻¹³ in integrated optics,¹⁴ and as windows and optical filters.¹⁵ Plasma polymerization is a well established technique but poorly understood because the plasma is very reactive and produces a large number of chemical species that form polymer films through chemical reactions whose mechanisms are very complex.¹⁶

On the other hand, despite progress in the technology of these polymers, we know little about their properties, such as mechanical stress,^{17,18} electrical,¹⁹⁻²¹ and optical properties²² as well as electronic bond structure.^{23,24}

In this article, we report on a study of the plasma process and the structural, optical, and mechanical properties of thin polymer films deposited by acetylene glow discharges. Optical emission spectroscopy was used to study the discharge environment. In particular, the actinometric technique was utilized to find trends in the concentrations of species present in the plasma which may play a role in the polymerization process.

The actinometric technique, which uses the emission from an inert probe gas (actinometer) to obtain relative concentrations of species of interest, is well established in current literature.^{25,26} This technique depends upon the fact that the excitation mechanisms of the species *x* and the actinometer *a* are predominantly by direct electron impact. In addition, the

excited states thus formed should decay only by photon emission. Finally, the threshold energies for both transitions should be the same. Actinometry relies on the fundamental relation²⁷

$$I_a = K_a N_a \eta_a, \quad (1)$$

where *a* refers to actinometer and *I*, *N*, and η are the intensity of emission, the concentration of the species in the ground state, and the excitation efficiency, respectively, and *K* is a constant. Thus, at a constant actinometer concentration of a few percent in the feed (which does not disturb the discharge), the concentration of the species of interest [*x*] is related to the concentration of the actinometer [*a*] by

$$[x]/[a] \propto I_x / I_a, \quad (2)$$

where *I_x* and *I_a* are the optical emission intensities of the species *x* and *a*, respectively.

The relative plasma CH concentration data were related to the C-H bond densities of the samples determined by transmission infrared reflection spectroscopy (IRS). By absorption ultraviolet-visible (UV-vis) spectroscopy some optical parameters, principally the refractive index and absorption coefficient, were also studied as a function of the deposition parameters. Residual stress measurements were also performed to investigate the role of intrinsic stress in the mechanical stability of the film.

II. EXPERIMENT

The experimental arrangement used was essentially the same as that described elsewhere.²⁸ Briefly, it consists of a Pyrex reactor of 7.5 cm internal diameter and 25.0 cm length, which opens into a bell-like structure 19.0 cm in diameter and 27.0 cm in height. Gases were fed to the reactor via needle valves and flowmeters (Datametrics, type 831).

TABLE I. Spectral data of species of interest.

Species	System	λ (nm)	Threshold energy (eV)
H	$2p^2P^0_{1/2}, 3d^2D_{3/2}$	656.3	12.09
CH	$A^2\Delta-X^2\Pi$	431.4	<11
N ₂	$C^1\Pi_u-B^1\Pi_g$	337.1	11.2
Ar	$4p^1(1/2)-4s^1(1/2)$	750.3	13.47

The radio frequency (rf) generator (120 MHz, 40 W) was connected to ring electrodes through an impedance matching circuit and through-line wattmeter.

Acetylene and the actinometers (argon and nitrogen) were supplied from gas cylinders. The gases were of 99.98% minimum purity. A Pirani gauge, previously calibrated to nitrogen with the use of a capacitance manometer (Datametrics, Barocel, type 600), was used for pressure indication.

The light from the plasma left the chamber via a quartz window and reached the slit of a 1-m-focal length monochromator (Spex Industries, model 14300). The output signal of the UV-vis photomultiplier was monitored on a chart recorder via an electrometer. Films for analysis by UV and infrared reflection spectroscopy (IRS) were prepared on quartz and KCl substrates, respectively. A UV-visible spectrophotometer (Perkin-Elmer, model Lambda 9) was used to obtain spectra and infrared analysis was performed using a Jasco (model IR 700) spectrophotometer. Film thickness was measured by an interferometric microscope (Varian, A-scope). The residual stress measurements were performed by the bending beam method,²⁹ using the apparatus described in a separate paper.³⁰

III. RESULTS AND DISCUSSION

A. Actinometry

Some of the species that are expected to play an important role in the film deposition (H, CH) were easily observed in the discharge. Table I lists the species of interest, the wavelength, and the respective excitation thresholds.

We used the nitrogen and argon actinometers which gave some indication of the behavior of the electron energy distribution as a function of a plasma parameter, in this case the pressure of acetylene.

The intensity of the light emitted by any chemical species x whose excitation resulted directly from electronic impact and whose de-excitation occurred by one photon emission is given by

$$I_x = KN_x\eta_x = K'\eta_x \int_0^\infty \sigma(E)N_e(E)dE, \quad (3)$$

where N_x is the ground state concentration of the species, η_x is the excitation efficiency, and $N_e(E)dE = E^{1/2}F_e dE$ represents the number of electrons per unit volume of the plasma in the energy range dE . Here, F_e is the electron energy distribution function (EEDF), $\sigma(E)$ is the excitation cross section

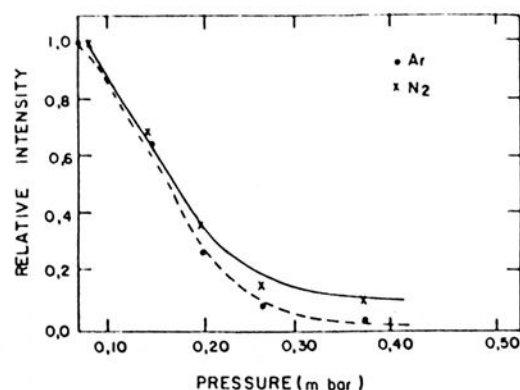


FIG. 1. Relative intensities of the actinometers argon and nitrogen measured as a function of the C₂H₂ pressure in discharges maintained at an applied rf power of 12 W.

tion to the state responsible for the emission, and K and K' are constants. Therefore it is apparent that, since the actinometer concentration remains constant in the discharge, variations in the emission intensity of the actinometer can be attributed to modifications in the EEDF. As the pressure of C₂H₂ changes, modification in both the plasma electron density and the average electron energy are to be expected, either of which will alter the EEDF. Thus, we propose, as previously,³¹ the use of a parameter A , defined as

$$A = \rho E, \quad (4)$$

where ρ is the mean electron density and E the mean electron energy. The parameter A therefore gives a rough indication of the activity of the plasma. Thus, by referring to this parameter, it is possible to avoid constant reference to an increase in the electron density or the electron mean temperature (or both).

Prior to each optical measurement or film deposition, the reactor was pumped down to 10^{-3} mbar. All the experiments were made at an applied rf power of 12 W and a flow rate of C₂H₂ in the range 0.68×10^{-2} – 3.38×10^{-2} Pa m³/s (1 Pa m³/s = 592 sccm), corresponding to an indicated pressure from 0.1 to 0.5 mbar. For these conditions, the nitrogen or argon actinometers were used at constant flow rate corresponding to 2% of the initial C₂H₂ pressure, i.e., 2% of 0.1 mbar during all of the experiments.

Figure 1 shows the light intensity emitted by the actinometers nitrogen and argon monitored as a function of the acetylene pressure in the discharge (the plots are normalized to one). Inspection of Fig. 1 shows that, for an increase in the C₂H₂ pressure, similar relative changes in the intensities of the two actinometers are observed. The similarity in the intensity curves of Ar and N₂ implies a similar influence of the increased C₂H₂ pressure on electrons of different energy.

To obtain trends in the relative concentration of the CH species we have normalized its optical emission intensity to that of the nitrogen line and to that of argon (spectral data are given in Table I). Although the threshold energy of N₂ to the state responsible for the transition measured here (11.2 eV) is closer to that of the transition of CH (<11 eV) than that of

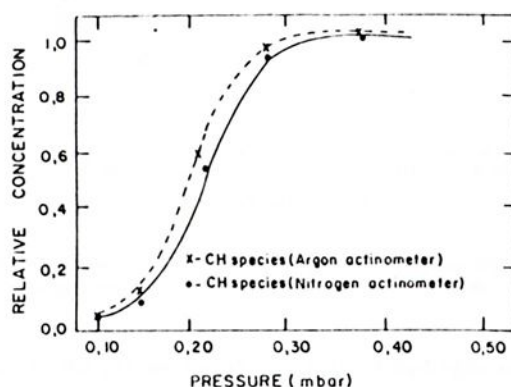


FIG. 2. Relative concentration of the CH species as a function of the C_2H_2 pressure at 12 W applied rf power (concentrations calculated using the actinometers Ar and N_2 are shown).

Ar (13.47 eV), the latter actinometer is preferable because Ar is an inert gas. In contrast, nitrogen is not only a diatomic molecule, but may also be incorporated into films deposited from plasmas of organic gases with nitrogen.

Figure 2 shows the trend in the concentration of CH in the plasma for experiments realized at pressures between 0.1 and 0.5 mbar, which are associated with different acetylene flow rates. A rapid increase is observed in the CH concentration in the discharge for pressures between 0.1 and 0.26 mbar and above this value the CH concentration remains fairly constant. This behavior may be considered the result of two competing factors, namely, the increase in the supply of C_2H_2 as the pressure is increased, and the simultaneous drop in the activity of the plasma. The first factor increases the supply of CH units; the second tends to reduce the degree of fragmentation.

It is clear from Fig. 2 that the choice of actinometer is not critical, but we prefer the use of Ar for the reasons already given above.

B. Infrared analysis

The films for analysis by infrared spectroscopy were grown at pressures of C_2H_2 between 0.1 and 0.5 mbar. Figure 3 shows an infrared spectrum characteristic of these films. The absorption bands due to C-H bonds are prominent in the spectrum of the film. The strong absorption at 2930 cm^{-1} arises from symmetrical and asymmetrical stretching modes in CH_2 and CH_3 groups. Asymmetrical and symmetrical bending modes in CH_3 groups give rise to the bands at 1440 and 1375 cm^{-1} , respectively. Other absorptions are due to $C=C$ (1624 cm^{-1}), carbonyl (1700 cm^{-1}), and hydroxyl (3500 cm^{-1}) groups. The last of these appears as a consequence of oxygen contamination, which may result from reactions with oxygen from water vapor or other oxygen-containing molecules still present in the reactor during film formation. It should be noted that the plasma polymers may contain a high concentration of free radicals, captured from the plasma.³² Thus, hydroxyl groups could arise from reactions between free radicals and the surrounding free oxygen.³³

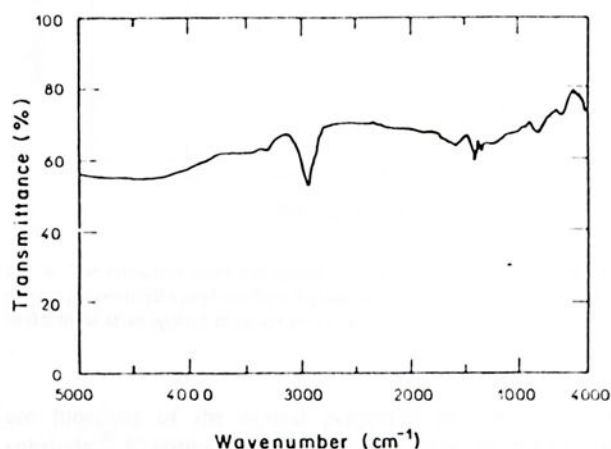


FIG. 3. Infrared spectrum of a typical plasma polymerized acetylene film. The discharge parameters were pressure = 0.2 mbar and applied rf power = 12 W. The film thickness was 6000 Å .

A quantitative evaluation of the relative C-H bond density can be made by calculation of the integrated absorption of the band at 2930 cm^{-1} . Figure 4 shows the integrated absorption of the C-H bond calculated by the method of Lanford and Rand³⁴ as a function of the C_2H_2 pressure in the discharge when the films were deposited. The increase in the C-H bond density is due to structural modification within the films. As a matter of fact, the power supplied to the discharge for a given pressure influences the deposition process, so that the increase in pressure results in greater quantities of CH in the plasma available for polymer deposition.

C. Correlation between deposition rate, IR analysis, and actinometry

Here, we discuss the correlation between the plasma CH concentration, the quantity of hydrogen in the polymer (C-H density) and the deposition rate of the film. The data of Figs. 2 and 4 show a strong correlation between the CH concen-

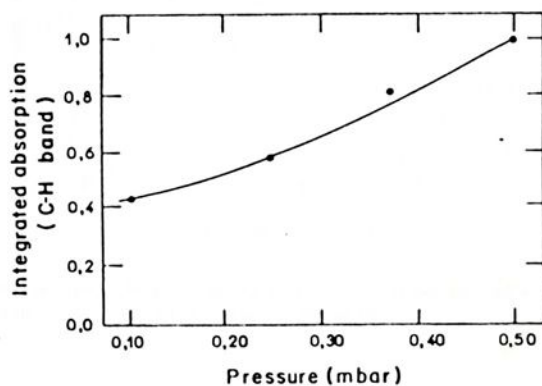


FIG. 4. Integrated absorption of the C-H band at 2930 cm^{-1} as a function of pressure used for the deposition. Films were prepared from acetylene at an applied rf power of 12 W.

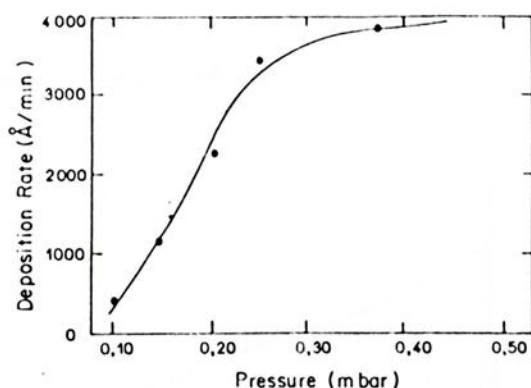


FIG. 5. Deposition rate of the plasma polymerized acetylene films as a function of the acetylene pressure at an applied rf power of 12 W.

tration in the plasma and the quantity of hydrogen in the polymer film. Both increase when the operating pressure of the system is increased.

Figure 5 shows the deposition rate of the plasma polymer films obtained as a function of C_2H_2 pressure in the system. It should be noted that the polymerization rate increases by a factor of 9 when the C_2H_2 pressure increases from 0.10 to 0.37 mbar.

To interpret these results we should remember that the electrons in the plasma are responsible for C_2H_2 fragmentation, thus producing many species in the discharge. The polymer deposition rate shows a very similar dependence on pressure as does the plasma CH concentration, independent of whether Ar or N_2 is used as the actinometer. This strongly suggests that the CH species in the plasma is one of the main precursors of polymer formation. This is in close agreement with the fact that higher concentrations of CH correspond to higher deposition rates of the polymer. In other words, these results are strongly indicative that the CH species is an elementary unit in the film formation process.

D. Optical properties

The refractive index and the optical absorption coefficient have been determined for various samples deposited from plasmas in acetylene. Using data from UV-visible transmission spectra, values of the refractive index for a photon energy of 1.25 eV were determined by a procedure described by Cisneros *et al.*³⁵ and are plotted in Fig. 6 as a function of the C_2H_2 pressure. The refractive index monotonically decreases from 1.74 to 1.63 as the pressure of the deposition increases from 0.1 to 0.5 mbar. The decrease in the refractive index can be attributed to the structural modification of the polymers with different quantities of hydrogen, and these values lie in the range 1.6–2.0 obtained for plasma polymerized C_2H_2 films by other authors.³⁶

For the computation of the optical transmission, the following equation was used

$$T = Ax / (Bx^2 + Cx + D), \quad (5)$$

where $x = \exp(\alpha d)$, α and d are the absorption coefficient and the thickness of the film, respectively. A, B, C, and D

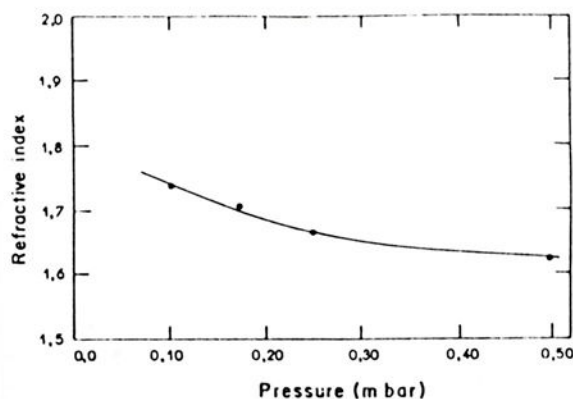


FIG. 6. The refractive index calculated at a photon energy of 1.25 eV for plasma polymerized acetylene films deposited at different pressures from 0.1 to 0.5 mbar at an applied rf power of 12 W.

are functions of the optical properties of the film and substrate.³⁷ Equation (5) was obtained from an expression given by Knittl³⁸ for a thin film deposited onto a weakly absorbing substrate.

Figure 7 illustrates the dependence of the optical absorption coefficient on the photon energy for various polymer films. In all the samples α rises sharply, showing an absorption edge similar to other materials such as amorphous hydrogenated carbon.³⁹ Differences in the optical absorptions of materials can be characterized by an optical gap. In our polymer films we defined as an optical gap, the photon energy E_{04} corresponding to the absorption at $\alpha = 10^4 \text{ cm}^{-1}$, as

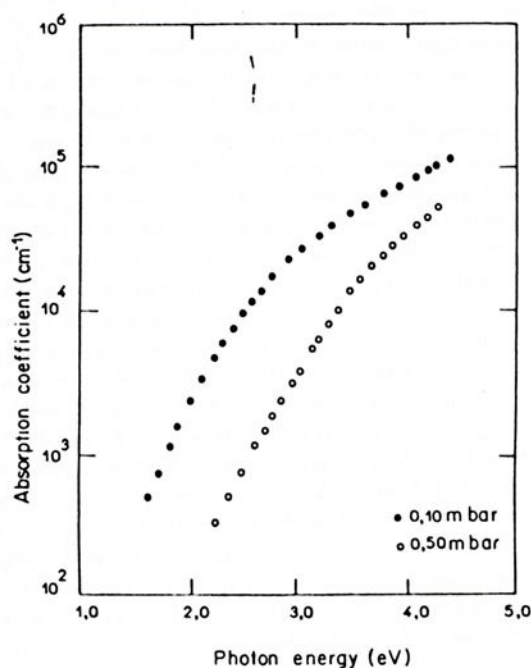


FIG. 7. The optical absorption coefficient of the plasma polymerized acetylene films calculated as a function of the photon energy.

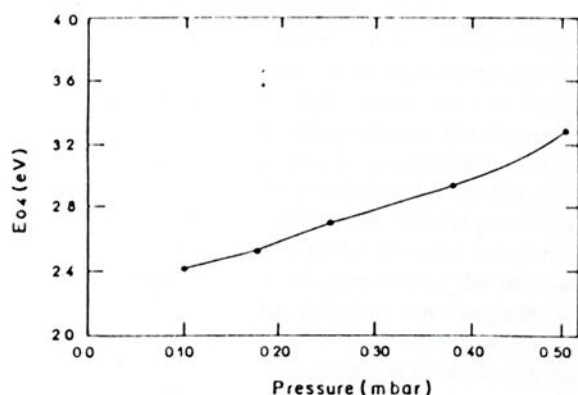


FIG. 8. The optical gap E_{04} of the plasma polymerized films as a function of acetylene pressure used for the deposition (applied rf power = 12 W.)

Freeman and Paul⁴⁰ have used to characterize the absorption edge of amorphous semiconductors.

Figure 8 shows a plot of values of the optical gap E_{04} as a function of the C_2H_2 pressure in the plasma deposition, obtained from the absorption curves like those of Fig. 7. The values of E_{04} increase as the pressure is increased in the range of 0.1–0.5 mbar. As shown in Fig. 4, the C–H bond density (quantity of hydrogen) in the sample prepared at 0.5 mbar is 2.3 times higher than the quantity of hydrogen in the sample deposited at 0.1 mbar. Thus, we can see that an increase in film hydrogen concentration can cause an increase in the optical gap of these polymers. It should be remembered that in many amorphous materials absorption can be described by the well-known Tauc model⁴¹ according to which

$$(\alpha E)^{1/2} = \beta(E - E_g), \quad (6)$$

where E_g is the optical gap and β is a constant. Since the optical data of our samples did not reveal a linear relationship between $(\alpha E)^{1/2}$ and E , the optical gap could not be determined by Eq. (6).

The random structure of the carbon chains in a plasma polymer makes theoretical interpretation of the experimental results rather difficult. However, it seems reasonable to suppose that some trends in the physical behavior of a *conventional* polymer must be followed by a plasma polymer. In conjugated polymers, for instance, the π bonds play a very important role in the electronic conduction, affecting the density of the states and the band gap. The density of π bonds is influenced by the hydrogen content. Hydrogen forms σ bonds with the carbon atoms at the expense of the π bonds. It may be noted that the attachment of hydrogen to the polymer affects bonds lengths, thus changing the band gap.

E. Residual stress measurements

The evolution of the residual stress as a function of film thickness for various plasma polymerized acetylene films is shown in Fig. 9. Each curve was obtained at a different discharge pressure. The values of the residual stress for the

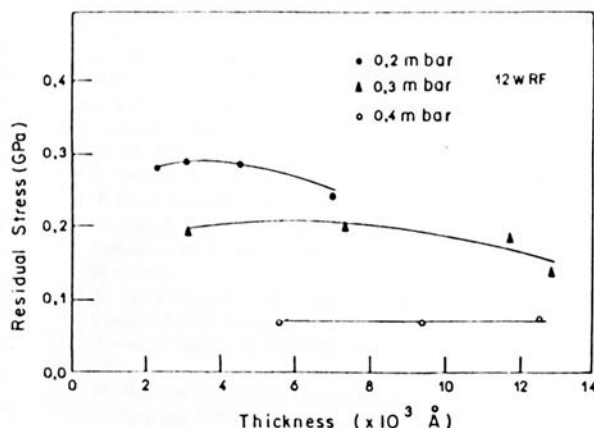


FIG. 9. Residual stress as a function of film thickness for the plasma polymerized acetylene films prepared at an applied rf power of 12 W.

films deposited at 0.2 mbar increase with the thickness in the interval of 2000–3000 $\text{\AA}$ and decrease between 3000 and 7000 $\text{\AA}$. The stress in the film prepared at 0.3 mbar increases between 3000 and 7000 $\text{\AA}$, decreasing thereafter. The values of the residual stress for polymers obtained at 0.4 mbar remain approximately constant between 5500 and 12 000 $\text{\AA}$. Comparing the three curves in the interval 3000–7000 $\text{\AA}$, we observe that at a constant thickness the stress decreases with increasing pressure. This behavior is also indicated by the curves corresponding to the films deposited at 0.3 and 0.4 mbar in the interval of thickness between 7000 and 12 000 $\text{\AA}$. Thus, films of the same thickness obtained at high pressure will be less stressed than those obtained at low pressure.

On the other hand, it is interesting to observe that the deposition rate of the polymers increases when the pressure increases, as shown in Fig. 5. So the residual stress decreases whereas the deposition rate increases. One possible explanation of this fact is that by increasing the pressure, the number of collisions between the reactive species of the gaseous phase increases too, because the mean free path decreases; consequently the chemical reaction rate will increase, increasing the polymerization rate. Plasma polymerization results in polymers which are products of the linking of *blocks* by the so-called *growth chain mechanism* described by Yasuda.⁴² The blocks are short carbon chains containing (or not) free radicals produced in the plasma when the acetylene molecule is broken. The successive building of these blocks produces an expansive effect in the film that is known as the *wedge effect*. This causes a compressive residual stress in the polymer film. Increasing the polymerization rate, the length of the blocks increases. The deposition of greater blocks decreases the wedge effect and consequently decreases the value of the residual stress in the films. When polymer films are deposited at low pressure, the mean free path is smaller than that of the initial situation (high pressure). So, the polymerization rate decreases because the reaction rate decreases in the gaseous phase. Therefore, blocks with smaller length will be deposited, increasing the wedge effect, and the residual stress value will be increased.

IV. CONCLUSIONS

Actinometric optical emission spectrometry measurements of film-depositing rf discharges of C_2H_2 revealed that the plasma activity falls as the system pressure increased. Analysis of the molecular structure of the thin films showed that hydrogen concentrations in the samples also depend on the pressure of C_2H_2 . The concentration of hydrogen increases when the pressure is increased. The deposition rate of the films is correlated with the concentration of CH species in the discharge and we concluded that the CH species constitute an elementary block in the plasma polymerization of acetylene. Modifications in the chemical structure of polymers prepared in rf discharges due to the increase in the hydrogen levels in these polymers can change the refractive index and the optical gap of these materials. The refractive index decreases with the increase in the hydrogen concentration of the films, while the optical gap increases. Hydrogen forms σ bonds with the carbon atoms at the expense of π bonds. At the same time, the attachment of hydrogen to the polymer affects bond lengths, thus changing the band gap. As previously observed, the residual stress depends on the thickness and the structural composition of the polymer films. Therefore, we can suppose that during the growth of the polymer, the wedge effect occurs due to the atomic packing, which produces compressive stress.

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STUDY OF THE MECHANICAL STABILITY OF HMDSN PLASMA POLYMERIZED THIN FILMS

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Introduction

The adhesion of thin films to different substrates is a subject of great importance in many technological issues, encompassing electronic industry where thin films are used in many kind of applications, as for instance in protective coatings, in food and drugs packaging, or like electronic devices where several superimposed layers are frequently required [1-3]. The degree of adhesion of thin films has received considerable attention of scientific community recently. The high degree of adhesion of films to their substrates or to another films is essential in most applications. However a combination of poor adhesion and high film stress is essentially troublesome. The word adhesion is frequently used in a broad sense to describe the sticking together of two materials with or without an intermediate layer and the terms autohesion and heterohesion have been introduced to describe situations where the two materials are identical or dissimilar, respectively. So, these words are used to describe complex situation since the average adhesive joint has two interfaces at which adhesive failure can occur and three regions of possible cohesive failure. The adhesion should be strictly reserved for the bonding at an interface between two different materials and carries the implication of intimate contact at the interface. There are several methods to characterize the adhesion as mechanical methods like Scotch-tape test, abrasion test, bend and stretch test, shearing stress test, direct pull-off methods, scratch test, peeling test [4-7] and non-mechanical methods like x-ray diffraction test and others[8]. These methods can be qualitative or quantitative. In addition of adhesion study, the residual stress has influenced the mechanical properties of thin films, specially the stability of these materials. Thin films are stressed even without the application of external loading and are said to possess internal or residual stresses. The origin and nature of these internal residual stresses are the sources of many mechanical effects in films. The presence of residual stresses is usually undesirable but there are cases where they are beneficial. Tempered



glass and shot-peened metal surfaces rely on residual compressive stresses to counteract harmful tensile stresses applied in service. In this work we deposited thin plasma polymer films using Hexamethyldisilazane (HMDSN) as monomer. These polymer were grown on glass substrates and the adhesion polymer-substrates was investigated. Residual stress measurements were also performed to investigate the role of intrinsic stress in the mechanical stability of the film.

Experimental

The experimental arrangement used for plasma polymer deposition was essentially the same one already described elsewhere [9]. Briefly, it consist of a Pyrex reactor of 17 cm internal diameter and 40 cm length. The HMDSN was fed to the reactor via needle valves and the experiment was carried out in continuous gas flow regime. The vacuum system was constituted by diffusion and mechanical pumps. The operating pressure was controlled by Pirani type gauge operating in voltage controlled mode. The HMDSN pressure was kept in 0,6 mBar and a negative d.c. supply was set in 800 V between two parallel electrodes with 5,5 cm of diameter whose separation was 1,5 cm. For adhesion measurements we deposited our polymers on microscopic glass substrates and two methods were used: the Adhesive Scotch-tape and a method adopted by the American Society for Testing and Materials (ASTM). In this test the polymer/substrate is immersed in boiling water and periodically examined to see if the surface coated layer starts to peel off from the glass. If the boiling time exceeds 8 hours, the adhesion is generally considered to be excellent. The residual stress measurements were performed by the bending beam method [10] using the apparatus already described in literature [11]. The polymer films were deposited on very thin microscopic glass substrate with 150 μm thickness.

Results and Discussions

It is shown in figure 1 the time dependence of the residual mechanical stress in plasma polymerized HMDSN of 0.9 μm thickness, grown up from a DC excited plasma kept at 800 V and 0.6 mbar. It is observed that the residual stress reduces to approximately 600% of the initial value, (measured immediately after the exposition of the film to the atmospheric environment), in 20 hours. In spite of its reduction the mechanical stress remains compressive during all the measurements. This behavior is mainly due to the recombination



processes of the free radicals with oxygen, nitrogen and water molecule present in atmospheric environment. The neutralization of these radicals stabilizes the surface causing relaxation of the residual stress due structural changes in polymeric chains. This essentially occurs because during the polymer formation many chemical units are aggregated to the chains without complete neutralization. These reactive sites may recombine among themselves or remain in certain positions of the polymeric chain, giving origin to chemical unstable units. Therefore the film may present a great amount of charged structures at the surface that will react with the components of atmosphere, when exposed to the air, in a rate that is not constant in time. These reactions may increase the degree of cross-linking causing the stabilization of the film. The adhesion of the films was measured for HMDSN polymerized over thin glass substrates. All the films resisted to the Scotch tape test, showing a excellent adhesion from this point of view. The films were submitted subsequently to the boiling water test with distillate water and seawater. The results obtained are shown in figure 2. It can be appreciated that the film submitted to action of boiling distillate water (fig.2.a) remained almost unchanged, presenting a small number of spots (white spots) without film. The remove here is attributed to small localized imperfections in film structure. In fig.2.b is observed that the action of the boiling seawater produced an expressive number of spots due to the corrosion processes produced by the chlorine and sodium ions present in the aqueous medium. It should be stressed here that the adhesion of our films were very high since they resisted for more than 8 hours to the boiling water environment, even the high corrosive seawater.

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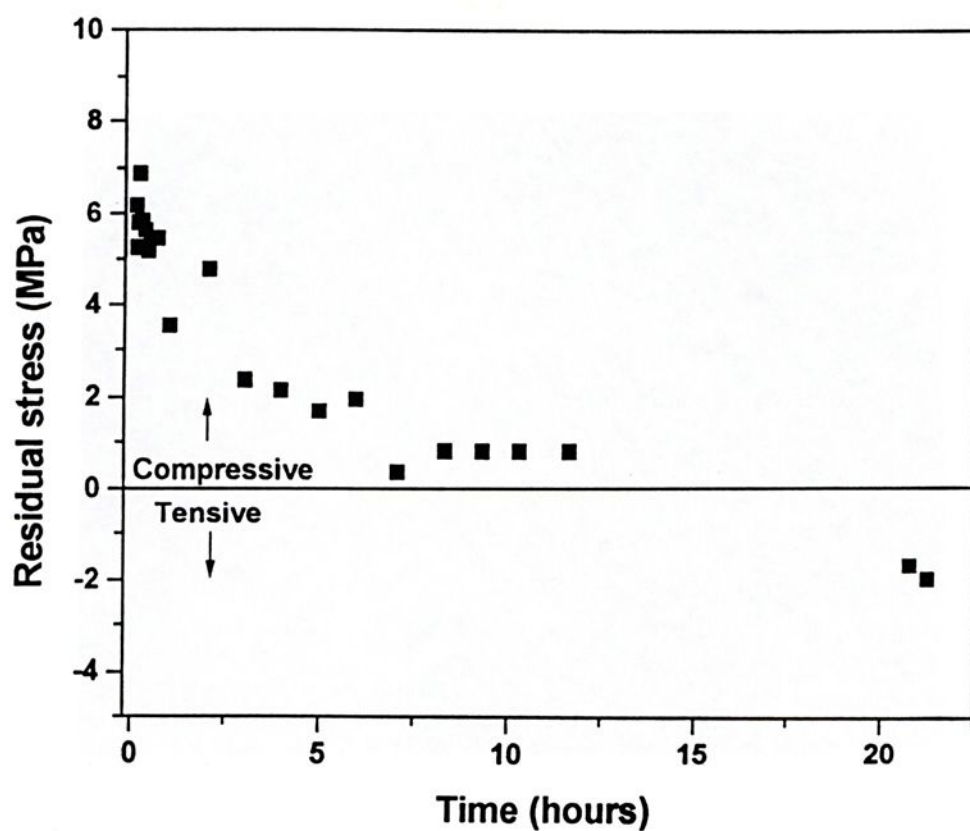


Fig. 1. Time dependence of the residual mechanical stress for plasma polymerized HMDSN films

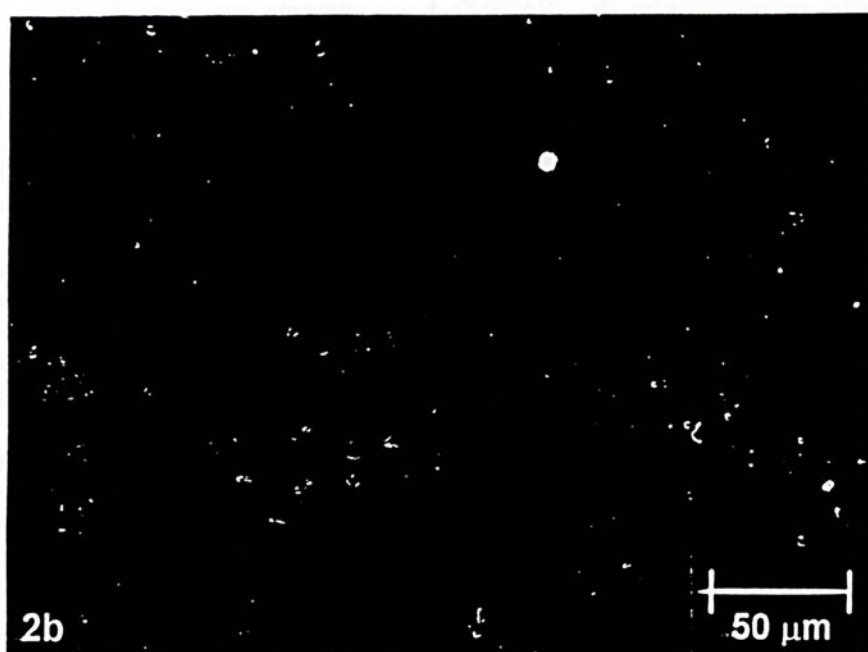
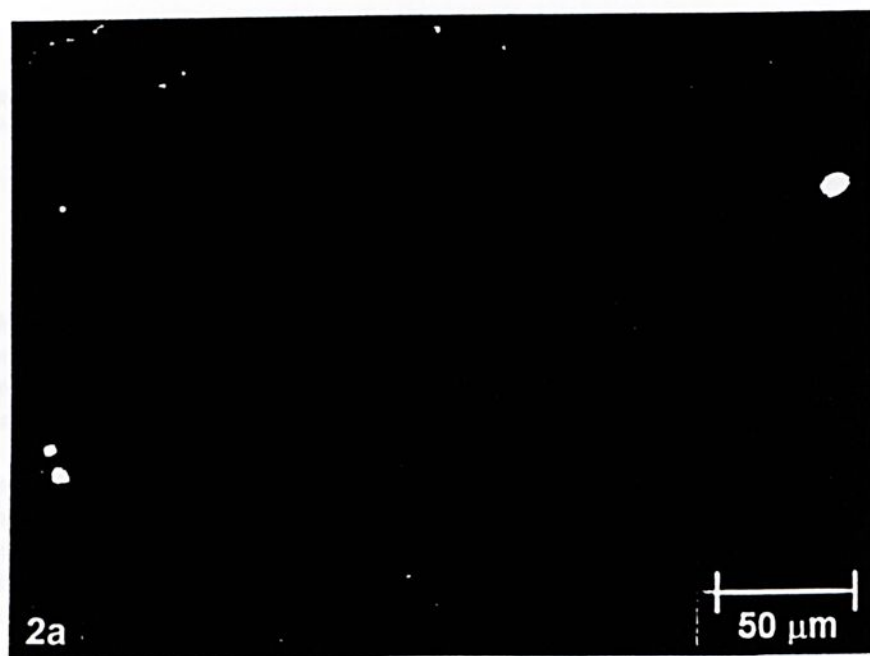


Fig. 2. Photographs of HMDSN films exposed to distillate boiling water(a) and boiling seawater (b). The white spots corresponds to regions where film was removed.

Thermal diffusivity measurements in C_2H_2 -plasma polymerized films using photoacoustic techniques

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Plasma polymerized thin films obtained from DC and RF (radio frequency) electrical discharges in hydrocarbons and organic vapours have been used in several technological applications at an increasing rate for many years [1–4]. The main reasons are that these polymers are resistant to the attack of acids and organic solvents and are pinhole free because their structures are composed of highly cross-linked two and three-dimensional chains, instead of one-dimensional chains as obtained in conventional processes [5].

In spite of the fact that plasma polymerization processes are not well understood, and that the properties of the polymers obtained are strongly dependent on plasma parameters, it is possible to control and reproduce thermal, optical, electrical and mechanical properties of such films [5, 6].

The great differences between the structures of plasma polymerized films and those obtained from the same monomer by conventional polymerization processes, are mainly due to the energies involved. The principal mechanism of molecular fragmentation within the plasma environment is electronic impact, encompassing energies varying from 1 to 4 eV [5, 6] which are at least one order of magnitude higher than the energies involved in conventional polymerization processes [5].

In this context it is extremely important to characterize the physical properties of plasma polymerized films, correlating them to the plasma parameters in order to establish which processes are the best to obtain a predetermined physical property.

This work reports, for the first time, the determination of the thermal diffusivity of plasma polymerized acetylene by amplitude measurements of the photoacoustic signal (PA). The polymeric films were grown over Al substrates 12 μm thick, from RF excited C_2H_2 discharges obtained within a small cylindrical plasma reactor, whose detailed description has previously been published [7, 8]. The C_2H_2 plasma was excited by a 10 W RF power supply operating at 10 MHz frequency. The discharge time of 45 min, at pressures of 67 Pa resulted in a 10 μm thick polymeric film.

The thermal diffusivity α of such films as determined directly from the theoretical fitting of

the sample's PA signal, which was obtained from the experimental set up schematically shown in the block diagram of Fig. 1. The acoustically modulated light from an Ar-ion laser illuminates the rear side of an open PA cell as shown in Fig. 1b. The signal generated by the microphone is detected through a lock-in amplifier locked at the light modulation frequency set by the pulse generator.

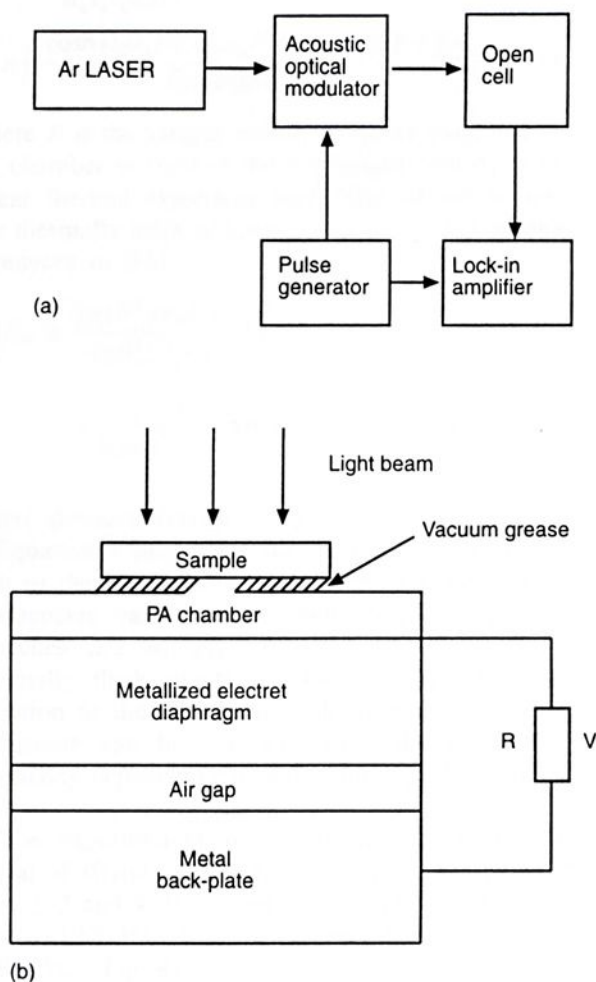


Figure 1 (a) Block diagram of the experimental setup used for PA signal measurements of plasma-polymerized films. (b) Schematic open photoacoustic cell using a front air chamber of a common electret microphone as the transducer medium [9].

With such a configuration, using the one-dimensional diffusion model of Rosencwaig-Gersho, the resultant PA signal is given by [9]:

$$\delta P = \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{2\pi l_g T_0 \kappa_s f} \frac{e^{i(\omega t - \pi/2)}}{\sinh(l_s \sigma_s)} \quad (1)$$

where $\gamma = c_p/c_v$ is the specific heat ratio of air, P_0 and T_0 are the ambient pressure and temperature, respectively, I_0 is the absorbed light intensity, f is the modulation frequency, and l_j , κ_j , α_j are the length, thermal conductivity and thermal diffusivity of material j , respectively. Here the subscript j denotes the sample (s) and the gas (g) media, respectively, and

$$\sigma_j = (1 + i)\alpha_j,$$

with

$$\alpha_j = \sqrt{\frac{\pi f}{\kappa_j}} = \frac{1}{\mu_j}$$

and

$$i = \sqrt{-1}$$

α_j is the complex thermal coefficient of the material j , and μ_j is the thermal diffusion length. In arriving at Equation 1 it is assumed that the sample is optically opaque to the incident light and that the heat flux into the surrounding air is negligible, conditions that are satisfied by the Al substrate used in our experiments.

In the range of frequencies for which the sample is thermally thin, i.e. $l_s \ll \mu_s$ or $l_s \alpha_s \ll 1$, Equation 1 can be reduced to

$$\delta P \cong \frac{\gamma P_0 I_0 \alpha_g^{1/2} \alpha_s}{(2\pi)^{3/2} T_0 l_g \kappa_s} \frac{e^{i(\omega t - 3\pi/4)}}{f^{3/2}} \quad (2)$$

Therefore theory predicts that the amplitude of the PA signal decreases as $f^{-3/2}$ as one increases the modulation frequency. As the frequency increases the sample changes its behaviour from thermally thin to thermally thick, i.e. $l_s \alpha_s \gg 1$. Under such condition one obtains from Equation 1:

$$\delta P \cong \frac{\gamma P_0 I_0 (\alpha_g \alpha_s)^{1/2}}{\pi T_0 l_g \kappa_s} \frac{e^{-l_s \sqrt{\pi f / \alpha_s}}}{f} e^{i(\omega t - \pi/2 - l_s \alpha_s)} \quad (3)$$

Equation 3 means that for a thermally thick sample, the amplitude of the PA signal decreases exponentially with the modulation frequency as

$$\frac{1}{f} \exp\left(-l_s \sqrt{\frac{\pi f}{\alpha_s}}\right)$$

The phase of the PA signal decreases linearly with $f^{1/2}$, namely

$$\phi = -\frac{\pi}{2} - l_s \sqrt{\frac{\pi}{\alpha_s}} f$$

Therefore one may obtain the thermal diffusivity α_s , of the sample, directly from the high-modulation-frequency behaviour of either the signal amplitude or its phase. In the case of the PA signal amplitude, α_s is obtained from the experimental data fitting of the coefficient

$$\beta = l_s \sqrt{\frac{\pi}{\alpha_s}}$$

in the argument of the exponential ($-\beta \sqrt{f}$). In the case of the PA signal phase data, α_s is obtained from the phase slope as a function of $\sqrt{f}$.

However in this range of frequency it is necessary to take into account the pressure changes due to the thermally induced surface dislocation of the samples. This dislocation is caused by the temperature gradient along the depth of the sample. The resultant thermoelastic bending of the sample cannot be neglected, especially in the case of thermally thick samples, as has been shown in the literature [10, 11].

In order to accomplish this, the thermoelastic equations must be coupled to the resulting temperature and pressure equations under the assumption of adiabatic expansion of the gas inside the PA cell [11]:

$$\delta P_{el} = \frac{3\alpha_T R^4 \gamma P_0 I_0}{R_c^2 l_g^2 \kappa_s \sigma_s^2} \times \left(\frac{\cosh(l_s \sigma_s) - (l_s \sigma_s/2) \sinh(l_s \sigma_s) - 1}{l_s \sigma_s \sinh(l_s \sigma_s)} \right) e^{i\omega t} \quad (4)$$

where R is the sample radius, R_c is the radius of the PA chamber in front of the diaphragm, and α_T is the linear thermal expansion coefficient of the sample. For thermally thick samples, i.e. $l_s \alpha_s \gg 1$, Equation 4 reduces to [11]:

$$\delta P_{el} \cong \frac{3\alpha_T R^4 \gamma P_0 I_0 \alpha_s}{4\pi R_c^2 l_g^2 \kappa_s f} \left[\left(1 - \frac{1}{l_s \alpha_s} \right)^2 + \frac{1}{(l_s \alpha_s)^2} \right]^{1/2} \exp[i(\omega t + \pi/2 + \phi)] \quad (5)$$

where $\phi = \arctan(1/l_s \alpha_s - 1)$.

Equation 5 shows that the thermoelastic contribution to the PA signal amplitude at high modulation frequencies varies as f^{-1} and its phase ϕ_{el} approaches $\pi/2$ as $\phi_{el} = \pi/2 + \phi$. Therefore, for a thermally thick sample, if the thermoelastic contribution to the PA signal is dominant, the thermal diffusivity can be evaluated from the modulation frequency dependence of either the signal amplitude or its corresponding phase.

The experimental results obtained for the PA signal of 10 μm thick polymer samples are shown in Figs 2, 3 and 4, for frequencies ranging from 25 Hz up to 1000 Hz (Figs 2, 3) and from 25 up to 3000 Hz, (Fig. 4).

The experimental data, shown in Fig. 2, for high-modulation frequency was fitted quite well by a function $S = B \exp(-\beta \sqrt{f})$, in close agreement with the theoretical predictions for thermally thick



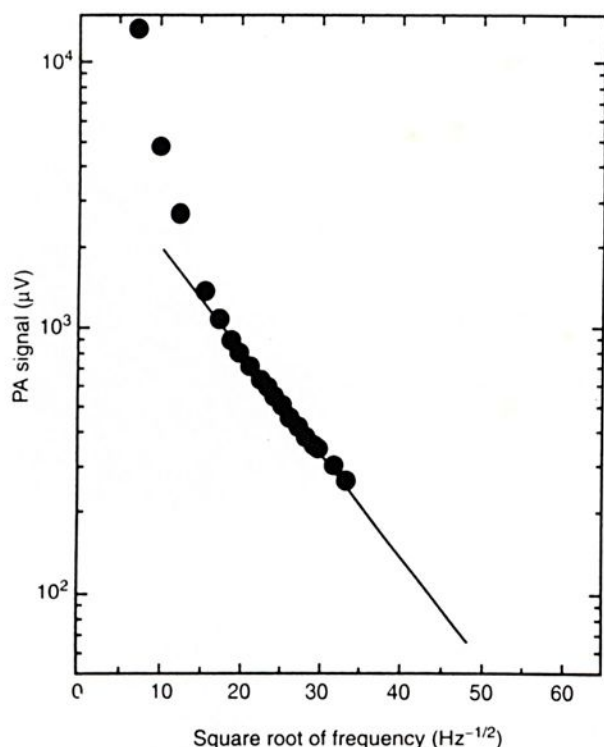


Figure 2 PA signal of C_2H_2 -plasma polymerized films for frequencies ranging from 100 to 1000 Hz. The frequency behaviour of the signal is in close agreement with the theoretical predictions for thermally thick samples ($S = Be^{-0.0438f^{1/2}}$).

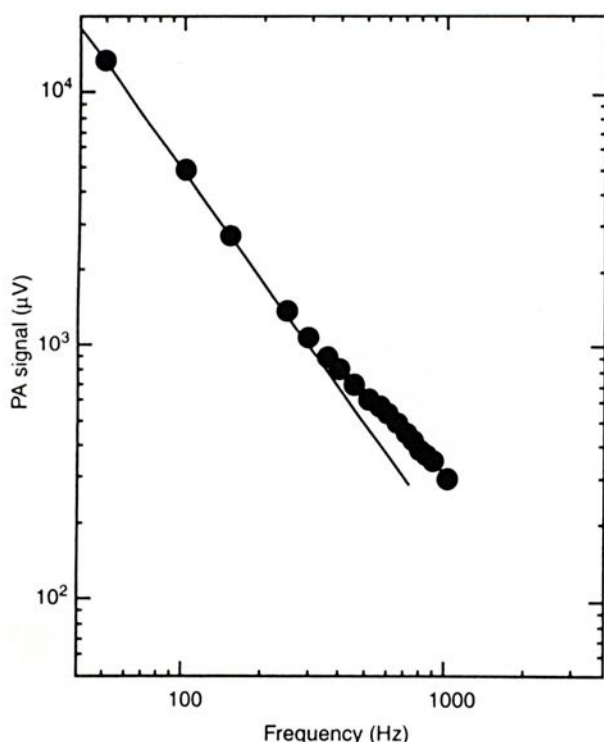


Figure 3 PA signal of C_2H_2 -plasma polymerized films showing the fitting for frequencies below 400 Hz. The frequency behaviour of the PA signal corresponds with that expected for thermally thin samples ($S = Af^{-1.43}$).

samples. The experimental value $\beta = 0.0438$ results in a thermal diffusivity value $\alpha = 1.64 \times 10^{-3} \text{ cm}^2/\text{s}$, which is in good agreement with values in the literature for polymers obtained by conventional polymerization processes [12]. In Fig. 3 the experi-

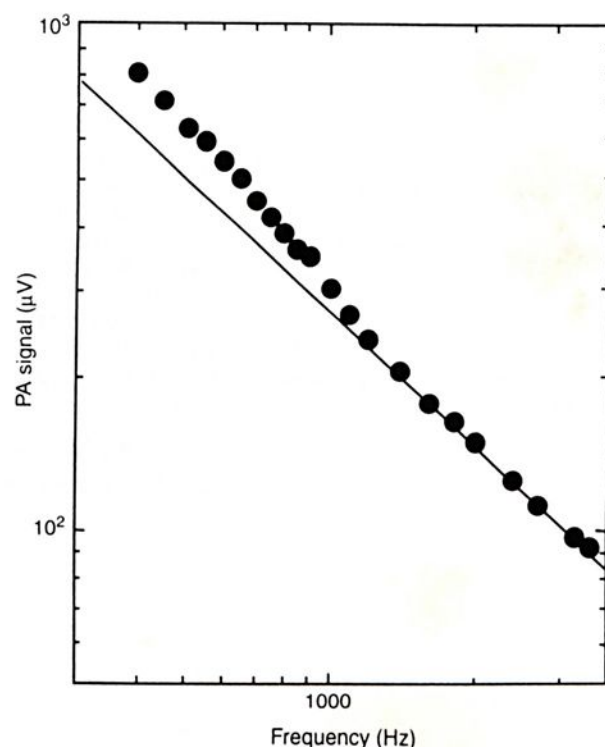


Figure 4 Pa signal of C_2H_2 -plasma polymerized films showing the fitting for the high frequency regime. The frequency behaviour of the PA signals of the sample show that thermoelastic bending of the films is the main mechanism of PA signal generation ($S = Cf^{-0.88}$).

mental data for frequencies below 400 Hz was fitted by a function $S = Ae^{-1.43}$ indicating that in this frequency range the sample is thermally thin. In Fig. 4 the experimental data was fitted for frequencies ranging from 1000 to 3000 Hz by a function $S = Ce^{-0.88}$. This frequency behaviour is a strong indication that for frequencies higher than 1000 Hz, thermoelastic bending of the polymeric film gives the main contribution to the PA signal.

To summarize, this work presented, to our knowledge, the first determination of the thermal diffusivity of plasma-polymerized polymers using photothermal techniques. The results obtained show that in spite of the structural differences between plasma-polymerized and polymers obtained by conventional polymerization processes, the thermal diffusivity is in the same order of magnitude indicating that the main mechanisms for heating transport are the same.

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