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# Photoinduced degradation in the electrical properties of normally and obliquely deposited $As_2Se_3$ thin films

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Dark conductivity in $As_2Se_3$ films was measured in the temperature range 300–400 K. It was found to be of the doubly activated type in high- and low-temperature ranges. The experimental results were analysed using the Meyer–Neldel rule. The effect of light soaking on the electrical transport properties of normally and obliquely deposited $As_2Se_3$ thin films were examined. It has been observed that light soaking results in the degradation of photocurrent, which nearly saturates in an hour. Dark conductivity is found to be smaller after light soaking than without it.

Key words: *chalcogenides; oblique deposition; Meyer–Neldel rule*

## 1. Introduction

In amorphous chalcogenide films, photostructural transformations have been extensively studied. It is well known that transformations are induced in some materials of the As–Se and As–S systems by band gap illumination, and are associated with certain changes in optical properties, such as the band gap and refractive index. These photoinduced changes can be increased by varying the deposition conditions, mainly the angle of deposition, since obliquely deposited films have a columnar structure and a smaller density of atoms [1]. As a result, large changes have been observed after photoillumination in obliquely deposited chalcogenide films [1–3].

Besides optical properties, various photoinduced phenomena [1, 2] have also been reported for photocurrent in amorphous semiconductors in recent years. Various models have been put forward in support of the observed light-soaked effects on photocurrent [3–5] and the decay of photocurrent [6]. It is well known that amorphous semiconductors undergo photoconductive degradation when exposed to light illumination. Light-induced effects on dark conductivities and photoconductivities in amorphous semiconductors are important subjects from both the fundamental and practical points

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of view [1, 2]. Specifically, the Staebler–Wronski effect, appearing in hydrogenated amorphous Si (a-Si: H) [3], poses serious problems in solar cell applications. Shimakawa et. al. [7] have reported a similar degradation phenomenon of photocurrent in chalcogenide glasses. The mechanisms of these photodegradation phenomena are assumed to be connected to the photoinduced creation of some kinds of defects. The transport properties of oblique films, however, have not been extensively studied, and therefore the purpose of the present paper is to investigate light-induced changes in the transport properties of $As_2Se_3$ films deposited at oblique incidence and to compare them with films at normal incidence. Thin films are key to exploiting the switching characteristics of chalcogenides. Also, thin films allow a current to flow through the highly resistive amorphous state at relatively low voltages.

## 2. Experimental details

Normal and oblique films of $As_2Se_3$ were prepared by the vacuum evaporation technique. The oblique films were deposited at the angle of 80°, this being the angle between the normal to the substrate and the direction of incidence of the evaporated atoms. Optical glass slides were used as the substrate for depositing the films. Evaporation was carried out on the substrates at room temperature in a vacuum of about $10^{-6}$ Torr from a molybdenum boat heater. A surface profiler (DekTek 3) was used to measure the thickness of the film. The films had thicknesses of the order of 1 μm. Conductivity measurements were done by evaporating aluminium contacts on the film in a coplanar configuration with a spacing of ~ 0.1 cm. The samples were annealed below the glass transition temperature for an hour. A running vacuum of the order of $10^{-3}$ Torr was maintained throughout the experiment. The temperature dependence of conductivity was measured in the range of 300–400 K. The temperature of the films was varied by inserting a heater into the cryostat and measured using a Chromel–Alumel thermocouple. A constant DC voltage, from a highly stabilized power supply, was applied across the sample, and the current was measured with a Keithly 610C electrometer.

Photocurrent and light soaking measurements were done using a tungsten halogen lamp (100 mW/cm$^2$). The cryostat had a window facing the film to let light fall on it. Different coloured filters were used to measure the spectral response of photocurrent.

## 3. Results and discussion

### 3.1. Dark current

The temperature dependences of dark conductivity for normal and oblique (80°) $As_2Se_3$ films are shown in Fig. 1. Dark conductivity was measured by warming the samples after rapid and normal cooling. Dark conductivity data can be described well by the standard expression

$$\sigma_{DC} = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

where $\sigma_0$ is the preexponential factor, $E_a$ is the activation energy for electrical conduction, $k$ is the Boltzmann constant, and $T$ the absolute temperature. It is clearly seen from the figure that there are two different temperature regions for conductivity.

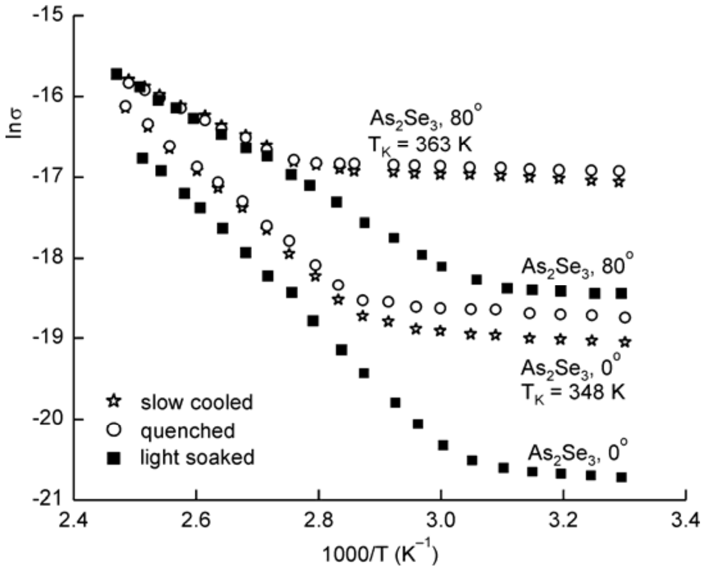


Fig. 1. Temperature dependence of dark conductivity ($\sigma$) for various cooling rates in $As_2Se_3$ normal and oblique films

Table 1. Activation energies and pre-exponential factors at various temperature ranges

| Sample[1] | Temperature | $E_a$ (eV) | $\sigma_0$ |
|---|---|---|---|
| $As_2Se_3$-0° (NC) | high | 0.57 | 1.47 |
| $As_2Se_3$-0° (Q) | | 0.54 | 0.657 |
| $As_2Se_3$-80° (NC) | | 0.31 | $1.2\times10^{-3}$ |
| $As_2Se_3$-80° (Q) | | 0.29 | $6.78\times10^{-4}$ |
| $As_2Se_3$-0° (NC) | low | 0.04 | $3.54\times10^{-7}$ |
| $As_2Se_3$-0° (Q) | | 0.039 | $3.24\times10^{-8}$ |
| $As_2Se_3$-80° (NC) | | 0.027 | $1.08\times10^{-7}$ |
| $As_2Se_3$-80° (Q) | | 0.018 | $8.9\times10^{-8}$ |

[1]NC – normal cooling, Q – quenched.

The activation energies and pre-exponential factors in the high- (360–400 K) and low- (350–300 K) temperature ranges are given in Table 1 for all the samples. The calculated values of activation energy and the pre-exponential factor in the high temperature region suggest that conduction is due to the thermally-assisted tunnelling of charge carriers in localized states in the band tails [8]. The observed decrease in activation energies in obliquely deposited films entails an increase in the conductivity. At low temperatures, the data suggest that conduction takes place in localized states near the Fermi level. The conductivity and pre-factor data were analysed using the Meyer –Neldel rule (MNR) [9].

According to MNR, the pre-factor $\sigma_0$ in Eq. (1) correlates with the activation energy $E_a$:

$$\sigma_0 = \sigma_{00} \exp\left(\frac{E_a}{E_{MN}}\right) \tag{2}$$

where the pre-factor $\sigma_{00}$ and the characteristic energy ($E_{MN}$) are positive constants. The values for $E_{MN}$ in various materials and processes have been reported to be between 25 and 100 meV [10]. A combination of Eqs. (1) and (2) gives a general expression for $\sigma_0$:

$$\sigma = \sigma_{00} \exp\left[\left(\frac{1}{E_{MN}} - \frac{1}{kT}\right) E_a\right] \tag{3}$$

This implies a single crossing point for different activation energies at a temperature $T_{MN} = E_{MN}/k$. At this temperature, $\sigma$ is independent of activation energy. In a plot of $\ln\sigma$ vs. $1/T$, the curves should show one common intersection at $T_{MN}$. Figure 2 shows the plot of $\ln\sigma_0$ vs. $E_a$. It can be seen from the figure that the MNR is satisfied for our films. The value of $E_{MN}$ is 32 meV.

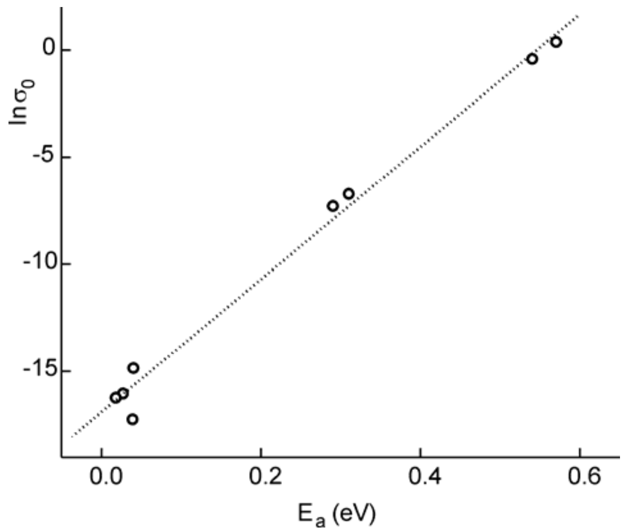


Fig. 2. Plot of $\ln\sigma_0$ vs. $E_a$ of normal and obliquely deposited $As_2Se_3$ films exhibiting the Meyer–Neldel rule

This type of variation in activation energy with a pre-exponential factor indicates the movement of the Fermi level towards the edge of the valence band with increasing temperature, resulting in an increase in conductivity.

### 3.2. Photocurrent

The variation of photocurrent $I_P$ with exposure time is shown in Fig. 3. It is observed that $I_p$ initially reduces with time and attains a nearly constant value after 1 hour of exposure in both normal and obliquely deposited films. This feature is qualitatively consistent with previous observations [11]. Obliquely deposited films exhibited a higher value of $I_p$ at all times. In general, photocurrent is directly related to the photoexcitation rate, the change in the lifetime of the carrier, and the change in mobility. Since in the present case both films were exposed to the same light, it is expected that a longer lifetime in obliquely deposited films is responsible for the observed higher photocurrent.

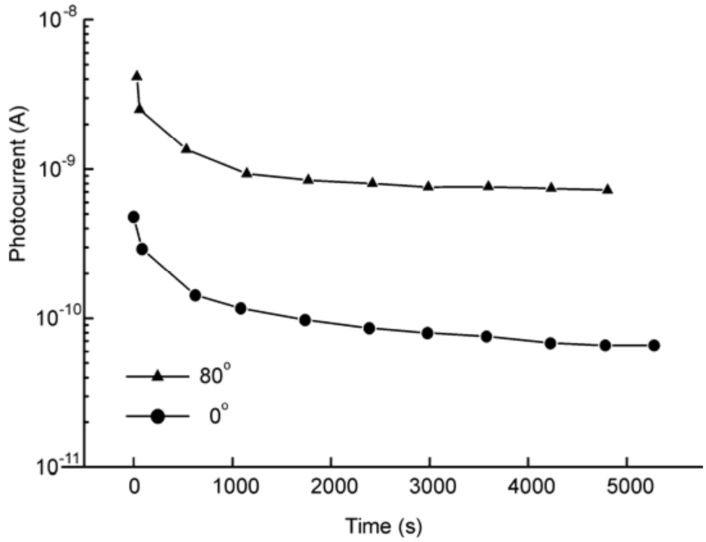


Fig. 3. Photocurrent in normal and obliquely deposited $As_2Se_3$ films as a function of exposure time

A higher photocurrent degradation rate was observed at an early stage of light soaking, as the defect generation rate is higher initially, but as time passes it decreases and finally becomes constant. The decrease in the rate of degradation with light soaking can be understood in terms of the difference between light-induced defect creation and annihilation. Since the annihilation component is directly dependent on the density of metastable defects, the density of defects increases more quickly initially. These photoinduced changes are reversible and can be annealed out near the glass transition temperature of 423 K.

Figures 4 and 5 show the photocurrent spectra before and after light soaking for an hour in normal and obliquely deposited $As_2Se_3$ films, respectively. At room temperature, light soaking gives rise to a decrease in the photocurrent over the entire investigated spectral range. It can also be seen from these figures that maximum in the photocurrent (~2 eV) appears at an energy greater than the band gap of the films (~1.79 eV) [12].

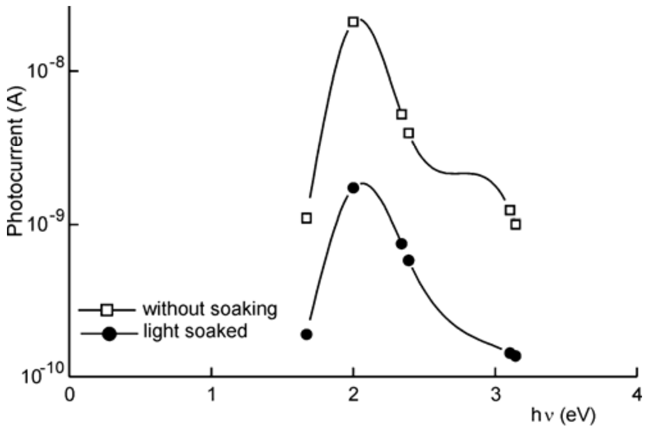


Fig. 4. Spectral dependence of photocurrent for light soaked and without light soaked $As_2Se_3$ normal films

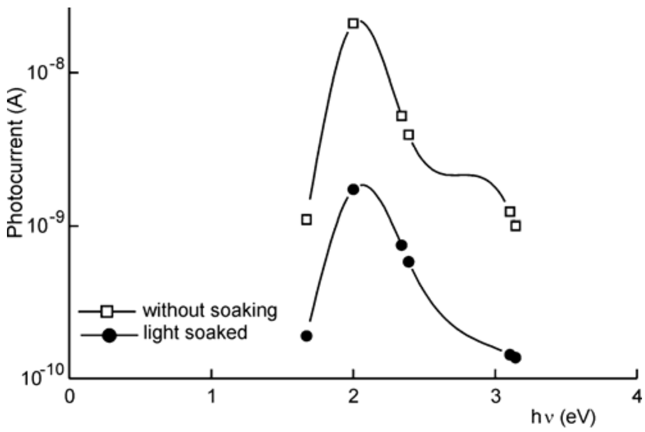


Fig. 5. Spectral dependence of photocurrent for light soaked and without light soaked $As_2Se_3$ obliged films

The decay of photocurrent in chalcogenide glasses due to light soaking can be understood on the basis of the charged defect model originally proposed by Mott [13]. According to the charged defect model, $D^-$ centres can act as recombination (or trapping) centres for photoexcited holes due to Columbic attractive forces, and accordingly the photocurrent decreases with light soaking at room temperature in a-$As_2Se_3$, because new $D^{-}$ centres (light induced metastable defects (LIMD)) are created by illumination. These photoinduced charged defects are metastable, and can recover to normal bonding structures when annealed at the glass-transition temperature. Shimakawa et al. have also proposed a similar model [7, 14]. The decrease in photocurrent is larger in the case of oblique films, which can be due to the photostructural changes induced by strongly absorbed light [15, 16]. Photo-darkening may accompany the creation of new localized states. It has been suggested [14] that these new localized states are close pairs of the charged $D^{+}$ and $D^{-}$ centres. Thus, the recombination of photoexcited holes will be more intense in oblique films then in normal incidence films.

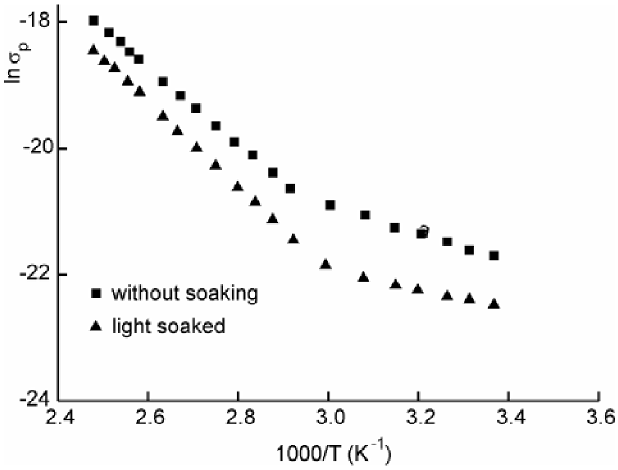


Fig. 6. Temperature dependence of the photoconductivity without light soaking and after light soaking in $As_2Se_3$ normal films

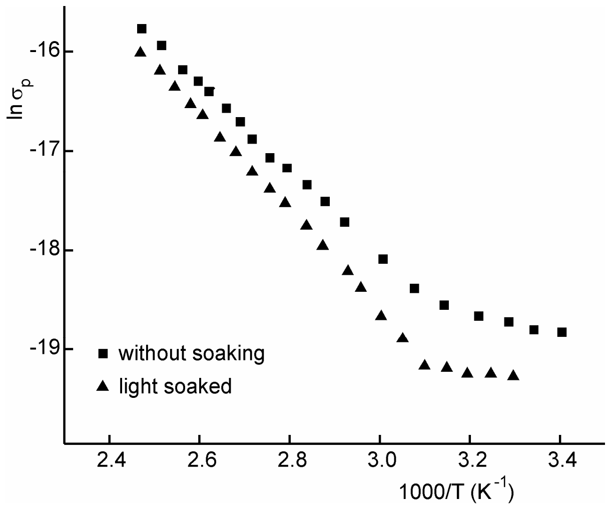


Fig. 7. Temperature dependence of the photoconductivity without light soaking and after light soaking in $As_2Se_3$ obliged films

The creation of defect states due to light soaking may result in a decrease in dark conductivity. The variation of dark conductivity with temperature is also shown in Fig. 1 for comparison. It is clear from this figure that in the low-temperature range dark conductivity after light soaking is nearly two orders smaller than the conductivity without light soaking, for both normal and obliquely deposited films.

Figures 6 and 7 show the temperature dependences of photoconductivities under the illumination of 100 mW/cm$^2$ in light-soaked and unmodified a-$As_2Se_3$ films. A thermally activated behaviour can be observed. Light soaking induces a decrease in photoconductivity. The temperature dependences of photoconductivity in a variety of different IV–V–VI chalcogenide semiconductors can be classified into three types, i.e. (a) type I, (b) type II, and (c) an intermediate between type I and type II. In type I, photoconductivity has a maximum at a specific temperature $T_m$ and generally higher values than the dark conductivity for $T < T_m$ and smaller than dark conductivity for $T > T_m$. Some amorphous materials from the IV–V–VI family show a different temperature dependence of photoconductivity, called type II behaviour, displaying no maximum in photoconductivity, the photoconductivity simply increasing slowly and monotonically with increasing temperature. In general, the photoconductivity is much smaller in this case than the dark conductivity.

In our case, the photoconductivity appears to be somewhat intermediate between type I and type II, as the magnitude of photoconductivity is much smaller than dark conductivity and it is activated in nature. Such a behaviour has been observed in $Ge_xAs_{1-x}$ ($x$ = 0.33, 0.50) and $GeTe_{1-x}$ for $0.3 \le x \le 0.5$ [17].

## 4. Conclusions

It can be concluded that photodegradation is larger in obliquely deposited films, similar to other photoinduced changes. These photoinduced changes in conductivity have been found to be reversible and can be removed by annealing near the glass transition temperature. Enhanced photodegradation may be due to the creation of new localized states, as is evident from the low value of dark conductivity after light soaking.

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