PHOTOCHEMICAL DEPOSITION OF Pd-LOADED AND Pt-LOADED TIN OXIDE THIN FILMS.

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ABSTRACT

Pd and Pt loaded tin oxide thin films have been successfully prepared by direct UV irradiation of amorphous films of β -diketonate complexes on Si(100) substrates. Tin oxide films loaded with 10, 30 and 50% Pd and Pt, were characterized by Auger electron spectroscopy (AES). The Auger peak intensity ratios of O $K_{L_{23}}$ to Sn M_{45} showed that as-deposited films consist of mixed tin oxide phases whereas annealed films consist mainly of single phase SnO_2 . The results showed that the stoichiometry of the resulting films is in relative agreement with the composition of the precursor films. The surface characterization of these thin films was performed using Atomic Force Microscopy (AFM). This analysis revealed that loaded tin oxide films have a much rougher surface than unloaded films, with rms roughness values ranging from 28-54 nm for as-deposited Pd- SnO_x films to 3.6-20 nm for as-deposited Pt- SnO_x films. It was also found that Pt-loaded tin oxide films present a better particle size distribution and uniformity when compared to Pd-loaded tin oxide films. These results demonstrate the potential use of these deposited films in the manufacture of gas-sensing devices.

Keywords: Tin oxide; Platinum; Palladium; photodeposition; thin films.

INTRODUCTION

In the last few decades the research interest in the gas-sensing field via semiconductor based devices has noticeably increased with a particular interest in the development of new materials. In this respect, a big effort is being exercised in the search for sensitive and selective materials. The functional properties of the materials depend on their microstructure (grain and agglomerate size, porosity, roughness, etc) and composition (doping, deviation from stoichiometry) [1]. In general, structural characteristics, depending on deposition conditions, have great effects on properties of materials [2].

Zinc oxide (ZnO) and tin dioxide (SnO_2) have long been used as gas sensing materials [3-6]. Although the oxides themselves are catalytically active, they are rarely used in isolation as their gas sensing characteristics are usually enhanced by the addition of small amounts of noble metal catalysts such as palladium or platinum which not only promote gas sensitivity but also improve the response times [4].

It has been shown that for SnO_2 films doped with noble metals, such as Pt and Pd, there is a decrease in operation temperature and enhancement of sensitivity to different gases [7,8]. Under noble metal loading, it is expected that clusters form at the surface of SnO_2 such as those observed in the case of Pd [9] and Pt [10]. These clusters will be in metallic or oxidized forms depending on the noble metal, the deposition process, the interacting gas and the sensor operation temperature.

SnO_2 thin films have been prepared by a variety of deposition techniques and noble metal additives can be introduced in several ways into a sensor: eg., sputtering and posterior thermal treatment [11,12], sol-gel techniques [13,14], and chemical vapour deposition [15,16] among others.

In the last few years we have developed a novel photochemical method for the deposition of a variety of metals and metal oxides thin films [17-19], which can be carried out at ambient temperature, from simple precursor compounds. This method consists in the direct irradiation of thin films of coordination complexes with ultraviolet light. The simplicity of the method allows for the deposition of very thin films of metallic materials or metallic oxides, depending on the reactions conditions, on substrates which are not affected by the UV light. The development of this method requires that the precursor complexes form stable amorphous thin films upon spin coating onto a suitable substrate and that photolysis of these films result in the photoextrusion of the ligands leaving the inorganic products on the surface (Eq 1).

where M= Metal; L= ligand.

In this work we report on the preparation and characterization of tin, palladium and platinum complexes to be used as source materials for the direct photochemical deposition of SnO_x , Pd- SnO_x and Pt- SnO_x thin films.

EXPERIMENTAL

General procedure

The FT-IR spectra were obtained with 4 cm^{-1} resolution in a Perkin Elmer Model 1605 FT-IR spectrophotometer. UV spectra were obtained in a Hewlett-Packard 8452-A diode array spectrophotometer. X-ray diffraction patterns were obtained using a D5000 X-ray diffractometer. The X-ray source was Cu 40 kV/30mA. Auger electronic spectra were obtained using a PHI double pass CMA at 0.85 eV resolution at the Surface Physics Laboratory, Department of Physics, Simon Fraser University. Sensitivity factors provided by PHI were used to obtain normalized Auger intensities. Atomic Force Microscopy was performed in a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in contact mode. Film thickness was determined using a Leica DMLB optical microscope with a Michelson interference attachment.

Solution photochemistry was carried out in 1 cm quartz cells, which were placed in a Rayonet RPR-100 photoreactor equipped with 254 nm lamps. Progress of the reactions was monitored by determining the UV spectra at different time intervals, following the decrease in UV absorption of the complexes. The solid state photolysis was carried out at room temperature under a UVS-38 254 nm lamp equipped with two 8W tubes, in an air atmosphere.

The substrates for deposition of films were borosilicate glass microslides (Fischer, 2x2 cm) and p-type silicon(100) wafers (1x1 cm) obtained from WaferNet, San Diego, CA. Prior to use the wafers were cleaned successively with ether, methylene chloride, ethanol, aqueous HF (50:1) for 30 seconds and finally with deionized water. They were dried in an oven at 110°C and stored in glass containers.

Synthesis of β -diketonate complexes.

The reagents used in the synthesis of tin, palladium and platinum β -diketonates were from Aldrich Chemical Co., and were used without previous purification. The method reported by Adams and Hauser [20,21] was used to obtain the β -diketonate, 1-phenyl-1,3-nonanedione. FT-IR data (film) ν_{CO} 1700(s), 1602(s), 1560(s); UV-Vis data λ (log ϵ) in CH_2Cl_2 : 314 nm (3.76), 248 nm (3.51). The sodium salt used in the synthesis of the tin complex, was prepared by the method previously described in the literature [21].

Bis (1-phenyl-1,3-nonanedionato) Sn(II)

The tin complex was prepared according to reported method [22,23]. Stannous chloride (1.0 g, 5.27 mmol) and Na(1-phenyl-1,3-nonanedionato) (2.42 g, 10.54 mmol) were loaded in a 250 mL flask under a nitrogen atmosphere. After addition of 80 mL of THF to the flask, the solution mixture was stirred at room temperature for 2 h. After filtration of the solution and removal of THF a pale yellow liquid was obtained. Purification of the crude product by distillation under reduced pressure afforded pale yellow $Sn(L)_2$ (70.3% yield). FT-IR data (film): ν_{CO} 1597.2 (s), 1525 (s) cm^{-1} . UV-Vis data λ (log ϵ) in CH_2Cl_2 : 330 nm (4.22), 254 nm (3.97), 232 nm (3.99). Anal: Calcd. for $C_{20}H_{18}O_4Sn$: C, 54.47; H, 4.11. Found: C, 54.41; H, 4.06.

Synthesis of β -diketonate Pd(II) and Pt(II) complexes.

For the synthesis of the Bis(1-phenyl-1,3- butanodionate)M(II) complexes where M= Pt or Pd, a method reported by W. Lin et al. was used [24]. To an aqueous solution of NaOH (250 mg in 10 mL) is added benzoylacetone (2 mmol) under constant stirring. After the addition of 1 mmol of the corresponding metal salt, PdCl₂ or PtCl₄, the mixture is stirred for 24 h at room temperature. The crude product is filtered and dried under vacuum, after which is purified by passing through a column packed with silica gel. The solvent is evaporated at room temperature until crystals are obtained. The pure complexes were characterized by FT-IR and elemental analysis.

(a) Bis(1-phenyl-1,3- butanodionate)Pd(II):

FT-IR data (film) ν_{CO} 1585(s), 1545(s), 1514(s)

UV-Vis data λ (log ϵ) in CH₂Cl₂: 354 nm (4.21), 258 nm (4.55), 232 nm (4.47)

Anal. Calcd. for C₂₀H₁₈O₄Pd: C, 56.02; H, 4.23; Found: C, 56.04; H, 4.10.

(b) Bis(1-phenyl-1,3- butanodionate)Pt(II):

FT-IR data (film) ν_{CO} 1580(s), 1518(s), 1486(s)

UV-Vis data λ (log ϵ) in CH₂Cl₂: 310 nm (4.56), 250 nm (4.28), 232 nm (4.21)

Anal. Calcd. for C₂₀H₁₈O₄Pt: C, 46.42; H: 3.51; Found: C, 46.21; H, 3.49.

Preparation of amorphous thin films

Thin films of the precursors complexes were prepared by the following procedure: a silicon chip was placed on a spin-coater. A portion (0.2 ml) of the solution of β -diketonate complex in CH₂Cl₂ was dispensed onto the silicon chip which was then rotated at a speed of 1500 rpm. Once the solvent evaporated, the motor was stopped and a thin film of the complex remained on the chip. The quality of the thin films was examined by optical microscopy (1000x magnification).

Photolysis of complexes as films on Si (100) surfaces.

All photolysis experiments were done following the same procedure. Here is the description of a typical experiment. A film of the diketonate complex was deposited on p-type Si(100) by spin-coating from a CH₂Cl₂ solution. This resulted in the formation of a smooth, uniform coating on the chip. The FT-IR spectrum of the starting film was first obtained. The chip was then placed under a UVS 254 nm lamp. After the FT-IR spectrum showed no evidence of the starting material, the chip was rinsed several times with dry acetone to remove any organic products remaining on the surface, prior to analysis. When glass substrates were used for deposition, the progress of the reactions was monitored by UV-Vis spectroscopy.

RESULTS AND DISCUSSION

The electronic spectra of thin films of the Sn⁺² complexes exhibited bands at 254 and 330 nm aprox. The observed absorption bands have been assigned to the various electronic transitions, the band at 254 nm corresponding to LMCT transition (ligand-to-metal charge transfer) while the absorption at 330 nm being assigned to an intraligand $\pi \rightarrow \pi^*$ transition. Although the photochemistry of several transition metal β -diketonates has been extensively investigated [25,26], no reports can be found in the literature concerning Sn complexes. We therefore carried out experiments to evaluate the photosensitivity of the Bis(1-phenyl-1,3-nonanedionato)Sn(II) complex in solution and as a film. In a previous paper we reported that when dichloromethane solutions of this complex were photolyzed with 254 nm UV light, a complete disappearance of the absorption bands of the complex could be observed after 30 min of irradiation [19]. This result demonstrates that the Sn diketonate complex is highly photoreactive in solution and that the photochemistry is initiated through the irradiation of the LMCT band at 254 nm.

In order to investigate the solid state photochemistry, films of the Sn complex were deposited on ITO glass by spin-coating and irradiated under air atmosphere with a 254 nm UV source. This led to the decrease of the absorptions associated with the ligand, as shown by the UV-Vis monitoring of the reaction (Fig. 1).

Fig. 1. Changes in the UV spectrum of Bis(1-phenyl-1,3-nonanedionato)Sn(II) complex thin film deposited on ITO glass upon ~7 min irradiation with 254 nm light (30 seg intervals).

The as-deposited tin oxide thin films on Si(100) substrate obtained by irradiation of Sn(II) diketonate complex were characterized by Auger electronic spectroscopy. In the AES spectrum (Fig. 2) is possible to observe a well resolved doublet signal at 423.8 and 432.2 eV corresponding to the Sn MNN transition assigned as ($M_4N_{45}N_{45}$) and ($M_5N_{45}N_{45}$). On the other hand, the oxygen signal was observed at 510.6 eV and associated to the $KL_{23}L_{23}$ transition. It has been established in some works [27,28] that the doublet signal for Sn in oxidized form appears clearly defined at 425 and 432 eV and the oxygen transition has been assigned to 510 eV. On the other hand, results reported for Sn metallic have indicated that the doublet signal is less resolved and shifted to higher energy values by approximately 5 eV. Values of 430 and 437 eV have been reported [27,28]. According to these results the as-deposited films show the formation of Sn in the oxidized form in an intermediate state, with little or nothing of Sn metallic present. Furthermore, an analysis after bombardment with Ar⁺ ions, showed only the presence of Sn in a 45.4% and oxygen in a 54.6%, with no signs of carbon contamination in the as-deposited films. The intensity ratio between the O and Sn Auger signals corresponds to a composition of SnO_{1.2}. The oxygen stoichiometry was estimated from the ratio of the Auger peak-to-peak heights of the O(KLL) line at a kinetic energy of 510.6 eV and the low-energy feature of the Sn(MNN) doublet at 423.8 eV.

Attempts to get an XRD spectrum of the as-deposited films were unsuccessful, which demonstrate the amorphous character of these films. Only after annealing at 900°C for 2 h in a continuous flow of synthetic air, X-ray diffraction peaks could be observed, at 2θ angles of 26.61, 33.89 and 37.95 degrees associated with the (110), (101) and (200) planes of tetragonal SnO₂ [JCPDS 21-1250].

Auger spectrum of the annealed film was determined and is shown in Fig. 3. It shows that the annealing treatment changes the shape of the Sn doublet and the O/Sn intensity ratio significantly, which results in a composition of approximately SnO_{1.9}. This broadening of the original peaks due to annealing may be attributed to different chemical environments of the tin atoms. Similar line distortions have been reported for as-deposited and annealed SnO_x films prepared by ion-beam assisted deposition [29].

Fig 2. Auger survey spectrum of an as-deposited SnO_x film (220 nm thick) photodeposited from Bis(1-phenyl-1,3-nonanedionato)Sn(II) after sputtering with Ar^+ for 120 s.

Fig 3. Auger survey spectrum of a SnO_x film (220 nm thick) photodeposited from Bis(1-phenyl-1,3-nonanedionato)Sn(II) and annealed at 900°C for 2 h under a flow of synthetic air.

AFM analysis revealed that the as-deposited SnO_x films (thickness = 220 nm) have a rough surface morphology with a rms roughness of 17.7 nm ($R_{\text{max}} = 226$ nm) as shown in Fig 4. In these films, grains are not well packed on the substrate, leaving relatively large mesopores in the films, and consequently having high porosity. These results are important since it has been reported that thickness and porosity of semiconductor films strongly influence the gas sensing properties to CO , H_2 and LPG [7].

Fig 4. AFM micrograph of an as-deposited amorphous SnO_x film photodeposited on Si(100) from Bis(1-phenyl-1,3-nonanedionato)Sn(II). Image size: $10 \times 10 \mu\text{m}$. Z-scale: 1000.0 nm.

Characterization of Metal (M)-loaded SnO_x thin films (M= Pt or Pd).

Precursor films were prepared by dissolving Bis(1-phenyl-1,3-nonanedionato)Sn(II) with 10, 30 and 50% of Bis(1-phenyl-1,3-butanedionato)M(II) (where M= Pt or Pd) (with respect to Sn complex) in CH_2Cl_2 and spin-coating at 1500 rpm on a silicon(100) substrate. After examination of the films by optical microscopy (1000x magnification), they were irradiated under a UV light (254 nm) for 48 h under air atmosphere. The FT-IR spectrum of the precursors deposited on Si(100) was easily detected and was used to monitor the reaction throughout the photochemical process. The loss of starting material was clearly evident, and at the end of the photolysis, after a 48 h irradiation period, there were no detectable absorptions associated with the diketone ligands in the FT-IR spectrum.

Pd-loaded SnO_x thin films.

Auger electron spectra for Pd loaded SnO_x films (10, 30, 50% of Pd) are represented in the Figs 5(a), 5(b) and 5(c) respectively. AES analysis for tin metal, establish that the $\text{M}_4\text{N}_{45}\text{N}_{45}$ transition for metallic Sn appears weakly in the form of doublet and shifted to higher kinetic energy (430 and 437 eV) with regard to the oxidized form of the Sn. These displacements to higher energy (near 5 eV), are observed for the as-deposited 10% Pd- SnO_x films, whose spectrum shows signals due to Sn $\text{M}_4\text{N}_{45}\text{N}_{45}$ transitions at 431.5 and 438.8 eV. This is also the case for the oxygen $\text{KL}_{23}\text{L}_{23}$ transitions which are observed at 518.7 eV. The positions of the most prominent tin peaks for the as-deposited 30% Pd- SnO_x films at 425.7 and 433.9 eV (rather than 430 and 437 eV for metallic tin) indicate that tin is primarily in an oxide form, and the good resolution of the doublet indicates that little or no metallic tin is present [30].

With respect to as-deposited 50% Pd- SnO_x thin films, the positions of tin signals corresponding to $\text{M}_4\text{N}_{45}\text{N}_{45}$ transitions are again shifted, appearing at 432.7 and 441.8 eV, whereas the oxygen KLL transitions are observed at 520.8 eV. Some authors [27,31] have attributed this finding to the presence of metallic Sn at the surface which leads to chemically shifted Auger lines. However, in our study no evidence for metallic Sn could be found. The change of the Sn Auger lines may be related to an intermediate and not fully relaxed oxidation state of the Sn atoms. The results confirm earlier conclusions that the chemical shift of Sn $\text{M}_4\text{N}_{45}\text{N}_{45}$ transitions band between SnO and SnO_2 is small and difficult to distinguish [27]. The C signals at 275 eV are most likely due to residual hydrocarbon contamination from organic precursors during photolysis.

Normally, the values for Pd M_{45}VV transitions are found between 330-336 eV [32]. In the Pd loaded films prepared here, this MVV Auger structure is found at 327.5 eV, and is rather well defined for pure Pd and but not for PdO. It is difficult to locate with precision the maximum of the MVV AES peak for PdO [32]. However, it is clear that its mean kinetic energy position is shifted in this case. The evolution of the $[\text{O}]/[\text{Sn}]$ composition ratio has been evaluated from intensity ratio $\text{I}(\text{O})/\text{I}(\text{Sn})$ where $\text{I}(\text{Sn})$ represents the peak area of Sn $\text{M}_4\text{N}_{45}\text{N}_{45}$ transition and $\text{I}(\text{O})$ the peak area of O KLL transition. This means that the information about the chemical composition of the structure only concerns the relative variation of the $[\text{O}]/[\text{Sn}]$ composition ratio and not its absolute value. This data for each element and a semi quantitative estimate of the composition of the films are shown in Table 1.

Fig 5. Auger survey spectra of photodeposited SnO_x films loaded with a) 10%Pd, b) 30%Pd and c) 50%Pd.

Table1. AES and AFM data for as-deposited Pd and Pt loaded SnO_x films.

	SnO_x	10% Pd SnO_x	30%Pd SnO_x	50%Pd SnO_x	10%Pt SnO_x	30%Pt SnO_x	50%Pt SnO_x
Auger Electron Energy (eV)							
Sn $M_{45}N_{45}N_{45}$	432.2	438.8	433.9	441.8	433.3	437.7	437.3
Sn $M_{55}N_{45}N_{45}$	423.8	431.5	425.7	432.7	424.8	429.8	429.4
O $KL_{23}L_{23}$	510.6	518.7	511.8	520.8	510.6	516.0	516.2
Pd $M_{45}VV$	---	333.6	330.3	336.4	---	---	---
Pt	---	---	---	---	64.4	62.4	62.3
% Additive AES							
Pd	---	7.84	22.26	37.26	---	---	---
Pt	---	---	---	---	12.91	28.55	53.0
[O]/[Sn]							
Surface	0.98	3.00	1.20	1.03	1.58	0.85	1.25
$\text{Ar}^+{}^1$	1.20	2.89	0.78	1.17	1.15	0.71	0.95
AFM Roughness							
Rms (nm)	17.7	34.9	54.4	28.0	19.7	3.60	14.8

¹ sputtering with Ar^+ for 120 s

In the table, from the evolution of the $[O]/[Sn]$ composition ratio one can observe that varies between 1.20 and 0.78 for most part of the photodeposits obtained. This means that the films consist of mixed phases of tin oxide, favoring mainly the formation of SnO .

Figs 6(a), 6(b) and 6(c) compare typical morphologies of the as-deposited revealed by AFM, and the images presented correspond to samples of SnO_x films loaded with 10, 30 and 50% of Pd respectively. We may observe in the 10% Pd- SnO_x films a flat surface with some Pd clusters with sizes ranging between 50 and 2000 nm aprox. deposited in some sectors over the surface.

Fig 6. AFM micrographs of as-deposited Pd loaded SnO_x films on Si(100) (a) 10% Pd loaded (b) 30% Pd loaded and (c) 50% Pd loaded tin oxide. Image size 10x10 μ m. With z-scale of 1000.0 nm.

The 30%Pd- SnO_x films show a rougher surface with increase agglomeration of clusters, with sizes varying between 50-1000 nm aprox. These clusters, although smaller than those found for 10% Pd- SnO_x , are distributed over a bigger surface area and therefore the rms roughness increases considerably, from 35 nm for the 10% Pd- SnO_x to 54.4 nm for the 30% Pd- SnO_x films.

Finally, we can observe that the 50% Pd- SnO_x films present a homogeneous distribution of clusters covering the entire surface. However the size of these clusters diminishes to 20-500 nm aprox. This translate into smaller rms

roughness (28.0 nm) when compared to SnO_x films with lower Pd content.

Pt-loaded SnO_x thin films.

Figs 7(a), 7(b) and 7(c) show the AES survey derivative spectra of SnO_x films loaded with 10, 30 and 50% of Pt respectively. It has been reported that the signals for Sn MNN transitions for Sn/Pt alloys, can be found between 428-430 and between 436-437 eV [30,33]. However, these energy displacements can vary depending on the synthesis conditions and composition of the sample. On the other hand, the Pt transitions can be found in a wide range of kinetic energy (25-300 eV) [30].

For the different photodeposits analyzed it was found that the $M_{45}N_{45}$ and $M_{545}N_{45}$ transitions assigned to Sn appear at 433 and 424 eV for the as-deposited 10% Pt - SnO_x , and at 437 and 429 eV for the as-deposited 30% Pt- SnO_x and 50% Pt- SnO_x . The signals pertaining to oxygen $KL_{23}L_{23}$ transition were located at 510 eV for the 10% Pt- SnO_x films and at 516 eV for the 30% Pt- SnO_x and 50% Pt- SnO_x films. Finally, the peaks associated to Pt in metallic state were found at 62 and 64 eV. All these results are shown in Table 1.

Fig 7. Auger survey spectra of photodeposited SnO_x films loaded with a) 10%Pt, b) 30%Pt and c) 50%Pt.

The [O]/[Sn] composition ratio obtained from each signal intensity, fluctuates between 1.58 and 0.71 for the different films. Just as in the previous case, intermediate Sn oxidation states exist, favoring the formation of SnO, more than the complete formation of SnO₂. The AES semi quantitative analysis gave the following results for Pt composition present in the as-deposited films: 12.9, 28.6 and 53.0%, values which correspond to the initial percentages of the mixtures prepared of the precursors (10, 30 and 50% of Pt).

Figs. 8(a), 8(b) and 8(c) compares AFM typical morphologies corresponding to as-deposited SnO_x films loaded with 10, 30 and 50% of Pt respectively. For the 10% Pt-SnO_x films it is observed that the Pt particles are distributed evenly throughout the surface, in comparison to Pd containing films. On the other hand, the size of the Pt particles is small and quite uniform (20-80 nm) compared to Pd clusters having a wide size range (50-2000 nm). However, the 30% Pt-SnO_x films present a significant change in surface morphology, with a flat and porous surface in which the Pt clusters are no longer observed indicating that the distribution of Pt on the SnO_x films appears to be very homogeneous and amorphous. The values of rms roughness for 30% Pt-SnO_x films (3.60 nm) are lower than those found for 10% Pt loaded films (19.7 nm). On the other hand, the 50% Pt-SnO_x films present a less flat and more porous surface, with a rms roughness value of 14.8 nm, and a homogeneous distribution of Pt throughout the surface. These findings are consequent with the AES semi quantitative analysis results, which showed that the percentages of Pt in the initial mixture are maintained in the final deposits. This characteristic can be attributed to the amorphous character shown by the precursor Pt complex when spin coated on the Si substrate. This is not the case for the Pd precursor complex which showed a more crystalline character, and this would explain the formation of clusters in the surface and its random distribution, in the as-deposited Pd-loaded SnO_x films.

(a)

(b)

(c)

Fig 8. AFM micrographs of as-deposited Pt loaded SnO_x films on Si(100) (a) 10% Pt loaded (b) 30% Pt loaded and (c) 50% Pt loaded tin oxide. Image size 10x10 μm. With z-scale of 1000.0 nm.

The presence of some pollutants such as carbon, may come from the photofragmentation of the precursor complexes during photolysis. The formation of species MC⁺ (where M = Pd or Pt) has been documented [34]. The absorption of light may cause dissociation of the M—O bonds and the formation of MC⁺, probably from the abstraction of a carbon atom from another β-diketonate complex.

CONCLUSIONS

Pd and Pt loaded SnO_x thin films have been successfully prepared by direct UV irradiation of amorphous films of β-diketonate complexes on Si(100) substrates. As-deposited films were characterized by Auger Electronic Spectroscopy (AES). Sn M₄N₄₅N₄₅ Auger transitions of as-deposited and thermally treated films show significant differences in peak shape, which are most likely due to differences in oxidation states of Sn. The Auger peak intensity ratios of O KL₂₃L₂₃ to Sn M₄N₄₅N₄₅ showed that as-deposited films consist of mixed tin oxide phases whereas annealed films consist mainly of single phase SnO₂. This is important since it has been reported that tin oxide films with mixed phases are better than single phase films for gas sensors [35].

The surface characterization using Atomic Force Microscopy (AFM) revealed that the microstructure of the films was significantly affected by loading with noble metal. Metal-loaded tin oxide films have a much rougher surface than unloaded tin oxide films, with rms roughness values ranging from 28-54 nm for Pd-SnO_x films to 3.6-20 nm for Pt-SnO_x films. As-deposited Pt-SnO_x films present homogeneously distributed grains and nanosize porosity whereas as-deposited Pd-SnO_x films showed a random distribution of grain size. These results demonstrate the potential use of these photochemically produced semiconductor oxide films in gas-sensing devices.

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REFERENCES

- [1] A.S. Ryzhikov, R.B. Vasiliev, M.N. Rumyantseva, L.I. Ryabova, G.A. Dosovitsky, A.M. Gilmudinov, V.F. Kozlovsky, A.M. Gaskov, *Mater. Sci. Eng. B* 96 (2002) 268.
- [2] H. Gong, Y. Wang, Z. Yan, Y. Yang, *Mater. Sci. in Semicond. Proc.* 5 (2002) 31.
- [3] H.W. Ryu, B.S. Park, S. Akbar, W.S. Lee, K.J. Hong, Y.J. Seo, D.C. Shin, J.S. Park, G.P. Choi, *Sens. Actuators B* 96 (2003) 717.
- [4] P. Mitra, H.S. Maiti, *Sens. Actuators B* 97 (2004) 49.
- [5] D.H. Kim, S.H. Lee, K.H. Kim, *Sens. Actuators B* 77 (2001) 427.
- [6] C.H. Shim, D.S. Lee, S.I. Hwang, M.B. Lee, J.S. Huch, D.D. Lee, *Sens. Actuators B* 81 (2002) 176.
- [7] M.H. Madhusudhana Reddy, A.N. Chandorkar, *Thin Solid Films* 349 (1999) 260.
- [8] A. Cabot, J. Arbiol, J.R. Morante, U. Weimar, N. Barsan, W. Gopel, *Sens. Actuators B* 70 (2000) 87.
- [9] R. Díaz, J. Arbiol, A. Cirera, F. Sanz, F. Peiro, A. Cornet, J.R. Morante, *Chem. Mater.* 13 (2001) 4362.
- [10] R. Díaz, J. Arbiol, F. Sanz, A. Cornet, J.R. Morante, *Chem. Mater.* 13 (2002) 3277.
- [11] C. Bittencourt, E. Llobet, P. Ivanov, X. Correig, X. Vilanova, J. Brezmes, J. Hubalek, K. Malysz, J.J. Pireaux, J. Calderer, *Sens. Actuators B* 97 (2004) 67.
- [12] S. Gupta, R. K. Roy, M.P.M. Pal Chowdhury, A. K. Pal, *Sens. Actuators B* 75 (2004) 111.
- [13] S. Capone, P. Siciliano, F. Quaranta, R. Rella, M. Epifani, L. Vasanelli, *Sens. Actuators B* 77 (2001) 503.
- [14] B. Esfandyarpour, S. Mohajerzadeh, S. Famini, A. Khodadadi, E. Asl Soleimani, *Sens. Actuators B* 100 (2004) 190.
- [15] P. Montmeat, C. Pijolat, G. Tournier, J-P. Viricelle, *Sens. Actuators B* 84 (2002) 148.
- [16] A. Salehi, *Sens. Actuators B* 96 (2003) 88.
- [17] G.E. Buono-Core, M. Tejos, J. Lara, F. Aros, R.H. Hill, *Mater. Res. Bull.* 34 (1999) 2333; G.E. Buono-Core, G. Cabello, B. Torrejon, M. Tejos, R.H. Hill, *Mater. Res. Bull.* 40 (2005) 1765; G.E. Buono-Core, M. Tejos, G. Cabello, N. Guzman, R.H. Hill, *Mater. Chem. Phys.* 96 (2006) 98.
- [18] G.E. Buono-Core, M. Tejos, G. Alveal, *J. Mater. Sci.* 35 (2000) 4873; G.E. Buono-Core, M. Tejos, G. Cabello, F. Aros, R.H. Hill, *Bol. Soc. Chil. Quim.* 47 (2002) 495.
- [19] G.E. Buono-Core, G. Cabello, J.L. Cayon, M. Tejos, R.H. Hill, *J. Chil. Chem. Soc.* 50 (2005) 541.
- [20] J.T. Adams, C.R. Hauser, *J. Am. Chem. Soc.* 66 (1944) 1220.
- [21] C.R. Hauser, T.M. Harris, *J. Org. Chem.* 30 (1965) 1007.
- [22] Kai Ming Chi, Chia- Ch'I Lin, Ya-Hui Lu, Ju Hsiou Liao, *J. Chin. Chem. Soc.* 47 (2002) 425.
- [23] H.K. Shin, K.M. Chi, J. Farkas, M.J. Hampden, T.T. Kodas, E.N. Duesler, *Inorg. Chem.* 31 (1992) 424.
- [24] L. Weibin, C.B. Wiegand, R.G. Nuzzo, G.S. Girolamy, *J. Am. Chem. Soc.* 118 (1996) 5977.
- [25] B. Marciniak, G. Buono-Core, *J. Photochem. Photobiol. A: Chemistry* 52 (1990) 1.
- [26] R. L. Lintvedt in "Concepts of Inorganic Photochemistry," A.W. Adamson y P.D. Fleischauer Eds., John Wiley & Sons, New York, Chap. 7, p. 299 (1975).
- [27] A. Lin, N. Armstrong, T. Kuwana, *Anal. Chem.* 49 (1977) 1228.
- [28] S.K. Sen, S. Sen, C.L. Bauer, *Thin Solid Films* 82 (1981) 157.
- [29] W.K. Choi, J.S. Cho, S.K. Song, H.J. Jung, S.K. Koh, K.H. Yoon, C.M. Lee, M.C. Sung, K. Jeong, *Thin Solid Films* 304 (1997) 85.
- [30] G. Hoflund, D. Asbury, *Thin Solid Films* 129 (1985) 139.
- [31] R. Ramamoorthy, M.K. Kennedy, H. Nienhaus, A. Lorke, F.E. Kruis, H. Fissan, *Sens. Actuators B* 88 (2003) 281.
- [32] M. Brun, A. Berthet, J.C. Bertolini, *J. Electron Spectrosc. Related Phenom.* 104 (1999) 55.
- [33] R. Bouwman, L.H. Toneman, A.A. Holscher, *Surf. Sci.* 35 (1973) 8.
- [34] P. Muraoka, D. Byun, J.I. Zink, *Coord. Chem. Rev.* 208 (2000) 193.
- [35] S.H. Park, Y.C. Son, W.S. Willis, S.L. Suib, K.E. Creasy, *Chem. Mater.* 10 (1998) 2389.