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Controlled synthesis of a textured CuSe(006) film by vacuum thermal treatment of a Se/Cu film structure

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A nanocomposite film consisting of crystalline CuSe and amorphous selenium (a-Se) was obtained by vacuum-thermal deposition. It has been shown for the first time that thermal heating of a CuSe/a-Se nanocomposite film in vacuum can transform it into a textured CuSe(006) film. It has been established that, at the temperature of 438 K, CuSe crystallites grow intensively in the (006) crystallographic plane. Using the X-ray diffraction analysis method and the technique for measuring the electrical resistance of the CuSe/a-Se composite film, the phase transformation temperatures at which monoclinic Se_8, trigonal t-Se, orthorhombic $CuSe_2$, and hexagonal CuSe are formed were determined.

Keywords: copper selenide, nanocomposite film, thermal heating, phase transformations, textured film.

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Copper selenides are semiconductor materials with the p-type conductivity. These materials may have different crystal lattices: tetragonal [1], rhombic [2], cubical and hexagonal [3].

Bandgap width E_g in copper-selenide films can vary in wide ranges from 2.0 to 2.3 eV and 1.1 to 1.5 eV for direct and indirect optical transitions, respectively [4–6].

Thin CuSe films are prepared by using pulsed laser ablation of mixed Cu and Se targets [7], thermal evaporation [8], solution growth [9], chemical bath deposition [10], electrodeposition [11], magnetron sputtering [12], etc.

We have established in [13,14] that, when stoichiometric CuSe films and nanocomposite CuSe/Se films are irradiated with a femtosecond laser, photocurrents depending on the rotation sense of the laser pump electric-field vector are generated in the films. The CuSe-based film structures may be used in designing and creating fast-response analyzers of the light circulation direction [15]. Thus, improvement of the vacuum-thermal evaporation technique for obtaining films with preset phase compositions is at present important.

The goal of this work was studying phase transformations taking place in the CuSe/a-Se composite film in heating it in vacuum and also revealing conditions for obtaining a textured stoichiometric CuSe(006) film.

The Se/Cu film structure was created in one vacuum cycle by sequential evaporation of Se and Cu weighed portions onto glass substrates 25×22 and 12×10 mm in size. During depositing the Cu and Se vapors, in the film system there proceeded a chemical reaction in the mode of explosive crystallization [16] with formation of the CuSe/a-Se composite film (a-Se is the amorphous selenium). The synthesized film thickness measured with an atomic-force microscope was 87 ± 4 nm.

Thermal heating of the CuSe/a-Se composite film to the temperature of 473 K with the rate of 4 K/min was performed in a vacuum chamber at the pressure of 10^{-3} Pa. The dynamic dependence of electrical resistance $R(T)$ (Fig. 1) exhibits extrema at the temperatures of $T_1 < T_2 < \ldots T_n$, which correspond to phase transformations; here n is the number of extrema. To prove that the revealed extrema correspond to the temperatures of phase transformations, the following experiments were carried out. First, a CuSe/a-Se composite film formed on the substrate 25×22 mm in size was heated to temperature $T_1 - \Delta T$, where $\Delta T = 5-15$ K. Once the preset temperature was reached, the furnace was switched off. After that, the sample was cooled to room temperature, withdrawn from the vacuum chamber, and studied with a diffractometer. After that, this sample was heated to temperature $T_1 + \Delta T$ and again analyzed with the diffractometer. Then the same cycle of operations was fulfilled at higher temperatures $T_2, \ldots, T_n$. The obtained dynamic dependence of R of the CuSe/a-Se composite film on T (Fig. 1) exhibits four maxima at $T = 308$, 323, 413, 433 K and four minima at $T = 313$, 358, 423, 443 K.

The phase analysis of the synthesized films was performed using diffractometer D2 PHASER (Bruker) operating at the wavelength of 0.154 nm (the characteristic CuK_α radiation of a copper X-ray tube). A diffractogram of the initial CuSe/a-Se composite film obtained at room temperature (298 K) demonstrates diffraction peaks only of the hexagonal CuSe phase with the crystal lattice parameters $a = 0.395$ nm, $c = 1.729$ nm (PDF 03-065-3562) (Fig. 2). The absence of diffraction peaks of crystalline Se evidences that Se contained in the CuSe/a-Se composite film is amorphous.

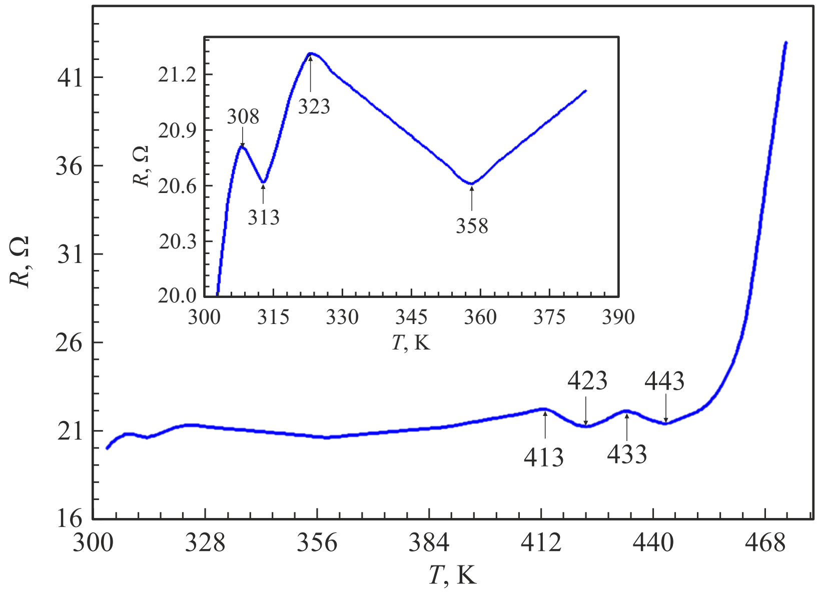

Figure 1. Dynamic dependence of electrical resistance R of the CuSe/a-Se composite film on temperature T of the substrate heating with the rate of 4 K/min. The inset presents the scaled-up basic dependence $R(T)$.

Diffractograms of the CuSe/a-Se composite film obtained after heating to 303 and 318 K are similar to that of the initial film obtained at room temperature (298 K). This makes it evident that heating of the CuSe/a-Se composite film to the preset temperatures (303 and 318 K) does not give rise to new crystalline phases in the film system. Along with this, in the dynamic dependence of electrical resistance R of the CuSe/a-Se composite film versus the glass substrate temperature T in heating them to 323 K there appear two extrema at the temperatures of 308 and 313 K (inset in Fig. 1). The maximum at $T_1 = 308$ K corresponds to the temperature at which, probably, chains Se−Se in the amorphous Se film get combined into rings Se_6 and Se_8. It is known that Se structures consisting of rings Se_8, Se_6 or chains Se−Se are flexible; this is why they easily transform one into another [17].

The minimum at $T_2 = 313$ K (inset in Fig. 1) corresponds to the selenium glass transition point (T_g). At this temperature, hard and fragile selenium transforms into viscous-flow liquid [18], which promotes Cu dissolution in the Se film and increase in electrical resistance R of the CuSe/a-Se composite film from 20.6 to 21.3 Ω (inset in Fig. 1).

In the CuSe/a-Se composite film diffractogram obtained after heating to 338 K, there appear diffraction peaks from the Se_8 monoclinic phase with the crystal lattice parameters $a = 1.285$ nm, $b = 0.807$ nm and $c = 0.931$ nm (PDF 01-073-6182). This phase manifests itself as a line with the scattering angle $2\theta = 23.44°$ (Fig. 2). Therewith, electrical resistance R of the CuSe/a-Se composite film decreases from 21 to 20.6 Ω (inset in Fig. 1). The Se_8 monoclinic phase was detected by the techniques of transmission electron microscopy and X-ray diffractometry in glassy Se films irradiated with a 632.8 nm laser with a low power density of 50 W/cm^2 [19]. The maximum at $T_3 = 323$ K (inset in Fig. 1) corresponds to the temperature of phase transformation from the amorphous Se to monoclinic Se_8. Along with the peak from the Se_8monoclinic phase, in the film system there appears a diffraction peak from the CuSe(006) hexagonal phase at angle $2\theta = 31.02°$ (Fig. 2). Intensity of this peak increases with increasing heating temperature of the CuSe/a-Se composite film, while intensity of the CuSe(103) peak at angle$2\theta = 30.38°$ decreases (Fig. 2). This means that, when the CuSe/a-Se composite film heating temperature increases, CuSe crystallites grow mainly in the (006) crystallographic plane.

During heating the CuSe/a-Se composite film, a transition from unstable monoclinic Se_8 to more stable trigonal Se(t-Se) takes place [17].

After heating the film to 368 K, the diffractogram begins demonstrating diffraction peaks from the Se trigonal phase at scattering angles $2\theta = 23.55$ and 29.74°. The elementary cell parameters were $a = 0.436$ nm and $c = 0.495$ nm (PDF 00-042-1425) (Fig. 2). Electrical resistance R of the CuSe/a-Se composite film increases from 20.8 to 21.6 Ω (Fig. 1). The minimum at $T_4 = 358$ K (inset in Fig. 1) corresponds to the temperature at which there begins nucleation and growth of crystallites of trigonal phase t-Se.

Further increase in the CuSe/a-Se composite film heating temperature to 398 K leads to a slight increase in concentration of trigonal t-Se and hexagonal CuSe crystallites. Therewith, intensity of diffraction peaks at scattering angles $2\theta = 29.74$ and 31.02° increases (Fig. 2). Electrical resistance R of the CuSe/a-Se composite film increases from 21.6 to 22.2 Ω (Fig. 1).

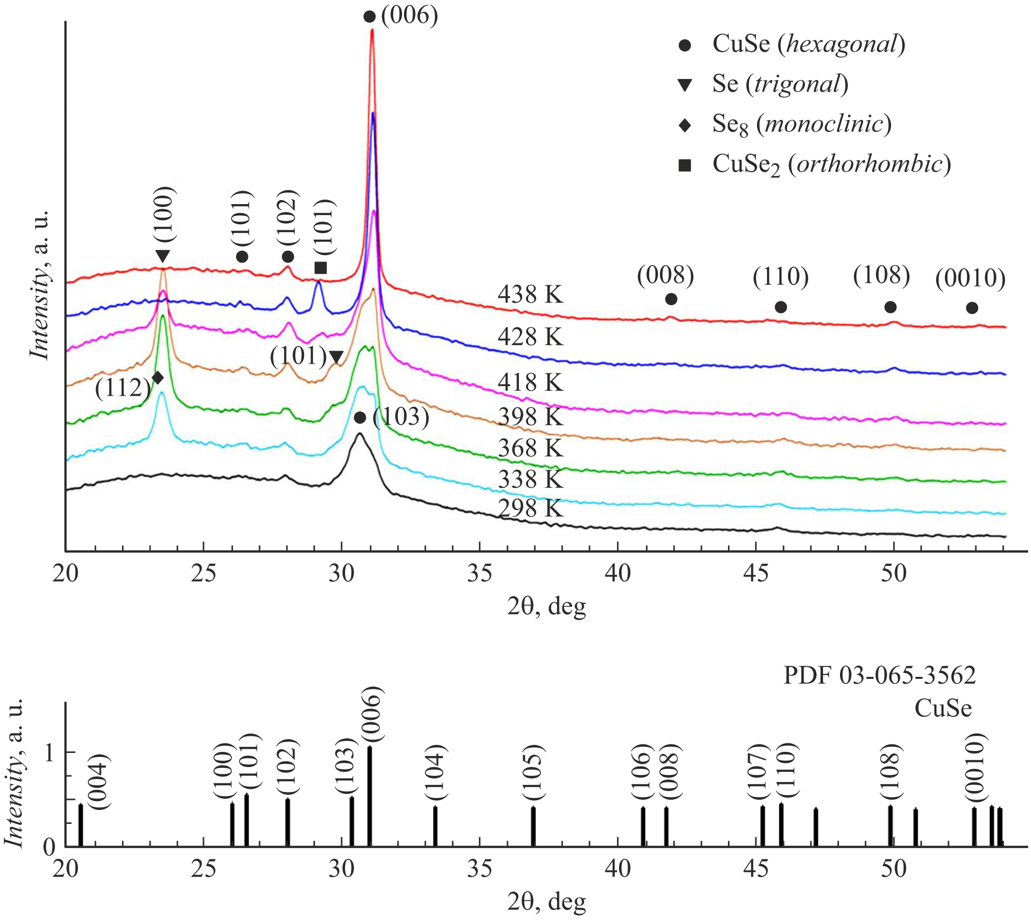

Figure 2. Diffractograms of the CuSe/*a*-Se composite film after heating it in vacuum of 10^{-3} Pa to different temperatures of 298−438 K (indicated at the curves), and also a histogram of diffraction reflections from completely disoriented polycrystalline CuSe (PDF 03-065-3562).

Heating of the CuSe/*a*-Se composite film to 418 K causes appearance in the diffractogram of manifestations of the phase that does not get formed at lower temperatures, namely, of orthorhombic $CuSe_2$ phase with crystal lattice parameters $a = 0.510$ nm, $b = 0.629$ nm and $c = 0.381$ nm (PDF 01-074-0280) (Fig 2). Excess Se contained in the CuSe/*a*-Se composite film begins reacting with Cu thus giving rise to $CuSe_2$ crystallites. The Se peak intensity at scattering angles $2\theta = 23.55$ and $29.74°$ decreases, and a new diffraction peak from $CuSe_2$ at angle $2\theta = 29.22°$ appears (Fig. 2). Electrical resistance R of the CuSe/*a*-Se composite film decreases from 21.6 to 21.2 Ω (Fig. 1). The maximum at $T_5 = 413$ K (Fig. 1) corresponds to the phase transformation temperature at which orthorhombic phase $CuSe_2$ emerges.

Heating of the CuSe/*a*-Se composite film to 428 K results in disappearance of the trigonal selenium diffraction peak at scattering angle 23.55° and growth of CuSe crystallites in the (006) plane, as well as in an increase in concentration of $CuSe_2$ crystallites (Fig. 2). However, when the film heating temperature increases to 438 K, the $CuSe_2$ phase decomposes with transformation to the CuSe phase and evaporation of excess selenium. As a result, a textured CuSe(006) film is formed, which is clearly seen from comparison of the obtained film diffractogram with the histogram of diffraction reflections from completely disoriented polycrystalline CuSe (PDF 03-065-3562) (Fig. 2). Electrical resistance of the CuSe/*a*-Se composite film decreases from 21.7 to 21.4 Ω (Fig. 1).

Thus, the paper demonstrates the possibility of controllable synthesis of a textured CuSe(006) film by vacuum-thermal heating of the CuSe/*a*-Se composite film. The heating temperature at which the textured CuSe(006) film arises was found to be 438 K. Using the method for studying the dynamic dependence of electrical resistance of the CuSe/*a*-Se composite film versus the substrate temperature, as well as the X-ray diffraction method, we succeeded in determining the temperatures of phase transformations of monoclinic Se_8, trigonal *t*-Se, hexagonal CuSe, and orthrhombic $CuSe_2$.

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Conflict of interests

The authors declare that they have no conflict of interests.

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