Thin Solid Films, 83 (1981) 267–271
ELECTRONICS AND OPTICS

SnO_2 FILMS PREPARED BY ACTIVATED REACTIVE EVAPORATION*

H. S. RANDHAWA, M. D. MATTHEWS AND R. F. BUNSHAH
Department of Materials Science and Engineering, University of California, Los Angeles, CA 90024 (U.S.A.)
(Received March 17, 1981; accepted April 7, 1981)

Transparent conducting films of SnO_2 doped with antimony were prepared on glass substrates by activated reactive evaporation for the first time. The sheet resistance and optical transmittance in the wavelength range 0.4–1.6 μm were studied as functions of various deposition parameters such as the ambient pressure of an 85%Ar–15%O_2 mixture, the substrate temperature and the antimony doping concentration in the Sn–Sb alloys. The sheet resistance and optical transmittance showed a strong dependence on the above-mentioned deposition parameters. The best results were obtained for a 90at.%Sn–10at.%Sb alloy evaporated in 85%Ar–15%O_2 at a partial pressure of about 5×10^{-4} Torr with a substrate temperature about 350 °C. These films, with a sheet resistance of 10 Ω/□ had an average transmittance of 95% over the wavelength range 0.4–1.8 μm. The film thickness was about 0.25 μm. Thicker films (about 0.5 μm) had a sheet resistance as low as 1.5 Ω/□ with an average transmittance 85% in the wavelength range 0.4–1.6 μm.

1. INTRODUCTION

Transparent conducting SnO_2 films have attracted a considerable interest in recent years, because of their potential use in optoelectronic devices such as heterojunction solar cells, display devices and image storage devices. In addition, SnO_2 has a refractive index in the range 1.6–1.9, making it suitable as an antireflection coating on silicon.

The techniques used to date to produce these films have been summarized by Vossen[1] and Haacke[2]. Although good-quality films have been produced by sputtering, this technique has the disadvantage of being a low deposition rate process. Moreover, the films produced by sputtering require a post-deposition heat treatment in appropriate ambients[3,4]. Reactive evaporation[5], chemical vapor deposition[6] and spray pyrolysis[7] techniques have also been reported for SnO_2 films, with varying degrees of success. The films prepared by spray pyrolysis are known to have large amounts of internal stress[1] as a result of high deposition temperatures.

* Paper presented at the International Conference on Metallurgical Coatings, San Francisco, CA, U.S.A., April 6–10, 1981.

0040-6090/81/0000-0000/$02.50

Recently, Nath and Bunshah[8] have reported a modified activated reactive evaporation (ARE) process for In_2O_3 and In_2O_3:Sn films. This technique yields high rates of deposition and requires no post-deposition treatments. In the present paper we report on the use of this modified ARE process to produce high quality SnO_2:Sb films.

2. EXPERIMENTAL DETAILS

The experimental arrangement used to produce these films is shown in Fig. 1 and is similar to the set-up described by Nath and Bunshah[8] for the preparation of In_2O_3 and In_2O_3:Sn films. Alloys of Sn–(0–15)at.%Sb were prepared by vacuum melting the two constituents (99.999%) which had been weighed in the proper proportions. A resistively heated molybdenum boat was used to evaporate Sn–Sb alloys onto chemically cleaned glass substrates. The ambient gas used had a composition of 85%Ar–15%O_2. The substrates were heated to the desired temperatures using a radiant heater; the temperature was monitored with a chromel–alumel thermocouple. In order to enhance the reactivity of tin and/or Sn–Sb vapor species with O_2 gas, a dense plasma was generated in the reaction zone by employing a thoriated tungsten electron emitter and an anode assembly. The plasma was confined to the reaction zone with the help of magnetic coils.

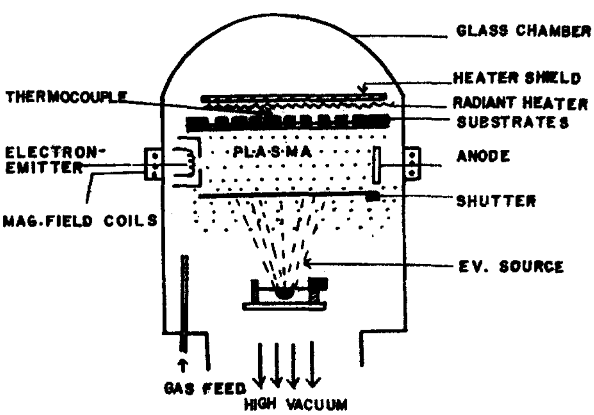

Fig. 1. The experimental arrangement employed for the deposition of SnO_2:Sb films by the ARE technique.

The transmittance spectra were recorded using a double-beam spectrophotometer. A standard four-point probe method was employed for the sheet resistance measurements.

3. RESULTS AND DISCUSSION

The transmittance spectra and the sheet resistance in SnO_2:Sb films showed marked dependences on the various deposition parameters, *i.e.* the antimony concentration, the partial pressure of the gas mixture and the deposition temperature. The variations in the sheet resistance and the optical transmittance as functions of the antimony concentration in the source material are as shown in Fig. 2. The ambient pressure of the 85%Ar–15%O_2 mixture gas was kept constant at about 10^{-4} Torr and a substrate temperature of about 300 °C was used for this purpose. The sheet resistance showed a rapid decrease with antimony concentration up to 10 at.% Sb in the Sn–Sb alloys. For antimony concentrations greater than 12 at.%, good quality films could not be obtained. The optical transmittance, however, is weakly dependent on antimony concentration. These results show that the optimum concentration of antimony for obtaining the lowest sheet resistance and the highest figure of merit (T^{10}/R_s, where T is the average transmission in the given wavelength range and R_s is the sheet resistance) is about 10 at.% in the Sn–Sb alloy. Other workers have reported this antimony concentration to be in the range 1–15 at.%, depending on the process employed[1,2,9,10].

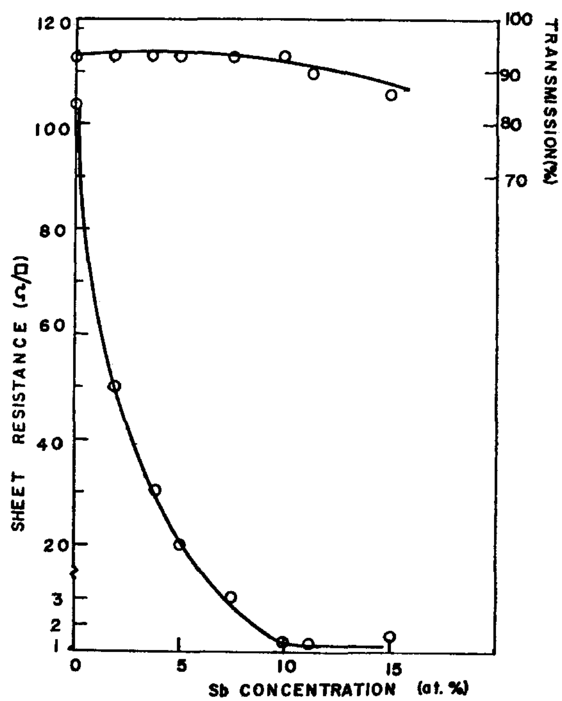

Fig. 2. Variations in sheet resistance and optical transmittance as functions of antimony concentration in Sn–Sb alloys.

The source material composition of 90at.%Sn–10at.%Sb was used for subsequent runs and the ambient pressure of 85%Ar–15%O_2 was varied while the source temperature was kept at 300 °C. The best results were obtained at an 85%Ar–15%O_2 pressure of about 5×10^{-4} Torr. These films exhibited an average transmittance of about 80% with a sheet resistance of about 5 Ω/□. A typical thickness for these films was about 0.5 μm. When an equivalent pressure of argon and a substrate temperature of about 300 °C was employed, the arrival rate of the Sn–Sb alloy at the substrate was found to be about 500 Å min^{-1}.

The substrate temperature in the vicinity of 300 °C was varied using a fixed partial pressure of 85%Ar–15%O_2 of about 5×10^{-4} Torr and an arrival rate of 90at.%Sn–10at.%Sb at the substrate of about 500 Å min^{-1}. The films deposited at 350 °C gave the best results. These films had a sheet resistance of about 1.5 Ω/□ with an average transmittance of 85% in the wavelength range 0.4–1.8 μm as shown in Fig. 3. The thickness of these 1.5 Ω/□ films was about 0.5 μm. Thinner films (about 0.25 μm) had a sheet resistance of 10 Ω/□ with an average transmittance of over 95% in the wavelength range 0.4–1.8 μm.

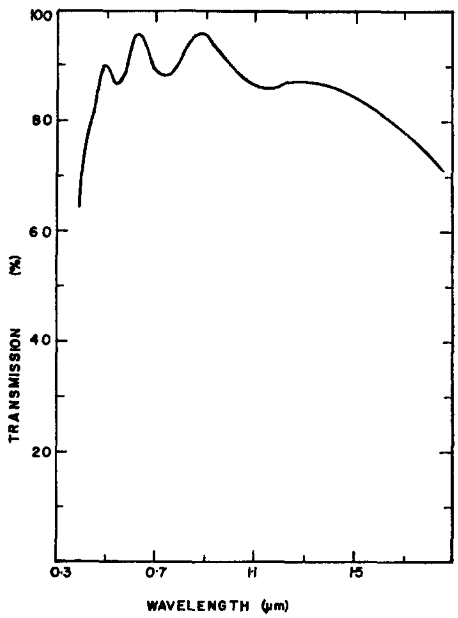

Fig. 3. Optical transmittance spectra for a typical 1.5 Ω/□ film in the wavelength range 0.4–1.8 μm.

TABLE I

COMPARISON OF THE AVERAGE OPTICAL TRANSMISSION AND SHEET RESISTANCE OF FILMS PRODUCED BY VARIOUS DEPOSITION TECHNIQUES

Process	*Material*	*Sheet resistance* (Ω/□)	*Average transmittance* (%) *in the range 0.4–1.6 μm*	*Reference*
ARE	SnO_2:Sb	10	95	Present work
ARE	SnO_2:Sb	1.5	85	Present work
ARE	In_2O_3:Sn	25	97	8
ARE	In_2O_3:Sn	2.2	88	8
Spray pyrolysis	In_2O_3:Sn	10–15	80	11
Spray pyrolysis	SnO_2:Sb	100	95	7
Reactive evaporation	In_2O_3:Sn	40–60	80	12
Reactive sputtering	In_2O_3:Sn	3–5	80	13, 14
D.c. sputter oxide	In_2O_3:Sn	2–3	80	15
R.f. sputter oxide	In_2O_3:Sn	2–3	80	16
	Cd_2SnO_4	2–3	80	17

It is of interest to compare the performance of the SnO_2 films prepared by the present technique with the transparent conducting films made by other techniques. Table I lists the results for different types of coatings prepared by a variety of techniques such as spray pyrolysis, chemical vapor deposition, reactive sputtering, reactive evaporation etc. It is seen that the SnO_2:Sb films prepared by the present technique demonstrate much better characteristics. The films have a transparency as high as 95% with a sheet resistance of 10 Ω/□. In addition to this, our technique does not require any post-deposition heat treatments. Further, the use of conventional evaporation geometry and short deposition times makes this technique an attractive and economical manufacturing technique for the production of transparent conducting films for a variety of applications, such as display devices, image storage devices and heterojunction solar cells.

In conclusion we showed that the modified ARE process can be used to produce high quality SnO_2:Sb films for use in a variety of applications.

REFERENCES

1 J. L. Vossen, *Phys. Thin Films*, *9* (1977) 1.
2 G. Haacke, *Annu. Rev. Mater. Sci.*, *7* (1977) 73.
3 W. R. Sinclair, F. G. Peters, D. W. Stillinger and S. E. Koonce, *J. Electrochem. Soc.*, *112* (1965) 1096.
4 V. M. Vaynshetyn, *Sov. J. Opt. Technol.*, *34* (1967) 45.
5 W. Spence, *J. Appl. Phys.*, *38* (1967) 3767.
6 R. F. Bartholomew and H. M. Garfinkel, *J. Electrochem. Soc.*, *166* (1969) 1205.
7 J. Kane, H. P. Schweizer and W. Kern, *J. Electrochem. Soc.*, *123* (1976) 270.
8 P. Nath and R. F. Bunshah, *Thin Solid Films*, *69* (1980) 63.
9 E. Shanthi, D. K. Pandya and K. L. Chopra, in F. de Winter and M. Cox (eds.), *Proc. International Solar Energy Society Congr., New Delhi, 1978*, Pergamon, New York, 1978, p. 698.
10 W. M. Feist, S. R. Steele and D. W. Ready, *Phys. Thin Films*, *5* (1975) 237.
11 J. Kane, H. P. Schweizer and W. Kem, *Thin Solid Films*, *29* (1975) 155.
12 D. Furuucki, *Microelectronics Society of Japan Meet.*, 1973.
13 J. M. Pankratz, *J. Electron. Mater.*, *1* (1972) 182.
14 W. W. Molzen, *J. Vac. Sci. Technol.*, *12* (1975) 99.
15 D. B. Fraser and H. D. Cook, *J. Electrochem. Soc.*, *119* (1972) 281.
16 J. L. Vossen, *RCA Rev.*, *32* (1971) 259.
17 G. Haacke, *Appl. Phys. Lett.*, *28* (1976) 622.