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DONOR- AND ACCEPTOR-LIKE CENTER REVEALING BY PHOTOCONDUCTIVITY OF AMORPHOUS THIN As_2Se_3 FILMS

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Measurements of photoconductivity and relaxation of positive and negative charge in amorphous thin As_2Se_3 layers are discussed. Photosensitive donor- and acceptor-like centers of 1.05 eV and 0.76 eV energies from valence band were revealed. These energies are constant and independent of light intensity in the range 1.5×10^9 - 1.5×10^{15} quanta/(cm^2s) and of energy of quanta. Wide quasicontinuously distribution trap centers with maximums at 0.62, 0.87 and 1.05 eV were found by relaxation measurements of positive and negative charge.

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1. Introduction

The measurement of a photoconductivity (PhC) is applied to determination of the different information about semiconductors, as the photosensitivity of a material and its spectral distribution law, the identification centers of trap, recombination of free charge carriers, etc. [1]. Detailed measurements of PhC glass semiconductors was studied for the first time in the paper of Kolomiets et al. [2], who have found the main PhC properties dependence of temperature and intensity of excited light.

Recently, in connection with development of the new concept about pair centers D^+ and D^- with variable valence and negative bond energy [3] and concept of “soft potentials” in disordered semiconductors [4] the attempt of combination of the data on photoconductivity, on optical and photoinduced optical absorption and on photoluminescence in common description scheme was made.

E.g., for massive glass semiconductor a-As_2Se_3, levels of 1.40 eV and 1.65 eV from valence band were revealed by measuring optical absorption [5], levels of 0.8-0.9 eV were revealed by measuring photoluminescence [6], and levels of 0.60 eV and 1.05 eV were revealed by measuring PhC dependence of temperature and light intensity at mono- and bimolecular recombination. These data are explained through configuration electron-phonon interaction diagram. Energy of interaction obtained for bulk a-As_2Se_3 is U_c = -0.45 eV [5].

We were interested in investigation of PhC for thin amorphous layers As_2Se_3 obtained by vacuum thermal evaporation which are in more disbalanced conditions than voluminous samples, to compare different experimental data on trap and recombination centers of free charge carriers. On this topic, a few published data exist.

In the present paper we investigate photoconductivity dependence on temperature and light intensity in a large interval of intensities and relaxation of positive and negative charge.

2. Experimental technique

We investigated properties of stationary PhC at the planar geometrical configuration of electrodes, because it characterizes properties of a sample more adequately, introduces less errors in calculation of PhC, do not depend of non-uniformity, of volume illumination, contact effects, etc. [1]. Monochrome He-Ne laser light (λ= 0.63 μm) was used for PhC excitation with maximal intensity $F_0 = 1.5 \times 10^{15}$ quanta/(cm^2s), which was loosened more than to 6 orders by neutral gauged filters. The spectral PhC dependence was measured at different temperatures using MDR-4 monochromator at illumination by a halogen lamp.

Amorphous As_2Se_3 films of thickness about 1.2 - 1.5 μm on glass substrates were investigated. They were obtained by thermal evaporation in vacuum. The source As_2Se_3 for evaporation was prepared by synthesis of elemental As and Se with cleanness not less than 10^{-5} %. On films, the Au contacts were made by thermal deposition in vacuum.

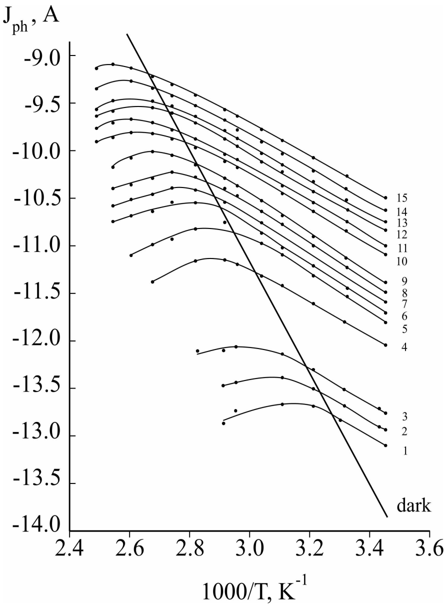

Fig. 1. Photoconductivity dependence of temperature for As2Se3 films at different light intensities (λ = 0.63 μm). Lines 1 – 15 correspond intensities from 1.5×10^{10} to 1.5×10^{15} quanta/cm^2.

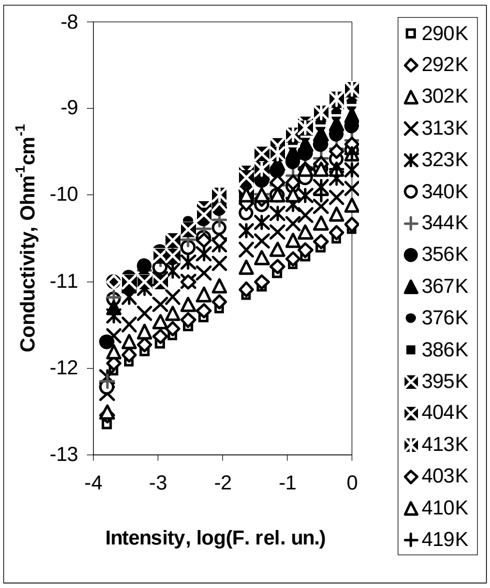

Fig. 2. Photoconductivity dependence of intensity for As_2Se_3 films at different temperatures (Lux-Ampere characteristic; λ = 0.63 μm)

The non-steady electrophotographic spectroscopy deep levels (NESDL) measurements were executed by a standard technique described in [7].

Before PhC measurements, films were subject to heat treatment in vacuum during 2 hours at 160 ^{0}C, to guarantee stationary properties of the material. Due to the strong dependence of electrical properties of amorphous As_2Se_3 films of humidity [8], and to eliminate effects of air humidity, all measurements were carried out in vacuum (10^{-5} bar). The maximum of applied electrical field for a sample was 600 V/cm. The sizes of contacts were about 1.5×0.3 cm^2, and distance between them was about 0.5 cm.

3. Results

It was found that for all measured samples the current-voltage characteristics were linear, and the Ohm's law was always satisfied. Hence we concluded the lack of influence of contacts to PhC measurements in a-As_2Se_3 layers. The measured stationary PhC in the temperature interval 286 - 413.4 K and at sample illumination intensity in range F_0 - 10^{-6} F_0 are shown in Fig. 1. Measurements of dark conductivity are shown also.

The measured dark conductivity is presented by a straight line in log σ_d – $(10^3/T)$ coordinates for all temperatures. Energy of activation corresponding to energy of a Fermi level (E_F) measured trough the conductivity of amorphous layers a-As_2Se_3 is 0.85 ± 0.03 eV.

PhC dependence of $(10^3/T)$ has mixed character, i.e., in the dependence of temperature exist positive and negative slopes, to which donor- and acceptor-like levels correspond. It was found that with increase of light intensity $\sigma_{ph}(10^3/T)$ is shifted without slope change. Even as light intensity is varied on 6 orders, the activation energy remain constant: $\Delta E_m = 0.20 \pm 0.04$ eV for donors and $\Delta E_m = 0.38\pm 0.02$ eV for acceptors. The maximum of $\sigma_{ph}(10^3/T)$ moves to higher temperatures at increase of light intensity (Fig. 1).

The activation energies are: $\Delta E_m = (E_D - E_V) - E_F$ and $\Delta E_b = (E_A - E_V)/2$.

Here q is the charge of an electron, k is Bolzmann constant, μ is mobility, E is electric field intensity, F is light intensity, v is thermal velocity of free carriers, σ_t is capture cross-section of centers, E_A and E_D are, correspondingly, energies of acceptor and donor centers, which are situated at different sides of the Fermi level, E_V is the energy at the edge of the valence band.

We obtained $E_A = 0.76$ eV, $E_D = 1.05$ eV, and the bond energy of centers $D1^+$ and $D2^-$ is equal $E_A - E_D = -0.29$ eV.

Lux-Amper characteristics exhibits the monomolecular, bimolecular and mixed recombination of charge carriers. The slope of acceptor type in the dependence $\sigma_{ph}(10^3/T)$ is $\gamma \approx ½$. Lux-Amper characteristics described above characterize also model of trap centres quasicontinuously distributed inside the forbidden band of the semiconductor. The dependence $\gamma(T)$ is of a kind $1/\gamma = T/T_0 - 1$ with characteristic temperature $T_0 = 590$ K. It means the distribution close to exponential inside the forbidden band [10].

The constant position of activation energy of both types of levels and its independence of energy of quanta of exciting light is apparently connected to transportation of carry with repeated trap. This transportation is dominant and is responsible for a current in amorphous semiconductors and is determined by exchange of carriers between zones and traps irrespective of places where this carrier was generated. At energies equal or higher than threshold, there is apparently an excitation $D1^+$ or $D2^-$ centers which results in neutral charge $D1^0$ or $D2^0$. These ones are thermally ionized and return the charge carrier in the conductivity or valence band. The further identification of the center model will be made after researches of photoconductivity, optical, luminescent and other properties.

Let's remark that in paper [7] PhC measurements in massive samples showed the results close to ours. The activation energies E_A and E_D given in that paper are 0.60 and 1.05 eV, correspondingly. The difference of these values is due to the relative unbalance of the thin amorphous layers comparatively to voluminous massive samples.

The obtained results of PhC measurements and electrophotografical spectroscopy led us to the dependence of energy distribution of centers inside a forbidden band in amorphous As_2Se_3 films shown in Fig. 4.

5. Conclusions

The PhC dependence of temperature dependence and of wide range of intensities (1.5×10^9 – 1.5×10^{15} quanta/(cm^{2}s)) and relaxation of accumulated positive and negative charges were measured in thin amorphous a-As_2Se_3 layers. The photosensitive centers of donor and acceptor types with activation energies 1.05 eV and 0.76 eV relative to valence band were retrieved, whose energies are constant and do not depend neither on intensity, nor from energy of exciting light in rather broad range of intensities and energies. The broad quasi-continuous energy distribution of trap centres of a donor and acceptor type with maxima was retrieved at 0.62, 0.87, 1.06 eV from measurements of relaxation of the accumulated charge.

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