

Modulated Dual-Beam Photoconductivity in Hot-Pressured a-As₂Se₃

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The effects of dual-beam illumination on the exponent ν in the power-law relationship, $I_{ph} \propto G^\nu$, between generating flux and photocurrent, as well as carrier lifetime, temperature and electric field dependent photocurrent were investigated in hot-pressured amorphous arsenic(III) selenide (a-As₂Se₃) with coplanar electrodes. For these measurements, we used a focused tungsten white light and HeNe/Ar laser red/blue light as a DC and modulated light, respectively. The photocurrent due to the DC light bias is perturbed by the modulated beam. The DC light creates free electrons and holes and thus changes the occupation of the semiconductor gap states through which recombination occurs. The second, mostly monochromatic, beam is used to probe recombination processes by altering the occupation of selected gap states, thereby modulating the photocurrent. The temperature variation of the exponent ν is obtained and compared for both single and dual beam illuminations in detail. At temperatures lower than about 200 K, the single beam values of ν are almost constant and close to 1.0, but the dual beam values of ν are larger than 1.0, and thus they show superlinear behavior. In temperature region between about 200 K and 250 K, both single and dual beam values of ν are almost coincident and decrease with increasing temperatures. However, above 250 K, they saturate. The photocurrent modulation spectrum, which is dependent on temperature and the intensity of DC light, is rich in information about gap states that act as recombination centers. The second beam has no significant effects on the modulation spectrum and thus the carrier lifetime. However, it is found that the carrier lifetime under illumination strongly depends on the excitation wavelength due to the different light absorption. Therefore, the two-beam method in our photocurrent measurements offers a sensitive way of probing the recombination of excess carriers trapped in tail states and defects. We also discuss the results in terms of photocurrent models proposed.

topics: dual-beam photocurrent, a-As₂Se₃, intensity- and temperature-dependence, lifetime, recombination

1. Introduction

Amorphous chalcogenides (e.g. Se, S, selenides or sulfides of Ge, As, etc.) have attracted a great deal of interest as they represent many unique properties [1]. These properties have been successfully explained by incorporating native defect states in the density of states (DOS), which are characterized by negative effective correlation energy [2]. It was postulated that these effects occur in concentration of 10^{17} – 10^{19} cm⁻³ and arise from under- and over-coordinated atoms (i.e., As and Se atoms in a-As₂Se₃, respectively), well-known as valence alternation pairs (VAPs) [3]. Experimental results in amorphous chalcogenides are consistent with the VAP model [4, 5].

The impact of amorphous semiconductors on science and technology is considerable, with these materials having application in solar cells, IR detectors, electronics and optical switches, inorganic resist, optical recording media and image processing systems [6, 7]. During the last decade,

efforts have been made to develop new vitreous materials, especially glassy chalcogenide materials (e.g., Se, S, selenides or sulfides of Ge, As, etc.) because of their attractive IR properties. Discovery and study of new materials, whose properties can be tailor-made, constitute the core of development of solid state technology. In spite of well-established technologies for preparation of these semiconductors and services fabricated, utility of such materials is restrained due to their discrete structural and electronic properties. Impurity effects in chalcogenide glasses may have importance in fabricating glassy semiconductors. It is known that illumination creates charged defect centers (D⁺ and D⁻) in amorphous chalcogenides [8, 9]. These defects act as recombination centers for photoexcited carriers and hence the number of photocarriers decreases with increasing illumination time (photodegradation), resulting in a decrease in the net charge.

The dual beam photocurrent technique [10–14] has been employed extensively to explore recombination centers for photogenerated carriers. Despite

that, the origin of the recombination kinetics, and thus the exponent ν in the power-law relationship $I_{ph} \propto G^\nu$, which reflects this complex phenomena is as yet still unclear. Many investigations have been done so far on evaporated glass films, but few on bulk glasses. In the present work, we especially examined the effect of second beam (tungsten focused light) on the exponent ν , the temperature dependence photocurrent, and the photocarrier lifetime in hot-pressed a-As₂Se₃ bulk samples. The temperature range covered was 20–30 K. We also compared our experimental results with the predictions of dual-beam photocurrent models proposed at high and low temperatures.

2. Experimental details

We produced the bulk samples of a-As₂Se₃ by using a hot pressured method in a fume cupboard. The materials used for these samples were from BDH chemicals with a high purity of 99.9992%. The hot pressured technique is well known in which the sample is obtained by cooling from the molten state. During cooling, the material is squeezed between two parallel plates (glasses in our case) to get smooth surfaces. The amorphous nature of glassy alloys has been verified by X-ray diffraction (XRD). The absence of any prominent peak in the XRD pattern indicates amorphous nature of the investigated sample. Figure 1 shows the X-ray diffraction of a bulky a-As₂Se₃ used. It gives an idea about whether its structure represents amorphous state or crystalline. The appearance of broad diffractions implies amorphous state. Meanwhile we should note that all of our chalcogenide samples are very brittle. Mostly we put co-planar Al or Au electrodes on the samples by using a suitable Al foil mask and a thermal evaporation unit. However, instead of using a crucible, the Al or Au ingots were evaporated directly from tungsten spiral. For electrode spacing, the different size Cu wires ranging between 0.1 mm and 0.2 mm were used as masks. Using of excess Al or Au ingots or long time evaporation cause the electrode space to be closed. Furthermore, one must be very careful to get a good vacuum before evaporation. Otherwise it is not possible to obtain good electrodes. The evaporated electrodes were left to dry inside the vacuum for a while (sometimes one or two days). This is intended to prevent the oxide contamination of the sample surfaces. External copper leads were contacted with Ag paint. The Ag paint must be left to dry for at least 20 min. However, using too much silver paint or too thick Cu wire causes the contacts to crack at low temperatures and under high voltages. Obviously this gives bad results for the photocurrent experiments and can lead to complete sample loss. Special care and experience are necessary to get good results. The current-voltage (I - V) measurements taken in dark proved that the contacts were perfectly ohmic. As noted previously [2], gold

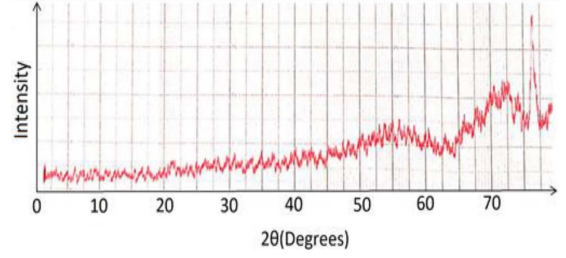


Fig. 1. XRD of the hot-pressed a-As₂Se₃.

contacts perform better in injecting hole carriers and thus give larger photocurrents than aluminium contacts for these a-As₂Se₃ chalcogenide samples.

The samples were excited by the 1.96 eV line of a HeNe laser or by the 2.54 eV line of Ar 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 analysed 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. The intensity of the excitation light was reduced by neutral density filters. Proper care was taken to avoid the thermal effects of tungsten light. It was passed through water and heat absorbing filters (KG3) before falling on the sample. The heat absorbing filter provides a cut at about 800 nm. A schematic representation of the experimental arrangement was given in [14].

3. Results and discussion

The quadrature frequency-resolved photocurrent (FRPC) response of the samples in the frequency interval between 10 Hz and 100 kHz was measured as a function of the intensity of the excitation light and temperature. Since the energy of the excitation light is much higher than the optical band gap of these materials (1.8 eV), we assume that the carriers are photoexcited between extended states and then a trap limited recombination occurs.

One of the main interest is the dependence of photocurrent I_{ph} on the photogeneration rate G :

$$I_{ph} \propto G^\nu. \quad (1)$$

It is differentially defined by:

$$\nu = \frac{d(\ln(I_{ph}))}{d(\ln(G))}. \quad (2)$$

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

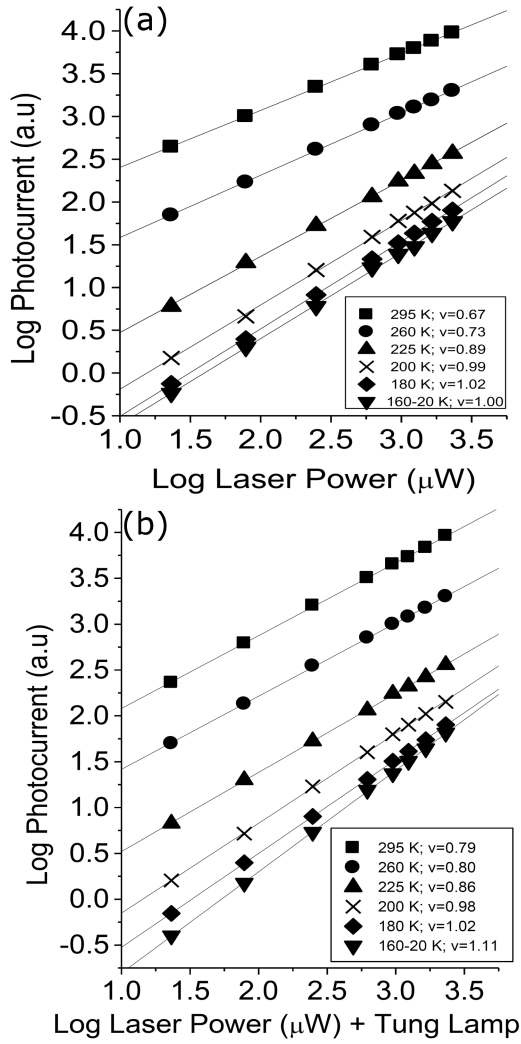


Fig. 2. Light intensity dependence of modulated photocurrent in a-As₂Se₃ at different temperatures: (a) single light (HeNe), (b) dual-beam (HeNe + tungsten).

Figure 2 shows the light intensity dependence of photocurrent at different temperatures under single and dual beam illuminations. According to (2), the plot between $\ln(I_{ph})$ and $\ln(G)$ should be straight line. The exponent ν is calculated from the slope of the curve plotted in Fig. 2 for each temperature.

The ν factor in (2) could qualitatively be associated with the amount of recombination centers located in energy gap; a higher value of ν -factor, in general, implies a higher rate of carrier recombination. In Fig. 3, the ν values were compared for single and dual beam illuminations as a function of temperature. Clearly the ν values for dual beam are larger than those of single light at low temperatures ($T < 200$ K) and high temperatures ($T > 250$ K). Furthermore, the ν values for dual beam increase with decreasing temperatures, while the ν values for single light are almost constant below 200 K. Also, under dual beam, the ν value shows a slight supralinear intensity-dependence with $1.0 < \nu < 1.11$.

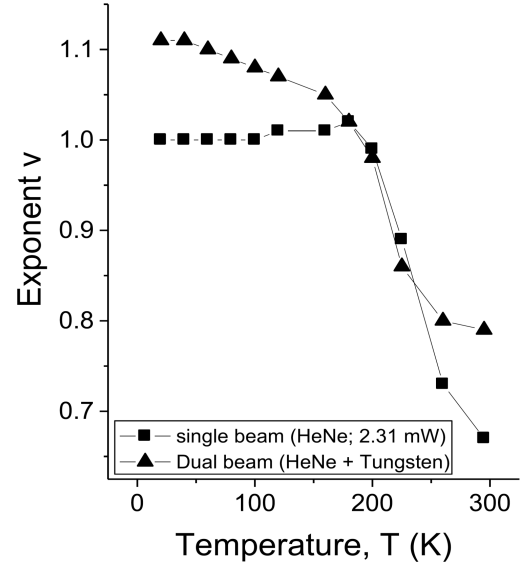


Fig. 3. Dual beam effect on the exponent ν in a-As₂Se₃ at temperature range 20–30 K.

Rose [16] reports that $\nu = 1$ corresponds to monomolecular recombination and $\nu = 0.5$ to bimolecular recombination. However, in the case of continuous distribution of localized states, the value of ν may be anywhere between 0.5 and 1.0 depending on the light intensity and the temperature range. As can be seen in Fig. 2, the values of exponent ν lie between about 0.5 and 1.0, indicating the presence of a continuous distribution of localized states in the energy gap. On the other hand, it is possible that the intermediate value of exponent ν is the result of limited number of traps, which are becoming saturated in the studied intensity range. It is clear from the figure that the exponent ν exhibits slightly supralinear intensity dependences, with $1.0 < \nu < 1.11$ in the temperature range of about 20–200 K. We should mention that reports of such power dependence greater than unity have also been reported in the literature [17–20]. This has been interpreted as a sensitization effect involving traps of different capture cross-sections in the lower-half of the energy gap.

We have also examined the temperature dependence of the photocurrent of hot-pressed a-As₂Se₃ samples used. Curves of Fig. 4 show a comparative typical Arrhenius plot of the logarithm of photocurrent I_{ph} against the inverse of temperature $1/T$, for three different single and dual beam illuminations. The single and dual beam curves are almost coincident for three illumination levels used. The light intensity (632 nm from HeNe laser) and modulation frequency were kept constant at 2.3 mW (about 2.3×10^{19} photons/(cm² s)) and at 10 Hz respectively for three cases. Obviously the temperature dependence of photocurrent indicates two regimes: (i) at low temperatures (≤ 200 K), the photocurrent tends to be constant, and (ii) at high temperatures (≥ 200 K), it increases very rapidly

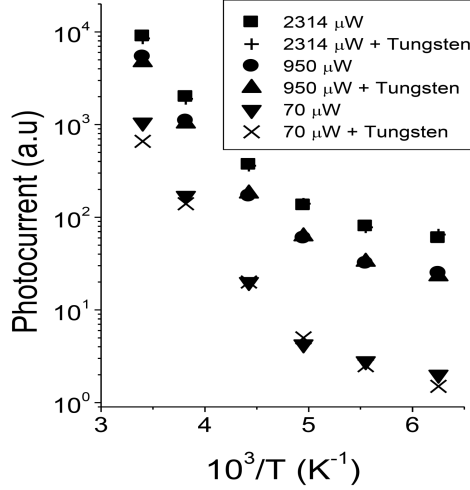


Fig. 4. Effect of the dual beam on the temperature-dependent photocurrent (modulation beam: HeNe).

with increasing temperatures. In this region, the photocurrent behaviour is approximately linear. It means that the photocurrent is an activated process, i.e.,

$$I_{ph} = I_0 \exp\left(\frac{-E_a}{k_B T}\right), \quad (3)$$

where I_0 is an initial constant, k_B is Boltzmann's constant. The activation energies (E_a) estimated from the slopes of $\ln(I_{ph})$ vs. $10^3/T$ curves are about 110.5, 123.5, and 147.5 meV for 2314, 950, and 70 μ W, respectively. Clearly the activation energy increases with decreasing single and dual beam illumination intensities, indicating that the position of the Fermi level is moving down to deeper energy levels. However, at low temperatures the intensity of photocurrent response under single or dual beam does not show an activated behavior. It means that the recombination processes do not depend on temperature in this temperature region due to tunnelling processes [21].

There are many transient photocurrent techniques [22, 23] aimed primarily at probing the thermalization of photoexcited carriers in amorphous materials. On a longer time-scale, the decay of the photocurrent in the presence of recombination gives information about both deep recombination centers and traps in thermal equilibrium with the band. The response time is generally measured by measuring the time for the photocurrent to decay to some fraction of its initial value. Measurement of the modulation frequency dependence of the photocurrent is a complementary method of measuring the response time [24]. Oscillatory modulation allows the investigation of details in the steady-state system response, whereas transient decay measurements average over a range of system conditions.

Lifetime can be measured in terms of the frequency-resolved spectroscopy (FRS) method [25]. This method has been widely applied to the study

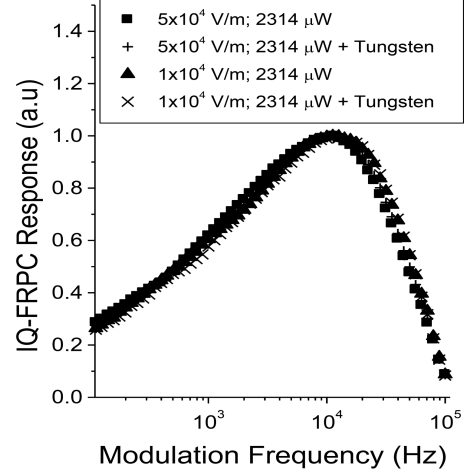


Fig. 5. In-quadrature frequency-resolved photocurrent (IQ-FRPC) response of a-As₂Se₃ at room temperature (290 K), for the indicated two different applied electric fields and illuminations. The spectra are normalized to their peak intensity values (modulation beam: HeNe).

of lifetime and recombination processes [26, 27] and references therein. According to FRS method, the in-phase and in-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 $\tau \propto 2\pi/f$ and ∞ . This treatment has been applied to frequency-resolved photocurrent (FRPC) response in amorphous materials [15, 28, 29].

Figure 5 shows the dual beam effects on the IQ-FRPC response at two different levels of applied electric fields. All curves are normalized to the respective signal heights at the maximum of the distribution. The single and dual beam curves are almost coincident and consist of a broad single peak. In other words, the monochromatic beam alone is not altered significantly by the DC pump photocurrent of the sample used. In the framework of the FRS method, Wagner et al. [28] reports 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

$$\tau = \frac{1}{2\pi f_{\text{peak}}}. \quad (4)$$

Using this relation and the data plotted in Fig. 5, a lifetime of about 14 μ s is calculated, which corresponds to the peak frequency of about 11220 Hz. At room temperature, the photocarriers may be thermally ionized from recombination or trapping states, in which only one recombination path is present. As can be seen from Fig. 5, the lifetime is found to be independent of applied electric field. However, it strongly depends on illumination intensity and temperature [30, 31].

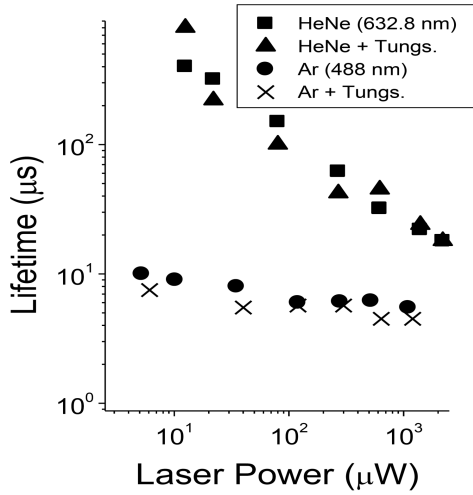


Fig. 6. The effect of tungsten white light on the lifetime of a-As₂Se₃ as a function of laser power for two different wavelengths of illumination.

Figure 6 shows the dual beam lifetime as a function of two different wavelengths (632.8 nm and 488 nm) of illumination intensities. As seen, the dual beam lifetime, τ , decreases with increasing illumination intensity for both cases. However, this decrease is larger and sharper for 632.8 nm illumination than that of 488 nm illumination. In both cases, all data points almost seem to lie on a straight line with constant slopes, suggesting that $(G\tau)$ is approximately independent of G as found by Street [32].

As is usually reported [24], the lifetime τ is given by

$$\tau = \frac{n}{G}, \quad (5)$$

where n is the carrier density which is proportional to photocurrent I_{ph} . And so, $n \propto I_{ph} \propto G^\nu$. Substituting this into (5) gives

$$\tau = \frac{1}{G^{1-\nu}}, \quad (6)$$

which is close to the dependence observed in Fig. 6. In our case, it is found that $\tau \propto G^{-0.73}$ and $\tau \propto G^{-0.14}$ for 632.8 nm and 488 nm illuminations respectively. The exponent of -0.73 of G in (6) leads to a stronger G -dependence of lifetime τ and thus of the photocarrier concentration, but -0.14 leads to a weaker G -dependence of τ at room temperature. However, the full interpretation of this result clearly needs a sufficiently detailed knowledge of the recombination mechanism, which is not presently available.

4. Conclusions

The amorphous nature of hot-pressured a-As₂Se₃ glassy alloys has been verified by XRD. The absence of any prominent peak in XRD pattern confirms amorphous nature of the investigated samples.

The exponent ν values in the power-law relationship of the intensity of the photocurrent on

the generation rate were compared for single and dual beam illuminations as a function of temperature. The ν values for dual beam illumination are found to be larger than those of single light at low temperatures ($T < 200$ K) and high temperatures ($T > 250$ K). Further ν value for dual beam illumination increases with decreasing temperatures, while its value for the single light illumination is almost constant below about 200 K. For $T < 200$ K, the ν value shows a slight supra-linear intensity-dependence with $1.0 < \nu < 1.11$ under dual beam, which is interpreted as a sensitization effect involving traps of different capture cross-sections in the lower-half of the energy gap. For temperatures between 200 K and 250 K, ν value decreases very sharply with increasing temperatures for both single and dual beam illuminations, which shows the presence of a continuous distribution of localized states in the energy gap.

The intensity of the photocurrent at a fixed frequency is also found to be temperature dependent. However, the second beam of tungsten light has no significant effect on the photocurrent produced by modulated single red light of HeNe laser. The high temperature regions of photocurrent vs. inverse temperature curves indicate an activated behaviour with an activation energy of 110.5 meV for the excitation intensity of 2314 μ W+tungsten. For lower excitation intensities, the activation energies increase due to the shift of the quasi-Fermi level.

The second beam (tungsten white light) also has no noticeable effects on the modulation spectrum and thus the carrier lifetime. A single broad distribution is observed to peak about 11220 Hz, which corresponds to the lifetime of 14 μ s. This lifetime is found to be independent of applied electric field at room temperature. However, we found that the lifetime behaviour of a-As₂Se₃ under illumination strongly depends on the excitation wavelength. This dependence can be related to the light absorption profiles.

Our single and dual beam results of the intensity- and temperature-dependence of photocurrent, and also of the room temperature carrier lifetime show that the recombination occurs through the trap states in the higher temperature region. Thus the release rate from traps controls both the photocurrent and also the carrier lifetime.

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