STUDY OF THE OXYGEN AND SUBSTRATE BIAS EFFECTS ON THE DEFECT STRUCTURE OF REACTIVE SPUTTER-DEPOSITED SnO_X FILMS

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Abstract

The effects of oxygen and substrate bias on the defect structure of reactive sputter-deposited $SnOx$ films were investigated. Samples were analysed using transmission electron microscopy (TEM), transmission electron diffraction (TED), X-ray diffraction (XRD) and positron annihilation spectroscopy (PAS). The oxygen played an important role in the film growth and surface morphology. TEM, TED and XRD showed that increasing of the oxygen partial pressure leads to the formation of films with different crystal phases. The void sizes also depended on oxygen partial pressure. The positron lifetimes and their relative intensities depended on the void concentration, the partial annealing of the vacancies and oxidation of SnO to $SnOx$. This investigation also showed that the mechanical strength of the films obtained at negative substrate bias is higher and the concentration of vacancy defects is smaller, than in the films prepared without substrate bias.

1. Introduction

In the recent years the research interest to SnO_X thin films has been renewed due to their industrial applications [1-7]. Specific uses have been found in liquid crystal displays, heated car windscreens, as a tool of ensuring mechanical reaction stability of glass bottles, transparent heat reflectors in sodium or incandescent lamps and as high quality optical elements [2]. Especially SnO_2 films are of great technological interest as transparent electrodes and as heat-reflecting filters, since in SnO_2 there is a high energy gap (3.6 eV) and it may possess high carrier concentrations [4,6].

The properties of deposited films are influenced by many factors which favour specific microstructures. Some of the most important factors affecting the microstructure of sputtered films are: kind and temperature of the substrate, rate of deposition of the condensing atoms, pressure of the working gas, substrate surface roughness, substrate bias and bombardment of the surface by ions or electrons. The changes in the film properties depend on the conditions of annealing, especially temperature range, time period and gaseous atmosphere (air, oxygen,

argon, vacuum, hydrogen). So, the properties of the films depend strongly on the preparation mode of and could vary considerably depending on the specific character of the technique used [7].

The present study is meant to contribute to the effect of oxygen and substrate bias on the defect structure of sputter deposited SnO_x films. The study was carried out using transmission electron microscopy (TEM), transmission electron diffraction (TED), X-ray diffraction and positron annihilation spectroscopy (PAS). Using PAS is provoked by the presence of point defects. Several studies have supposed that dislocations and vacancies play a major role in determination of the thin films properties (see, for example, refs. 8-13).

2. Experimental

2.1 Samples

The SnO_x films with thickness, d, of 1 μm, were deposited on tin plates of diameter 20 mm by d.c. reactive magnetron sputtering in argon-oxygen atmosphere at different oxygen partial pressures. The film thickness and deposition rate, v_d, have been measured during the deposition using a quartz oscillator MIKI FFM. The substrate temperature was not controlled during the deposition, but it was permanently <100 °C. The total pressure was kept constant ($P_{total}=8x10^{-3}$ mbar). Two kind of films were obtained-without substrate bias and at bias of -120 V. The source material was 99.99% pure tin. The samples were left to cool at room temperature after deposition before being removed from the vacuum system. Table I summarizes the deposition parameters of the samples studied. The last column in the Table I electric current was kept constant (I = 0.3 A). The films have been devided into four sets according to partial oxygen pressure.

TABLE I. DEPOSITION PARAMETERS OF THE SAMPLES STUDIED

	Sample	Bias a) (V)	d b) (μm)	P_{O2} x10^{-4} c) (mbar)	O_2 d) (mol %)	v_dx10^{-4} e) (μm/s)	N, f) (W)	Class g)
Set I								
	1	0	1	5.0	6.2	18.0	90	A
	1*	-120	1	5.0	6.2	18.0		B
Set II								
	2	0	1	8.0	10.0	6.5	84	A
	2*	-120	1	8.0	10.0	6.5		B
Set III								
	3	0	1	11.0	13.7	0.7	75	A
	3*	-120	1	11.0	13.7	0.7		B
Set IV								
	4	0	1	14.0	17.5	0.4	78	A
	4*	-120	1	14.0	17.5	0.4		B

a) Substrate bias in volts
b) Sample thickness in microns
c) Oxygen partial pressure during deposition
d) Oxygen concentration
e) Deposition rate
f) Target sputtering power
g) Sample classification using the A/B scheme described in the text

2.2 X-ray, TEM and TED measurements

X-ray diffraction studies were performed using a URD6 (DDR) difractometer with monochromatic CuK_α radiation. The TED patterns were obtained by electron microscope ÝMB 100 Ë at accelerating voltage of 75 kV. The films for these measurements had been deposited on <100> oriented single KCl crystals and were detached from the substrate by dissolving KCl substrate in distilled water.

2.3. Positron annihilation

For positron lifetime measurements, two identical samples were used. $^{22}NaCl$ radioactive source, sealed between two thin (0.723 mg/cm^2) kapton foils, was sandwiched by the samples. The positron lifetime spectrometer used is based on a fast-fast type coincidence circuit and provides 260 ps time resolution (FWHM). The activity of the source was (13±1) μ Ci. About $1.2x10^6$ counts were collected for each spectrum. The samples were measured at least four times. The spectra have been analyzed by Positronfit Extended Program. The lifetime spectra were corrected for source lifetime components by the computer program LAYER, based on the Monte Carlo method [15, 16]. To get the net effect of the positron annihilation in the films, two types of lifetime measurements were done for positron incidences from the film side and from the substrate side of the samples ("face-to-face" and "back-to-back" case correspondingly).

In the back-to-back case only one positron lifetime is needed to fit the spectra. This lifetime, τ_3 , was kept constant in the face-to-face spectra processing with 3 lifetimes. To minimized the scattering of the results the ratio $(I_1+I_2)/I_3$ was fixed to the value obtained by LAYER for the fraction of positrons annihilating in the SnO_x films. All the samples were measured as-obtained except for the sample #1 (class A) which was measured twice, the second time after low temperature annealing.

In addition to the positron lifetime we have also measured the Doppler broadening of the 511 keV annihilation γ-line using a high purity germanium detector of energy resolution 1.17 keV FWHM at 514 keV gamma line of ^{85}Sr. Each spectrum, containing more than 10^6 counts was collected for 10^4s. Eight spectra have been recorded for each pair of samples.

The annihilation gamma line was characterized by the usual shape S and W parameters. The S parameter is defined as a ratio of the counts from the annihilation line central region ($0<|\Delta E_\gamma|<0.933$ keV) and the total counts number N_{tot} in the line. The W parameter is the ratio of the counts in the annihilation line (2.33 keV$<|\Delta E_\gamma|<$7.31 keV) wings and N_{tot}. S(W) parameter for the face-to-face case can be written as [17]

$$S = f\, S_{film} + (1-f)\, S_{sub}$$
$$W = f\, W_{film} + (1-f)\, W_{sub}$$

where f is the fraction of positrons annihilating in the film and $S_{film}(W_{film})$ and $S_{sub}(W_{sub})$ are characteristics of the film and the substrate respectively. As the film thickness is the same for all samples (f=const) we have not separated the S_{film} (W_{film}) from S(W). All conclusions based on S(W) values are valid for $S_{film}(W_{film})$ as well. By checking linearity of the S parameter versus the W parameter Liszkay et al [12] introduce a method for analysing data which directly show that the same vacancy defect could be present in all the films.

FIG. 1. TEM micrograps (magnification, x30000) and TED patterns of samples 1, 2, 3 and 4.

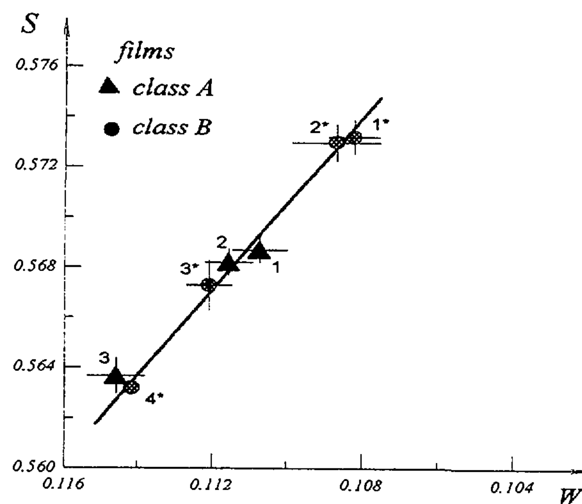

FIG. 2 Annihilation parameter S as a function of annihilation parameter, W, in vacuum d.c.magnetron sputtering thin SnO_x films

3. Results and discussion

Tin oxide films are usually composed of a mixture of different phases. The dominant phase depends sensibly on the deposition and/or annealing conditions. When the substrate is amorphous, the magnetron d.c. reactive sputtering technique usually leads to amorphous highly defective tin oxide films with α-Sn precipitates [6]. Variations in the substrate temperature T_s change the film structure from amorphous to crystalline [5]. The formation of SnO can be prevented by introducing oxygen during deposition. In our TEM studies the substrates have been <100> oriented single KCl crystals and SnO_x layers were polycrystalline.

3.1 TEM, TED and X-ray diffraction studies

i) Figure 1 a-d show TEM micrographs of films, deposited at different partial oxygen pressures. It is evident that oxygen plays an important role in the film growth as it was shown in [18]. The film surfaces, deposited at $P_{O2} = 5x10^{-4}$ mbar (Figure 1- a) indicate a very small-sized polycrystalline structure and a smooth surface. The surface morphology of film, deposited at $P_{O2} = 8x10^{-4}$ mbar (Figure 2- b) differs considerably from that one of the first type of films. They are homogeneous too, but the grain size is larger. TEM micrographs of films, deposited at $P_{O2} = 1.4x10^{-3}$ mbar shows a coarse grain structure (Figure 1-d).

In Figure 1 a-d the selected area of electron diffraction patterns are presented too.The majorα-Sn, SnO and SnO_2 reflections have been identified. Diffraction data provide evidence for the presence of SnO_2 even at low oxygen concentration (6.2 mol % O_2). The Sn_2O_4 phase appears at partial oxygen pressure of $P_{O2} = 1.1x10^{-3}$ mbar (10 mol % O_2). The Sn_2O_3 phase is present in the films, obtained at $P_{O2} = 1.4x10^{-3}$ mbar (17.5 mol % O_2), while the β-Sn - phase appears only in sample 3 (13.7 % O_2).

The results from TEM and TED clearly show that increasing of the oxygen partial pressure leads to formation* of films of different grain size and a mixture of different phases. In the viewpoint of the rate of deposition, the high v_d leads to formation of small - sized structure, which is in accordance with other results.

ii) In general, X-ray diffraction studies do not allow to characterize structurally the films, because of their small thickness.

3.2. Positron annihilation lifetime (PAL) results

The PAL data for all of the samples studied are listed in Table II. For comparison, the characteristic lifetimes in Sn and SnO_2 are shown as well. In the "back-to-back" experiment only one lifetime component was found - $\tau = 204.0$ ps for samples class A and $\tau = 196$ ps for samples of class B. These values are close to the results for bulk lifetime in Sn [19,20]. In the "face-to-face" case three distinct lifetime components are necessary to fit the spectra with τ_3 fixed to the "back-to-back" value.

Only the lifetimes and their relative intensities, I_1 and I_2, for positron annihilation in the films are presented in the table.

The longer lifetime τ_2=1200-2000 ps is characteristic for pick-off annihilation of orthopositronium (o-Ps) the bound triplet state of electron and positron. As o-Ps can be formed only in comparatively large free volume holes [22] our results enable us to affirm that such large voids exist both in the films and in the interfaces between the films and their substrates and in both simultaneously.

The first lifetime τ_1=320-380 ps is considerably longer than the positron lifetime in the bulk of SnO_2 τ_b=220 ps (the results for sample 3, class A will be discussed below). Such long lifetimes are characteristic for annihilation of positrons trapped in mono- and divacancies. So,

TABLE II. PAS DATA FOR THE SAMPLES STUDIED ($\bar{\tau} = \sum_{i=1}^{N} \tau_i I_i$ IS MEAN POSITRON LIFETIME IN THE CORRESPONDING FILMS)

Sample	class	τ_1, ps	I_1, %	τ_2, ps	I_2, %	$\bar{\tau}$, ps
1	A	378(4)	84.89(4)	1960(39)	15.14(4)	617(8)
2	A	322(3)	90.55(2)	1792(55)	9.45(2))	460(6)
3	A	247(1)	94.87(4)	1197(67)	5.13(4)	296(4)
4	A	345(5)	92.86(9)	1432(162)	7.14(9)	423(14)
1*	B	319(5)	84.89(4)	1164(263)	15.11(4)	447(40)
2*	B	360(1)	97.52(2)	1346(295)	2.48(2)	409(8)
3*	B	365(5)	98.02(4)	1541(231)	1.98(4)	388(8)
4*	B	372(2)	97.59(2)	1857(288)	2.41(2)	408(8)
1 annealed for 75 min at t=130°C in air		218(5)	89(1)	1090(46)	11(1)	248(2)

Sn bulk	vacancy	
$\tau = 201$ ps [19]	$\tau = 242$ ps [19]	
199 ps [20]		
SnO_2		
$\tau_1 = 195 \pm 10$ ps	$I_1 = 78.9 \pm 6.3\%$	[21]
$\tau_2 = 463 \pm 14$ ps	$I_2 = 21.2 \pm 1.1\%$	

it could be considered that τ_1 is a mixture of at least three lifetimes - one due to free annihilation in the bulk of the films, second - due to annihilation of positrons trapped in mono- or divacancies and the third, of 125 ps, due to self annihilation of para-positronium (p-Ps the bound singlet state).

From the results shown in the table the following conclusions, concerning the quality of the films, could be made:

1. In both classes of the samples, the increase of the partial oxygen pressure leads to decrease of the concentration of the large voids (I_2 decrease). This decrease of the void concentration is accompanied by decrease of the void sizes (τ_2 decrease) in the samples of class A. This behaviour of the voids can be connected with the film grain sizes (Figure 1). Only sample #4 (class A) drops out from the above mention systematic. It is interesting to note that this film is the only one deposited after restoring the same experimental conditions in the vacuum chamber after opening. This is indicator for the well known sensitivity of the film structure relative to the strictly required experimental conditions of their preparation.

2. The void sizes in the samples of class B increase with the increase of the partial oxygen pressure (τ_2 increases).

3. The contribution of trapped positron annihilation in τ_1 decreases in the samples of class A (τ_1 decrease) with increasing of the P_{O2}.

4. Taking into account the relatively large contribution (about 5%) of p-Ps annihilation in τ_1 for sample #1*, class B, which caused a considerable decreasing of τ_1 it can be consider

that the kind of vacancies able to trapped positrons in all samples of class B is the same (τ_1 is almost independent of P_{O2}).

5. The small value of τ_1 for sample #3, class A, the most probably is connected with the presence of β-Sn phase in the film (see section 3.1).

6. The changes of lifetimes and their relative intensities after annealing of sample #1, class A, (see table 2) can be explained by the decreasing of void concentration, the partial annealing of the vacancies and oxidation of the SnO to SnO_2. The last statement is based on the proximity of τ_1 to the value of bulk lifetime of positrons annihilating in SnO_2. Of course, the value of τ_1 remained larger than that required from the trapping model [23]. This is due to incomplete annealing of the vacancies in the film.

3.3. Doppler broadening of annihilation line

The S-parameter as a function of the W-parameter is shown in Figure 2 As can be seen all experimental points fit well to straight line of slope R=1.7±0.1. According to [12] if the measured (S_{film}, W_{film}) values in the different films lie on the same straight line on the (S, W) plane, the types of the defects in the samples are similar.

Our results show that the mechanical strength of the films obtained at negative substrate bias is higher, the adhesion of films to substrates is higher and the concentration of vacancy defect smaller than in films prepared without substrate bias. This is due to ion bombardment of the films during their deposition.

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References

1. E. Leja, T. Pisarkiewicz and A. Kolodziej, Thin Solid Films, 67, p. 45 (1980)
2. H. De Waal and F. Simonis, Thin Solid Films, 77, p. 253 (1981)
3. P. Grosse and F. J.Schmitte, Thin Solid Films, 90, p. 309 (1982)
4. J. Geurts, S. Rau, W. Richter and F. J. Schmitte, Thin Solid Films, 121, p. 217 (1984)
5. D. Das and R.Banerjee, Thin Solid Films, 147, p. 321 (1987)
6. F.C.Stedile, B.A.S.De Barros,Jr., C. V. Barres Leite, F. L. Freire, Jr., I. J. R. Baumvol and W. H. Schreiner, Thin Solid Films, 170, p. 285 (1989)
7. L.I. Popova, M. G. Michailov and V.K.Georgiev, Thin Solid Films, 186, p.107 (1990)
8. R.L. Frost, A.B.Dewald, M.Zaluzec, J.M.Rigsbee, B.Nielsen and K.G.Lynn, J. Vac. Sci. Technol., A8, 4, p.3210 (1990)
9. C.Lopez Gil, M.F.Ferreira Margues, A.P. de Lima, M.T.Vieira and A.Cavaleire, Materials Science Forum, vols. 105-110, p.1137 (1992)
10. J.P.Schaffer, A.J.Perry and Brunner, J.Vac.Sci.Technol., A10, 1, p.193 (1992)
11. J. Brunner, A.J.Perry, J.P.Schaffer and W.D.Sproul, Materials Science Forum, vols.105-110, p.913 (1992)
12. A.Liszkay, C.Corbel, L.Baroux, P.Hautojarvi, M.Bayhan, A.W.Brinkman and S.Tatarenko, Appl.Phys.Lett.64, 11, p.1380 (1994)
13. N.Nancheva, P.Docheva, N.Feschiev, M.Misheva and N.Djourelov, Scripta Metallurgica et Materialia, vol.33, 4, p.575 (1995)

14. P.I.Docheva, PhD Thesis, Technical University, Russe (1991)
15. R.B.Gregory and W.Su, Nucl.Instr.Meth. in Phys. Res., B62, p.1 (1991)
16. R.B.Gregory and W.Su, Mat.Sci.Forum, vols.105-110, p.1875 (1992)
17. K.Saarinen, P.Hautojarvi, J.Keinonen, E.Rauhala, J.Raisanen and C.Corbel, Phys. Rev.B43, 4249 (1991)
18. K.Suzuki and M.Mizuhashi, Thin Solid Films, 97, 119 (1982)
19. K.P.Gopinathan, World Scientific Publ. Co. Pte. Ltd. Singapore, p. 527 (1985)
20. M.A.Monge and J. del Rio, J. Phys.: Cond. Matter, 6, p. 2643 (1994)
21. M.Bertolaccini, A.Bisi, S.Gambarini and C.Zappa, J.Phys.C: Solid State Phys., vol.4, 734 (1971)
22. H.E.Schaefer, R.Wurschum, R.Birringer and H.Gleiter, Phys.Rev.B38,14, 9545 (1988)
23. A.Vehanen, P.Hatojarvy, J.Johansson, J.Jli-Haupala and P.Moser, Phys.Rev. B(1982)762