JOURNAL OF MATERIALS SCIENCE 24 (1989) 1305–1308

Electron spin resonance and electrical properties of co-evaporated SiO/SnO_2 thin films

M. H. ISLAM, C. A. HOGARTH, K. A. LOTT*
*Department of Physics and *Department of Chemistry, Brunel University, Uxbridge, Middlesex UB8 3PH, UK*

Electron spin resonance (ESR) measurements are reported for various compositions of SiO/SnO_2 thin films and indicate a decrease in the value of spin density for increasing SnO_2 content in the SiO. Annealing of the device further reduces the value of the spin density. The electrical activation energy and resistivity have been found to increase after annealing of the device and the results are compared with the optical and ESR measurements.

1. Introduction

The electron spin resonance (ESR) measurement is a useful technique for estimating the density of unpaired electrons on dangling bonds in thin armorphous dielectric film specimens. Timson and Hogarth [1] first reported an ESR study on thin SiO films and on composite films of SiO/B_2O_3. They found the spin density in SiO to be associated with a large number of dangling bonds (10^{18}–10^{20} cm^{-3}, depending on the rate of evaporation) and with the addition of B_2O_3 into SiO some of these bonds were saturated and the spin density decreased. Similar results have also been found [2] with the addition of other oxides such as GeO_2, In_2O_3, V_2O_5 and BaO to SiO. The dangling bond density decreased further after annealing of the device [3]. Brodsky and co-workers [4] reported a correlation between the spin density, electrical conductivity and optical band gap of the material and similar results have also been reported by Al-Ramadhan and co-workers [5] and Lewis and colleagues [6]. Chittick [7] reported that the decrease of the electrical conductivity after annealing of the device may be associated with the decrease in the value of spin density in the specimen during the annealing process.

In the present paper the ESR measurements on as-prepared and annealed films of SiO and SiO/SnO_2 are reported and an attempt has been made to correlate the results of the effect of annealing on the spin density, electrical conductivity and optical band gap.

2. Experimental work

Thin films of SiO and SiO/SnO_2 were prepared on cleaned 2 cm × 1 cm fused silica substrates which had been fused onto a special mounting to fit the ESR spectrometer. The devices for electrical measurements were made on 7059 Corning glass substrates. The composite films of SiO/SnO_2 were prepared by a co-evaporation technique [8] in a Balzers Ba510 coating unit (Berkhamstead) at a pressure of about 4×10^{-4} Pa. Two quartz crystal monitors were used in order to control the rate of evaporation of the two oxides individually. Tantalum and tungsten boats were used for SiO and SnO_2 respectively. The thicknesses of the films were measured using a Sloan Instruments Angstrometer (model M-100). The ESR and electrical measurements were made on as-prepared and annealed films. Annealing of the films was performed at 473 K in a vacuum of about 10^{-3} Pa for 2 h. The ESR measurements were made at room temperature using a Varian E3-EPR spectrometer working at X-band and at the same modulation amplitude, time constant and magnetic field scan of 3400 gauss and at a microwave frequency of 9.33 GHz. Only the amplifier sensitivity was changed as required for different samples. Calibration of the spectrometer was performed using a crystal of copper sulphate of known spin concentration (3×10^{15} cm^{-3}) and contained in a Pyrex cell. The electrical measurements were performed in a vacuum of pressure about 10^{-3} Pa and in the temperature range 294 to 383 K.

Results and discussion

Fig. 1 shows the ESR spectrum at room temperature for SiO and different compositions of SiO/SnO_2 thin films of fixed thickness ($\approx$ 260 nm), measured at $g = 2.004$. The line shapes of the ESR signal in SiO and SiO/SnO_2 thin films are nearly Lorentzian in form. The general form of the signal is the same as that for SiO except that the strength of the signal, which is proportional to the concentration of dangling bonds, decreases as the SnO_2 content increases in the composite films of SiO/SnO_2 (Fig. 1). The second integral of the curves is directly proportional to the spin density and the absolute values have been calculated by comparing with the known spin concentration of copper sulphate (3×10^{15} cm^{-3}). The calculated values of spin density for SiO and different compositions of SiO/SnO_2 are given in Table I. The value of spin density for SiO is found to be 1.5×10^{20} cm^{-3} and is in good agreement with the previously reported value [1]. The variation of spin density with the content of SnO_2 in SiO is shown in Fig. 2 (curve a) and Fig. 2 (curve b) shows the same variation after annealing of the films. It may be seen that the spin density

0022–2461/89 $03.00 + .12

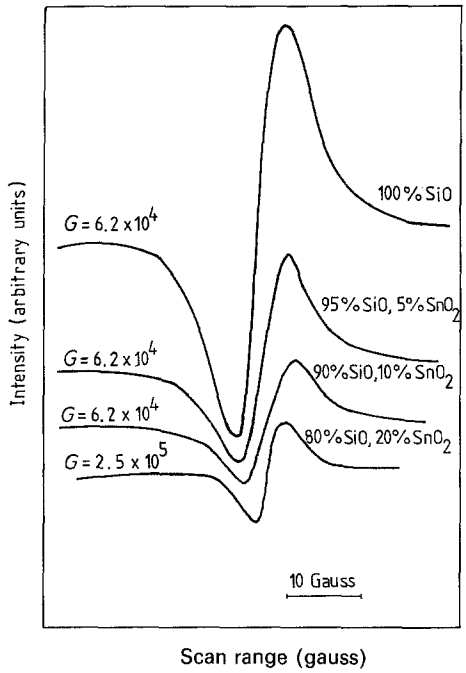

Figure 1 ESR spectrum for as-prepared SiO and SiO/SnO_2 thin films of thickness ~ 260 nm. (G = Receiver gain).

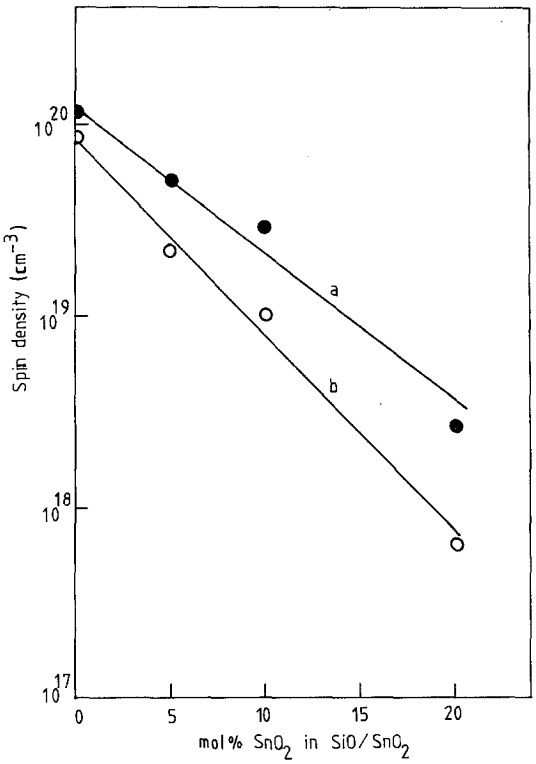

Figure 2 The variation of spin density with composition of SiO/SnO_2 films of thickness ~ 260 nm: (Curve a) before annealing (curve b) after annealing.

decreases with the increase of SnO_2 content in the films of SiO/SnO_2 and this decrease is about two orders of magnitude resulting from the introduction of 20 mol % SnO_2 into SiO. The results are similar to those reported earlier for other mixed oxide thin films [2]. This reduction in the spin density may well be due to the partial satisfying of the unpaired electrons on the dangling bonds in SiO by the addition of SnO_2.

Fig. 2 (curve b) shows that annealing of the device further reduces the spin density. This may be due to the re-arrangements of atoms and removal of some voids in the matrix as has been suggested by different authors [3, 9]. It is possible that the increase in temperature causes a softening of the material and facilitates the re-arrangments of atoms inside the lattice with a resulting successive saturation of the free valencies [10].

The effects of annealing on the current–voltage characteristics have been studied on a number of samples. All the samples were annealed in vacuum at 473 K for 2 h. Fig. 3 shows typical V–I characteristics at 296 K before and after annealing of the device. It is observed that the conductivity decreases after annealing of the film. A typical V–I characteristic (before and after annealing) at various temperatures for an Al–90 mol % SiO/10 mol % SnO_2–Al device is shown in Fig. 4. The activation energies (before and after annealing of the device) have been calculated from the plot of log I against $1/T$ (Fig. 5) according to the following relation:

$$I = I_0 \exp(-\Delta E/kT) \quad (1)$$

TABLE I The values of spin density before and after annealing for different compositons of SiO/SnO_2 thin films (thickness ~ 260 nm)

Film composition	Spin density (cm^{-3})	
	Before annealing	After annealing
100% SiO	1.15×10^{20}	8.80×10^{19}
95 mol % SiO 5 mol %	5.07×10^{19}	2.16×10^{19}
90 mol % SiO 10 mol % SnO_2	2.79×10^{19}	1.02×10^{19}
80 mol % SiO	2.52×10^{18}	6.15×10^{17}

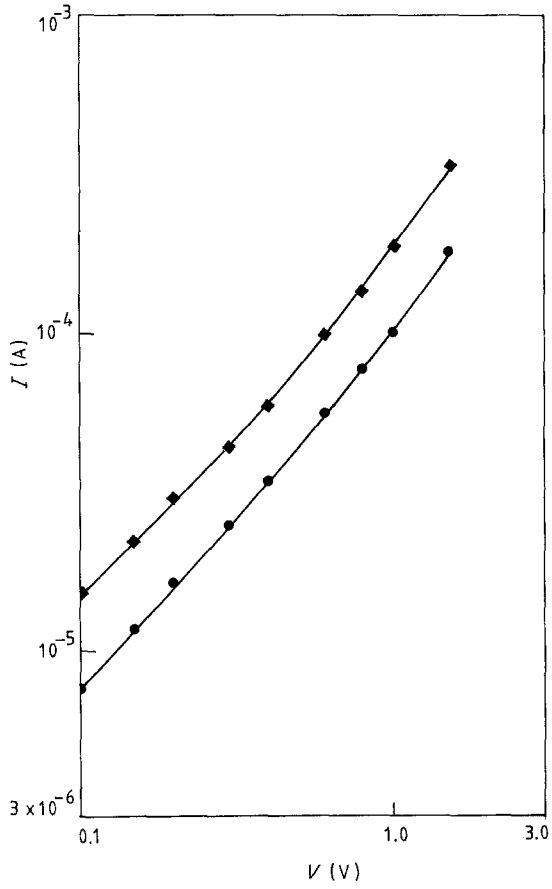

Figure 3 Effect of annealing on the V–I characteristic of an Al–90 mol % SiO/Al device with insulator thickness ~ 150 nm. (■) before annealing, (●) after annealing.

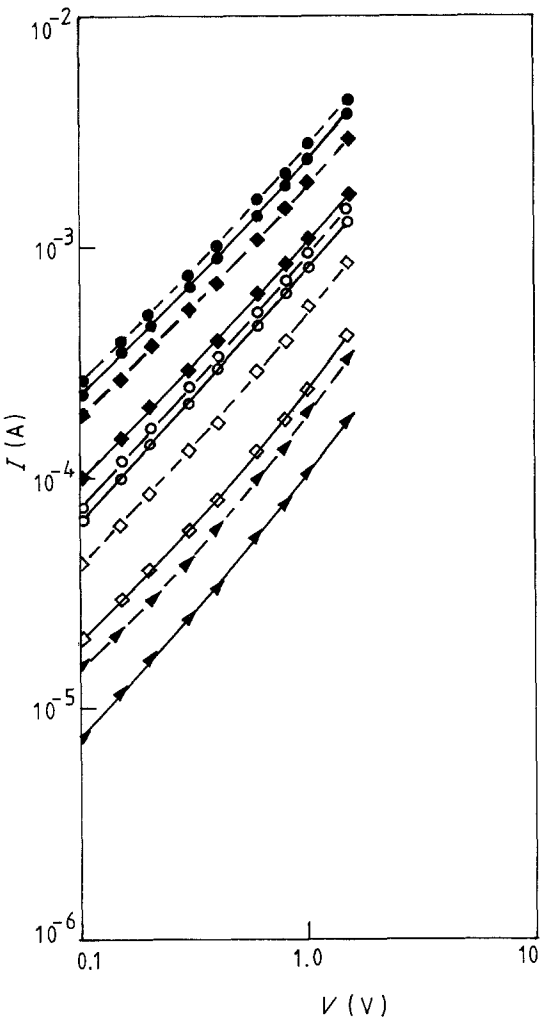

Figure 4 *V–I* characteristics (before and after annealing) at different temperatures for an Al–90 mol % SiO/10 mol % SnO_2–Al device of insulator thickness ~ 150 nm; (– – –) before annealing; (——) after annealing. Temperatures: (●) 383 K, (■) 353 K, (○) 339 K, (□) 313 K, (▲) 294 K.

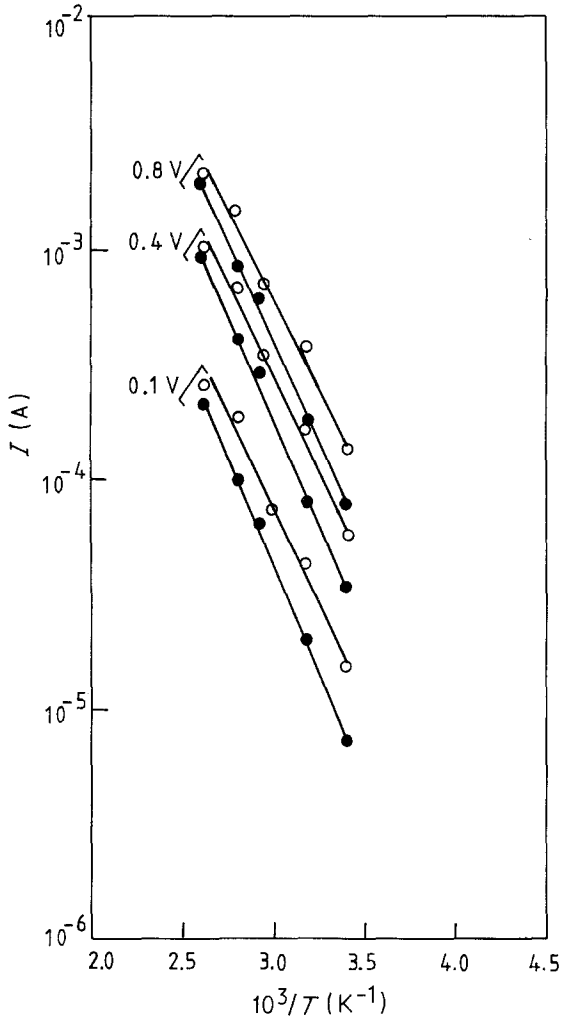

Figure 5 Plots of log *I* against 1/*T* from the data of Fig. 4, at three fixed bias voltages (○) before annealing, (●) after annealing.

where I is the current through the sample, ΔE the activation energy, k the Boltzmann constant, T the absolute temperature and I_0 is a constant.

After annealing of the device, both the activation energy and resistivity (at 296 K) are increased from 0.35 to 0.39 eV and from 3.57×10^7 to $6.25 \times 10^7\ \Omega$cm respectively. The values of the different parameters before and after annealing for a typical sample (90 mol % SiO/10 mol % SnO_2) are given in Table II. It is observed that a correlation exists between electrical conductivity, optical band gap and electron spin density. The increase of activation energy is in good agreement with the result of the optical study that the optical band gap also increased after annealing of the device. Chittick [7] and Walley and Jonscher [11] have also found in a-Ge and in a-Si that the resistivity at room temperature and high temperature activation energy increases after annealing of the samples. According to them, the annealing process appears to be associated with the removal of some defect centres or dangling bonds resulting in an increase of resistivity and activation energy. It is observed from the ESR measurements that the spin density decreased after annealing of the device (Table I) which clearly indicates that the increase of the resistivity and activation energy after annealing of the device may be due to a decrease in the density of dangling bonds.

TABLE II The values of various parameters (before and after annealing) of a 90 mol % SiO/10 mol % SnO_2 thin film

Parameter	Before annealing	After annealing
Spin density (cm^{-3})	2.79×10^{19}	1.02×10^{19}
Optical band gap* E_{opt} (eV)	1.98	2.04
Electrical activation energy (eV)	0.35	0.39
Resistivity (Ωcm)	3.57×10^7	6.25×10^7

*Islam and Hogarth [12]

References

1. P. A. TIMPSON and C. A. HOGARTH, *Thin Solid Films* **10** (1972) 321.
2. K. I. ARSHAK, PhD Thesis, Brunel University, Middlesex (1986).
3. K. I. ARSHAK and C. A. HOGARTH, *Thin Solid Films* **137** (1986) 281.
4. M. H. BRODSKY, R. S. TITLE, K. WEISER and G. D. PETTIT, *Phys. Rev.* **B1** (1971) 2632.
5. F. A. S. AL-RAMADHAN, K. I. ARSHAK and C. A. HOGARTH, *J. Mater. Sci.* **19** (1984) 3687.
6. A. J. LEWIS, G. A. N. CONNELL, W. PAUL, I. R. PAWLICK and R. J. TEMKIN, in Proceedings of the Conference on Tetrahedrally Bonded Amorphous Semiconductors, Yorktown Heights, New York (American Physical Society and IBM, New York 1974) p. 27.
7. R. C. CHITTICK, *J. Non-Cryst. Solids* **3** (1970) 225.
8. C. A. HOGARTH and L. A. WRIGHT, in Proceedings of the International Conference on Physics of Semiconductors, Moscow (Nauka, Leningrad, 1968) p. 1279.

9. M. H. BRODSKY and R. S. TITLE, *Phys. Rev. Lett.* **23** (1969) 581.
10. S. LUBY, *Thin Solid Films* **8** (1971) 333.
11. P. A. WALLEY and A. K. JONSCHER, *ibid.* **1** (1968) 367.
12. M. H. ISLAM and C. A. HOGARTH, *Phys. Status Solidi* (*a*) **99** (1986) 503.

Received 29 January
and accepted 13 June 1988