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Amorphous arsenic chalcogenide films modified using rare-earth complexes

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Abstract

The optical absorption and current–voltage characteristic of amorphous arsenic chalcogenide As_2X_3 (X = S, Se) films modified by rare-earth complexes with organic mixed-ligands have been studied. The following two types of complexes were used: europium dipivaloylmethanate $Eu(thd)_3$ and lanthanide diethyldithiocarbamates $Ln(ddtc)_3$ (Ln = Pr, Eu). It was shown that the use of rare-earth mixed-complexes with similar volatility to the chalcogenide volatility permits the deposition of amorphous films by thermal evaporation. The decrease in absorption coefficient at the Urbach's edge after introduction of the europium dipivaloylmethanate complexes containing oxygen in arsenic selenide has been revealed. The type of organic ligands, incorporated in the amorphous matrix, determines the shape of current–voltage characteristic. The observed results have been discussed on the basis of the different rigidity of the structure of amorphous arsenic chalcogenides.

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1. Introduction

Chalcogenide vitreous semiconductors (ChVSs) exhibit a number of interesting optical and electrical properties under various applications as recently reviewed in, for example, [1]. ChVSs are pointed out to be promising materials for telecommunications and integrated optical systems because they are transparent over a wide range of wavelengths in the infrared (IR) spectral region, possess high refractive index, low phonon energy and can be easily fabricated. ChVSs containing rare-earth (RE) ions are employed in designing optical fibers in the near-IR region for various telecommunication devices. The wide-band multicomponent glasses are used mainly for that purpose, e.g. the systems like Ga–La–S, Ge–Ga–Se, Ge–As–S, As–Se–S, As–S. RE sulphides [2], chlorides, or oxides [3] are most frequently applied as a modifying component, whereas RE elements themselves are used rarely [4].

The method of preparation of arsenic chalcogenide As_2X_3 (X = Se, S) thin films modified by RE complexes with organic ligands and its electrical and optical properties are reported in the present paper. The key feature of technological approach is the co-evaporation of inorganic material (ChGSs) and a volatile complex from the separate sources. Criteria of RE complexes selection as a modifying component were described in details in [5]. It should be pointed at the main factors appear to be volatility and thermal stability of the complexes under chalcogenide evaporation conditions. Two types of the mixed-ligand compounds were found: lanthanide dipivaloylmethanates with *o*-phenanthroline – $Ln(thd)_3(Phen)$ [6] and

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lanthanide diethyldithiocarbamates with *o*-phenanthroline – Ln(ddtc)$_3$(Phen) [7]. The key distinction between these compounds is the elements surrounding RE ion. The central sphere was formed by six oxygen atoms and two nitrogen atoms in the case of dipivaloylmethanates, and oxygen is replaced by sulfur atoms in the other compounds.

2. Experimental

Glasses with the composition As_2Se_3 and As_2S_3 were synthesized by melting of appropriate amounts of As, Se or S in fused silica ampoules, which were subsequently evacuated to 10^{-6} Torr, at 980 K in rotating furnace. The compounds Ln(ddtc)$_3$(Phen) (Ln = Pr, Sm, Eu) and Eu(thd)$_3$(Phen) were synthesized by conventional methods [6,7] and identified by elemental analysis and IR spectroscopy. The films were thermo-evaporated under vacuum (10^{-6} Torr), and the process conditions were optimized in experiment so as to ensure the best possible uniformity of the films with the required thickness and composition reproducibility controlled by the ratio [ChVSs]/[complex compounds] in the film. Film thickness was measured by means of interferometric microscope and varied in the range 0.2–5.4 μm. The chemical and phase compositions of the films were determined and described in [5].

The current–voltage characteristics measurement was conducted for a ‘sandwich’ type structure of the sample with the aluminum electrodes. The accuracy of current–voltage characteristic measurement was ±10%. Absorption spectra were recorded in the region 0.5–2.5 μm with Perkin Elmer Lambda 900 spectrophotometer. The surface morphology was examined by atomic force microscope (AFM) in a Solver Pro-NT–MDT system with tripod scanner and a I-shaped silicon tip. The scanning regions ranged from 20 × 20 to 1 × 1 μm recorded in air at the room temperature.

3. Results

The optical absorption edge spectra of the As_2Se_3 and As_2S_3 amorphous films containing different RE complexes have the following peculiarities:

(i) Amorphous arsenic sulphide films modified by Ln(ddtc)$_3$ or Eu(thd)$_3$ have an increased absorption coefficient which corresponds to the growth of characteristic Urbach's edge energy and the darkening of the material (Fig. 1).

(ii) Amorphous arsenic selenide films modified by Eu(ddtc)$_3$ or Eu(thd)$_3$ have a decreased absorption coefficient in the photon energy region 1.4–1.9 eV which corresponds to the reduction of characteristic Urbach's edge energy and the bleaching of the material (Fig. 2).

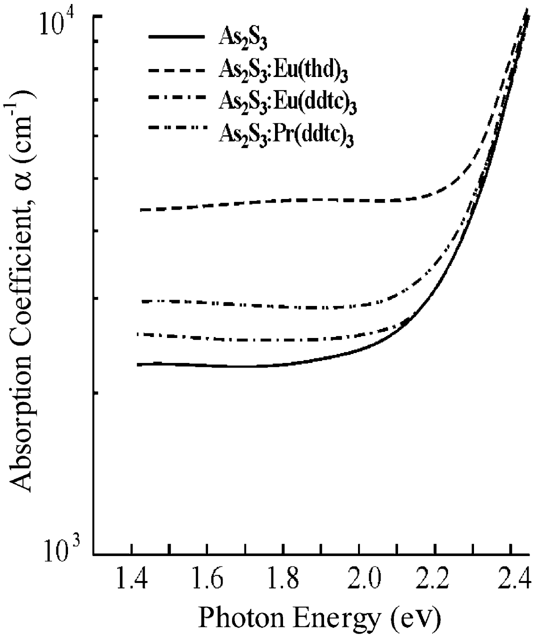

Fig. 1. The absorption spectra of As_2S_3 film and As_2S_3 films modified by Ln(ddtc)$_3$ (Ln = Pr, Eu) and Eu(thd)$_3$. The concentration of RE ions in the samples is 1.4 at.%.

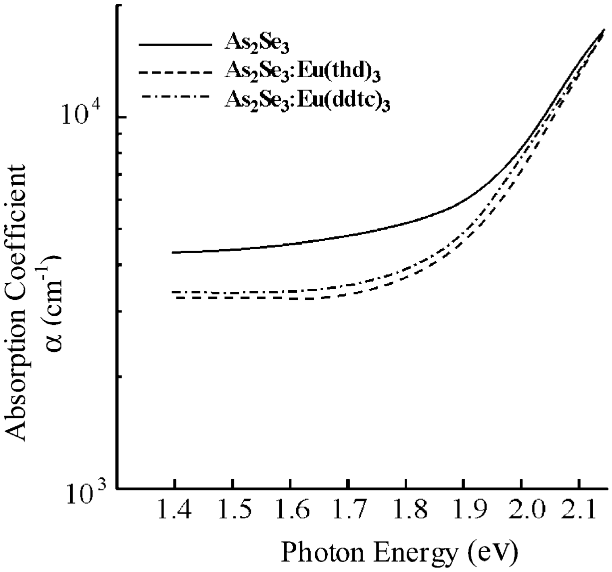

Fig. 2. The absorption spectra of As_2Se_3 film and As_2Se_3 films modified by Eu(ddtc)$_3$ and Eu(thd)$_3$. The concentration of RE ions in the samples is 1.4 at.%.

The darkening effect and especially photodarkening effect have been studied extensively in As-chalcogenide glasses for the past three decades, bleaching has been observed rarely. Therefore current–voltage characteristics measured for arsenic selenide films have revealed the bleaching. Fig. 3 shows current–voltage characteristics of As–Se films modified by Ln(thd)$_3$ and Ln(ddtc)$_3$ measured at a room temperature. As seen, the type of organic ligands incorporated in amorphous matrix has a fundamental importance and determines the shape of characteristics. In the case of oxygen-free complex Ln(ddtc)$_3$ a shift of

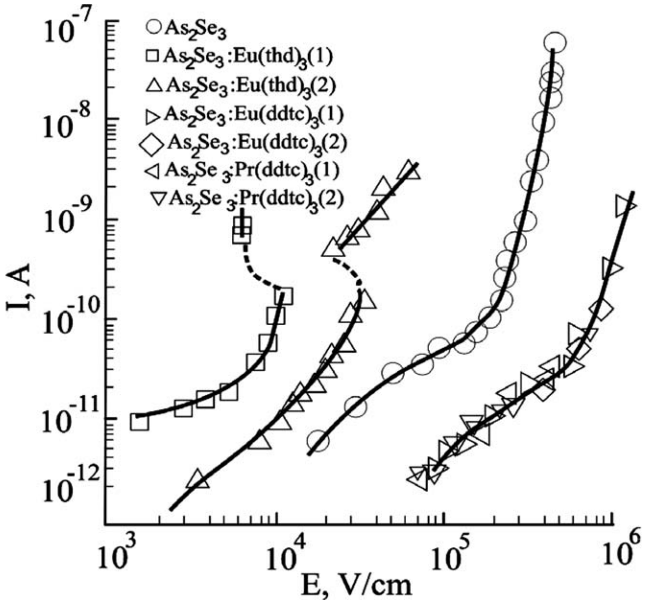

Fig. 3. Current–voltage characteristics of As_2Se_3 film and As_2Se_3 films modified by Ln(ddtc)$_3$. (Ln = Eu, Pr) and Eu(thd)$_3$. The concentration of RE ions in the labeled (1) samples is 0.7 at.% and in the labeled (2) samples is 1.4 at.%.

the crossover of the liner and non-linear regions in the current–voltage characteristics is observed in comparison with non-modified As–Se film. As seen, the crossover point is shifted to higher electrical fields. In the linear region and in the non-linear region the curves are parallel to each other. If oxygen containing complex Eu(thd)$_3$ was used for modification, the current–voltage characteristic is shifted to the low field up to the region with negative differential resistance. In the material, containing Eu(thd)$_3$, the conductivity of the films has significantly increased. The temperature dependences of the conductivity of these films were measured in the range 200–300 K. The decrease of activation energy from 0.70 to 0.25 eV with an increase of RE ions concentration from 0.7 to 1.4 at.% has been observed.

4. Discussion

The conducted experiments have revealed the important role of an amorphous matrix, which was used for modification by the complex compounds. The structures of the stoichiometric glasses As_2Se_3 and As_2S_3 were studied by many authors. The pyramidal structural units are considered to be the main ones such as $As(X_{1/2})_3$ (orpiment crystal structure). The molecules As_4Se_4 (realgar crystal structure) form isolated units [10]. Recently the experimental studies have appeared which allowed stating new hypotheses about the structure and, accordingly, the rigidity of these glasses. In particular, the quasitetrahedral units, in which the arsenic atom is fourfold coordinated are supposed to exist also together with the main units in the As-rich glasses As–Se. The part of such structural units could make ∼0.3 from a total amount of the arsenic atoms according to [8].

The experimental data of the fourfold coordinated arsenic existence absents in stoichiometric glass As_2S_3. But the clusters such as As_4S_4 in the monomeric form are observed in this glass [9,10]. The rigidity of As_2Se_3 and As_2S_3 glasses is larger compared with the rigidity of the chalcogen-rich glasses of the same systems. The arsenic selenide is supposed to be more rigid due to increased coordination of part of arsenic atoms comparing to the arsenic sulfide at matching a rigidity of stoichiometric compositions among themselves.

The rigidity distinction of the initial matrix could be a reason of the observed distinctions in properties at modification by the complex compounds. The formation of microheterogeneous structures with appropriate boundaries between them is more probable in a rigid matrix As_2Se_3 than in a matrix As_2S_3 at introduction of the concerning large complex Eu(thd)$_3$. According to [11] the presence of a negative resistance region (see Fig. 3) is typical for ChVSs possessing the local change of amorphous film morphology, leading to formation of microheterogeneities, which are able to create conducting channels. The study of a film surface using the AFM has allowed observing the following result, which represented in Fig. 4. The surface morphology of a modified by Eu(thd)$_3$ film (Fig. 4(a)) is more structured in comparison with one of non-modified As_2Se_3 film (Fig. 4(b)). We observed an increase in roughness, which is demonstrated to be complex compound. The

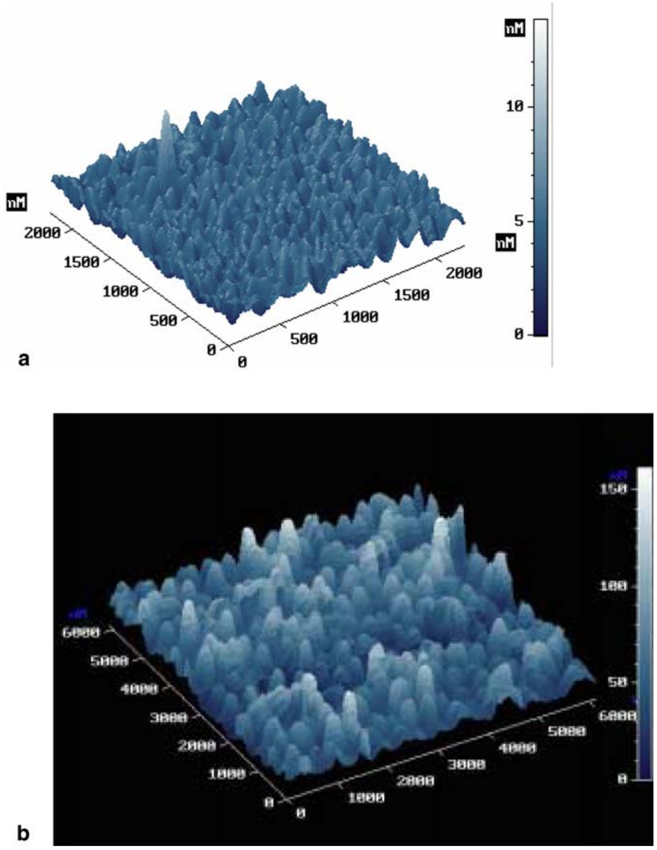

Fig. 4. AFM images of non-modified As_2Se_3 film (a) and As_2Se_3 film modified by Eu(thd)$_3$ (b).

surface of amorphous non-modified films is irregular with a typical roughness of ∼5 nm, a typical roughness increase in some times after modification.

5. Conclusions

The study of electrical properties of arsenic selenide and arsenic sulfide films modified by rare-earth complexes reveals the influence of ligand type on the feature of current–voltage characteristics. The most significant changes are typical for the films containing the complexes with oxygen $Eu(thd)_3$.This phenomena may be connected with the formation of microheterogeneitites in arsenic selenide films during modification.

Acknowledgment

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