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Electron spin resonance and some electrical and optical properties of GeO_2/SiO_x thin films

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Electron spin resonance measurements show a reduction in the spin density associated with unpaired electron dangling bonds of a mixed complex of co-evaporated GeO_2/SiO_x films compared with that of SiO_x films investigated under similar conditions. Unlike the behaviour of BaO/GeO_2 complex films, these samples show a decrease in the optical gap as the thickness increases for films of fixed compositions. However, it increases as the SiO percentage increases in films of the same thickness. D.C. measurements at low applied fields below 10^5 V cm^{-1} agree well with the spin density results.

1. Introduction

Brodsky *et al.* [1] have shown that for α-Si a correlation between the spin density, N_s, and electrical conductivity, as well as with the optical properties, exists. A similar behaviour has been observed by Lewis *et al.* [2] for sputtered α-Ge. Timson and Hogarth [3] correlated the reduction of the spin density of SiO films with the extremely high resistance for applied electric fields less than 10^5 V cm^{-1} obtained from d.c. measurements.

The present work is an attempt to correlate electron spin resonance (ESR) results with d.c. electrical measurements and the variations in optical energy gaps for films prepared under the same conditions.

2. Experimental work

Co-evaporated thin film samples of GeO_2/SiO were deposited on to 3 cm × 1 cm fused silica substrates which had been fused on to a special mounting to fit the ESR spectrometer. For optical and electrical measurements Corning 7059 glass substrates were used. All substrates were held at 100° C to improve adhesion during the evaporation process. Two quartz crystal monitors were used as described by Hogarth and Wright [4], in order to control the evaporation rates of both oxides individually, the silicon and germanium oxides being evaporated from tantulum and molybdenum boats, respectively, at a pressure of approximately 8×10^{-6} torr. Films of thickness between 240 and 730 nm were prepared at evaporation rates between 0.5 and 2 nm sec^{-1}.

Optical absorption measurements were performed at room temperature using a Perkin-Elmer Model 402 spectrometer in the ultraviolet-visible range. This was equipped with two source beams, the reference beam and the sample beam. The absorption spectrum of the evaporated films only could be obtained by cancelling the effect of the glass substrate on placing another cleaned substrate in the path of the reference beam. ESR measurements were made at room temperature. The spectrometer was a Varian E3-EPR equipment working at X-band and at the same modulation amplitude, time constant and magnetic field scan for each specimen. Only the amplifier sensitivity was changed as required by different samples.

The area of the second integral of the output signal is directly proportional to the spin density. The derived value is then used in conjunction with the specimen volume and instrument sensitivity to give a figure proportional to the spin cm^{-3}. Calibration of the spectrometer in absolute spin cm^{-3} was performed using aqueous copper sulphate solution of known spin concentration and containined in a Pyrex cell. ESR measurements were carried out on both SiO and GeO_2/SiO films at the same magnetic field of 3400 G and at a microwave frequency of 9.33 GHz.

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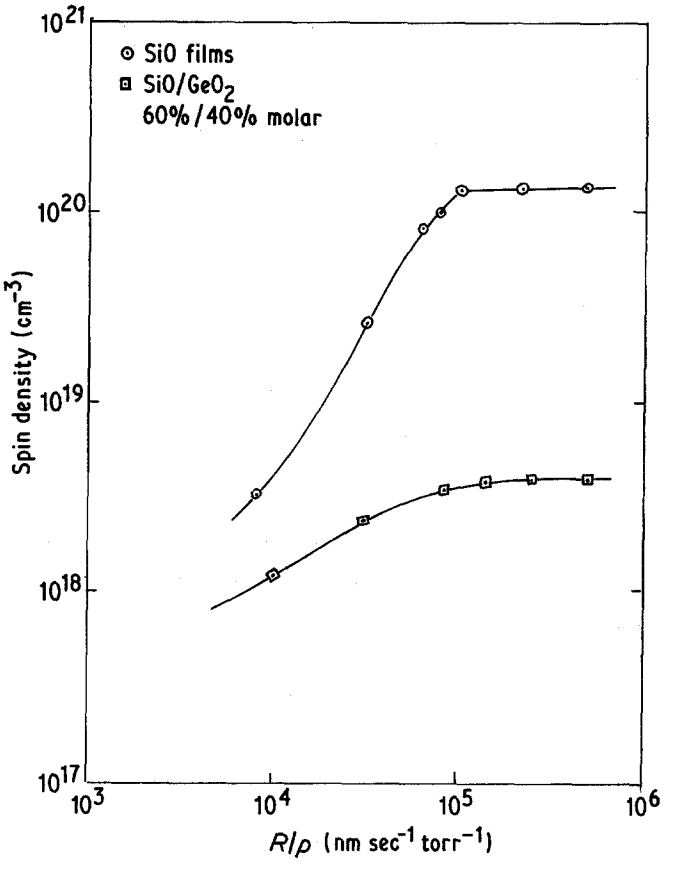


Figure 1 A plot of spin concentration against R/p for 60% SiO/40% GeO_2 thin films.

3. Results

Strong ESR signals at g = 2.00 were found in films of silicon oxide, were symmetrical and of nearly Lorentzian shape; weaker asymmetrical ESR signals were observed in films of GeO_2/SiO. Fig. 1 shows the spin density (cm^{-3}) plotted against the rate of deposition per unit ambient pressure, R/p. In the higher extremes of the parameter R/p, a high spin density for both types of films was found. At the lower extremes of R/p a lower spin density is measured. In the high extreme, the spin density of GeO_2/SiO is reduced by a factor of 35 indicative of the reduction in the numbers of dangling bonds. In the low extreme it is reduced by a factor in the range of 4 to 10. This is a consequence of the increased oxidation produced by the addition of GeO_2 to SiO. In line with the above results, direct current measurements on 782 nm thick films of GeO_2 with a composition 80% SiO/20% GeO_2 and using copper electrodes, were made. Fig. 2 shows the circulating current as a function of the applied voltage at different temperatures. At fields below 10^5 V cm^{-1} the films showed very high values of d.c. resistance in the

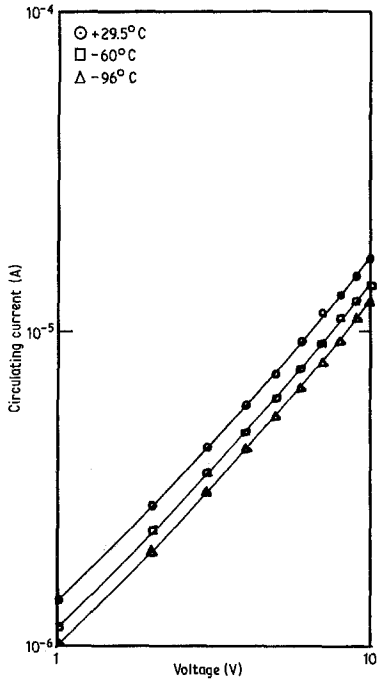
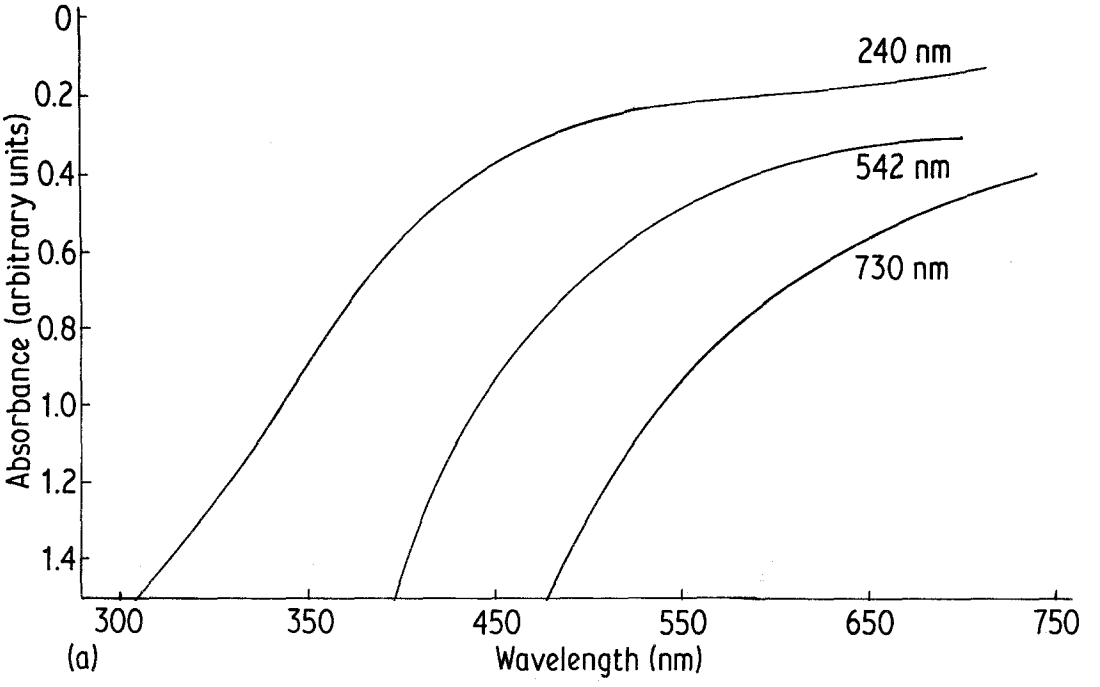


Figure 2 Current–voltage characteristic of a Cu–80% SiO/20% GeO_2–Cu film at three temperatures.



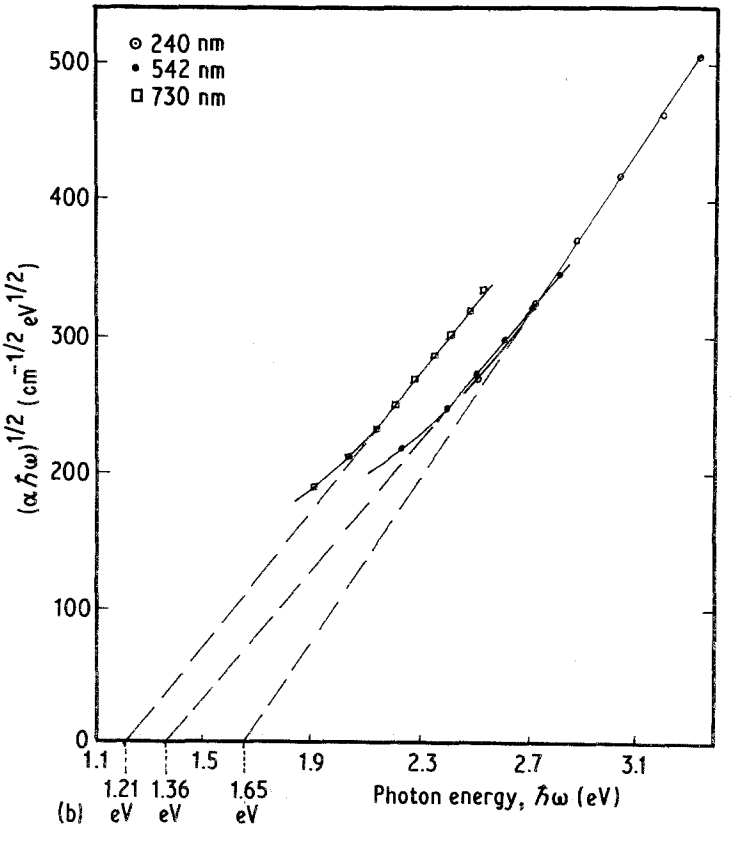


Figure 3 (a) Absorbance as a function of wavelength for samples of composition 60% SiO/40% GeO_2 and different thicknesses. (b) $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ for three samples of 60% SiO/40% GeO_2 having nominally the same composition but of different thicknesses.

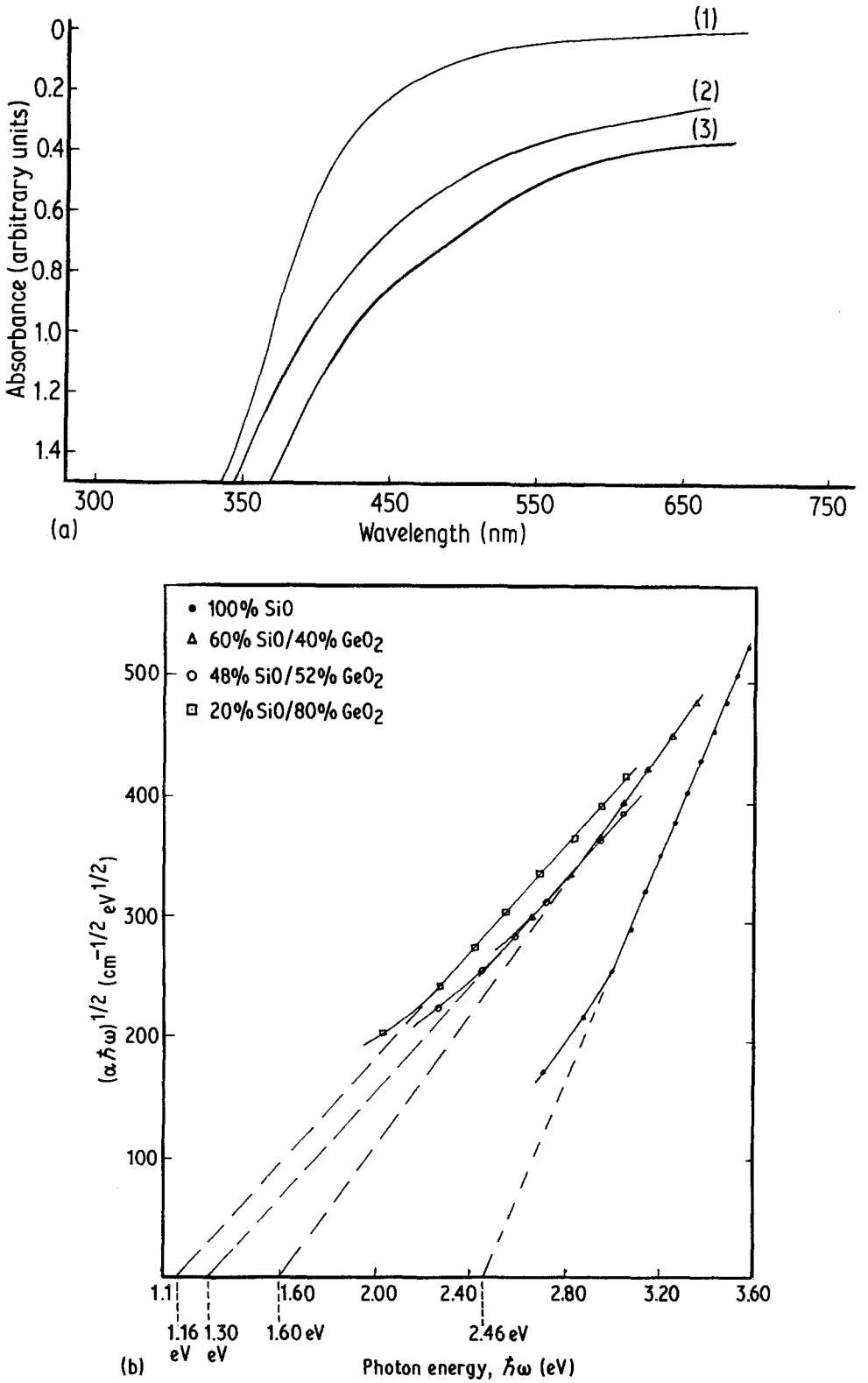


Figure 4 (a) Absorbance as a function of wavelength for samples of the same thickness (400 nm) but having different compositions (1) 100% SiO; (2) 60% SiO/40% GeO_2; (3) 20% SiO/80% GeO_2. (b) $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ for samples having nominally the same thickness (400 nm) but of different compositions.

range from 10 kΩ to 1 MΩ. The activation energy value is 0.54 eV compared with the reported value of 0.47 eV for SiO films, a result which agrees well with the spin density results, but the results are different from the decrease in the activation energy value of SiO/B_2O_3 films reported by Timson and Hogarth [3] since with our films the value of activation energy tends to decrease slightly at the higher voltages.

Tauc [5] showed how the shape and position of the absorption edge for the high adsorption 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, and E_{opt} is the optical energy gap. Considering our optical absorption results, Fig. 3a shows the absorbance in arbitrary units as a function of the wavelength in nm for samples of the same compositions 60% SiO/40% GeO_2 but of different thicknesses. It is evident that in the thicker films (730 and 542 nm) the absorption starts to increase in the visible region while the thinner films of 240 nm it starts to increase in the ultraviolet region. Fig. 3b shows the variation of optical energy gap, E_{opt}, with thickness of films having fixed composition as above and it seems to increase as the film thickness decreases.

Fig. 4a shows the absorbance variation with the wavelength for films having a fixed thickness of 400 nm but different composition. Fig. 4b displays the increase in molar percentages of SiO added to GeO_2. A value of $E_0 = 2.46$ eV obtained for 100% SiO is in good agreement with earlier reported values of E_{opt}.

4. Discussion

From ESR studies carried out by Timson and Hogarth [3] on SiO/B_2O_3 complexes, it is evident that the reduction in the spin density compared with that of SiO films only is due to the reduction in the number of unpaired electrons on dangling bonds within the disordered matrix. Our results on GeO_2/SiO_x complexes confirm the above results and give support to the notion of the dangling bonds being satisfied within the matrix.

When two suitable oxides are mixed together, appropriate impurities are added to amorphous material. This reduces the number of unpaired electrons, and hence the overall free carrier density is consistent with an increase in the overall disorder in these materials, especially from the electrical conduction point of view, where the d.c. conduction decreases as the spin density decreases.

The contamination of our samples may be fairly high due to their preparation under a vacuum of 10^{-5} to 10^{-6} torr and to them being exposed to air when taken out of the deposition chamber to be measured under atmospheric pressure. It is obvious that the contamination must play some role in the reduction of the spin density.

Increased disorder and the presence of defects is known to reduce the value of the optical gap [6]; in other words it increases the number of the localized states, thus reducing the value of E_{opt}.

In ESR the dangling bonds play a major role in the concept of the increase or decrease of the spin density but we believe they would not play a significant role with respect to optical energy gap variations as the film composition changes.

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References

1. M. H. BRODSKY, R. S. TITLE, K. WEISER and G. D. PETTIT, *Phys. Rev.* **B1** (1971) 2632.
2. A. J. LEWIS, G. A. N. CONNELL, W. PAUL, I. R. PAWLIK and R. J. TEMKIN, Proceedings of the Conference on Tetrahedrally Bonded Amorphous Semiconductors, Yorktown Heights, New York, March 1974 (American Physics Society and IBM, 1974) p.27.
3. P. A. TIMSON and C. A. HOGARTH, *Thin Solid Films* **10** (1972) 321.
4. C. A. HOGARTH and L. A. WRIGHT, Proceedings of the 9th International Conference on the Physics of Semiconductors, Moscow, July 1968 (Acad. Sci., USSR, 1968) Vol. II, p. 1274.
5. J. TAUC, *Phys. Status Solidi* **15** (1966) 627.
6. S. CHAUDHURI, S. K. BISWAS. A. CHAUDHURY and K. GOSWAMI, *J. Non-cryst. Solids* **54** (1983) 179.

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