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## LETTER TO THE EDITOR

# Optical energy gap of amorphous selenium: effect of annealing

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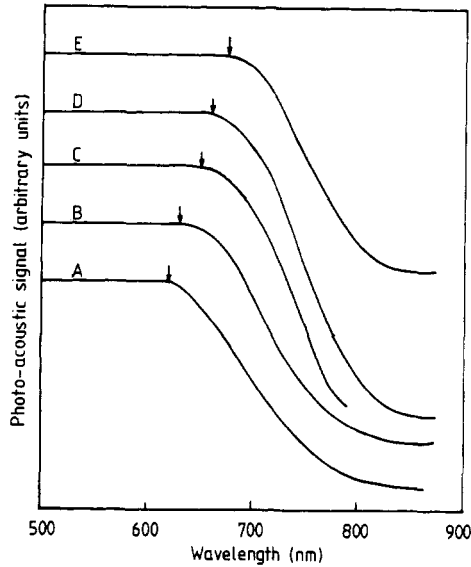
**Abstract.** The optical energy gap of amorphous Se powder has been determined by a photo-acoustic method and has been found to be  $1.99 \pm 0.02$  eV. On annealing, the gap decreases linearly as a function of annealing temperature towards that of the crystalline selenium.

A surprising result was recently reported by Chaudhuri *et al* (1983) regarding the effect of annealing on the optical energy gap,  $E_{op}$ , of a thick amorphous selenium (a-Se) film. For a 4200 Å thick a-Se film, they found that  $E_{op}$  is 1.76 eV, decreasing to 1.09 eV after annealing for 15 minutes at 70 °C. They further found that repeated annealing finally reduced  $E_{op}$  to 0.14 eV. We have cast doubts in an earlier Letter (Bhatnagar and Reddy 1985) on this reported enormous decrease in  $E_{op}$  of a-Se.

In this Letter we report a systematic study of the effect of annealing on the  $E_{op}$  of a-Se employing photo-acoustic spectroscopy (PAS) measurements on powdered samples of a-Se. We also note that as yet there is no report in the literature on the effect of annealing on the  $E_{op}$  of *bulk* a-Se. The usefulness of photo-acoustic spectroscopy in determining the energy gap of semiconductors is well established and has been demonstrated earlier by various workers (Somoano 1978, Subranmanyam and Bhatnagar 1979, Wong 1980).

Amorphous selenium was prepared from 99.999% pure selenium by the conventional ice–water quenching technique. The amorphous nature of the prepared samples was checked by x-ray diffraction method. The a-Se was finely powdered and few grams of fine powder was enclosed in a quartz tube under a vacuum of  $10^{-5}$  Torr. Samples were annealed at 50, 100, 150 and 200 °C. For each anneal temperature, the samples were isothermally annealed for 15, 30 and 60 minutes. PAS was performed on amorphous and crystalline selenium, and the annealed samples at room temperature using a micro-processor-controlled photo-acoustic spectrometer with an optical range of 200 to 2600 nm. Each spectrum was normalised with respect to carbon black, the reference material.

PAS of unannealed amorphous and annealed a-Se are shown in figure 1. In the plots of photo-acoustic signal against wavelength of the incident radiation, a sudden increase in the signal at 800 nm for a-Se is due to the non-radiative transitions between their valence and conduction bands. The wavelength at which the signal gets saturated is interpreted as being the value of the absorption edge or the energy gap of the semiconductor. Energy gaps measured by this procedure for a-Se and crystalline selenium (c-Se) are  $1.99 \pm 0.02$  eV and  $1.85 \pm 0.02$  eV respectively. Energy gaps of amorphous samples annealed at various temperatures and for different times are listed in table 1.



**Figure 1.** Photo-acoustic signal versus wavelength: A, amorphous selenium; B, a-Se annealed at 50 °C; C, a-Se annealed at 100 °C; D, a-Se annealed at 150 °C; E, a-Se annealed at 200 °C; vertical arrows indicate the region where the signal saturates which refers to the energy gap.

**Table 1.** The energy gaps of amorphous samples annealed at various temperatures for various times

Sample	Annealing temperature (°C)	Annealing time		
		15 min	30 min	60 min
Amorphous selenium	50	1.96	1.96	1.96
	100	1.90	1.90	1.90
	150	1.87	1.87	1.87
	200	1.83	1.83	1.83

The values of  $E_{op}$  for a-Se and c-Se are in a good agreement with previous results (Lanyan 1963, Al-Ani and Hogarth 1984, Fisher 1972, Moreth 1979, Weiser and Stuke 1971). It is seen from the table that the annealing of a-Se does decrease the energy gap  $E_{op}$ . However, for any given temperature of annealing, 15 minutes is found to be long enough to stabilise the change as no further change in  $E_{op}$  was observed (even up to 60 minutes) for all the anneal temperatures tried here. The a-Se powder annealed at 200 °C was found to be crystallised.

Figure 2 shows the measured energy gap versus anneal temperature  $T_A$ . It is found that the energy gap of a-Se decreases linearly as a function of anneal temperature towards the energy gap value of c-Se.  $E_{op}$  for a-Se annealed at 200 °C is  $1.83 \pm 0.02$  eV which is the same as  $E_{op}$  for c-Se within experimental errors.

One could imagine the possibility that the annealing of a-Se (even at low temperatures) could produce some crystalline pockets in an otherwise amorphous Se matrix and

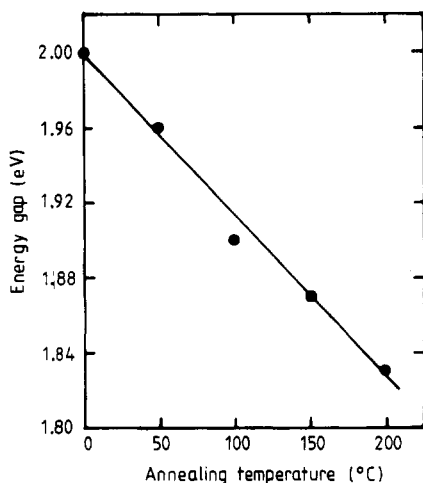
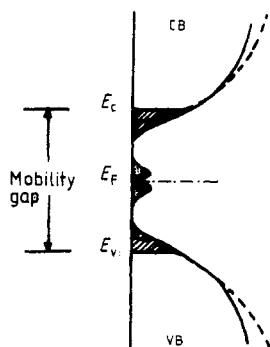


Figure 2. Energy gap of a-Se versus annealing temperature.

what we measure could be a volume average of the energy gap. However, the PAS technique is very sensitive, and in this case one would expect the photo-acoustic signal to show two shoulders rather than a single one in the spectrum. Since we do not observe any second shoulder in the plots of PAS signal against wavelength, we believe that our annealed samples are homogeneous whether they are amorphous or crystalline. Moreover, if there were such volume fractions of crystallised material within an amorphous sample at a given  $T_A$ , they should have increased as a function of time, which we do not observe. Hence, the observed decrease in  $E_{op}$  on annealing is a real effect and not a spurious one.

We make an attempt to understand the result of figure 2 within the Mott-CFO model (Mott 1967, Cohen *et al* 1969). Due to the randomness in the medium, a few states will be pulled into the band gap and the sharp band edges will be replaced by tails stretching into the gap. These tails contain localised states. However, the room temperature is too high to let the electrons remain trapped in the localised states, so we expect at least a great reduction in the number of truly localised states if not their complete disappearance. Another phenomenon that is responsible for the reduction in the number of *single-electron* localised states in chalcogenides is the formation of *paired-electron* states due to the polaron effect (Anderson 1975)—neutral dangling bonds can attract electrons or holes to give rise to charged localised states; dangling bonds with pairs of electrons ( $\uparrow\downarrow$ ) are formed due to strong attractive interaction between electrons produced by electron-lattice interaction. These two-electron states exist with high density in the middle of the band gap and pin the Fermi energy. Apart from the possibility of existence of localised states due to the intrinsic defects, our sample is pure enough to yield any significant localisation due to extrinsic impurities.

Thus, if any single-electron localised states are present, we expect they should exist in the deep tails with rather small density, i.e. the 'mobility edges' should be sitting deep into the band tails (figure 3). These localised states must be *very strong* ones to have survived the high temperature and should clearly be sustained by the spatial regions offering very strong potential fluctuation which appear with low probability (hence low density). As we will discuss, our results indicate that our samples do contain such localised states despite the high temperature.



**Figure 3.** Schematic plot showing single-electron localised states in the band tails and the mobility gap. In broken line is shown the density of states for crystalline material. The middle of the gap contains bipolaron states which pin the Fermi energy  $E_F$ ; the single-electron density of states is zero in this region.

Photo-excitation will occur mainly from the extended states in the valence band for two reasons: (a) localised states are so scarce and (b) excitation from localised states requires extra energy. When the photons are able to impart sufficient energy to cause excitation to the conduction band, it will mainly occur into the extended-states region because (a) again the localised states in the conduction band are scarce and (b) the 'bipolaron' states (discussed above) do not produce optical absorption. Thus, the optical energy gap that we measure is essentially the 'mobility gap'. The fact that we find  $E_{op} \approx E_{mob}$  for the unannealed sample to be greater than  $E_g$ , the crystalline energy gap, indicates that the strongly localised states are present in the system. They appear over a range of 0.1 eV which is about 1% of the band width, in agreement with certain rough estimates (Mott and Davis 1979).

As the temperature increases, the amorphous nature decreases, disorder increases and the regions of strong fluctuations become more and more rare. Consequently, the localised states reduce in number, the tails shrink and the mobility edges  $E_c$  and  $E_v$  move deeper into the tails. Eventually their movement stops and they coincide with the band edges to mark the crystallisation. At this stage  $E_{op}$  should become the same as  $E_g$ , as we find. What is interesting is that the approach to crystallinity happens linearly, i.e. the trajectory of mobility edges in the small disorder region is linear as has been found theoretically (Weaire and Srivastava 1977).

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