

Sb-contained thin films Structural and electric properties

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First results of experimental study of the structure of Sb_2Se_3 and NaSbSe_2 thin films by means of transmission electron microscopy and electron diffraction methods are reported. Structural and morphological peculiarities of crystal growth in films are discussed. Some electrical properties, in particular, current–voltage characteristics in metal–semiconductor (MS) structures: $\text{In}/\text{Sb}_2\text{Se}_3$ and $\text{In}/\text{NaSbSe}_2$, are presented.

Key words: *chalcogenide semiconductor; thin film; structure; current–voltage characteristics*

1. Introduction

Investigations of multicomponent semiconductor compounds allow one to expand possibilities of their practical applications in modern microelectronics and photonics [1–5]. In amorphous films of multicomponent chalcogenides containing alkali metals, physical and chemical properties of prospective active elements may be varied in a wide range of functional characteristics. Bulk NaSbSe_2 has been reported [3] as a perspective photoelectric semiconductor material ($T_{\text{melt}} = 1013 \text{ K}$). The compound is formed by the equimolar ratio of Na_2Se and Sb_2Se_3 in the ternary Na–Sb–Se system [4]. NaSbSe_2 crystallizes in a NaCl-like cubic lattice with the lattice constant $a = 5.96 \text{ \AA}$. Sb_2Se_3 crystallizes in the orthorhombic system, with the following lattice parameters: $a = 11.6 \text{ \AA}$, $b = 11.7 \text{ \AA}$, $c = 3.97 \text{ \AA}$. Amorphous thin films of semiconductor chalcogenides have principally new perspectives for applications as aggressive gas environment and electric field sensors [1]. Sb-contained semiconductor materials seem to be attractive not only for structural studies (the question is still open), but also as a subject

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of electric investigations. Their electrical properties were not studied until recently. Electrical characteristics of the semiconductor materials p-Sb₂Se₃ (the gap $E_g = 1.16$ eV) and p-NaSbSe₂ ($E_g = 1.36$ eV) have not been investigated. We should note that there are practically no references concerning the electrical behaviour of these materials. The paper reports on structural characteristics of the films and for the first time on the electric field-induced characteristics of metal–semiconductor (MS) structures In/Sb₂Se₃ and In/NaSbSe₂.

2. Experimental

Sb₂Se₃ thin films were grown by thermal evaporation from a quasi-closed system. As was shown earlier [2], this technique gives a good possibility to obtain films of chalcogenides with the compositions corresponding to those of the initial material. The films were condensed at 10^{-3} Pa on glass substrates, at various temperatures of substrates: $T_s = 300$ K and $T_s = 400$ K with the rates of deposition from 0.1 to 0.5 nm/s. The thickness of the films was estimated to be 40–80 nm. The nanostructure of the films was studied by methods of electronography and transmission electron microscopy. Cluster-like and whisker-like structure of the films was revealed (Fig. 1).

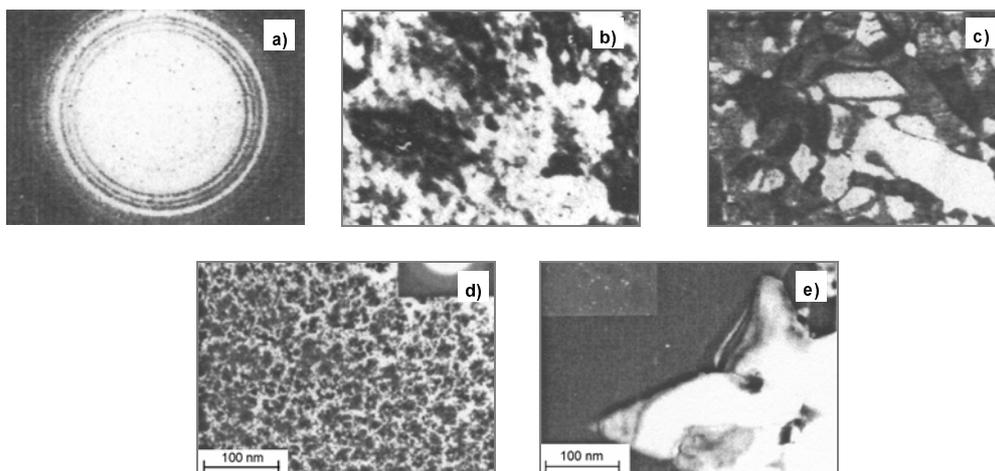


Fig. 1. TEM images of Sb₂Se₃ films deposited onto (001) NaCl substrates, $T_s = 293$ K [3]: microdiffraction pattern (a), after vacuum annealing during 15 h at 493 K (b), and at 593 K (c); the film grown on the glass substrate under $T_s = 500$ K, crystalline nano-whiskers are observed (d); the micrograph of NaSbSe₂ film deposited onto glass substrate, $T_s = 400$ K. The rectangles in Figs. d) and e) show microdiffraction patterns illustrating the amorphous structure of the films under study

The properties of the films under external electric fields are completely unknown. To investigate the electric field-induced characteristics of the compounds, one should fabricate metallic contacts working as quasi-ohmic ones or as active elements, i.e., barrier-like structure; in the active mode, charge carriers flow through such a contact

due to the monopolar injection from the metal [7]. As we have mentioned above, there is no information about properties of the barrier (i.e., formation, height, width etc.). We have studied some structural and electric field-induced properties of NaSbSe₂ thin films prepared by the pulse laser deposition (PLD) technology [6]. Here we report similar investigations of the samples obtained by the thermal evaporation technique. In order to make electrical experiments In contacts of $\sim 2.0\text{--}3.5\text{ mm}^2$ area were deposited on the films for non-destructive current–voltage studies. Electric measurements were carried out at the room temperature under electric fields up to $5\cdot 10^4\text{ V}\cdot\text{m}^{-1}$.

3. Results

Figure 2 shows experimental current–voltage characteristics (IVC) obtained for Sb₂Se₃ films deposited on both cold and hot substrates.

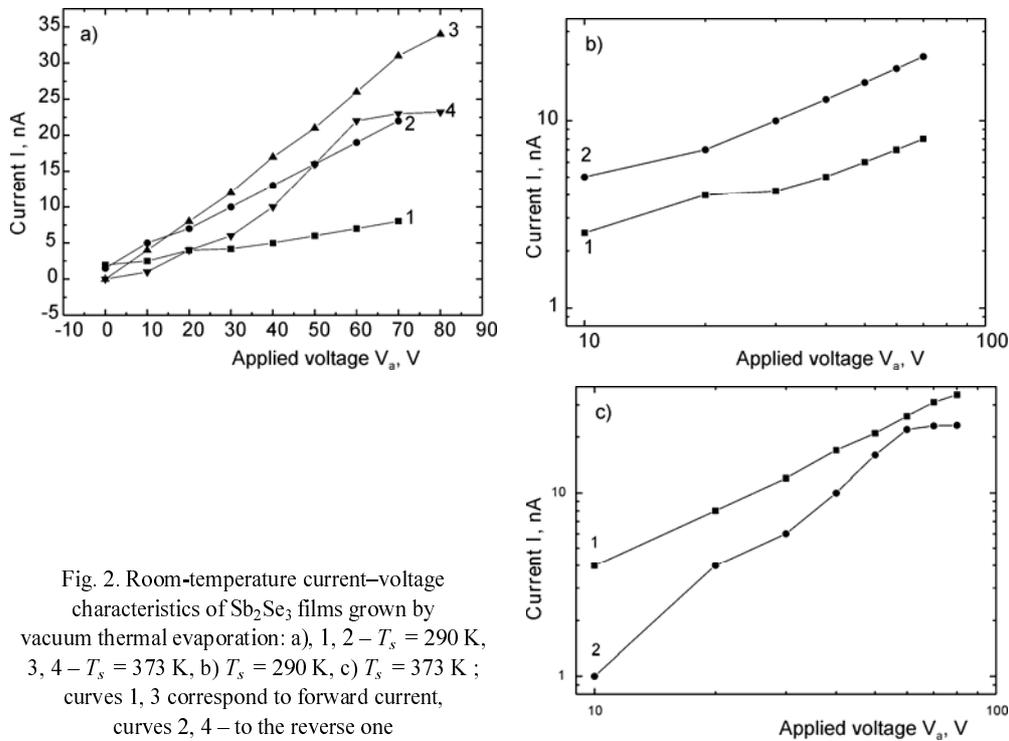


Fig. 2. Room-temperature current–voltage characteristics of Sb₂Se₃ films grown by vacuum thermal evaporation: a), 1, 2 – $T_s = 290\text{ K}$, 3, 4 – $T_s = 373\text{ K}$, b) $T_s = 290\text{ K}$, c) $T_s = 373\text{ K}$; curves 1, 3 correspond to forward current, curves 2, 4 – to the reverse one

Qualitatively, the “cold” IVC (Fig. 2b) can be described as follows:

$$I \propto V_a^m \quad (1)$$

where V_a stands for the applied voltage and $m = 0.6\text{--}0.8$.

Unlike this case, “hot” samples (i.e., grown at $T_s = 400$ K) exhibited diode-like characteristics (Fig. 2c):

$$I_{f1} \propto V_a^m, \quad I_{f2} \propto \exp\left(\frac{eV_a}{nk_B T}\right) \quad (2)$$

where I_{f1}, I_{f2} are currents corresponding to the forward sections of the experimental IVC, $m = 3.5, n = 1.04$. The reverse current is:

$$I_r \propto V_a^m \quad (3)$$

where $m \approx 0.9$.

Experimental data for NaSbSe₂ films are plotted in the Fig. 3a–c.

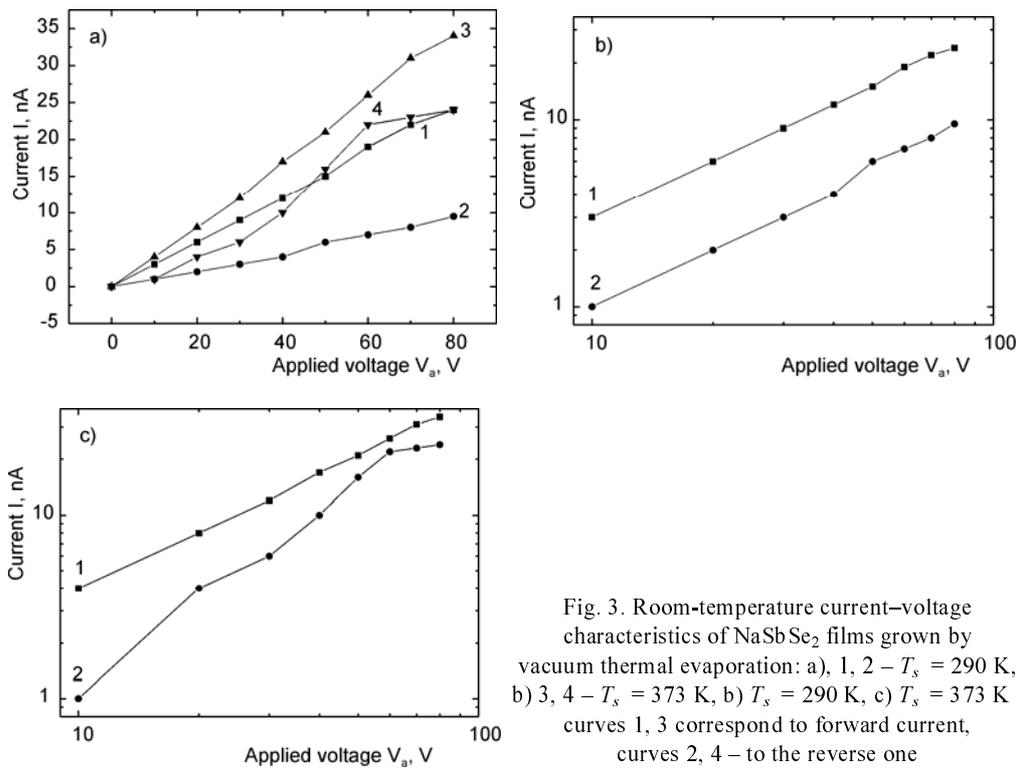


Fig. 3. Room-temperature current–voltage characteristics of NaSbSe₂ films grown by vacuum thermal evaporation: a), 1, 2 – $T_s = 290$ K, b) 3, 4 – $T_s = 373$ K, b) $T_s = 290$ K, c) $T_s = 373$ K ; curves 1, 3 correspond to forward current, curves 2, 4 – to the reverse one

Figure 4 illustrates experimental and calculated IVC of the NaSbSe₂ film. As is shown, the forward and reverse sections are alike and are well described by the velocity saturation mode:

$$J \sim \frac{2\varepsilon_0\varepsilon_s v_{\text{sat}} V_a}{L^2} \quad (4)$$

In this expression, v_{sat} stands for the carrier saturation velocity, experimentally determined by so-called threshold voltage on the forward section of the IVC, L is the thickness of the film, ε_0 is the permittivity of free space, and ε_s is the relative electric permittivity.

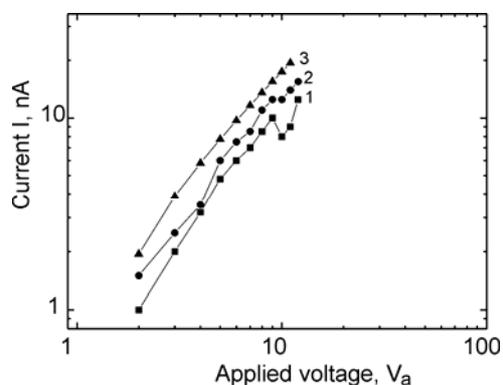


Fig. 4. Room-temperature experimental (1, 2) and calculated (3) current-voltage characteristics of NaSbSe₂ films deposited onto the “cold” substrate

Sb₂Se₃ films deposited onto the “hot” substrate demonstrate IVC typical of metal–semiconductor structures [7]. Unlike these layers, the films grown on the “cold” substrates, as well as NaSbSe₂ layers exhibit IVC which are characteristic of structures metal–amorphous semiconductor [8].

4. Conclusions

The growth conditions and the surface structure as well as electric field-induced characteristics of semiconductor Sb-contained thin films were investigated. The structural research performed by means of tunneling electron microscopy demonstrated a crystalline whisker-like surface relief of the Sb₂Se₃ films. Such a surface is observed only for the films grown by the pulsed laser deposition technology.

The experimental data obtained under study of the electric field-induced characteristics (room-temperature current-voltage functions) enabled us to estimate charge transfer mechanisms in the films under applied electric field (the power law-like dependences are observed) and made it possible to simulate numerically electrical behavior of the investigated films.

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