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Effect of Atmosphere and Dopants on Sintering of SnO₂

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(Dedicated to Professor Dr. Drago Kolar in memory of a great scientist and a great man)

Abstract: Tin oxide is an n type semiconductor material with a high covalent behavior. Mass transport in this oxide depends on the surface state promoted by atmosphere or by the solid solution of aliovalent oxide doping. The sintering and grain growth of this type of oxide powder is then controlled by atmosphere and by extrinsic oxygen vacancy formation. For pure SnO₂ powder the surface state depends only on the interaction of atmosphere molecules with the SnO₂ surface. Inert atmosphere like argon or helium promotes oxygen vacancy formation at the surface due to reduction of SnO₂ to SnO at the surface and liberation of oxygen molecules forming oxygen vacancies. As a consequence surface diffusion is enhanced leading to grain coarsening but no densification. Oxygen atmosphere inhibits SnO₂ reduction by decreasing the surface oxygen vacancy concentration. Addition of dopants with lower valence at the sintering temperature creates extrinsic charged oxygen vacancies that promote mass transport at the grain boundary leading to densification and grain growth of this polycrystalline oxide.

Keywords: Tin oxide; Sintering; Dopants; Sintering atmosphere.

Резюме: Оксид олова – это полупроводниковый материал типа n с высокими ковалентными свойствами. Перенос массы в данном оксиде зависит от состояния поверхности, на которое влияет атмосфера или твердый раствор алиовалентного оксида. Спекание и рост зерен в этом оксиде регулируются атмосферой и примесным образованием кислородных вакансий. В случае чистого SnO₂ состояние поверхности зависит только от взаимодействия молекул атмосферы с поверхностью SnO₂. Нейтральные атмосферы, какими являются аргон и гелий, влияют на образование кислородных вакансий на поверхности вследствие восстановления на поверхности SnO₂ в SnO и освобождения молекул кислорода, образующих вакансии кислорода. Результат этого – ускорение поверхностной диффузии, приводящей к укрупнению зерен, но не к уплотнению. Атмосфера кислорода замедляет восстановление SnO₂ уменьшением концентрации поверхностных вакансий кислорода. Добавка присадок с более низкой валентностью при температуре спекания влияет на образование вакансий кислорода,

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которые ускоряют перенос массы по границам зерен и приводят к уплотнению и росту зерен данного поликристаллического оксида.

Ключевые слова: Оксид олова; спекание; присадки; атмосфера спекания.

Сadržaj: Калај-оксид је полупроводнички материјал *n*-типа са јако израженим ковалентним својствима. Пренос масе у овом оксиду зависи од стања површине на које утиче атмосфера или допирање чврстим раствором алиовалентног оксида. Синтеровање и раст зрна код овог типа оксида је тада контролисано атмосфером и примесним образовањем ваканција кисеоника. За чисти прах SnO_2 стање површине зависи само од интеракције молекула атмосфере са површином SnO_2 . Инертне атмосфере, као што су аргон или хелијум, утичу на формирање ваканција кисеоника на површини због редукције SnO_2 у SnO на површини и ослобађања молекула кисеоника који формирају ваканције кисеоника. Последица овога је убрзање површинске дифузије, што доводи до укрупњавања зрна, али без згушњавања. Атмосфера кисеоника инхибира редукцију SnO_2 смањењем концентрације површинских ваканција кисеоника. Додатак допаната са нижом валенцом на температури синтеровања утиче на образовање ваканција кисеоника које потпомажу транспорт масе на границама зрна и доводе до згушњавања и раста зрна овог поликристалног оксида.

Кључне речи: Калај-оксид; синтеровање; допанти; атмосфера синтеровања.

I. Introduction

Tin oxide polycrystalline ceramics are *n*-type semiconductors that have been widely used as gas sensors [1-2], electrodes for electric glass melting furnaces, and in thin films as electrochromic devices, crystal displays, photodetectors, solar cells and protective coatings [3-8]. However, the use of SnO_2 ceramics is limited by the low densification of this oxide during sintering due to the dominance of non-densifying mechanisms for mass transport such as surface diffusion or evaporation-condensation [9-10]. These mechanisms promote coarsening of SnO_2 leading to low densification of this ceramics [11].

Several processes and sintering aids have been used to improve SnO_2 densification by forming reactive liquid phase or extrinsic defects by solid state solution [12-18]. Liquid phase is the densifying mechanism when additives such CuO and Bi_2O_3 are used. MnO_2 , ZnO , CoO and Li_2O are known to form solid solutions with SnO_2 .

Since tin oxide ceramics are very sensitive to the atmosphere [11], the interaction of gases with the SnO_2 surface promotes charge transfer and defect creation during sintering of this oxide. In this paper the effect of atmosphere (argon, oxygen, and argon with water vapor) on the pore and grain size evolution as well as densification of SnO_2 will be considered. The addition of CoO or MnO_2 to SnO_2 creates charged oxygen vacancies at the sintering temperature. These oxygen vacancies as well as Mn^{2+} , Mn^{3+} , or Co^{2+} ions substituting Sn^{4+} are segregated at the grain boundaries and improve mass transport leading to densification and grain growth.

II. Experimental procedure

SnO₂ powder used in this study was supplied by Backer showing the following characteristics: surface area = 7.5 m²/g; purity 99.9%; mean particle size = 0.12 μm. Pellets were prepared by pressing the powder in a cylindrical die followed by isostatic pressing at 210 MPa.

The pellets were sintered in an electrical alumina tube furnace with one closed end, and the temperature was controlled by a Pt/Pt-13% thermocouple inserted into the area of the hot zone. For the purpose of adequate gas input into the furnace a thin alumina tube open at both ends was passed through a rubber stopper and connected by rubber tubing to the gas system. Another Pt/Pt-13%Rh thermocouple was used to measure the temperature of the sample placed inside the tube furnace. The exhausted gases were bubbled in oil after passing through an opening in the alumina tube.

Atmosphere control was maintained by metering the bottled argon or oxygen gases through a flow meter and then was passed through a drying column and bubbled through a gas-washer used to introduce a specific amount of water vapor to argon. The argon that was bubbled through the gas-washer was passed through a heated rubber tube, to prevent condensation of the water vapor, into the tube furnace. The partial pressure of water vapor mixed with argon was measured at the entrance to the tube furnace by weighing the amount of water collected by a tube containing zeolite and silica gel, in a given period of time.

Bulk densities of SnO₂ compacts were measured by displacement using a mercury picnometer. Pore size distribution was determined in each sample using a mercury porosimeter Micromeritics model 9210. The mid pore diameter was defined as the pore corresponding to the mercury pressure where half of porosity was achieved. Surface areas of the green sample and sintered samples were measured from the pore size distribution curves as described in former work [11].

III. Results and discussions

III.1 Influence of atmosphere on coarsening and pore size evolution of SnO₂

The results after characterization of SnO₂ samples sintered in dry argon and oxygen during 1 h at several temperatures are listed in Tab. I. As observed in this table, pores grew with temperature without densification. The decrease in surface area, after sintering in dry argon, from 4.28 m²/g at 1000°C to 0.99 m²/g at 1250°C with no densification is related to pore growth from 0.110 μm at 1000°C to 0.512 μm at 1250°C.

Considering that the bulk density remains constant for all temperatures and time considered in this study, the following analysis can be made. Supposing that pores have a spherical geometry in a compact with the total pore volume per gram of material V_p , the following relationship can be written:

$$V_p = KNd_p^3, \quad (1)$$

where N is the total number of pores per gram of material, d_p is the mid pore radius and K is a geometrical constant.

The surface area of N spherical pores will be:

$$S = 3KNd_p^2. \quad (2)$$

Tab. I Physical characteristics of SnO₂ compacts sintered at several temperatures in dry argon and oxygen during 1 h.

Temp. (°C)	Atmosphere	Mid pore diameter (μm)	Surface area (m ² /g)	Bulk density (g/cm ³)
900	Ar	0.084	5.60	4.1
1000	Ar	0.110	4.28	4.1
1100	Ar	0.205	2.38	4.1
1200	Ar	0.360	1.41	4.1
1250	Ar	0.512	0.99	4.1
1000	Ar + 69 torr H ₂ O	0.126	3.68	4.1
1000	Ar + 171 torr H ₂ O	0.157	3.15	4.1
1000	O ₂	0.091	5.68	4.1
1200	O ₂	0.209	2.24	4.1

Combining equations (1) and (2) results in:

$$S = \frac{k^* V_p}{d_p}, \quad (3)$$

where k^* is a geometrical factor which is constant if the total pore volume remains constant and the pore geometry does not change with sintering. For spherical and cylindrical geometries the constant of equation 3 will be 6 and 4 respectively.

Fig. 1 shows the plot of surface area as a function of the inverse of mid pore diameter of SnO₂ pellets, sintered in dry argon, for temperatures ranging from 900 to 1250°C and for time ranging from 30 to 240 min. As observed in this figure the plot is a straight line that can be extrapolated to the original with $k^* = 4.8$. This result demonstrates that during sintering of SnO₂ the pore geometry remains constant. Moreover, the value for the geometric factor k^* obtained in these conditions is intermediate between the spherical and cylindrical geometry. This is expected since SnO₂ compacts have particles relatively uniform and equiaxial.

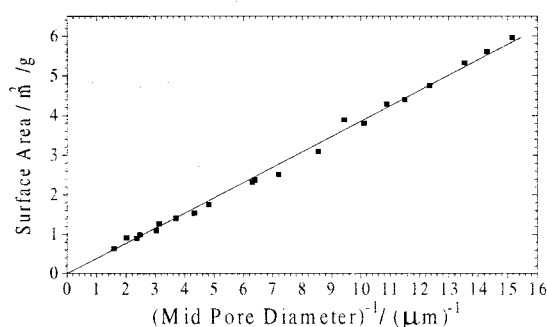


Fig. 1 Surface area versus reciprocal of mid pore diameter of SnO₂ pellets sintered in dry argon for temperatures ranging from 900 to 1250°C and times from 30 to 240 min.

Although the results of Fig. 1 demonstrate that pore growth is due to elimination of small particles by transferring the mass to large particles, the exact mechanism of grain growth cannot be defined at this point. Both Ostwald Ripening for grain growth controlled by fluid phase (evaporation/condensation) or fast grain boundary motion can perfectly explain this pore growth behavior.

Fig. 2 shows two SEM micrographs obtained in SnO₂ pellets sintered in dry argon at two different sintering temperatures (900 and 1200°C). Both micrographs show the same characteristics but at a different scale. This indicates that the microstructure remains uniform during the process of grain growth.

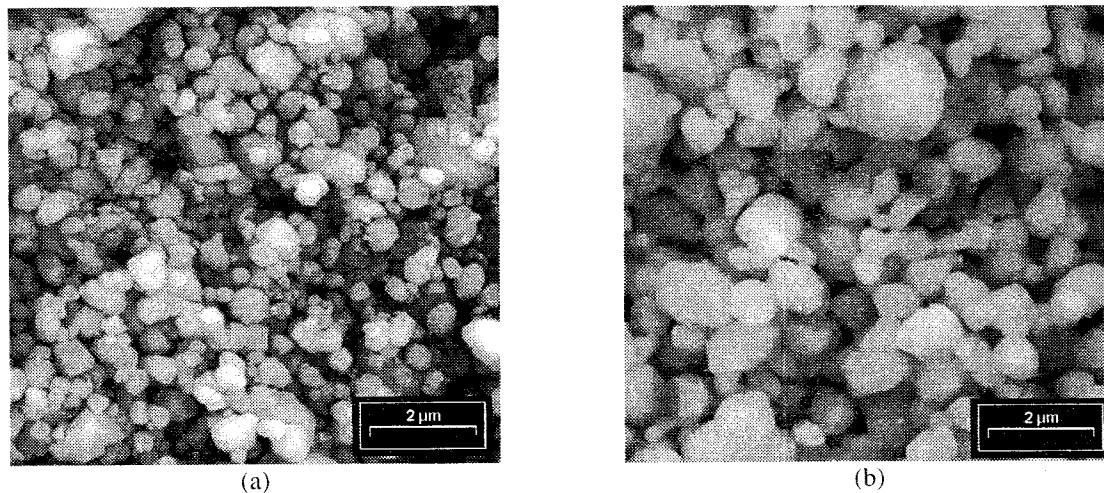


Fig. 2 SEM micrograph of SnO₂ pellets sintered in dry argon during 1 h: (a) 900°C; (b) 1200°C.

The sintering atmosphere has a large effect on sintering of SnO₂ compacts as demonstrated by Quadir and Readey [19] using hydrogen atmosphere. In a dry argon atmosphere one possibility is the evaporation of SnO₂ forming SnO(g) and O₂ according to:



SnO(g) and O₂ can be combined and precipitate in a large particle surface leading to grain growth (Ostwald Ripening). Another possibility is evaporation from the convex surface of two neighboring particles with precipitation of SnO₂ in the neck leading to neck growth up to a critical value and then grain boundary motion. The thermodynamic calculated value for the free energy of reaction (4) at 1485 K is 67 Kcal/mol, corresponding to oxygen partial pressure of 2×10^{-7} atm. This value is not far from that obtained experimentally by Hoening [20] at the same temperature (3.5×10^{-7} atm), indicating that evaporation-condensation might control the coarsening of SnO₂ ceramics for temperatures higher than 1200°C.

Mass spectrometry was used to determine desorbed species from the SnO₂ surface for temperatures up to 1500°C in dry helium. As shown in Fig. 3 between 300 and 600°C CO₂, OH and H₂O are desorbed from the SnO₂ surface. Desorption of these species should result in a high oxygen vacancy concentration at the SnO₂ surface. The evaporation of oxygen is effective for temperatures above 1200°C as shown in this figure.

Another possibility for liberation of oxygen from the SnO₂ surface is the reaction:



This reaction is effective for a neutral or reducing atmosphere resulting in the reduction of Sn⁴⁺ to Sn⁺² and creation of oxygen vacancies at the SnO₂ surface. In an oxygen atmosphere the rate of evaporation is reduced as observed in Tab. I in agreement with reactions 4 and 5. Moreover, the oxygen partial pressure calculated for high temperatures using equations 4 and 5 indicates that equation 4 is more effective and agrees with the experimental results [20].

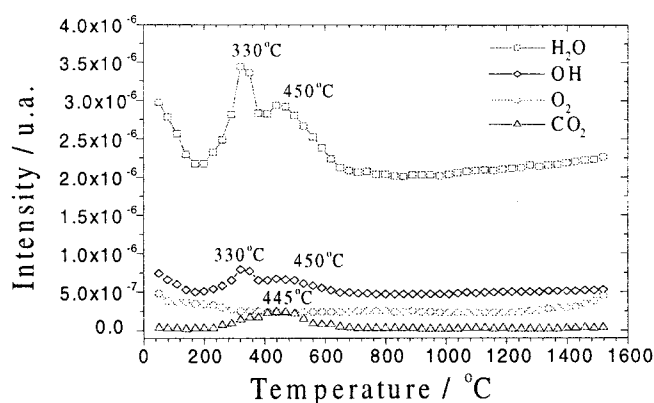


Fig. 3 Mass spectrometry for SnO_2 pellets.

Water vapor was found to accelerate pore growth during sintering. As observed in Tab. I pore growth is accelerated with water vapor partial pressures. This is due to a chemical interaction of water molecules with the SnO_2 surface and formation of oxygen vacancies after desorption of species as observed by mass spectrometry (Fig. 3).

III.2 Effects of transition metal oxide addition on sintering and electrical properties of SnO_2

Transition metal oxides such as ZnO , MnO_2 and CoO form a limited solid solution in SnO_2 with formation of extrinsic oxygen vacancies. The addition of 0.5 mol% of MnO_2 to SnO_2 leads to 95% of theoretical density of SnO_2 [21]. However, there is a controversy about the sintering mechanism of this system. Whether a liquid phase forms is not known since there is no data on the eutectics or phase diagram of this system. However, the formation of MnSnO_3 and Mn_2SnO_4 is reported in the literature [21]. The addition of small amounts of CoO to SnO_2 (>0.5 mol%) also leads to high density of this ceramics. Fig. 4 shows linear shrinkage as a function of temperature for both systems, containing 0.5 to 2.0 mol% of MnO_2 or CoO . As observed in this figure, linear shrinkage starts at lower temperatures as the CoO or MnO_2 concentrations increase. The final relative densities of samples sintered in a dilatometer, using a constant heating rate of $10^\circ\text{C}/\text{min}$, for temperatures up to 1400°C are higher than 99%. This indicates that these dopants are extremely effective in promoting densification of SnO_2 , even for low dopant concentrations.

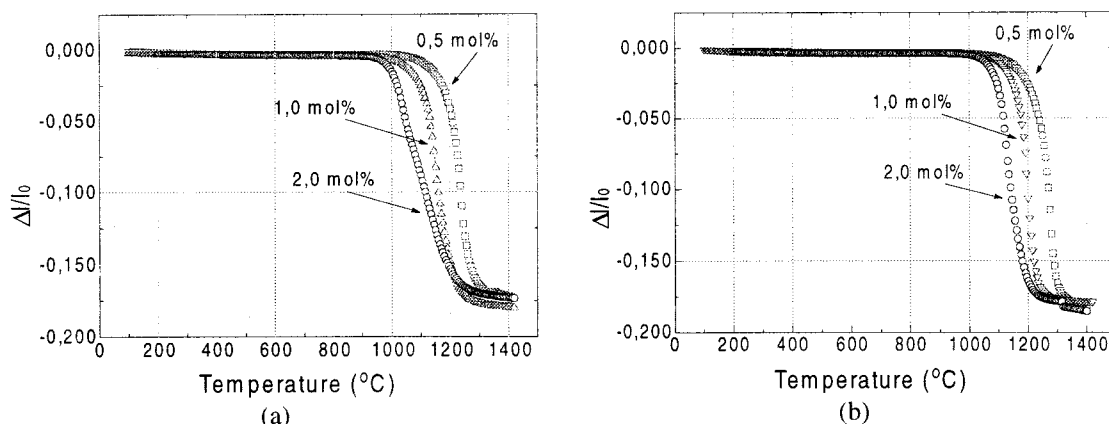


Fig. 4 Linear shrinkage rate versus temperature for the systems: (a) $\text{SnO}_2\text{-CoO}$ and (b) $\text{SnO}_2\text{-MnO}_2$.

Although the two systems show similar densification behavior the micrograph in Fig. 5 shows trapped pores for CoO doped SnO₂ indicating that the nondensifying mechanisms appear to be dominant at lower temperatures when compared to the system doped with MnO₂.

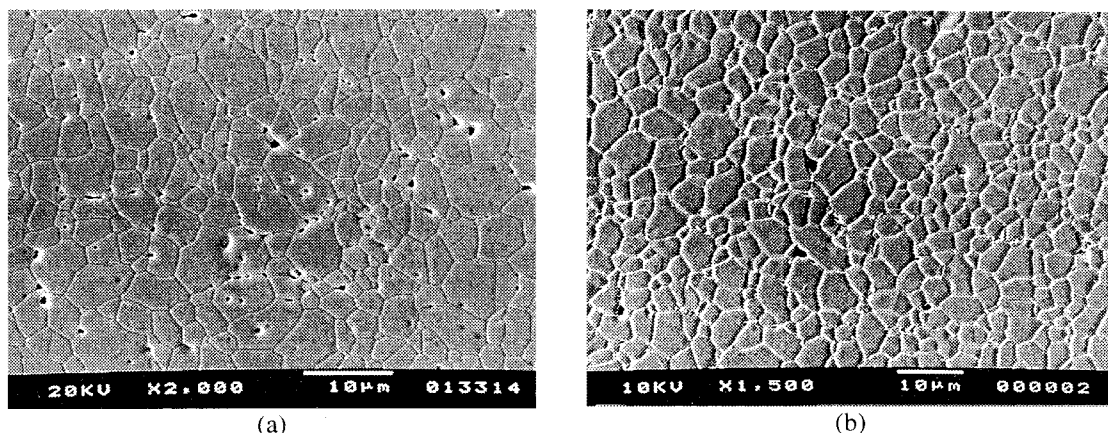


Fig. 5 Secondary electron micrographs for SnO₂ with 0.5 mol% additives: (a) CoO; (b) MnO₂.

X-ray diffractograms for compositions SnO₂ + 8 mol% MnO₂, before and after sintering at 1400°C with a constant heating rate of 10°C/min show that only a SnO₂ phase is observed after sintering, indicating the formation of a solid solution even after cooling. Otherwise, the XRD for compositions SnO₂ + 8 mol% CoO sintered in the same conditions shows two phases after cooling, SnO₂ and Co₂SnO₄. Considering that this second phase is not observed at high temperature X-ray diffraction, this phase forms during cooling.

Thermal analysis (DTA/TG) of SnO₂.CoO and SnO₂.MnO₂ up to 1550°C did not show the presence of endothermic reactions related to liquid-phase formation. Moreover, an increase in the dopant concentration does not promote a change in the microstructure and shifts the temperature at which the linear shrinkage starts, which are not characteristics of an eutectic system.

The absence of experimental evidence of an eutectic liquid suggests that the densification observed in the studied systems is not associated with liquid-phase sintering. Thus, the sintering of both systems containing up to 2 mol% of MnO₂ or CoO seems to be controlled by diffusion in the solid state. As is well known, diffusion-controlled processes of oxides depend strongly on the defect chemistry and on the nature and concentration of foreign atoms. Therefore, modifying SnO₂ crystals by adding CoO or MnO₂ could alter the sintering mechanisms and rate. SnO₂ is a n-type semiconductor with native oxygen vacancies compensated by electrons. For diffusion-controlled processes like sintering, the slowest diffusion species should determine the overall rate of sintering. Since oxygen is the rate controlling diffusion species [22] in SnO₂, increasing the oxygen vacancy (V_O) concentration would increase the sintering rate. Thus considering that for temperatures higher than 1100°C Mn(IV) is reduced to Mn(II), the following reactions are proposed for both systems:



These results are in accordance with Yuan et al. [17] who showed that Li^+ also acts as an acceptor in SnO_2 and hence improves the densification rate. Contrary to these results, Nb_2O_5 doped SnO_2 does not improve densification of the system due to the fact that Nb_2O_5 is an electron donor, which increases the electrical conductivity of SnO_2 as shown by Gouvea [23]. Then the following equation controls the defect formation in SnO_2 :



To rationalize the role played by dopants and vacancies in the electrical properties, the electronic structure of doped and undoped SnO_2 was calculated as a function of the dopant type (niobium, cobalt and chromium) and concentration, as well as with oxygen surface concentration. The calculations were made using the Gaussian 94 package at the Roothann Hartree Fock (RHF) level of theory. The results show that the energy gap is reduced when oxygen vacancies are formed (Tab. II), the system becomes a n type semiconductor and electronic conduction is therefore increased. When the dopant Nb^{5+} is added the electrical conductivity of the SnO_2 ceramic also increases. Otherwise, the addition of Co^{2+} and Mn^{2+} , although forming oxygen vacancies in the SnO_2 structure, decreases the electrical conductivity of this ceramic.

Tab. II Calculated band gap and Fermi energies for SnO_2 .

Cluster Model	HOMO (eV)	LUMO (eV)	Band gap (eV)	Fermi energy (eV)
$(\text{SnO}_2)_{15}$	-6.93	-2.84	4.08	-4.89
$(\text{SnO}_2)_{14}\text{SnO}$	-6.48	-3.92	2.55	-5.20
$(\text{SnO}_2)_{13}(\text{NbO})_2$	-6.76	-4.27	2.48	-5.52
$(\text{SnO}_2)_{13}(\text{CoO})_2$	-6.05	-3.43	2.62	-4.74
$(\text{SnO}_2)_{13}(\text{MnO})_2$	-6.49	-2.42	4.07	-4.46

IV Conclusions

Sintering of undoped SnO_2 compacts in atmospheres of Ar, Ar plus H_2O vapor and O_2 , in the range of 900 to 1250°C, leads to coarsening with no densification. Reduction of Sn^{4+} to Sn^{2+} by evaporation of oxygen at the surface and desorption of chemically adsorbed species on the SnO_2 surface control coarsening at temperatures bellow 1000°C by surface diffusion. Evaporation and condensation of SnO_2 according to the reaction: $\text{SnO}_2 \Leftrightarrow \text{SnO}(g) + \frac{1}{2}\text{O}_2(g)$ control the mass transport for temperatures above 1000°C and are responsible for coarsening of SnO_2 ceramics.

Densities above 99% of the theoretical density were obtained during sintering of MnO_2 or CoO -doped SnO_2 ceramics (up to 2 mol%). Experimental evidence indicates that these dopants act as acceptors leading to the creation of additional oxygen vacancies in SnO_2 , increasing the densification rate of this oxide.

Acknowledgments

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