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Influence of substrate temperature on the electrical and optical properties of amorphous germanium films

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Abstract. The influence of substrate temperature on electrical and optical properties of the amorphous germanium films deposited under well-defined conditions has been investigated. DC electrical conductivity in the temperature range of 80–573°K has been measured. In the low temperature region Mott's $T^{-1/4}$ law of conductivity is obeyed. The estimated values of T_0 and N show significant decrease with change in T_s in steps of 50°K. Similar results are seen in annealed films. The values of activation energy and optical energy increase with T_s.

Keywords. Amorphous germanium; annealing; substrate temperature; density of states; optical energy gap; d.c. electrical conductivity.

1. Introduction

Although much work has been carried out on the structural, electrical and optical properties of amorphous germanium (a-Ge), the many aspects towards a basic understanding of a-Ge have still remained a challenging problem. This is due to the strong dependence of properties such as density, structural transformation kinetics, electrical conductivity, thermopower, magneto-resistance, optical absorption and optical constants etc observed on various deposition parameters, subsequent ageing, annealing treatment and adsorption effects.

An amorphous thin film obtained by condensation of vapour atoms onto the substrate consists of various defects in the films like voids, vacancies, divacancies, dangling bonds (unsatisfied bonds) etc and these defects arise due to various preparation conditions during deposition and pre- and post-deposition treatments of the films. Thermally-activated continuous rearrangement is possible in amorphous materials if the amorphous matrix contains micropolycrystalline regions which may occur in various deposited films and if finite adatom mobility exists during the condensation process. Though the existence of the so-called ordered region of $\simeq 14$ Å dimensions (Graczyk and Choudhari 1973) hardly supports the microcrystalline nature of a-Ge films, the sharp dependence of several properties of a-Ge films on various deposition parameters (Walley 1968; Bauer and Galeener 1972; Zavetova and Koc 1972; Goebel *et al* 1973) can be understood only on the assumption of a finite adatom mobility during the condensation process of the film. Therefore, for a satisfactory interpretation of the properties, a clear understanding of the atomic rearrangement during and after deposition of a-Ge film is necessary. This is because any rearrangement in the structure of films causes a change in the number of defects thus providing a variation in the density of states in the mobility gap and therefore in the properties. Studies on the variation of angle of deposition (Chopra and Pandya 1974), annealing (Walley 1968; Brodsky *et al* 1970; Brodsky and Title 1969; Paesler *et al* 1974; Paul and Mitra 1973) and oxygenation (Walley 1968; Lecomber *et al*

1974) in a-Ge revealed a decrease in the density of states with an increasing angle of incidence, annealing temperature T_A and the presence of oxygen during deposition respectively.

We have utilized the substrate temperature as a parameter while studying the d.c. electrical conductivity of vacuum-evaporated a-Ge films in the temperature range 80–573°K. The optical absorption of samples deposited at various substrate temperatures has also been studied.

2. Experimental

2.1 *Sample preparation*

Sample films of a-Ge were prepared by evaporating intrinsic (99·99% pure) Ge from molybdenum boat onto the clean glass substrates with predeposited Al contacts held at various substrate temperatures. The six substrate temperatures chosen were in the range of 300–500°K in steps of 50°K. The angle of deposition was $\simeq 80°$. The deposition rate was $\simeq 100$ Å/sec. All evaporations were made using a conventional vacuum system with an oil diffusion pump (pressure during deposition 10^{-5} torr). Film thickness was measured using an interferometric technique. The thickness of the film was 1000–1500 Å.

2.2 *DC conductivity measurement*

The low temperature d.c. conductivity was measured by transferring sample films after deposition to the cryostat (Chandole and Shah 1981) evaluated at a pressure of 10^{-3} torr. The sample conductance was measured at various stable temperatures between room temperature and upto 130°K. While measuring the conductance, pressure contacts were used and the temperature was recorded using a calibrated copper constantan thermocouple fixed on a glass plate near the sample. High temperature d.c. conductivity was measured from room temperature to 573°K in vacuum and $\simeq 10^{-5}$ torr pressure. The sample conductance was measured at different temperatures. While measuring the conductance, pressure contacts were used. Both at low and high temperatures, conductance was measured by determining a voltage drop across a standard resistor using a d.c. micro-voltmeter TFM 12.

If the natural logarithm (ln) σ_{dc} vs $T^{-\frac{1}{4}}$ is plotted using a low temperature σ_{dc} data, we get a straight line plot, the slope of which will be $T_0^{\frac{1}{4}}$. Thus using experimentally obtained values of T_0, the values of density of states at E_F, $N(E_F)$ were obtained using the relation (Ambegaonkar *et al* 1971) $T_0 = 16\alpha^3/KN(E_F)$ where $\alpha = 10^7\,\text{cm}^{-1}$ and k is the Boltzmann's constant. Also by plotting ln σ_{dc} vs $1/T$ for high temperature σ_{dc} data, the values of E_{act} were determined for various sample films from the slope of the plots. The values of $N(E_F)$ and E_{act} are shown in table 1. The values of ln σ_{dc} vs $T^{-\frac{1}{4}}$ and ln σ_{dc} vs $1/T$ plots are shown in figures 1 and 2 respectively.

2.3 *Optical absorption*

The optical absorption of the sample films was measured using a double beam spectrometer (Cary 17D) in the near infrared range (8000–20000 Å). The refractive index

Table 1. Electrical and optical data of a-Ge films.

Substrate temperature T_s(°K)	Hopping parameter T_0(°K)	Density of states $N(E_F)(\text{eV}^{-1}\,\text{cm}^{-3})$	Activation energy E_{act}(eV)	Optical energy E_g^{op}(eV)
300	5.39×10^7	3.44×10^{18}	0.32	0.86
350	7.72×10^7	2.40×10^{18}	0.33	0.88
400	1.60×10^8	1.16×10^{18}	0.35	0.90
450	1.99×10^{18}	9.33×10^{17}	0.36	0.93
500	2.93×10^8	6.32×10^{17}	0.45	0.96

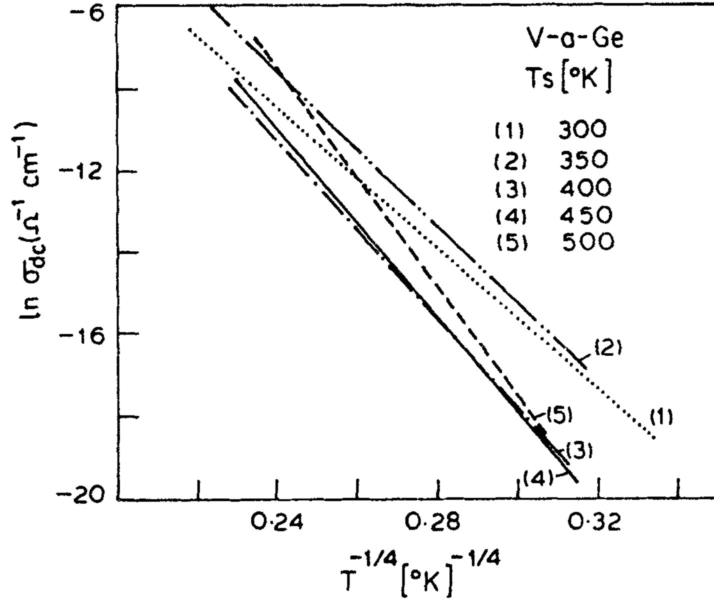

Figure 1. Low temperature measurement data plotted for a-Ge films with different T_s values.

(n) of the sample films was determined by identifying the order of interference peak obtained from transmission maximum and transmission minimum (Wales *et al* 1967). An average value of n was calculated and used for further calculation. Following Brodsky *et al* (1970) for a film of thickness, the value of transmission T is given by

$$T = \frac{(1-R_1)(1-R_2)(1-R_3)\exp(-\alpha t)}{1-R_2R_3[1-|R_1R_2+R_1R_3(1-R_2)^2|\exp(-\alpha t)]},$$

where R_1 is the film to air reflection coefficient $=[(n-1)/(n+1)]^2$, R_2 is the film substrate reflection coefficient $=[(n-n_s)/(n+n_s)]^2$, R_3 is the air to substrate reflection coefficient $=[(1-n_s)/(1+n_s)]^2$, α is the absorption coefficient, n, the refractive index of glass and n_s is the refractive index of the film. It is found that $R_3 \ll R_2 < R_1$, so that the above formulae can be approximated to the form

$$T = (1-R_1)(1-R_2)(1-R_3)\exp(-\alpha t).$$

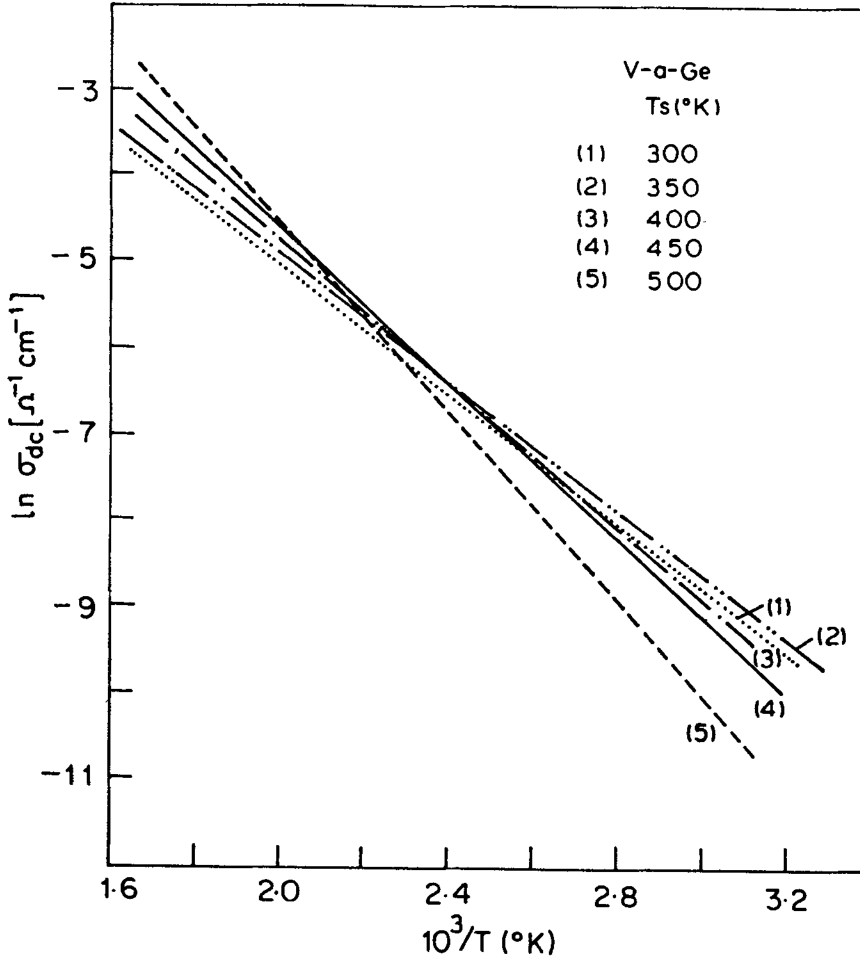

Figure 2. High temperature measurement data plotted for a-Ge films with different T_s values.

From the value of T measured experimentally, α can be calculated using the above equation. When absorption is plotted as $(\alpha h\nu)^{\frac{1}{2}}$ vs $(h\nu - E_g^{op})$, a straight line fit for the above data (particularly at the high absorption region) is observed. Extrapolating this to $\alpha = 0$ gives the value of E_g^{op}. By measuring T experimentally, the plots of α vs $h\nu$ and $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$ for all samples were obtained to study the absorption edge and to calculate the E_g^{op} respectively. The E_g^{op} data are summarized in table 1 and plots α vs $h\nu$ and $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$ are shown in figures 3 and 4 respectively.

3. Results and discussion

The low temperature dependence of d.c. conductivity in a-Ge films deposited at $T_s = 300°$K and at elevated T_s is shown in figure 1. Mott's $T^{-\frac{1}{4}}$ law of conductivity is verified in each case. As the resistivity of the films increase with higher T_s values $T^{-\frac{1}{4}}$ plots shift towards the lower conductivity region. The values of T_0 obtained

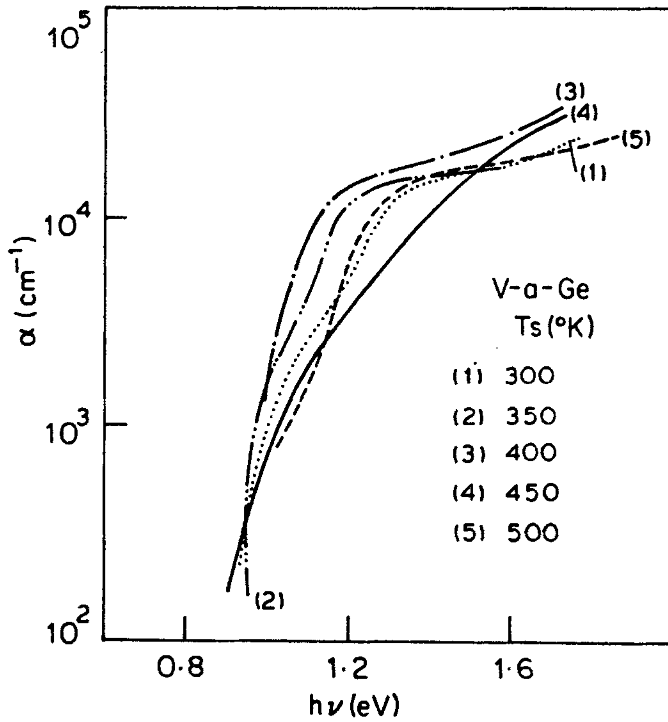

Figure 3. Absorption coefficient (α) vs photon energy ($h\nu$) plotted for a-Ge films with different T_s values.

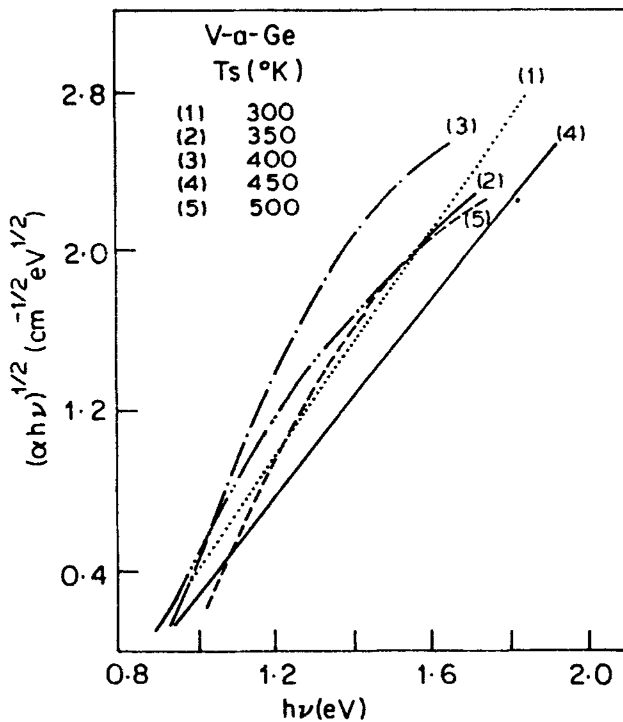

Figure 4. $(\alpha h\nu)^{\frac{1}{2}}$ vs photon energy ($h\nu$) plotted for a-Ge films with different T_s values.

from the $T^{-\frac{1}{4}}$ plots increase with increasing value of T_s. Thus $N(E_F)$ is smaller in films deposited at elevated T_s. This observation agrees with the studies on annealed (Hasegawa *et al* 1978; Paul and Mitra 1973; Narasimham 1977; Koc *et al* 1972) and oxygenated a-Ge films (Zavetova and Koc 1972; Lewis *et al* 1974; Kubler *et al* 1979). The temperature dependence of the conductivity of a-Ge films deposited at various T_s is shown in figure 2. Although the conductivities of the film with $T_s = 300°K$ and films with increased T_s differ considerably from each other, the general features of the temperature dependence behaviour are found to be similar as the value of E_{act} decreases rapidly with decreasing temperature and at the same temperature E_{act} is higher for films with higher T_s. This effect is similar to that observed in annealed (Pierce and Spicer 1971), oxygenated and obliquely deposited (Chopra and Pandya 1974) a-Ge films. The optical absorption coefficients α of the a-Ge films deposited at $T_s = 300°K$ near the fundamental absorption edge behave nearly in the same manner as that reported by Theye (1971) with increasing T_s. The curves α vs $h\nu$ and $(\alpha h\nu)^{\frac{1}{2}}$ vs $h\nu$ (figures 3 and 4 respectively) for a-Ge films shift towards higher energies. The value of E_g^{op} for a-Ge film deposited at $T_s = 300°K$ is in accordance with that reported by Theye (1971). Similar results are reported for optical absorption studies carried out over annealed (Brodsky *et al* 1970; Hasegawa and Kitagawa 1978; Koc *et al* 1972; Theye 1971, 1974; Pandya and Chopra 1976), oxygenated (Mott and Davis 1979) and obliquely deposited a-Ge films (Chopra and Pandya 1974). The shift of fundamental absorption edge towards higher energies and increase in E_g^{op} values with increasing T_s is also reported by other workers (Pandya and Chopra 1976; Theye 1970; Connell *et al* 1973; Donovan and Spicer 1970).

In general, films deposited at high T_s are of high density and coordination number but they have a fair density of impurities, voids, vacancies, dangling bonds, etc. In such cases trends of these properties with increasing film density allow the effect of dangling bonds, voids, impurities etc to be separated out from those of matrix itself. This happens at crystallization temperature because there is a gradual modification in the electrical and optical properties of films with increasing T_s below crystallization temperature. Density, refractive index, resistivity, activation energy and optical energy gap values tend to increase upto limiting values and this is characteristic of most ideal amorphous state of the matrix. Deposition of films at quite high T_s may produce high density films closer to those of the hypothetical pure perfectly co-ordinated network i.e. pure crystalline films (Connell *et al* 1973). According to Theye (1971) the ideal amorphous state and complete crystallization state of vacuum evaporated a-Ge films occur at 400°C and 500°C respectively. These limiting states have characterized E_g^{op} values as 1 eV and 0·8 eV respectively. Our films have preparation conditions similar to that of Theye (1971) and the observed changes in the electrical and optical properties of our sample films below crystallization temperature, can be interpreted as showing progressive transformation of the as-deposited film towards a most ideal amorphous state. Our annealing supports such a modification in the film structure with T_s as we obtained a value of $E_g^{op} \simeq 0{\cdot}99$ eV (comparable to $\alpha \simeq 1$ eV, a characteristic value of E_g^{op} indicating perfect amorphous state) in a-Ge annealed at $T_A = 300°C$ for 6 hr (Delit and Shah 1983).

The role of T_s determining such a transformation in the structure of the film and thereby the properties may be understood with the possible existence of finite adatom mobilities. Though adatom mobility is considered very small, it may be finite in the films deposited with the increased temperature of T_s since adatom may get

more thermal activation energy from the surface of substrate compared to that of the film deposited into room temperature substrates. As a result the rearrangement may be different for different T_s. The resulting gradual change in the structure of films with T_s may be related to the probability that a high energy adatom configuration may transform to a lower energy adatom configuration during deposition of a monolayer (Connell *et al* 1973).

The fact that density of defect states at E_F decreases with increasing T_s below recrystallization temperature (table 1) supports the explanation that there is a gradual transformation of the as-deposited films towards a most ideal amorphous state with well-defined specific properties. The increase in T_0, E_{act} and E_g^{op} data with T_s (table 1) below crystallization temperature also confirms the above explanation as the data reflect the properties of the increasing amorphous state of the matrix. Similar reports on sputtered a-Ge films (Connell *et al* 1973) have shown that the main structural changes are due to densification of the structure with the elimination of voids, dangling-bonds etc.

Thus, similar to annealing and oblique deposition studies, the trends of electrical and optical properties of vacuum-evaporated a-Ge films reflect the same cycle indicating an evolution of the film structure towards an ideal amorphous state with increasing T_s below crystallization temperature ($\simeq 300°C$). For higher $T_s > 300°C$ we may expect the modification of the film structure towards recrystallization which, according to annealing studies, are expected to start at about $T_A \geqslant 400°C$. This is obvious since densification of the matrix after an ideal amorphous state will result in recrystallization of the structure. Such changes in the films with elevated T_s may be detected by performing structural studies in films with elevated T_s as seen in the case of annealed films (Theye 1971).

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