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Polaron Conduction and Optical Absorption of Amorphous Selenium Films

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The temperature dependence of electrical conductivity in amorphous selenium films is investigated. The experimental results show a polaronic conduction in the states near the Fermi level, in agreement with Mott's model. Optical absorption measurements show the rate at which the valence band states fall off with energy into the energy gap.

The mechanism of electronic conduction in amorphous materials is not yet understood. Because of the disordered lattice structure, the energy band structure cannot be as readily derived for these materials as it has been for periodic lattices. Nevertheless, it is believed that valence and conduction bands do exist for the amorphous structure, but a true band gap of forbidden energies between the valence and conduction bands probably does not exist. Instead, energy states at the band edges may smear or tail into a pseudo-gap. Within this pseudo-gap the states are localized, and outside the pseudo-gap, in the valence and conduction bands, the hole and electron states are nonlocalized as in the valence and conduction bands of crystalline semiconductors [1, 2]. Electronic conductivity could take place by hopping of carriers in the localized states. In order to identify the mechanism of conduction for amorphous selenium, we have conducted measurements of the temperature dependence of conductivity on various amorphous selenium films.

Electrical Conductivity

Amorphous selenium films were prepared by thermal evaporation of spectral pure selenium in a vacuum of $\sim 10^{-5}$ torr at an evaporation rate of 15 Å per second from a tantalum boat onto quartz plates. The samples were provided with silver electrodes. The so-formed contacts are not blocking. Measurements were made for two different voltages applied to the sample: 1500 and 2000 volt using a stabilized high voltage power supply. The current which flowed through the sample was measured by a Vibrating Reed Electrometer sensitive to detect currents as low as 10^{-15} A. Figure 1 shows the dependence of the current intensity (plotted on log scale) on the reciprocal temperature at different applied voltages. Sample thickness of 1553 Å and 6550 Å (determined by interferometric methods [3] were used. The 2000 V curve shows a change of slope around 240 K. For temperatures above 240 K, the slope of the straight line is independent of the applied voltage and gives an activation energy about 0.43 eV, whereas for temperatures below 240 K the activation energy is strongly influenced by the applied voltage. The presence of more than one activation energy was observed on As_2Se_3 samples [4]. Rossiter and Warfield [5] reported a change in the mobility activation energy with temperature in amorphous selenium. Several activation energies in the conductivity of amorphous silicon layers were observed [6] and interpreted as a result of the hopping process. Moreover, the existance of a critical tem-
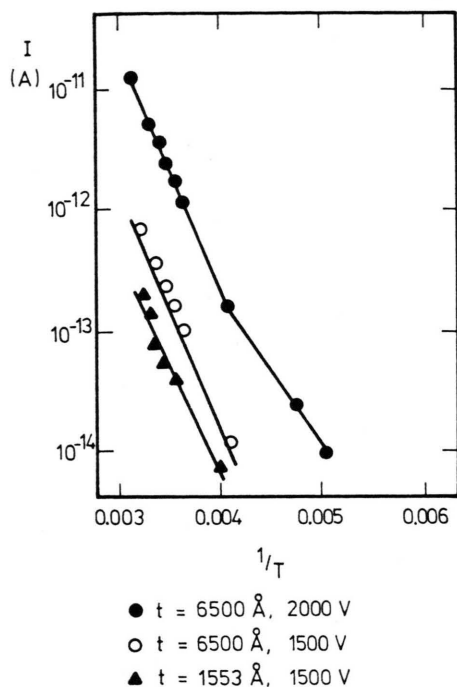
Fig. 1. Current intensity in amorphous selenium films plotted in log scale versus reciprocal temperature.

perature at which the activation energy changes suggests the possibility of polaron conduction [7]. Hempel [8] has suggested a polaronic conduction for selenium.

Mott [9] studied the conductivity for energies E near an energy E_c, which separates localized and non-localized states, and derived, for the localized states, an expression for the polaron mobility,

$$\mu(E) = (\nu_p \, a^2 \, \Phi \, e/KT) \exp\{-W/KT\} \qquad (1)$$

with W the hopping energy, ν_p the phonon energy $(10^{13} \text{ sec}^{-1})$, and a the distance between atoms. The approximation $\nu_p = 10^{13} \text{ sec}^{-1}$ is valid only if $W > K \Phi_D$ with Θ_D the debye temperature. It is not valid for impurity conduction at low temperatures. Φ is a number depending on the overlap between wave functions. It contains the factor $\exp\{-2\,\delta R\}$ if the overlap between states is small (δ is the rate at which the atomic wave function falls off with distance and R is the mean distance between the states near the Fermi level). If, however, the overlap is considerable this factor will be of order unity. Moreover, as $E \to E_c$ each localized state will overlap a large number of others and Φ becomes much larger than unity.

Polarons arise from the interaction between an electric field created by a localized electron and the polarization field of the lattice. For temperatures above $\frac{1}{2}\Theta_D$ polarons move by hopping with a mobility given by expression (1). For temperatures below $\frac{1}{2}\Theta_D$, when the conductivity depends on the behaviour of electrons with energies near E_F, only those electrons with energies $\sim KT$ below E_F have a significant probability of hopping and W tends to zero.

Mott [10] found that the conductivity, when hopping is not between nearest neighbours but between more distant centres, should obey

$$\ln \sigma = A - B\,T^{-1/4} \qquad (2)$$

where A and B are constants. Figure 2 shows the dependence of the current intensity, plotted in log scale, on $T^{-1/4}$. For temperatures below 240 K, the curve is a straight line in full agreement with relation (2). Therefore, one may consider that the conduction arises from polaron transport by a hopping
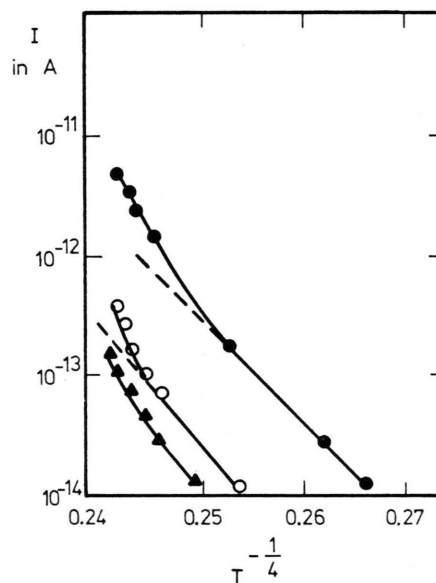

Fig. 2. Current intensity versus $T^{-1/4}$ at different voltages.

process in the localized states near the Fermi level.

For temperatures above $\frac{1}{2}\Theta_D$ (~ 240 K) the conductivity is related to the temperature [11] by the relation $\sigma = D\,T\,\mu = \sigma_0 \exp\{-W/KT\}$. The value of W was obtained from the plot of log σ versus $1/T$ and is equal to 0.43 eV.

Inspite of the presence of injected carriers, due to high electric fields applied on the sample, the

theories of conduction by hopping process and polarons can be used [12], since the quasi-thermal equilibrium is conserved.

Optical Absorption

The optical absorption edge of nearly all amorphous materials is characterized by an exponential or Urbach [13] dependence of the absorption constant α on the photon energy $h\nu < E_g$:

$$\alpha(h\nu) = \alpha_0(T) \exp\left\{\gamma[h\nu - E_g(T)/KT]\right\}$$

α_0 is the normalized transition strength, γ a constant of order unity and E_g the energy gap. Urbach behaviour is observed in some crystalline materials, however a unique explanation for the effect has not yet been found.

For the amorphous phase, because of the small spatial overlap between those states in the valence and conduction bands which are localized, optically induced transitions between these occur with low pro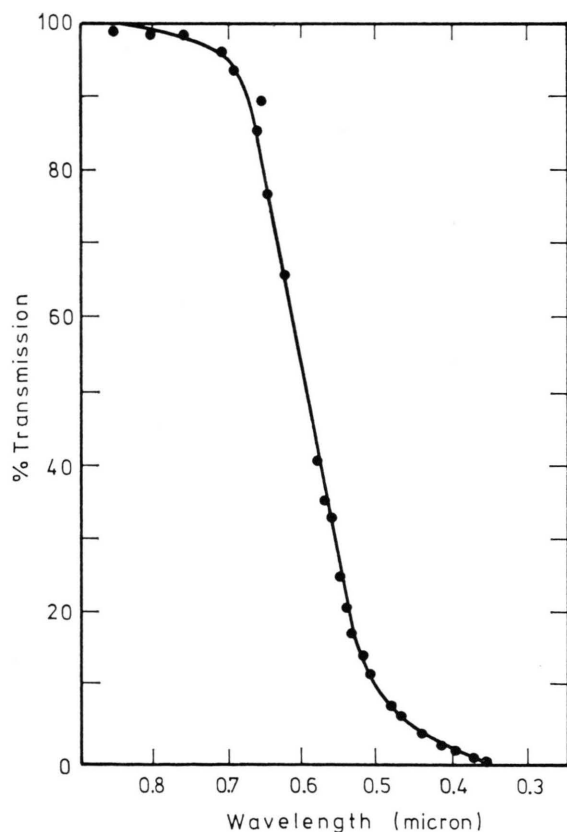bability. However, transitions from the valence band tail to nonlocalized states in the conduction band should contribute appreciably to the absorption. Simple calculations [14, 15] show that the absorption coefficient as a function of photon energy should reflect the rate at which the valence band states fall off with energy into the gap.

Optical transmission measurements were carried out on amorphous selenium films, using a Beckman UV spectrophotometer D.U. Figure 3 shows the variation of sample transmission with the wavelength for film thickness 1553 Å. The transmission falls off rapidly for wavelengths lower than 7500 Å. The variation of the absorption coefficient, calculated from transmission data, with incident photon energy $h\nu$ is shown in Figure 4. The plot of the
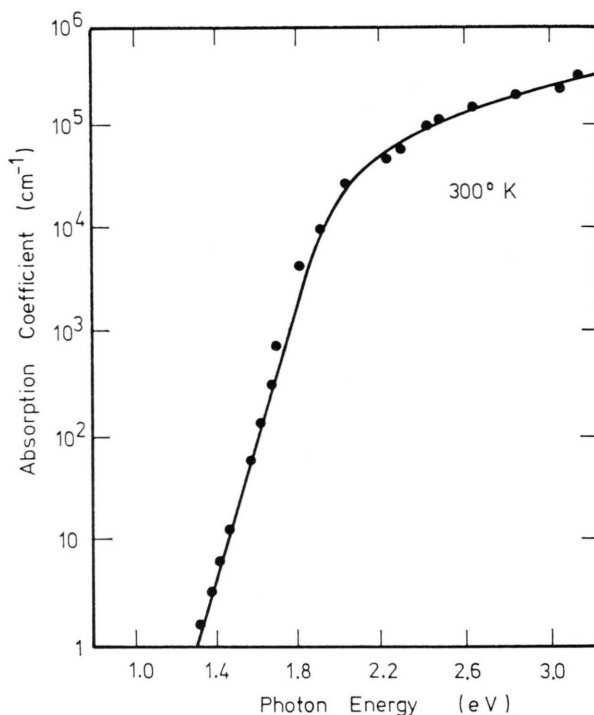

Fig. 4. Optical absorption coefficient versus photon energy.

logarithm of the absorption coefficient against $h\nu$ is a straight line in the region characterizing the Urbach behaviour.

At high values of the optical absorption coefficient ($10^4 - 10^6$ cm^{-1}) deviations from the Urbach behaviour occur in selenium. These, it is believed, occur at photon energies corresponding to excitations final states beyond the band tail (where the

Fig. 3. The dependence of sample transmission on the wavelength.

density of states are large). A reasonable fit to the curve in this region has been obtained using the conventional formula for semiconductors with parabolic bands

$$a \sim \left[\frac{h\nu - E_g}{h\nu} \right]^n$$

with a value of $n = 2$, which is close to the value suggested by Mott.

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