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Analysis of bias field influenced recombination processes in narrow gap Sb_2Se_3 films

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Abstract

The influence of bias field on photoconductivity was studied for a-Sb_2Se_3 films over the temperature range 253–343 K. The dependence of the photoconductivity on the intensity, temperature and bias field reveals the presence of both monomolecular and bimolecular recombination regimes. The photosensitivity and differential lifetime are found to be maximal at low bias voltage (10 V). We find that the electric field induces an increase in the recombination parameter (γ) with increase in the bias field, which plays an important role in the phase transformations (amorphous to crystalline) in electrical switching devices. The negative-U defect states are found to be at 0.36 ± 0.06 and 1.02 ± 0.09 eV above the valence band mobility edge for a-Sb_2Se_3 semiconductor.

1. Introduction

Studies of conduction phenomena in binary chalcogenide systems have attracted increased interest recently due to the applications in various switching devices [1, 2]. The applications in data storage devices make use of reversible and irreversible switching properties, which can be induced by electric field, light or both [2, 3]. The influence of external parameters leads to a microscopic relaxation of the structure due to the changeable nature. The inherent disorder and defects present in the amorphous state are assumed to be responsible for this nature [4]. In phase change random access memory (PRAM), electrical currents of different magnitudes pass from an electrode in contact with a phase change material and the Joule-heating effect is used to apply heat for the reversible transformation. The power consumption in the memory device is proportional to the area of the contact electrode, electrical conductivity and melting temperature of the phase change material. The large values of the electrical conductivity, crystallization temperature and time required for crystallization of $Ge_2Sb_2Te_5$ (used as a phase change material in optical memories) limits the applicability in PRAM technology [5]. The semiconducting system Sb_2Se_3 has recently been investigated as a substitute material for electrically erasable phase change memories with low power consumption [3]. Thus, it is of great importance to understand the influence of defect states on the transport processes and, hence, the metastability behind the transformation.

The measurement of photoconductivity is a valuable technique for understanding the recombination processes and density of defect states [4, 6–8]. Decrease in the dark conductivity as well as the photoconductivity after prolonged illumination has been observed in Sb_2Se_3 films, similar to the Steabler–Wronski effect observed in a-Si:H [1]. This has been considered due to the broadening of the pre-existing thermal defect states upon illumination. Baily and Emin have observed conduction through thermally assisted small polaron hopping in amorphous Sb_2Te_3 samples [9]. Indeed, much work has been done on understanding the conduction processes in these disordered materials, but a proper understanding of the threshold switching has not been achieved until now. This requires understanding of the different transport properties in various experimental conditions. In the present work, we report the bias field effect on the steady state photoconductivity in thermally evaporated Sb_2Se_3 films.

2. Experimental design

The conventional melt quenching technique was used to prepare the sample in the bulk form. The appropriate amounts

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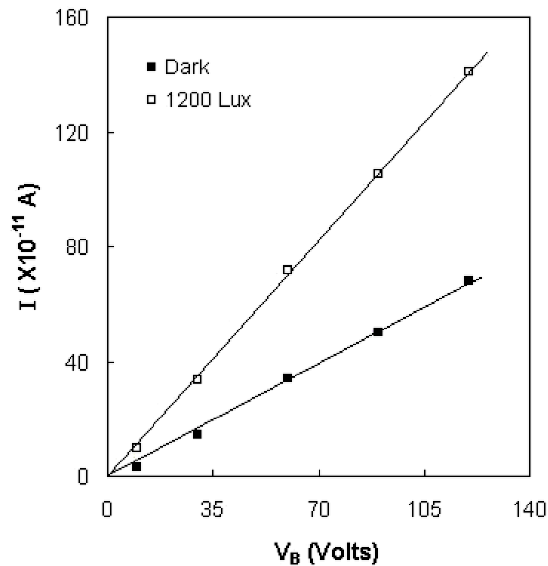

Figure 1. Current–voltage plot for a-Sb_2Se_3 films at room temperature.

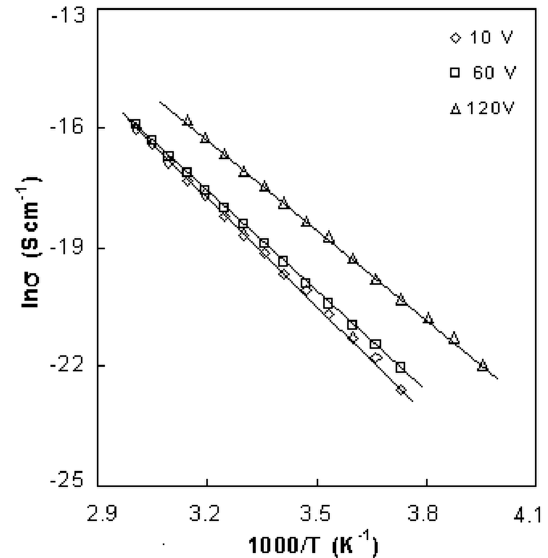

Figure 2. Variation of $\ln\sigma$ versus $1000/T$ for a-Sb_2Se_3 films at different bias fields.

of the precursor materials (Sb and Se) were taken in well-cleaned ampoules. These ampoules were then sealed in a vacuum of 10^{-5} Torr and heated at 850 °C for 45 h. The source material (Sb_2Se_3) in bulk form was used for the deposition of the films on pre-cleaned glass substrates. The thin films were deposited in a high vacuum coating unit (HINDHIGHVAC, model No. 12A4D) under a pressure of 10^{-5} Torr. The amorphous nature was confirmed by the absence of any sharp peak in the x-ray diffraction patterns. The thickness of the films (~1 μm) was measured by using Tolansky's interference method with a sodium vapor lamp as the light source. Pre-deposited Al electrodes with spacing ~1 mm in coplanar geometry were used for the transport studies in the dark and in light.

For electrical studies, the samples were placed in a specially designed metallic cryostat with a heater and thermocouple to measure the temperature. All the measurements were made in a running vacuum of the order of 10^{-4} Torr. The bias field was varied by using a power supply (0–120 V) and the resulting current was measured by using a digital picoammeter (DPM-111, Scientific Equipments, Roorkee). A 500 W tungsten halogen lamp (Halonix, India) was used with a heat-absorbing filter to illuminate the films. By changing the distance between the sample and the light source, the intensity was varied and measured through a digital luxmeter (LX-102, Taiwan). Optical measurements were performed at room temperature using a Shimadzu UV-160A spectrophotometer.

3. Results and discussion

Figure 1 shows the current–voltage (I–V) characteristics for a-Sb_2Se_3 films at different bias voltages in dark conditions and in light. The straight lines passing through the origin confirm the ohmic nature of the contacts for the present material. The slope of the plots defines the differential conductance ($=\mathrm{d}I/\mathrm{d}V$) and its value is found to be 56 nS and 117 nS in dark and illuminated conditions, respectively. An increase in the value of differential conductance with light illumination is expected due to the decrease in the resistivity of the sample. The variation of the dc conductivity (σ) as a function of temperature at different bias fields for a-Sb_2Se_3 films is shown in figure 2. It has been observed that the dark conductivity increases with increase in temperature and bias voltage. It also exhibits an activated temperature dependence of the form $\sigma = \sigma_0 \exp(-\Delta E/kT)$, where σ_0 is the pre-exponential factor, ΔE is the activation energy for dc conduction. The activation energy and pre-exponential factor values change from 0.75 eV and 3.7×10^4 S cm^{-1} at 10 V to 0.64 eV and 2.3×10^3 S cm^{-1} at 120 V as calculated from the slopes and intercept on the y-axis respectively. These values suggest that the band conduction takes place through extended states [10]. The value of ΔE is greater than half of the optical gap ($E_o = 1.20$ eV) for all the bias fields used. Similar results have also been reported in the literature for the doping of different metal impurities in some binary systems, namely Sb_2Se_3 and As_2Se_3 films [11, 12].

The decrease in σ_0 with increase in the bias field is discussed as follows. The trap limited mobility increases only slightly with field [13] or remains constant [14]. This implies that there is a decrease in the density of localized states with increase of the electric field. This is possible if the carriers drift in the higher localized states with increase of the electric field besides being thermally agitated in the tails of the localized states, while the decrease in the dc activation energy with increase in the bias field can be due to the reduction in the number density of states with a shift of the Fermi level $N(E_F)$ towards the valence band edge. Consequently, the increase in the bias field leads to a decrease in the dc activation energy and an increase in the room temperature conductivity.

The time dependence of the photocurrent with different bias fields was also studied. Photodegradation in the photocurrent has been observed for all the fields used. The

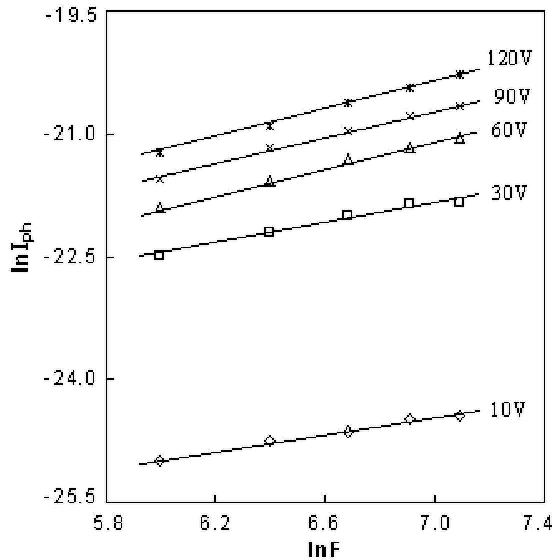

Figure 3. Plots of photocurrent against intensity with different bias fields for a-Sb_2Se_3 films.

Table 1. Calculated values of photosensitivity (S), recombination parameter (γ) and differential lifetime (τ_d) for a-Sb_2Se_3 films at various bias fields.

V_B	S	γ	τ (s)
10	2.3	0.50	48.5
30	2.2	0.67	28.2
60	1.9	0.78	26.3
90	1.7	0.83	25.4
120	1.6	0.91	25.1

important parameter in photoconductivity measurements is the photosensitivity ($S = I_{ph}/I_d$) at a particular temperature and intensity. The values of the photosensitivity at room temperature with different bias fields are summarized in table 1. The intensity versus photocurrent plots for different bias fields are shown in figure 3. This obeys the power law $I_{ph} \propto F^{\gamma}$, where I_{ph} is the photocurrent, F is the light intensity and γ is the exponent that determines the recombination mechanism. The values of exponent γ at different bias fields are summarized in table 1. The value of $\gamma = 0.5$ indicates a bimolecular recombination mechanism, whereas $\gamma = 1.0$ indicates a monomolecular recombination mechanism. If the value of the exponent lies between 0.5 and 1.0, an exponential distribution of traps is present in the gap [7, 9]. In this case, the value of the exponent is 0.5 with a bias supply of +10 V, which indicates a bimolecular recombination mechanism. Further increase in the bias field increases the exponent to 0.91 at a bias field of 120 V. Since this value is near to that for the monomolecular recombination, the recombination mechanism changes from bimolecular to a monomolecular with increase in the bias field.

The decrease in the photosensitivity and a change in the recombination process with increase in the bias field for a-Sb_2Se_3 films can be understood as follows. The decrease in both the dc activation energy and the pre-exponential factor show an increase in the carrier concentration with increase in the bias field. Therefore, the density of equilibrium thermal carriers exceeds that of photogenerated carriers as we increase the bias field and, consequently, there are fewer photogenerated carriers in the photoconduction process, which leads to the decrease in photosensitivity. The increase in the carrier concentration in the dark with increase in bias field makes the concentration of the photogenerated carriers smaller as compared to that of the equilibrium majority carriers. The rate of recombination now becomes proportional to that for one type of carriers and results in a change in the recombination process.

The recombination time is effectively dominated by the rate of trap emptying, which is much larger than the carrier lifetime. Thus, the results can also be discussed by assuming an enhancement in the rate of de-trapping of charge carriers from their neutral defect states with increase in the bias field. As a result of faster de-trapping process, a decrease in differential lifetime of the carrier at higher bias fields has been observed. Since the photosensitivity depends on the nature of defect states, which is greatly influenced by the change in the field, leads to a decrease in the photosensitivity.

These results have also been analyzed by using the concept of differential lifetime and the localized–localized recombination. For the localized–localized recombination, the spatial distribution of carriers is important; the transition probability and recombination coefficients are functions of the distance between the pairs of electron and hole traps. Hence the process of recombination can only be described using a distributed time constant. The differential lifetime, τ_d, is given by the relation $\tau_d = -[I_{ph}(dI_{ph}/dt)]^{-1}$. The plots of ln I_{ph} versus t are straight lines for the timescale 5–60 s after stopping the illumination. As the bimolecular recombination does not have a single decay time constant, for comparison its values are calculated only from the straight line plots in this time interval. This indicates that the decay process occurs through non-dispersive bimolecular recombination. The values of the calculated differential lifetime τ_d at different bias fields are summarized in table 1. The value of τ_d decreases sharply from 48.5 s at 10 V to 28.2 s at 30 V, while with further increase in the bias field, it decreases slowly. This variation may be due to the change in the rate of trap emptying and carrier lifetime with increase in the bias field.

Figure 4 shows a plot for dark and photocurrent data measured at different light intensities as a function of temperature in the range 253–343 K with a bias supply of 10 V. The maxima in the photocurrent shifting to the higher temperature side with increase in the light intensity has been observed. The observed photocurrent behavior is quite similar to that observed for amorphous chalcogenide semiconductors [6, 15]. At low temperatures and high intensities, i.e. when the photocurrent is higher than the dark current, a bimolecular recombination regime leads to an exponential increase in I_{ph} with increase in the temperature. The low temperature slope, the activation energy for bimolecular recombination (ΔE_b), is calculated using the relation $\sigma_{ph} \propto \exp(-\Delta E_b/kT)$. The value of ΔE_b is 0.18 ± 0.03 eV at 1500 lux.

In the high temperature region, a broad maximum in photoconductivity is observed which becomes more

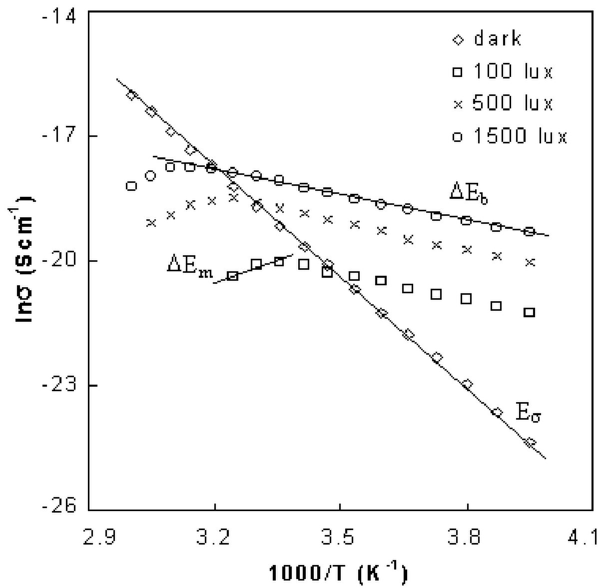

Figure 4. Temperature dependence of the dark conductivity and photoconductivity for a-Sb_2Se_3 films at 10 V biasing supply.

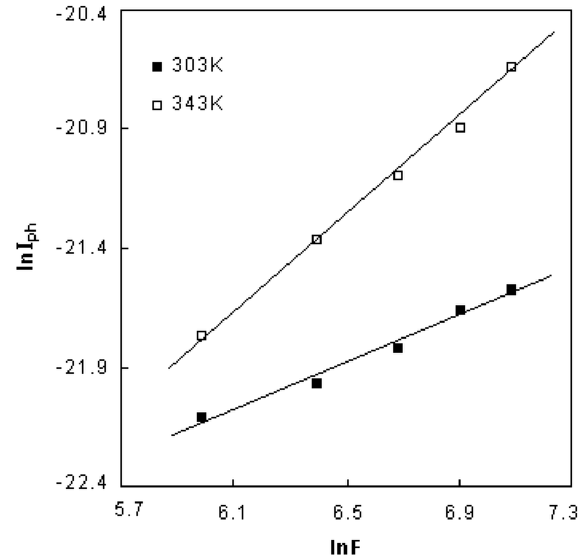

Figure 5. The dependence of the photocurrents on the light intensity at two different temperatures for a-Sb_2Se_3 film samples.

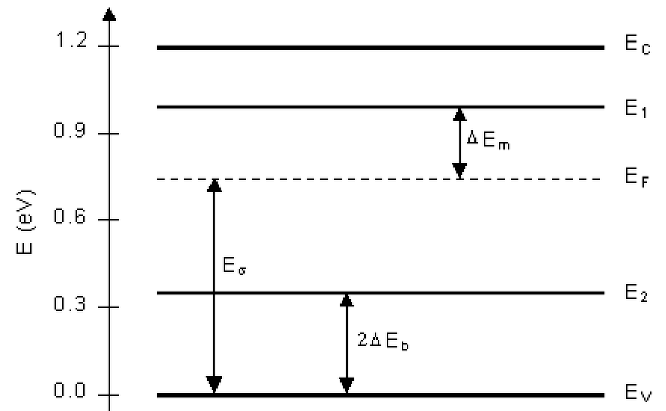

Figure 6. Energy level diagram for the negative-U defects in a-Sb_2Se_3 films.

pronounced at low intensity (100 lux). For high temperature and low intensity, the photoconductivity becomes smaller than the dark conductivity, monomolecular recombination takes over and a photocurrent exponentially decreasing with temperature was observed. For this region, the activation energy for monomolecular recombination (ΔE_m) is calculated by using the relation $\sigma_{ph} \propto \exp(\Delta E_m/kT)$. It is difficult to calculate the precise value for ΔE_m, as only a limited number of data points are available in the higher temperature region. The estimated value of ΔE_m is 0.27 ± 0.08 eV at 100 lux.

The intensity dependence of the photoconductivity has also been studied at two different temperatures. Figure 5 shows the photocurrent variation with light intensities at two different temperatures. These plots indicate a power law variation. The value of the exponent is 0.51 at lower temperature (303 K), while $\gamma \sim 1.0$ is found on the higher temperature side. Between these two extreme cases, γ lies between 0.5 and 1.0. In single-trap analysis [6], the value of $\gamma = 1$ corresponds to the case of monomolecular recombination and $\gamma \sim 0.5$ to bimolecular recombination. However, in the case of exponential distribution of traps, the value of γ is anywhere between 0.5 and 1.0 depending on the intensity and temperature range. These results can be explained on the basis of a model proposed by Simmons and Taylor [16].

The positions of the defect energy states E_1 and E_2 above the valence band edge can be written as $E_1 = \Delta E + \Delta E_m$ and $E_2 = 2\Delta E_b$ respectively. For chalcogenide semiconductors, these centers have been identified as negative-U centers, i.e. charged defects with negative effective correlation energy [17]. From this, the approximate locations of the energy states E_1 and E_2 have been calculated for Sb_2Se_3 films and are shown in figure 6. The figure depicts that E_F is not pinned between the middles of these two defect states and is located towards the conduction band edge. A similar discrepancy has also been observed for Se and $Ge_{22}Se_{78}$ films. The Fermi level lies towards E_1 for a-Se, while it is towards E_2 for $Ge_{22}Se_{78}$ films [18, 19]. This shows that D^+ and D^- centers will act as discrete traps for photogenerated electrons and holes ($D^+ + e \rightarrow D^0$ and $D^- + h \rightarrow D^0$) and create the neutral D^0 sites. Due to polaronic lattice deformation, these D^0 sites produce energy levels approximately midway between the band edges and the Fermi level, as shown in figure 6.

The pronounced field effects observed in the presence of light are due to the appearance of some light induced metastable defects. The photoexcitation results in pairs of electrons and holes which thermalize in the band states and the tail states up to certain depths E_1 and E_2, respectively. The recombination is monomolecular, when the density of thermal carriers exceeds that of the photoexcited carriers and is bimolecular, when there are more photoexcited carriers than thermal ones as the rate of recombination is governed by the photogenerated carriers and equilibrium carriers in the dark [20]. Thus, at low electric field, the number of photogenerated neutral defects is greater than the equilibrium

value, causing bimolecular recombination, while at high electric field the number of photogenerated neutral defects is less than the equilibrium value, causing a monomolecular recombination in the present case [21]. Therefore, the increase in the equilibrium concentration of carriers with lower concentration of photogenerated ones at high bias fields may result in the observed changes in the recombination mechanism.

4. Conclusions

The dark conductivity and steady state photoconductivity measurements as a function of temperature and light intensity reveal the presence of defect levels in the band gap with negative correlation energy for Sb_2Se_3 films. The values of the dc activation energy, pre-exponential factor, photosensitivity and differential lifetime have been found to decrease while the recombination parameter increases with increase in the bias field. Higher photosensitivity at low bias fields and smaller differential lifetime at higher bias field were observed.

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