

Modulated Photoconductivity Studies of a-As₂Se₃ Thin Films

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Abstract

Modulated photocurrent measurements in amorphous arsenic triselenide (a-As₂Se₃) is reported. Particular focus is paid towards photocarrier lifetimes as a function of temperature, and applied electric field (i.e. dc) were determined by using the quadrature frequency-resolved spectroscopy method. The activation energy from the photocurrent as a function of temperature was determined to be about 125 meV for a constant illumination intensity of 2.3 mW. Its value was found to be almost independent of the applied electric field. The exponent ν in the power law relationship ($I_{ph} \propto G^\nu$) between generating flux and photocurrent was obtained under different electric fields. The electric field dependence of photocurrent at various temperatures was also measured. A very little non-ohmic contact behavior was observed at low fields and at high temperatures.

Key Words: Amorphous As₂Se₃, Photoconduction, recombination, lifetime, trapping.

1. Introduction

The importance of amorphous semiconductors to science and technology is considerable, with these materials having application in solar cells, IR detectors, electronics and optical switches, optical recording media and image processing systems [1–5]. During the last decade, many efforts have been made to develop some new vitreous materials, especially glassy chalcogenides (e.g., a-Se, a-SeTe, a-As₂Se₃, a-As₂Te₃, etc.) because of their attractive properties. Discovery and study of new materials, whose properties can be tailored-made, constitute the core of development of solid state technology. In spite of well-established technologies for preparation of these semiconductor chalcogenide glasses and services fabricated, utility of such materials is restrained due to their discrete structural and electronic properties. Effects of the impurities in chalcogenide glasses may have importance in the fabrication glassy semiconductors. It is now known that illumination creates charged defect centers (D⁺ and D⁻) in amorphous chalcogenide gasses [6, 7]. These defects act as recombination centers for photoexcited charge carriers and hence the number of photocarriers obtained decreases with increasing illumination time (photo-degradation), resulting in a decrease in the net charge on the thin film layers. The decrease in the net charge will result in the decrease of repulsion force.

Although there have been numerous attempts, both theoretical and experimental in the literature, the nature of the recombination processes, and thus physical mechanism responsible for the photocurrent of chalcogenide amorphous semiconductors at low temperatures, is still an unsolved problem at present. The

study of frequency-resolved photocurrent as a function of temperature, applied field, excitation wavelength and light intensity in amorphous chalcogenide semiconductors is a valuable tool to developing a good understanding of the recombination processes and distribution of localized states which control the frequency-resolved photocurrent kinetics. However, in spite of the extensive studies, the interpretation of experimental data remains difficult. We believe that our experimental results will help to study this problem.

In this work, we mainly determined the photocarrier lifetime, the exponent ν in the power-law relationship $I_{ph} \sim G^\nu$, and their dependences on the electric field and temperature in a-As₂Se₃. We also attempted to interpret our experimental results in the frame of predictions of photoconductivity models proposed at high and low temperatures.

2. Experimental

Our sample of a-As₂Se₃ was a thin film prepared by standard thermal evaporation. The thermal evaporation, like other vacuum techniques, is a thin-film preparative technique. It is most widely used method for producing amorphous thin films by deposition from a vapor. The starting compound is vaporized and the material is deposited on a substrate. In practice, the evaporation is performed in vacuo to reduce contamination. In the thermal evaporation chamber, the starting compound is evaporated from a crucible (mostly carbon, or ceramic types) surrounded by a tungsten spiral resistance (heating element) which allows a large current to pass through it. By using a suitable Al foil mask, it is possible to produce many samples of the same type, in one evaporation. Further details of the thermal evaporation technique can be found in reference [1] (pages 6-9).

The material used for our sample was acquired from BDH Chemicals and had a purity of 99.9992%. During evaporation of the film, the work chamber pressure was maintained at less than 10^{-6} Torr. The substrate (Corning 7059 glass) was held at room temperature (295 K). The thickness of sample was on the order of 1 μ m. Gold contacts were then evaporated on the film in coplanar configuration. The spacing between the contacts was 0.13 mm. Copper wires were placed on the gold layers with electrically conductive silver paint.

The sample was excited by the 1.96 eV line of a HeNe laser. An acousto-optic modulator (IntraAction Corp., Model AOM-125) was used to modulate the light sinusoidally in the frequency range of 10 Hz to 100 kHz. The modulation amplitude amounted to 46% of the bias light intensity. The modulated photocurrent signal excited in this way was measured and analyzed by a lock-in amplifier (SR 530 Stanford Research System). During the measurements the sample was kept in a helium exchange-gas cryostat in which the temperature could be varied between room temperature and 20 K. The vacuum pressure of the cryostat was about 10^{-6} Torr. Light intensities were varied by using a set of neutral density filters.

3. Results and Discussion

In-quadrature ($\phi = 90^\circ$) frequency-resolved photocurrent (IQ-FRPC) response of a-As₂Se₃ in the frequency interval between 10 Hz and 100 kHz was measured as a function of temperature, intensity of the excitation light and applied electric field. Since the energy of the excitation light (1.96 eV) is much higher than the optical band gap of this material (1.8 eV), we assume that the carriers are photoexcited between extended states and then a trap limited recombination occurs.

Figure 1 shows the IQ-FRPC response at various temperatures. The light intensity (at 632.8 nm) from HeNe laser was kept constant at 2.31 mW ($\sim 2.3 \times 10^{19}$ photons \cdot cm $^{-2}$ \cdot s $^{-1}$) during measurements. The applied electric field was 5×10^4 V/cm.

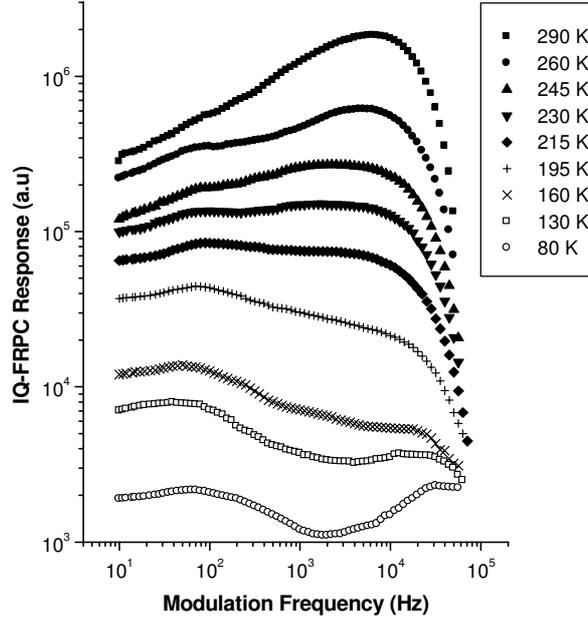


Figure 1. In-quadrature frequency-resolved photocurrent (IQ-FRPC) response of a-As₂Se₃ at various temperatures. Excitation light intensity is 2.31 mW with the wavelength of 632.8 nm.

Lifetime can be measured in terms of the frequency-resolved spectroscopy (FRS) method [8]. This method has been widely applied to the study of lifetime and recombination processes [9–11]. According to FRS method, the in-phase and quadrature photoluminescence response in amorphous materials have been treated in detail and showed that the quadrature response function gives the lifetime distribution of the system whereas the in-phase response is the integral of the lifetime distribution between the limits $\tau \propto 2\pi f^{-1}$ and ∞ . This treatment has been applied to frequency-resolved photocurrent response in amorphous materials [12–15]. In the framework of the frequency-resolved photocurrent method, Wagner et al. [12] suggest that for a system with a single characteristic time τ the quadrature frequency-resolved spectrum is a symmetric line of half-width 0.7 decades peaked at the frequency

$$\tau = 1/(2\pi f_{peak}). \quad (1)$$

Using this relation and the data plotted in Figure 1, a room temperature (290 K) lifetime of 22.5 μ s was calculated. However, this main peak starts to disappear at low temperatures and a second peak, corresponding to a lifetime of 2.53 ms at 80 K, comes to be dominant. This result provides a way of distinguishing between capture and recombination rates. If the carriers move in extended states, and detrapping is not important, then only one peak is expected in the IQ-FRPC, corresponding to the total capture rate into localized levels. At higher temperatures, the carriers may be thermally ionized from recombination or trapping states. Simple models indicate that a second lifetime proportional to the detrapping rate will be seen even if only one recombination path is present. However, because the release rate is thermally activated both the second lifetime and the strength of its contribution will be strongly temperature dependent [13, 16].

Figure 2 shows the IQ-FRPC response at different levels of applied electric fields. This spectra was obtained for a constant excitation light intensity of 2.31 mW and room temperature (290 K). A single, broad distribution is observed to peak at 11.22 kHz. From Equation (1), the corresponding carrier lifetime is calculated as 14.2 μ s, which is independent of applied electric field.

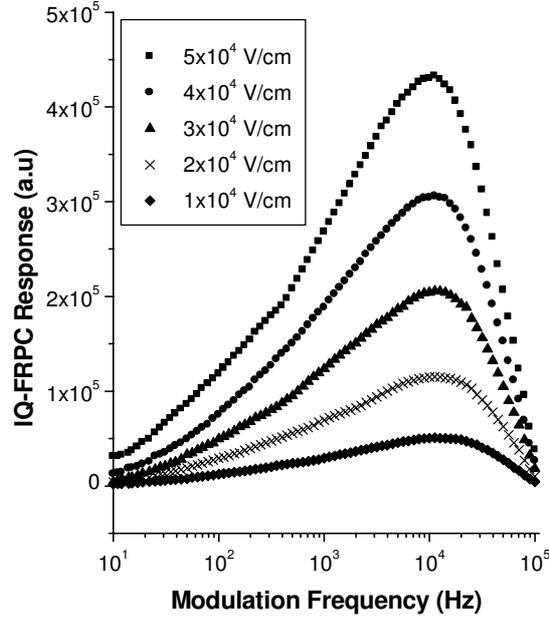


Figure 2. IQ-FRPC response of a-As₂Se₃ under various applied electric fields. Excitation light intensity is 2.31 mW with the wavelength of 632.8 nm. Data were taken at room temperature (290 K).

Figure 3 shows the temperature dependence of photocurrent for various levels of applied electric field. It indicates three regions: (i) At low temperatures, $T \leq 100$ K, the photocurrent becomes temperature independent and can be explained by a theory of energy loss hopping of photocarriers through a distribution of localized band tail states [17–18]. According to this theory, at low temperatures, the photoexcited carriers can only lose energy by tunneling to lower energy states, such as localized tail states or by recombination. (ii) At intermediate temperatures, $100 \text{ K} \leq T \leq 200 \text{ K}$, the photocurrent starts to rise with temperature by several orders of magnitude. As the temperature increases the excess electrons start to hop in the tail of the conduction band, giving rise to photocurrent while holes are still immobile because they are trapped in deeper states immediately after thermalization [19]. (iii) At high temperatures, $T \geq 200 \text{ K}$, the photocurrent increases rapidly and almost linearly with increasing temperatures. The photocurrent I_{ph} (proportional to photoconduction, σ_{ph}) produced by the thermal activation of photocarriers, follows the exponential relation [20–21],

$$I_{ph}(\sim \sigma_{ph}) = I_o \exp(-E_a/kT) \quad (2)$$

where I_o is a prefactor, k is the Boltzmann's constant, and E_a is the activation energy. The value of E_a can be calculated from the slope of a linear plot of $\ln(I_{ph})$ vs. $1000/T$. An average E_a value of about 125 meV of this linear plot was determined at all applied electric fields measured. At intermediate temperatures, however the E_a decreases with decreasing temperatures. At low temperatures, the photocurrent approaches a constant value and the activation energy becomes zero, as expected. At high temperatures, the transport of photocarriers can be described by the multiple trapping model [22–23], in which injected carriers thermalize in a broad distribution of localized band tail states, moving to deeper energies as a result of thermal activation to transport states and subsequent retrapping.

An alternative interest for recombination kinetics in chalcogenide glasses is the dependence of photocurrent I_{ph} on the photogeneration rate G :

$$I_{ph} \propto G^v, \quad (3)$$

and can be written by a differential form

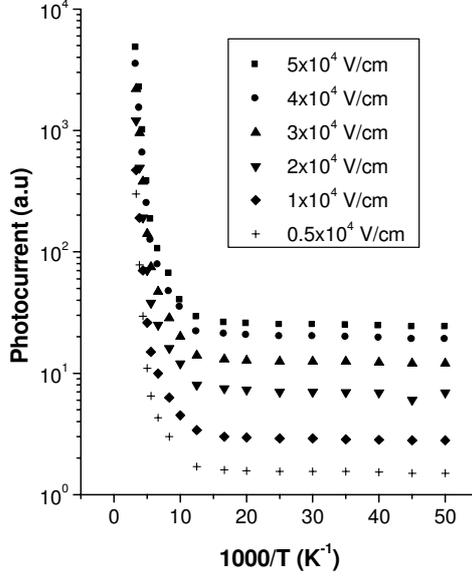


Figure 3. Photocurrent vs. inverse temperature at various levels of applied electric fields. Excitation light intensity is 2.31 mW with the wavelength of 632.8 nm.

$$\nu = d [\ln(I_{ph})] / d [\ln(G)]. \quad (4)$$

It is now well known that the value of the exponent ν differs in various chalcogenide materials. In most cases, a sublinear dependence is found and the exponent ν in this power-law relation has quite complicated variations with temperature, photon energy, light intensity and applied electric field [15, 24–25].

Figure 4 shows the excitation light intensity dependence of photocurrent for six applied electric fields determined at a constant modulation frequency of 10 Hz and temperature of 290 K. Rose [24] suggests that $\nu = 1$ corresponds to monomolecular recombination and $\nu = 0.5$ to bimolecular recombination. However, in the case of continuous distribution of traps the value of ν may be anywhere between 0.5 and 1.0, depending on the intensity and the temperature range. As can be seen from Figure 4, the values of exponent ν lie between 0.55 and 0.58. The dependence of ν on the applied electric field is weak. The result of $\nu \sim 0.55$ – 0.58 , indicates a continuous distribution of traps within the mobility gap. It was already reported that the value of ν is independent of excitation wavelength [15]. However, its value depends on the temperature [26].

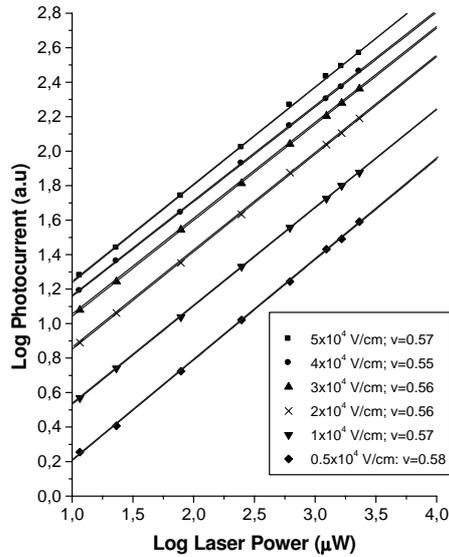


Figure 4. Excitation light intensity-dependence of photocurrent at various levels of applied electric fields. Data were taken at room temperature (290 K).

Figure 5 shows the photocurrent vs. applied electric field at various temperatures. The excitation light intensity and modulation frequency were kept constant at 2.31 mW and 10 Hz. Current-voltage measurement taken in the dark proved that the Au contacts deposited on the a-As₂Se₃ sample were perfectly ohmic. The dark conductivity of a-As₂Se₃ at room temperature was around $10^{-12}\Omega^{-1}\cdot\text{cm}^{-1}$. However, as seen from Figure 5 the current-voltage relation shows a very little nonlinearity at very low fields ($\leq 2 \times 10^4$ V/cm) and at high temperatures (≥ 200 K) under the illumination. However, we have no an exact explanation for this result at present. It may be due to the increase of photocarrier release rate which is thermally activated at high temperatures.

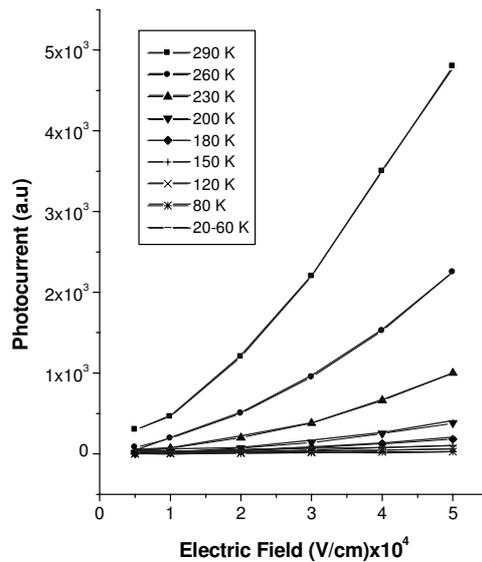


Figure 5. Electric field-dependence of photocurrent at various temperatures. Excitation light intensity was kept constant at 2.31 mW with the wavelength of 632.8 nm.

4. Conclusion

In-quadrature frequency-resolved photocurrent response (IQ-FRPC) of a-As₂Se₃ thin film sample between 10 Hz and 100 kHz was measured as a function of the intensity of the excitation light, temperature and applied electric fields. The temperature range covered was 20–295 K. We observed that the IQ-FRPC response shows a single broad peak (main peak) at room temperature, and its lifetime (22.5 μ s) does not depend on the temperature and applied electric field. Below about 260 K, a weak peak (the second peak) was discovered in the IQ-FRPC spectra at low frequency range, in addition to the main peak. Its lifetime was determined as 2.53 ms. We suggest that this second peak can be related to detrapping rate. It splits away markedly from the main peak as the temperature drops.

The high temperature regions of photocurrent vs. inverse temperature curves at different applied fields show an activated behavior with an activation energy of 125 meV for an excitation intensity of 2.31 mW.

The exponent ν in the power-law relationship of the intensity of the photocurrent on the generation rate is found to be weakly applied electric field-dependent between 0.5×10^4 V/cm and 5×10^4 V/cm. Its value was determined in the range $\nu \sim 0.55$ – 0.58 , indicating a continuous distribution of localized states.

The current-voltage measurements under the illumination show that a very little non-ohmic contact behavior at low applied electric fields ($\leq 2 \times 10^4$ V/cm) and high temperatures (≥ 200 K). However, we have no clear explanation for this result.

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