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Correlation between electron spin resonance, electrical conductivity and optical absorption edge of co-evaporated thin films of the dielectric system SiO/V_2O_5

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Measurements of electron spin resonance, d.c. and a.c. electrical conduction and optical absorption of thin film samples of SiO/V_2O_5 prepared by a co-evaporation process at a pressure in the range 8×10^{-6} to 3×10^{-5} torr are reported. It is found that the spin density of the mixed system decreases by about one order of magnitude compared with that of an SiO film deposited under similar conditions. This reduction correlates with the d.c. electrical conductivity which also decreases as the V_2O_5 content of the complex SiO/V_2O_5 films increases. At the same time the optical energy gap also decreases. At lower temperatures (down to 198 K), a.c. conductance measurements give evidence of hopping conduction. D.c. conductance shows a transition from hopping conduction to free-band (extended state) conduction at about 263 K.

1. Introduction

The addition of B_2O_3 to SiO is known to reduce the dielectric losses in the composite thin films and thus renders the films more suitable for dielectric application [1, 2]. When B_2O_3 is added to SiO the dangling bond density of the resulting films shows a sharp decrease by more than two orders of magnitude [3]; a minimum occurs at around 3% B_2O_3 and then the density slowly increases. Timson and Hogarth [4] published the results of electron spin resonance (ESR) studies on SiO films and of composite films of SiO and B_2O_3 and have found a decrease in the dangling bond density of the order of five times on the addition of B_2O_3 to SiO, and this was also consistent with the reduction in the number of conduction electrons. Recently, Ilyas and Hogarth [5] have reported on the optical absorption of the system SiO/B_2O_3 of different compositions and found that the optical energy gap increases with the addition of B_2O_3 to SiO. They argued that this effect was due to the reduction in the spin density and thus the density of unpaired electrons on unsaturated bonds and hence the band tailing decreases, resulting in an increase in the forbidden energy gap. It is generally known that the addition of other suitable oxides to dielectric oxide materials can reduce the spin density by bonding via the dangling bonds and thus they will reduce the number of electrons and hence spins on the dangling bonds. We have recently carried out measurements on GeO_2/SiO thin films [6], and have found that the reduction in the spin density associated with unpaired electrons on dangling bonds is consistent with the decrease in d.c. electrical conductivity. Where the optical energy gap decreases with the addition of GeO_2 to SiO, the latter was attributed to the localized states being extended further into the normally delocalized region on the density-of-states curve [7].

Thomas *et al.* [8] have shown that the number of spins in amorphous silicon thin films is a linear function of the thickness of the samples when the plot extrapolated to zero thickness, yielded a significant residual spin density.

Following the above work on various amorphous systems, we report measurements on the SiO/V_2O_5 thin film system which resembles to a certain extent similar properties reported previously on the system SiO/GeO_2.

2. Experimental work

The mixed films of SiO and V_2O_5 used for electrical conduction measurements were deposited on clean Corning 7059 glass substrates held at a temperature of 100 to ~ 120° C and at an ambient pressure between 8×10^{-6} and 3×10^{-5} torr in a Balzers BA 510 coating unit, using the co-evaporation technique described by Hogarth and Wright [1]. The evaporation rates were of the order of $2\,\mathrm{nm\,sec^{-1}}$. Fused silica substrates of dimensions 3 cm x 1 cm which had been fused on to a special mounting so as to fit the spectrometer were used for the ESR measurements. The optical absorption measurements were made on films of thicknesses ~ 500 nm deposited on Corning glass. For ESR and electrical measurements, thicknesses between 250 and 900 nm were used; the measurements of absorbance were made by using a Perkin–Elmer ultra-violet–visible spectrometer model 402 equipped with two source beams, the reference beam and the sample beam, to eliminate the effect of the glass substrate. ESR measurements were conducted as described in recent work [6] using a Varian E3-EPR equipment. Electrical measurements were made using conventional methods.

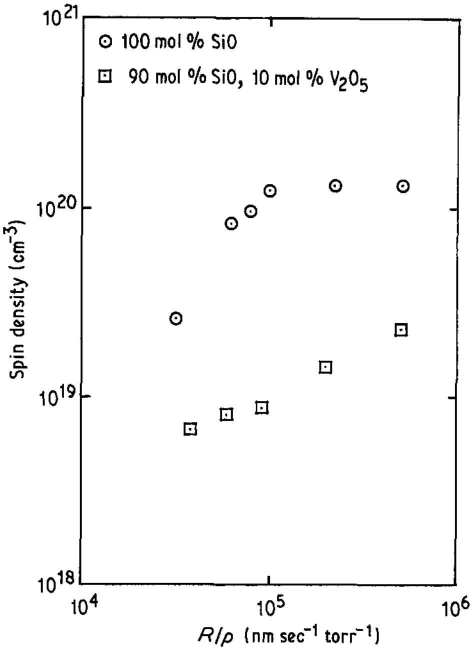

Figure 1 Spin concentration as a function of R/p for two thin films, where R is the rate of deposition and p is the total gas pressure during evaporation.

3. Results

ESR signals were measured at $g = 2.00$ for films of SiO and for the system SiO/V_2O_5. Fig. 1 shows a high spin density of the order of $10^{20}\,\mathrm{spin\,cm^{-3}}$ for SiO films only. Adding 10% V_2O_5 to the system lowered the spin density by about one order of magnitude. A lowering of the spin density by about two orders of magnitude has been observed with the increase in molar percentage of up to some 50 to 60 mol% V_2O_5 in a mixture of SiO/V_2O_5 as shown in Fig. 2. A linear relation has been obtained, Fig. 3, between the number of spins $\mathrm{cm^{-2}}$ plotted as a function of film thickness for samples having composition nominally 90 mol% SiO/10 mol% V_2O_5 and thickness of not less than 500 nm, thus establishing a bulk property of the material. Extrapolation of the lower part of the plot gives a value of $\simeq 1 \times 10^{13}\,\mathrm{spin\,cm^{-2}}$ indicative of significant residual spin density at zero thickness. From the data presented in the figure, we obtained a density of spins per unit volume of $2.33 \times 10^{19}\,\mathrm{spin\,cm^{-3}}$.

A decrease in the electrical conductivity has been noted with the increase in the molar percentages of V_2O_5 in these films as shown in Fig. 4. The temperature dependence of the electrical conductivity in the range 165 to 413 K has been measured

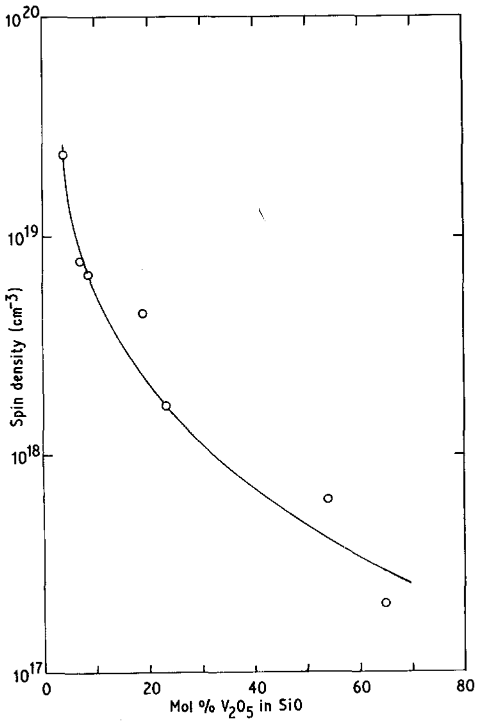

Figure 2 Variation of spin density with molar percentage of V_2O_5 in SiO thin films.

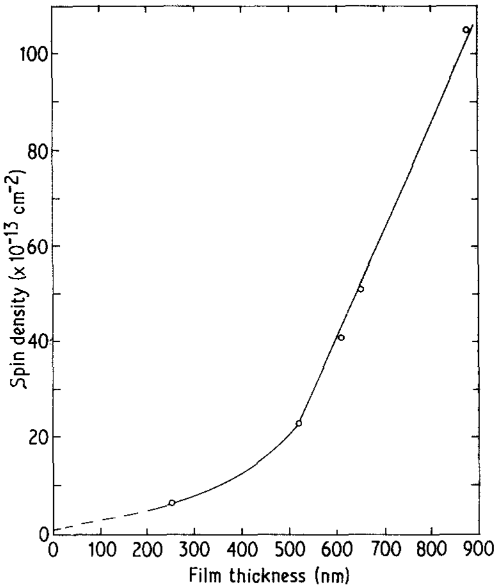

Figure 3 Dependence of area spin density on film thickness for an SiO/V_2O_5 thin film.

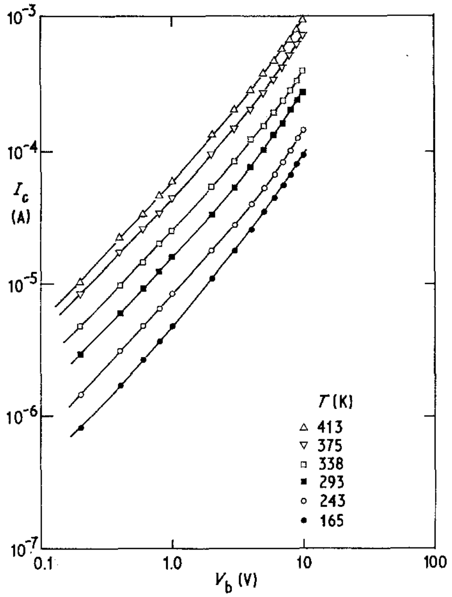

Figure 5 Voltage–current characteristics of an SiO/V_2O_5 thin film at several temperatures.

on a sample 620 nm thick and of composition 57 mol% SiO/43 mol% V_2O_5 with top and base copper electrodes, as shown in Fig. 5. Analysis of the high-field conduction has revealed that the Schottky process of conduction was dominant, with activation energy $\Delta E \simeq 0.15$ eV as shown in Fig. 6. At low temperatures between 165 and 273 K, the conductivity was found to be governed by a hopping conduction associated with an activation energy $\Delta E \simeq 0.01$ eV. The transition from hopping conduction to free-band conduction was noted at about − 10° C.

This is further confirmed by measurements of a.c. conductance G plotted against frequency f at 198 K, on a log–log scale, as shown in Fig. 7; the slope of this straight plot ($\simeq 0.6$) falls within the

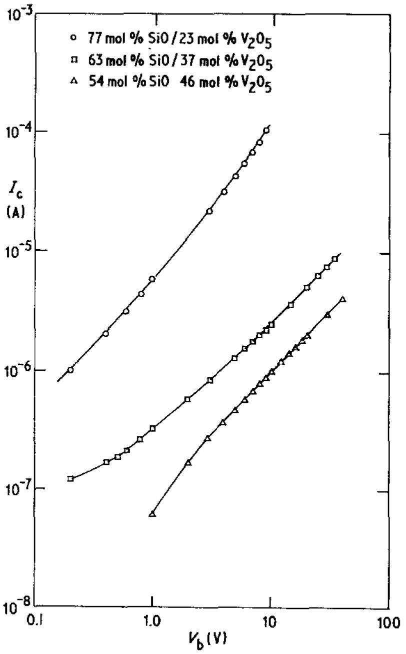

Figure 4 Dependence of circulating current (I_c) on applied voltage (V_b) for three compositions of SiO/V_2O_5 films.

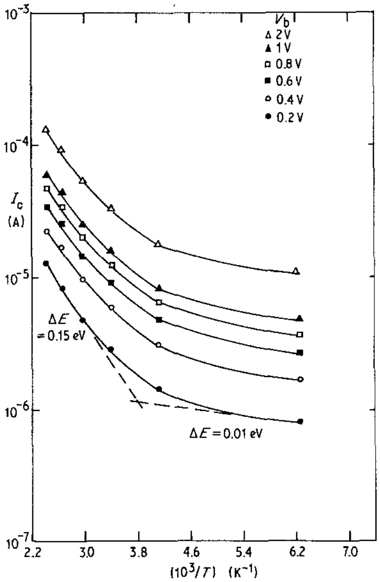

Figure 6 Circulating current (I_c) as a function of inverse temperature at different applied voltages (V_b) for an SiO/V_2O_5 thin film.

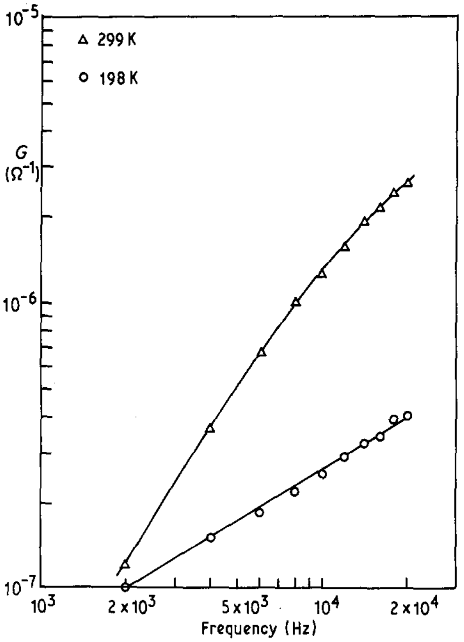

Figure 7 Dependence of a.c. conductance on frequency, measured at two temperatures for an SiO/V_2O_5 thin film ($V_{r.m.s.} = 1$ V).

limit $0.5 < s < 1$ which characterizes the presence of hopping conduction as a dominant process at low temperatures according to the Pollak and Geballe equation [9] describing this process, $\sigma(\omega) = A\omega^s$, where A is a complex constant, ω is the angular frequency, $0.5 < s < 1$, and $\sigma(\omega)$ is the conductivity at angular frequency ω. At room temperature, however, the log G/log f behaviour is not linear and therefore the conduction is not purely hopping. It contains a component which decreases with frequency, probably free-band conduction, which is known to decrease with increasing frequency.

In order to study the effect of the composition on the optical gap shifts, we have carried out measurements on samples of nominal thickness 500 nm but having different compositions. Tauc [10] showed how the shape and position of the absorption region could be represented by an equation of the form $\alpha(\omega) = A(\hbar\omega - E_{opt})^2/\hbar\omega$, where α is the absorption coefficient for non-direct transitions, ω is the angular frequency of the radiation, A is a constant, E_{opt} is the optical energy gap, and $\hbar$ is Planck's constant.

Our results were found to obey the above relation, as shown in Fig. 8, where $(\alpha\hbar\omega)^{1/2}$ is plotted against the photon energy $\hbar\omega$.

It is evident that the optical energy gap decreases as the molar percentage of V_2O_5 increases in the mixed oxides of SiO/V_2O_5 as indicated in Figs. 8a and b. This result is consistent with the earlier reported [6] value of 100% SiO film which is 2.46 eV.

4. Discussion

Reduction of the spin density of SiO films is achieved by adding V_2O_5 which tends to compensate the spins on the dangling bonds. Other methods of reducing the spin density include annealing [11], oxidation [12] and hydrogenation [13]. Results of such experiments have shown that there is a change in the shape of the absorption edge of amorphous silicon films with oxygen

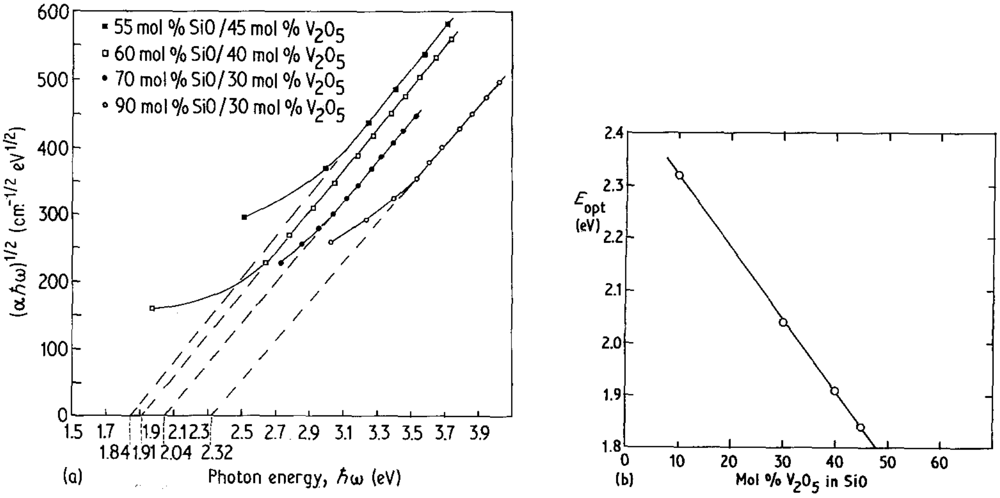

Figure 8 (a) Dependence of $(\alpha\hbar\omega)^{1/2}$ on photon energy for SiO/V_2O_5 thin films having different compositions (thickness ~ 500 nm). (b) Optical energy gap as a function of V_2O_5 content of SiO/V_2O_5 thin films.

incorporation and this leads to the conclusion that the effects of annealing and of oxygen are basically the same and are to be attributed to internal surfaces being rendered inactive. Other workers [14, 15] provided evidence that oxygen incorporation can shift the absorption edge, and Moss *et al.* [16] have found significant structural changes with ~ 10% oxygen contamination of amorphous silicon.

Our films were deposited at a pressure of the order of 8×10^{-6} to 3×10^{-5} torr which will facilitate the inclusion of some foreign atoms and oxygen incorporation into the films, thus increasing the number of localized states in the forbidden gap of the amorphous structure and probably leading to a shift of the optical absorption edge smaller than that of the pure SiO films as the composition of V_2O_5 increases in the mixed system. As reported [6, 17], the effect of dangling bonds on the optical properties is not easily calculable. The large surface area and dangling bonds should cause strain and field effects affecting the fundamental absorption edge and may vary from sample to sample because of their growth and thermal histories.

As has been seen, the thickness of the samples has a significant effect on the area density of spins of the unpaired electrons on the dangling bonds; the latter increases linearly with the thickness of the samples (500 nm and over), indicative of a bulk property of the films. This is in agreement with results reported by Thomas *et al.* [8] on evaporated amorphous silicon. Our value of $\simeq 1 \times 10^{-13}$ spin cm^{-2} of the residual spin density at zero thickness film could be due to spins on external surfaces, while the linear increase with thickness of the number of spins corresponds to spins uniformly distributed in the volume of the sample as explained by Thomas *et al.* for amorphous silicon films.

As shown in Fig. 4 the electrical conductivity decreases with the increase of molar percentage of V_2O_5 added to the system SiO/V_2O_5. At low applied voltages before the contact current saturates to the Schottky–Richardson level, the conductivity is governed by bulk processes, and at low temperatures there is insufficient energy available to excite electrons into the conduction band and the dominating transfer mechanism will be the hopping of electrons from one site to another within the localized states of the forbidden gap.

Finally, a satisfactory correlation is found to exist for all the three properties, ESR, electrical and optical, studied. For instance if the electrical conductivity is high so is the spin density and optical energy gap. Our argument above agrees with the conclusion of Bahl and Bhagat [11] with the emphasis on the incorporation of additional oxygen into the matrix as the main cause for the reduction of the optical gap, apart from its obvious effect on the electrical and ESR properties.

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References

1. C. A. HOGARTH and L. A. WRIGHT, Proceedings of the International Conference on Physics of Semiconductors, Moscow (1968) p. 1279.
2. H. VARDHAN, G. C. DUBEY and R. A. SINGH, *Thin Solid Films* 8 (1971) 55.
3. G. C. DUBEY, K. SAHU, T. R. REDDY and G. C. TRIGUNAYAT, *ibid.* 61 (1979) L17.
4. P. A. TIMSON and C. A. HOGARTH, *ibid.* 10 (1972) 321.
5. M. ILYAS and C. A. HOGARTH, *J. Mater. Sci. Lett.* 2 (1983) 535.
6. K. I. ARSHAK, F. A. S. AL-RAMADHAN and C. A. HOGARTH, *J. Mater. Sci.* 19 (1984) 1505.
7. N. F. MOTT and E. A. DAVIS, "Electronic Processes in Non-Crystalline Materials" (Clarendon Press, Oxford, 1979).
8. P. A. THOMAS, D. LÉPINE and D. KAPLAN, "Tetrahedrally Bonded Amorphous Semiconductors" (American Institute of Physics, New York, 1974) p. 47.
9. M. POLLAK and T. H. GEBALLE, *Phys. Rev.* 122 (1961) 1742.
10. J. TAUC, *Phys. Status Solidi* 15 (1966) 627.
11. S. K. BAHL and S. M. BHAGAT, *J. Non-Cryst. Solids* 17 (1975) 409.
12. S. K. BAHL, S. M. BHAGAT and R. GLOSSER, *Solid State Commun.* 13 (1973) 1159.
13. *Idem*, Proceedings of the 5th International Conference on Amorphous and Liquid Semiconductors, Garmisch, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974) p. 69.
14. S. KOC, M. ZÁVĚTOVÁ and J. ZEMEK, *Thin Solid Films* 10 (1972) 165.
15. M. L. KNOTEK and T. M. DONOVAN, *Phys. Rev Lett.* 30 (1973) 652.
16. S. C. MOSS, P. FLYNN and L. O. BAUER, *Phil. Mag.* 27 (1973) 441.
17. M. H. BRODSKY and R. S. TITLE, *Phys. Rev. Lett.* 23 (1969) 581.

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