ELECTRICAL CONDUCTION AND PHOTOCONDUCTION IN a-Se_{0.6}Te_{0.4}

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The DC conductivity and photoconductivity of a–Se_{0.6}Te_{0.4} is studied in the temperature range from 150 K to 300 K. From the temperature dependence of the dark current, the thermal activation energy of 0.14 eV was obtained. The lux–ampere characteristics at different temperatures and voltages between electrodes show that photocurrent is proportional to the flux of light to the power γ . The activation energy of the carriers from dangling–bond levels was obtained from the photocurrent variation with temperature.

1. Introduction

Recently, due to many applications in various fields, the chalcogenide glasses are studied with growing interest. The alloys based on amorphous selenium are remarkable from two points of view: in fundamental studies and for applications in xerography or other solid state devices. Some properties are specific to the binary amorphous $\text{Se}_x \text{Te}_{1-x}$ alloys [1–3]. We have chosen a– $\text{Se}_{0.4} \text{Te}_{0.6}$ due to its interesting properties. For example, in the paper of R. Arora and A. Kumar [1] pointed out interesting dielectric properties of such types of compounds.

The present paper reports the conductivity and photoconductivity measurements in thin layers of $a-Se_{0.6}Te_{0.4}$. It is well known that for selenium the valence

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band bottom is formed by ion-pair states (the bonding states are deep states in the valence band) and the antibonding states represent the conduction band [4]. The structure of amorphous selenium is a mixture of long-helical chains and eight membered rings with covalent bonds existing between atoms within the molecular units and Van der Waals forces between neighbouring units. The a-SeTe structure is completed by the open rings of tellurium, the ratio of interchain and intrachain separations being smaller. Taking into account that every end of the structural chain means dangling-bond defect, the result of dark- and photo-conductivity measurements are interpreted in terms of a theoretical model which considers the thermal or optical transitions between the valence/conduction bands and defect states.

The DC conductivity was measured in the temperature range from 150 K to 300 K for various voltages applied between electrodes. The photoconductivity characteristics were performed for the same temperature and voltage range, with the intensity of light flux in the range of $10^{12} - 10^{15}$ photons/cm²s. In order to determine the light flux dependence of the photocurrent, the lux–ampere characteristics at different temperatures and voltages were measured and the value of γ ($I_{ph} \sim \Phi^{\gamma}$) parameter was obtained.

2. Experimental

Selenium (60%) and tellurium (40%) of 5–nines purity were sealed in an evacuated (10⁻⁴ mbar) quartz ampoule. At 10⁻⁵ mbar vacuum the mixture was annealed 1 h at 350 °C and then 1 h at 500 °C, the last step being finished by slowly decreasing the temperature (50 °C/h). The result was Se_{0.6}Te_{0.4} of polycristalline structure with large microcrystallites. By grinding this material, a powder was obtained with grains ranging between 1 μ m and 10 μ m. Thin films of a–Se_{0.6}Te_{0.4} have been obtained by thermal vacuum evaporation (at 10⁻⁵ mbar) of this powder onto cleaned optical glass substrates. We have cleaned these supports with deionizated water (12 MΩcm) to be sure that there are not electrical changes at substrate–film interface. During vacuum deposition, the temperature of the substrates was mantained at 300 K. The thickness of films was about 1 μ m. A coplanar structure with a separation between electrodes of about 1 mm was obtained by standard vacuum evaporation of Al electrodes.

To avoid the modification of surface states by the adsorbtion of different types of molecules, the measurements were made in vacuum (10^{-4} mbar) in a cryostat with a quartz window and heater mounted inside which allowed the measurement of darkand photo-conductivity at various temperatures of the sample. The temperature varied between 150 K and 300 K and was measured with a cooper-constantan thermocouple that was in good contact with the sample. For the measurements under light, the sample was illuminated with white light $(0.5 - 5 \text{ mW/cm}^2)$. The DC voltage applied across the sample was in the range 1 - 40 V.

3. Results and discussion

The ohmic character of the sample for voltage up to 30 V is shown in Fig. 1 in the absence as well in the presence of light. The mechanism of the electronic

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conduction is generally obtained from the temperature dependence of conductivity [5]. Figure 2 shows that $\log I_{dark}$ versus $10^3/T$ is a straight line. If one considers that $I = \sigma U/d$, where d is the distance between electrodes, it is easy to observe that the plot in Fig. 2 is described by the well-known relation:

$$\sigma_{DC} = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right),\tag{1}$$

where ΔE is the activation energy for DC conduction and k is the Boltzmann's constant. From the slope of the straight line, the value of ΔE is found to be 140 meV.



Fig. 1. The ohmic character of the sample in the absence as well as in the presence of light.



Fig. 2. The temperature dependence of the dark current and photocurrent.

Figure 3 represents the steady state photoconductivity at different voltages between electrodes. From these lux–ampere characteristics, it is observed that pho-

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to current is proportional to the light flux to the power γ , $I_{ph} \sim \Phi^{\gamma}$, with γ around 0.5. Theoretically for single-type of carriers in a semiconductor with one single trap-level, the variation of the number of photogenerated carriers, δn , is given by Mott relations:

$$\delta n = \begin{cases} \frac{G}{2C_n n_0} & \text{for small photogeneration} \\ \sqrt{\frac{G}{C_n}} & \text{for high photogeneration,} \end{cases}$$
(2)

where n_0 is the concentration of thermally generated carriers, C_n is the capture coefficient and G is the photogeneration rate.



Fig. 3. Lux-ampere characteristics of Se_{0.6}Te_{0.4}.

In the ohmic domain of the current–voltage characteristics, the photocurrent is given by $I_{ph} = e\mu\delta nU/d$, where e is the electron charge, U is the voltage applied between electrodes separated at distance d and μ is the electron–photogenerated mobillity.

The photogeneration rate is related to the incident light flux \mathcal{I} , by:

$$G = \eta \frac{\mathcal{I}(1-R)[1-\exp(-\alpha d)]}{d}$$
(3)

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where η is the quantum efficiency, α the absorption coefficient and R the reflectivity of the sample.

Both conduction and photoconduction mechanisms are based on the recombination kinetic using the dangling-bond levels. In the simplest case, the atom from the end of the chain or open ring atomic units has an electron, and from electrical point of view this defect is neutral (D^0). But the chalcogenides are materials with negative correlation energy, and defect-sites with two electrons are favoured. This means network of negatively charged defects (D^-) and positively charged defects (D^+) with corresponding levels in the gap, pinning the Fermi level near the middle of the gap. The D^- and D^+ -defects act as shallow acceptors and donors for trapping processes. For thermally activated conduction processes one electron/hole transforms D^+/D^- in D^0 defect with activation energy for release.

In accord with the Frank–Condon principle, the optical excitation of electrons takes place in a much shorter time than the time in which the structure can relax. The electron is trapped in the level close to the bottom of the conduction band and in this way, the level D⁺ is transformed into D⁰–level by D⁺ + $e_{cb} \rightarrow D^0$. This electron from D⁰–center can recombine with the hole trapped on D⁻–level into D⁰ (D⁻ + $e_{vb} \rightarrow D^0$) or can be emmitted into conduction band to participate in conduction mechanisms. Therefore, the number of photocarriers is equal to the excess of D⁰–centers which appear by illumination. Mott proposed the relation:

$$\sigma_{ph} \sim \Delta N \exp\left(-\frac{W}{kT}\right) \tag{4}$$

where W is the activation energy from dangling-bonds level into conduction/valence band.

Under these conditions, the value $\gamma = 0.5$ for flux–ampere characteristics is in good agreement with the supposition that the recombination processes take place between an electron trapped on D⁺–level and a hole traped on D⁻–level, a bimolecular recombination.

The activation energy in Eq. (4) can be obtained from the photocurrent variation with temperature. Figure 2 shows such a dependence and the shape of the curve is typical for amorphous semiconductors. A maximum in the temperature dependence of photoconductivity is observed, like a variety of amorphous materials [5–9]. In the region of temperature above the maximum, the photocurrent is smaller than the dark current and varies exponentially with 1/T. This is the region of high temperature. Immediately bellow the maximum, the photoconductivity decreases exponentially with 1/T, in accord with Eq. (4).

In the low-temperature region, the photocurrent is higher than the dark current and approaches a constant value asymptotically. Here the temperature dependence of carrier density is compensated by the temperature variation of the mobility.

The region of intermediate temperature is very interesting because the energy of photoconduction can be obtained: W = 88.7 meV using Eq. (4). Usually, the thermal activation energy is higher in the dark conditions than the activation energy for photoconduction. The rate of recombination is given by the photocarriers and

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the activation energy corresponds directly to the depth of traps in the gap. The mechanism of recombination has the following steps: the excess of photogenerated electrons and holes are located on D⁰-centers. After stopping the illumination, the D⁰-centers are transformed by the recombination process $2D^0 \rightarrow D^+ + D^-$. Therefore, the recombination is a process between localized states.

Concerning the DOS in the mobility–gap, it can be evaluated from the dark conductivity from the relation $\log(I_{dark}) = fT^{-1/4}$. For our samples, it is 3.4×10^{19} cm⁻³eV⁻¹. Figure 3 shows also, an nonlinear dependence of the lux–ampere characteristic at U = 40 V. In our opinion, taking into account that we have supposed the same value for mobility of the photogenerated and thermally generated carriers, this is due to the non–ohmic behaviour of the dark current–voltage characteristic.

4. Conclusions

In summary, it is clear that $a-Se_{0.6}Te_{0.4}$ represents a structure of density of states in the gap based on dangling bonds which have a great influence on the transport phenomena. For the conductivity, an activation energy of 140 meV has been obtained, whereas the steady state photoconductivity is an activated process with W = 88.7 meV. The photocurrent follows a power law and has a square root dependence on the light intensity. The bimolecular recombination between the dangling-bonds sites is used to explain $I_{ph} \sim \Phi^{\gamma}$.

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ELEKTRIČNA VODLJIVOST I FOTOVODLJIVOST U a-Se_{0.6}Te_{0.4}

Proučavana je istosmjerna električna struja i fotostruja tankih filmova Se_{0.6}Te_{0.4} u temperaturnom području od 150 K do 300 K. Iz temperaturne ovisnosti tamne struje nađeno je da aktivacijska termička energija iznosi 140 meV. Mjerenja pokazuju da je fotostruja proporcionalna s Φ^{γ} , gdje je Φ svjetlosni tok.

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