Bulgarian Journal of Physics 25 Nos 3/4 (1998) 171-176

A STUDY OF DEFECT STRUCTURE OF SPUTTER-DEPOSITED SnO_x FILM USING THE DOPPLER BROADENING OF THE ANNIHILATION LINE*

N. NANCHEVA, P. DOCHEVA
Department of Physics, Technical University
7017 Rousse, Bulgaria

M. MISHEVA, N. DJOURELOV
Faculty of Physics, University of Sofia
5 J. Bourchier Blvd, 1164 Sofia, Bulgaria

Received 4 April 1997

Abstract. SnO_x films, grown on tin substrates via d. c. magnetron sputtering have been studied using Doppler broadening of the annihilation line. The results showed that the oxygen and the substrate bias play an important role in the film growth. The mechanical strength and the adhesion of the films obtained at negative substrate bias are higher.

PACS number: 78.70.Bj 68.55-a

1. Introduction

The research interest to SnO_x thin films has been renewed due to their industrial applications [1-7]. Especially SnO_2 films are of great technological interest as transparent electrodes and as heat-reflecting filters, because SnO_2 has a high energy gap (3.6 eV) and it can possess high carrier concentrations [4, 6]. A previous series of papers [1-7] reported data received by a variety of techniques. However, the properties of the films depend strongly on the mode of preparation and could vary considerably from one technique to another [7].

The purpose of the present study is to investigate the effect of oxygen and substrate bias on the defect structure of sputter deposited SnO_x films. The investigation was carried out using Doppler broadening of annihilation line (DBAL). The reason for using positron annihilation is that it responds to the presence of point defects. Many studies have suggested that dislocations and vacancies play a major role in determining the properties of thin films (see, for example, Refs [8-13]).

*This work is dedicated to the late Assoc. Prof. M. Minev (Technical University, Rousse).

2. Experimental

The SnO_x films, with thickness d of 1 μm, were deposited on tin plates of diameter 20 mm by reactive d. c. magnetron sputtering in argon-oxygen atmosphere at different oxygen partial pressures. The oxygen concentration was in the range of 6.2–17.5 %. 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 always $T < 100\,°C$. The total pressure was kept constant ($P_{total} = 8 \times 10^{-3}$ mbar). Two kinds of films were obtained: without substrate bias and at a bias of -120 V. The source material was 99.99 % pure tin. The films were allowed to cool to room temperature after deposition before being removed from the vacuum system. Table 1 summarizes the deposition parameters of the samples studied. The last column in the Table 1 gives the film classifications (A or B) based on the bias voltage. During the deposition the current was kept constant ($I = 0.3$ A). The target sputtering power N was in the range of 75–90 W. For more detailed study of the influence of negative substrate bias a second set of samples has been prepared at the same conditions as sample 1 and bias from -40 V to -140 V.

Table 1. Deposition parameters of the samples studied

	Sample No	Bias (V)	d (μm)	$P_{O_2} \times 10^4$ (mbar)	O_2 (%)	$v_d \times 10^4$ (μm/s)	N (W)	Class
Set I	1	0	1	5.0	6.2	18.0	90	A
	1*	−120	1	5.0	6.2	18.0		B
	2	0	1	8.0	10.0	6.5	84	A
	2*	−120	1	8.0	10.0	6.5		B
	3	0	1	11.0	13.7	0.7	75	A
	3*	−120	1	11.0	13.7	0.7		B
	4	0	1	14.0	17.5	0.4	78	A
	4*	−120	1	14.0	17.5	0.4		B
Set II	5	−40						
	6	−60						
	7	−80	1	5.0	6.2	18.0	90	A
	8	−100						
	9	−120						
	10	−140						

The 511 keV annihilation line was measured 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 10^4 s. Eight spectra have been recorded for each pair of samples. Due to the Doppler effect, the width of the 511 keV annihilation line is dependent on the momentum distribution of the annihilating electron-positron pair. Since the electrons move, on the average, slower in open-space defects than where the ions are more dense, the positron localization in defects gives a narrowing of the annihilation line. Thus a sharpening of the centre of the Doppler distribution about the 511 keV value indicates trapping and annihilation at defects (vacancies, dislocations, voids or grain boundaries).The wing regions of the

spectrum represent annihilation events with higher energy core electrons [14]. The line shape is different for different materials and it is also sensitive to positron trapping by lattice defects. Various line shape parameters (S, H, W) characterizing the width of the annihilation line are used [15, 16]. Changes of these parameters can be used to follow various phenomena like the defect concentration of the samples. The momentum density narrowing that results from positron-defect trapping is presented in Fig. 1. The cross-hatched areas illustrate the regions of integration involved in the peak height S and in the tail or wing W parameter.

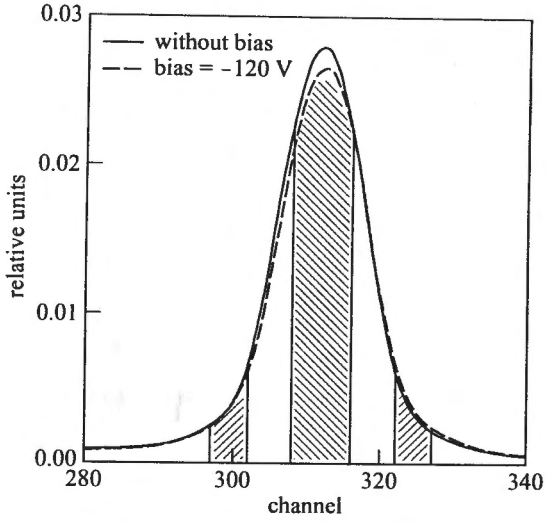

Fig. 1. Doppler-broadened energy spectra of samples 1 and 10

In our investigation 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 in 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}.

3. Results and Discussion

It is well-known that, in general, an increase in S corresponds to an increase in the defect concentration of the sample [15]. Our results from the momentum distribution showed that S and W parameters vary from one sample to the other. According to [10] the measured $S(W)$ can be presented as

$$S = fS_{\mathrm{f}} + (1 - f)S_{\mathrm{s}} \tag{1}$$

where $f = 0.11$ is the part of positrons annihilating in the film [17], S_{f} and S_{s} are the values of the S parameter in the film and substrate, respectively. For all samples

studied f and S_s are constants. It is obviously from (1) that in this case the variations of S and S_s are the same. Because of this we used only the measured $S(W)$ parameter.

We have many problems with the adhesion of the samples class A. This is the reason that the dependence of $S = F(P_{O_2})$ and $S = F(v_d)$ for the samples class B are presented in Figs 2 and 3. From Fig. 2 it is clear that the increasing of the oxygen partial pressure leads to decreasing of the S parameter (defect concentration). The increasing of the deposition rate v_d leads to the increasing of S parameter (Fig. 3), i. e. the oxygen pressure and deposition rates influence defect concentrations in the opposite way.

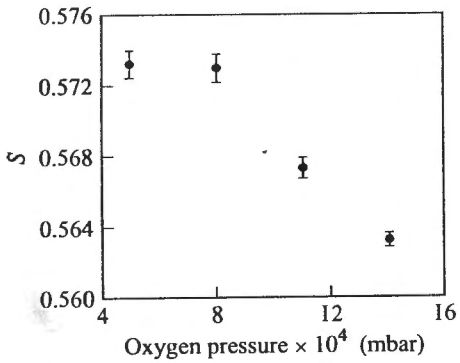

Fig. 2. Annihilation S parameter of samples of class B (Set I) as a function of partial oxygen pressure

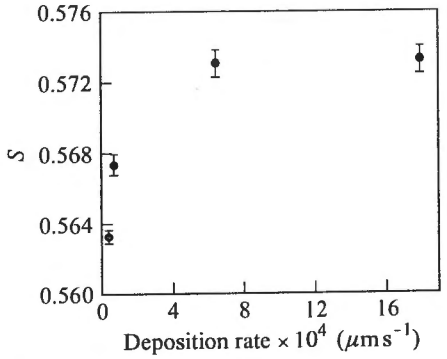

Fig. 3. Annihilation S parameter of samples of class B (Set I) as a function of deposition rate

Liszkay et al. [12] suggested a method for data analysis which directly shows that the same vacancy defect can be present in a set of samples by checking the linearity of the S versus W parameter. The S parameter is associated mainly with the annihilation of free-positrons with valence electrons and positrons, trapped in a vacancy or in a vacancy cluster and self-annihilation of p-Ps. W parameter is associated with the annihilation of positrons with core electrons and pick-off annihilation of o-Ps. If the regions, used for the calculation of S and W parameters are not adjacent, as it is in the present case, a linear relationship between S and W can occur in two cases:

(i) If in the samples, besides annihilation of free positrons, there exist only one type of defects trapping positrons. In the case of existing of several types of defects, one of them must be predominant [12].

(ii) If it can be assumed that several annihilation species are formed in the samples at $t = 0$, and they proceed to annihilation without interconversion, provided that certain relationships between the relative concentration of the species exist [18].

Figure 4 presented the annihilation parameter S as a function of the annihilation parameter W. As it can be seen all experimental points fit well to the straight line of slope $R = 1.7 \pm 0.1$. According to [18] this means that all samples have the same defect structure.

In Figure 5 $S = F(W)$ dependence is presented for samples of Set II. All experimental points again fit well to the straight line of slope $R = 1.1 \pm 0.1$, i. e. these

samples have the same defect structure but it is different from the dependence of the samples of Set I.

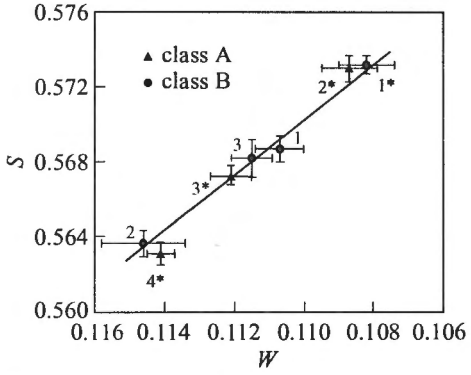

Fig. 4. The S parameter as a function of a W parameter for samples of Set I

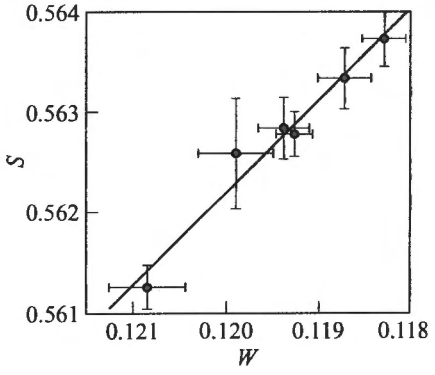

Fig. 5. The S parameter as a function of W parameter for samples of Set II

The variation of the S with bias voltage is presented in Fig. 6. This dependence is in accordance with the results of Zhang et. al. [19] about the variation for the resistivity with bias voltage. From the figure it is clear that increasing of the negative substrate bias leads to decreasing of defect concentration. In our opinion this is due to the "compressing" effect of Ar^+ positive particles bombardment when the substrate has a negative bias potential [20].

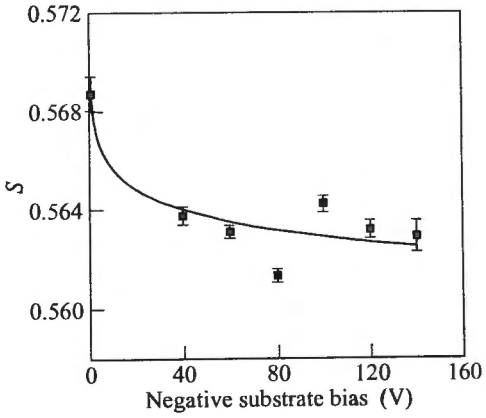

Fig. 6. Annihilation S parameter as a function of the values of negative substrate bias for samples of Set II

4. Conclusion

1. Oxygen plays an important role in the film growth. The increasing of partial oxygen pressure leads to decreasing of defect concentration.
2. Samples prepared at different partial oxygen pressure (Set I) and samples prepared at different negative substrate biases (Set II) have different defect structures.

3. The mechanical strength and the adhesion of the films obtained at negative substrate bias are higher.

Work is in progress to clarify the influence of the substrate bias in detail.

Acknowledgements

This work has been supported in part by the National Science Fund, Ministry of Education and Science (Bulgaria) under Contract F486.

References

1. E. Leja, T. Pisarkiewicz, A. Kolodziej. *Thin Solid Films* **67** (1980) 45.
2. H. De Waal, F. Simonis. *Thin Solid Films* 77 (1981) 253.
3. P. Grosse, F. J. Schmitte. *Thin Solid Films* **90** (1982) 309.
4. J. Geurts, S. Rau, W. Richter, F. J. Schmitte. *Thin Solid Films* **121** (1984) 217.
5. D. Das, R. Banerjee. *Thin Solid Films* **147** (1987) 321.
6. F. C. Stedile, B. A. S. De Barros, Jr., C. V. Barres Leite, F. L. Freire, Jr., I. J. R. Baumvol, W. H. Schreiner. *Thin Solid Films* **170** (1989) 285.
7. L. I. Popova, M. G. Michailov, V. K. Georgiev. *Thin Solid Films* **186** (1990) 107.
8. R. L. Frost, A. B. Dewald, M. Zaluzec, J. M. Rigsbee, B. Nielsen, K. G. Lynn. *J. Vac. Sci. Technol.* **A8 4** (1990) 3210.
9. C. Lopez Gil, M. F. Ferreira Margues, A. P. de Lima, M. T. Vieira, A. Cavaleiro. *Materials Science Forum* **105–110** (1992) 1137.
10. J. P. Schaffer, A. J. Perry, J. Brunner. *J. Vac. Sci. Technol.* **A10** (1992) 193.
11. J. Brunner, A. J. Perry, J. P. Schaffer, W. D. Sproul. *Matenrials Science Forum* **105–110** (1992) 913.
12. A. Liszkay, C. Corbel, L. Baroux, P. Hautojarvi, M. Bayhan, A. W. Brinkman, S. Tatarenko. *Appl. Phys. Lett.* **64 11** (1994) 1380.
13. N. Nancheva, P. Docheva, N. Feschiev, M. Misheva, N. Djourelov. *Scripta Metallurgica et Materialia* **33** (1995) 575.
14. Positrons in Solids (Ed. P. Hautojarvi, Springer-Verlag, Berlin Heidelberg New York 1979).
15. I. K. Mac Kenzie, J. A. Eady, R. R. Gingerich. *Phys. Lett.* **A33** (1970) 279.
16. J. L. Campbell. *Appl. Phys.* **13** (1977) 365.
17. N. Nancheva, P. Docheva P. Hadjijska, M. Misheva, N. Djourelov, D. Elenkov. *Scripta Metallurgica et Materialia* **37** (1997) 1957.
18. M. Misheva, N. Djourelov, F. M. A. Margaca, I. M. Miranda Salvado, G. Passage. *J. Phys.: Conds. Matter* **8** (1996) 6313.
19. H. Zhang, Y. Zhang, W. Xu. *Vacuum* **45** (1994) 145.
20. J. F. Smith. Microwaves & RF (1982) 54.