

I. PHYSICS

Solid State Physics

ELECTRICAL CONDUCTIVITY MEASUREMENTS OF EVAPORATED SELENIUM FILMS IN VACUUM

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In vacuum, variation of electrical conductivity of evaporated selenium films deposited on glass substrates with thickness (500 to 4420 Å) and temperature (30 to 150 °C) has been done. Electrical resistivity of the films increases with thickness from 500 to 3400 Å and then decreases for thicker ones. Qualitative explanation for this unusual observation is given in terms of high oxide contents in thinner films and surface-space charge double layer. Thermal activation energy is found to decrease with increase in films thicknesses. Temperature coefficient of resistance (TCR) in films is also calculated. It is found to be negative and in magnitude increases with decrease in temperature or increase in thickness.

Keywords: Electrical conductivity of selenium films.

INTRODUCTION

In the last few years, tremendous interest has been shown both in the study of theoretical and experimental properties of amorphous selenium films because of their commercial applications in rectifiers, photocells, the vidicon, xerography etc.

Hartke (1962), Lanyon and Spear (1961) found conduction in thick amorphous selenium films to be space charge limited, while Vautier (1972) showed it to be polaronic in the lower temperature range (–100 °C to 20 °C). Studies of Roberts (1971) asserted that conduction processes in this elemental semi-conductor could be understood in terms of normal energy band picture. Looking to the drastic fall in resistivity of selenium in presence of approximately 50 ppm oxygen molecules (LaCourse *et al.*, 1970; and Twaddell *et al.*, 1972), increase in crystallinity of amorphous selenium films after annealing (Samantary & Nigam 1976), it was decided to study electrical conductivity of selenium films with thickness variation in vacuum during heating and cooling cycles. Thermal activation energy and temperature coefficient of resistance of these films are reported.

MATERIALS AND METHODS

Various selenium films of 500 to 4420 Å thick were obtained by vacuum deposition technique on glass substrates by resistive heating of pure selenium powder (99.5%) from molybdenum boat. To maintain similar conditions of evaporation in all cases, film deposition was always started at about 3×10^{-5} torr pressure. During film

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deposition pressure did not exceed 5×10^{-5} torr and after film deposition it fell to about 1×10^{-5} torr and remained there during measurements in vacuum.

Thickness of the films was controlled by Quartz Crystal Thickness Monitor, which was pre-calibrated by Newton-Fizeau Interferometric method. Rate of evaporation was kept $5 \text{ \AA}/\text{sec}$. The area of the film was $0.2 \text{ mm} \times 25 \text{ mm}$, which we obtained by shadowing the substrate by a copper wire during silver contact deposition. Leads from silver deposited electrodes were taken with the help of cleaned spring slips. After the films had attained steady value of electrical resistance in vacuum at room temperature, changes in their electrical resistance with temperature from 30 to $150 \text{ }^\circ\text{C}$ were measured during heating and cooling cycles. The heating was 2 to $3 \text{ }^\circ\text{C}$ per minute. To measure electrical resistance of films, stabilized d.c. power supply was connected in series with films and a standard resistance. Potential drops across film and a standard resistance were measured by vernier potentiometer with accuracy $1 \text{ } \mu\text{V}$. Temperature of the films was measured by copper-constantan thermocouple placed on the same side of the film. For all measurements sufficient time was devoted to secure stability before taking readings.

RESULTS AND DISCUSSION

Electrical resistivity of vacuum deposited selenium films at room temperature as a function of film thickness has been shown in Fig. 1. Curves 1, 2 and 3 represent stable value of resistivity after deposition, after an annealing cycle (from 30 to $150 \text{ }^\circ\text{C}$ and back to $30 \text{ }^\circ\text{C}$), and in residual vacuum after 25 hours respectively. Film resistivity increases with thickness up to 3400 \AA and then decreases.

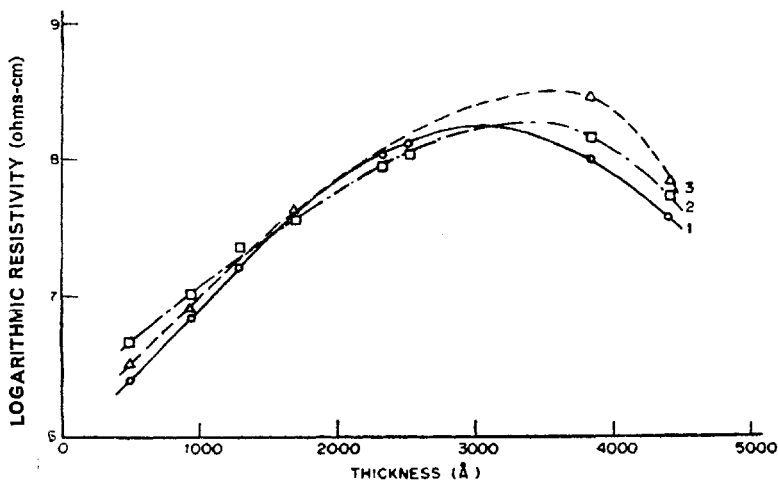


FIG. 1. Electrical resistivity versus thickness. Curve 1 — Stable value after film deposition, 2 — After an Annealing cycle, and 3 — After 24 hours in residual vacuum.

This initial increase in the resistivity with the increase of film thickness is contradictory to the Fuchs (1938) and Sondheimer (1952) size effect theory. Similar

trend was also observed by Chaudhuri (1974) in tellurium films. In their experiments, resistivity increased up to the film thickness of 1500 \AA and then decreased. They attributed this unusual behaviour of the resistivity with films thicknesses to the structure of the films. They said that at lower thicknesses film had become uniform and more or less like single crystal film, which is quite contradictory to the existing general observations and theories of film growth structure on amorphous substrates. This initial increase in resistivity for selenium films could be understood in terms of high oxide contents in thinner films and surface-space charge double layer which exists on surface of a semi-conductor.

This double layer possesses different concentrations of charge carriers, mobility and the Hall coefficient (Petritz, 1958), and is produced by surface-charge distribution, counterbalanced by space-charge region. Surface-charge distribution arises due to trapping of holes, electrons and impurity ions at the surface of a semi-conductor. In our case, these trappings could be due to amorphous structure of selenium films and chemisorption of oxygen molecules. The chemisorption traps are often separated from the bulk material by an oxide layer (Schrieffer, 1955). Space-charge region extending to a depth of 10 to $10,000 \text{ \AA}$, gives rise to electrostatic potential energy at the surface of the film, consequently charges are depleted from the space-charge region, giving a layer of high resistivity (Bardeen, 1947).

The selenium films are deposited in residual vacuum of 3×10^{-5} torr i.e., in presence of about 1.14×10^{16} gas molecules ($\approx 2.2 \times 10^{15}$ oxygen molecules) striking per unit area of the substrate per sec., where approximately 13 monolayers could be formed in a second. LaCourse *et al.* (1970) found resistivity of pure selenium (10^{17} ohms-cm) decreased by six orders of magnitude in presence of 50 ppm oxygen molecules. The resistivity of our films is in the range of $10^7 - 10^9$ ohms-cm, showing that their surfaces are in the oxidised state. The thinner films are expected to have higher oxide concentration (because of their formation in early vacuum and capillaries extending up to surfaces—creating easy accessible places for oxygen penetration) than the thicker ones and thus tend to have lower resistivity than the later ones.

Thus, the resistivity of selenium films is governed by two factors, namely, the oxide contents in thinner films and the surface-space charge double layer. The oxide formation reduces the resistivity, while the latter factor increases the resistivity of the films till their thicknesses approach the double layer thickness (about 3400 \AA in our case). For films thicker than the double layer thickness, the effect of oxide content and double layer becomes constant and their resistivity is dominated by the size effect on the electron free path in the bulk and thus resistivity decreases onwards with increasing thickness.

Effect of heating (30 to $150 \text{ }^\circ\text{C}$) on resistance of some of the selenium films in vacuum is shown in Fig. 2a. While heating, two main features are observed in almost all films. First, drastic fall in electrical resistance around 40 to $50 \text{ }^\circ\text{C}$ and second, dip in electrical resistance between 80 to $130 \text{ }^\circ\text{C}$. These two features can be understood in terms of structural changes in specimens. At room temperature selenium films possess amorphous structure (Chopra, 1969). As the temperature

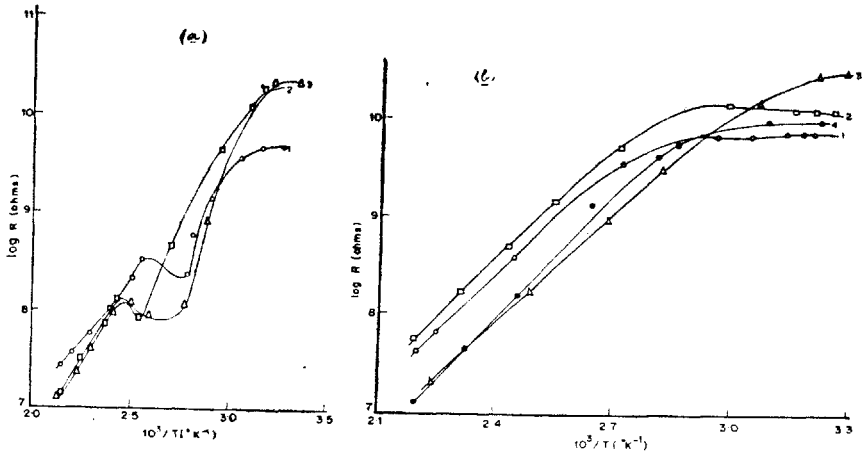


FIG. 2. (a) Resistance versus reciprocal of temperature on heating. Curve 1 — Film 500 Å, 2 — Film 1700 Å, and 3 — Film 3850 Å thick. (b) Resistance versus reciprocal of temperature on cooling. Curve 1 — Film 500 Å, 2 — Film 950 Å, 3 — Film 2530 Å, and 4 — Film 4420 Å thick.

increases, selenium films lead to irreversible phase transformation from amorphous to crystalline structure, which is observed in our case between 40 to 50 °C and try to attain stable configuration between 80 to 130 °C. X-ray diffraction studies by Samantary and Nigam (1976) also find irreversible structural changes in amorphous selenium films by heat treatment under similar conditions and attain stable crystalline trigonal structure at 110 °C.

Heating upto 150 °C completes the structural changes in vacuum deposited selenium films. No dip in electrical resistance is observed during reverse or cooling cycles (i.e. 150 to 30 °C), because of films having undergone irreversible phase transformations and attained trigonal structure. These are separately shown in Fig. 2b.

Thermal activation energy of the films is calculated from the straight portions of the cooling curves (i.e. fig. 2b) between log R and $1/T$, by using the relation,

$$\Delta E_r = \frac{\Delta (\log R)}{\Delta (1/T)} \times 2.303 \times k \times 2.303 \text{ eV}$$

where k is the Boltzmann constant and T , the absolute temperature. This calculated activation energy is found to decrease with increase of the film thickness as shown in Table I.

TABLE I

Decrease of activation energy

Thickness in Å	500	950	2330	2530	3000
Activation energy in eV	1.59	1.55	1.48	1.46	1.12

Temperature coefficient of resistance (TCR) is also calculated for various films at different temperatures from Fig 2*b* using simple relation.

$$\text{TCR} = \frac{1}{R_{rt}} \cdot \frac{R_t - R_{rt}}{T_i - T_{rt}}$$

where R_t is the film resistance at arbitrary temperature T_i , and R_{rt} the film resistance at room temperature T_{rt} .

Negative TCR is observed and it decreases in magnitude with increasing temperature but for thinner films it first increases and then decreases as shown in Fig. 3. However, at higher temperature (150 °C) all the films yield the same TCR, which is $-0.66 \times 10^{-2} \text{ } ^\circ\text{C}$.

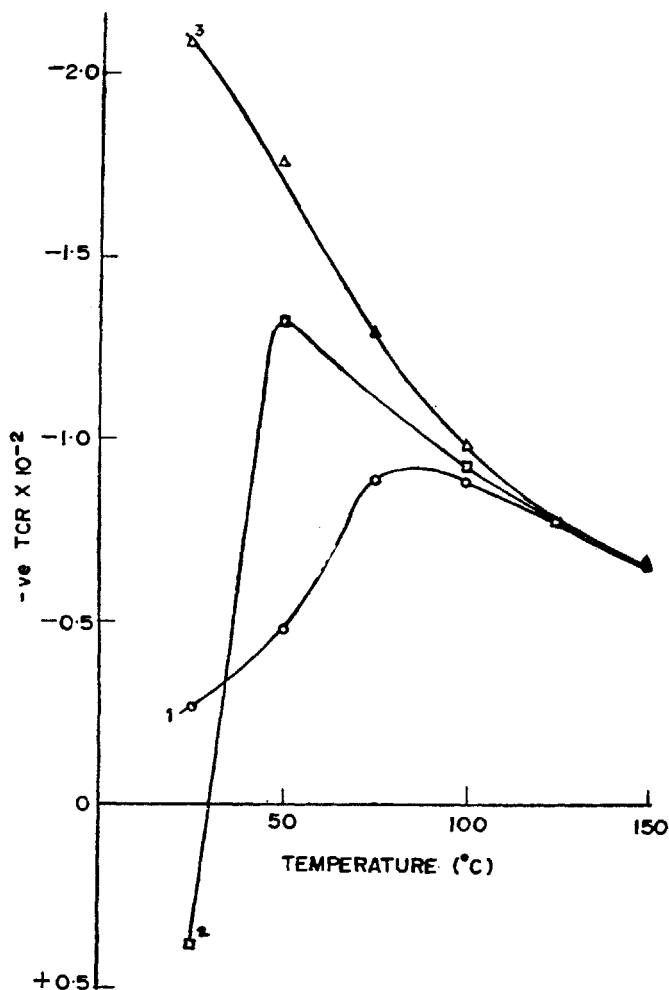


FIG. 3. Negative TCR versus temperature. Curve 1 — Film 500 Å, 2 — Film 950 Å, 3 — Film 2530 Å thick.

Neugebauer and Webb (1962) developed a theory for electrical conduction in ultra thin films which in a modified form could be applied to semi-conductor continuous films. Apart from the term tunnelling probability (which is negligible for continuous films like ours) their expression for electrical conduction reduces for semi-conductor continuous films as:—

$$\sigma = C. \exp(-e^2/\epsilon r + E_g)/2kT, \quad \dots(1)$$

where $(e^2/\epsilon r + E_g)$ is thickness dependent thermal activation energy term, ϵ , the dielectric constant of the substrate, r , approximated as film thickness, E_g , the energy band gap and C , the constant.

From the activation energy term, it is obvious that film activation energy decreases with increasing film thickness, which explains our observation.

From eqn. (1), TCR is expressed as

$$\text{TCR} = \frac{1}{\rho} \cdot \frac{d\rho}{dT} = \frac{-(e^2/\epsilon r + E_g)}{2kT^2}.$$

Thus negative TCR decreases in magnitude with increasing temperature and thickness of the films. The negative TCR highly depends on temperature than thickness (r), as former comes in the denominator of the whole term and also in square form. Consequently, at higher temperature the effect of thickness is negligible and all films of different thicknesses yield the same TCR. However, for thinner films initial increase in TCR with increase of temperature is inconclusive, possibly the double layer having different concentration of carriers or oxide contents may be playing dominating role in a complicated manner.

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