

BRIEF COMMUNICATIONS

EFFECT OF THERMAL TREATMENT OF PbTe FILMS ON THEIR IR SPECTRA AND SURFACE STRUCTURE

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This is a study of n-type PbTe films produced by deposition from gas-dynamic vapor flows onto glass substrates. It is found that short-term steady heating of these films at 300–400°C in air causes significant changes in their spectral and structural properties because of competition between an increased concentration of deformation defects owing to mismatch of the coefficients of linear thermal expansion of the film and substrate and the healing of these defects.

Keywords: microstructure, chalcogenide film, reflection spectrum, deformation defect.

Introduction. Narrow-band chalcogenide semiconductors and structures based on them are used as active media in IR photodetectors [1], terahertz injection lasers [2], and thermoelectric converters [3]. Nevertheless, there is a significant lack of data on the relationship between the spectral and structural properties of these compounds. The purpose of this paper is to discover such a relationship by studying the IR spectra and surface microstructure of PbTe films.

Experiment. Films were synthesized by depositing PbTe from a gas-dynamic flow of the vapor onto condensing substrates of multicomponent glass (microscope cover glasses). This technique produces crystals with a columnar structure oriented perpendicular to the plane of the substrate [4]. The film thicknesses were 1.5–2.0 μm. No special steps were taken to protect them from oxidation. The surface (supermolecular) structure and elemental composition of the films were studied with a LEO-1420REM scanning electron microscope (Carl Zeiss, Germany). Reflection and absorption spectra were recorded on a Nexus IR-Fourier spectrometer (Thermo Nicolet, USA) in a mirror reflection mode at an angle of 20°. The phase composition was monitored with a DRON-2.0 x-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.154184$ nm).

Results and Discussion. Figure 1 shows microphotographs of PbTe films deposited on substrates with temperatures $T_{\text{sub}} = 60$ and 90°C before and after subsequent steady thermal processing in air at different temperatures T_{ann} for 3 min. Figure 1a shows that the surface structure of a film with $T_{\text{sub}} = 60^\circ\text{C}$ before thermal processing consists of grown elongated crystalline granules of length ~ 1 μm with a large number of pores with dimensions of several hundred nm between them. After thermal processing at $T_{\text{ann}} = 300^\circ\text{C}$ the pores vanish and the film surface becomes much more uniform with granules of size ~ 0.1 μm (Fig. 1b). Thermal processing at $T_{\text{ann}} = 350^\circ\text{C}$ leads to further densification of the film and to the appearance of a large number of randomly oriented inhomogeneities on the surface with sizes up to 0.5 μm (Fig. 1c), while at $T_{\text{ann}} = 400^\circ\text{C}$ the concentration of the latter decreases (Fig. 1d). For the film with $T_{\text{sub}} = 90^\circ\text{C}$ the change in the surface structure on heating to $T_{\text{ann}} = 300^\circ\text{C}$ (cf. Fig. 1a' and b') and the reduction in the concentration of inhomogeneities on going from $T_{\text{ann}} = 350^\circ\text{C}$ to 400°C (cf. Figs. 1c' and 1d') are much less marked than for the film with $T_{\text{sub}} = 60^\circ\text{C}$. It should be noted that no changes were observed in the phase composition of the annealed films; at all temperatures they retained a cubic structure with a [100] texture, while for the film with $T_{\text{sub}} = 60^\circ\text{C}$ the atomic Pb:Te ratio was 70:30 and remained invariant under thermal processing to within the relative error of $\pm 15\%$.

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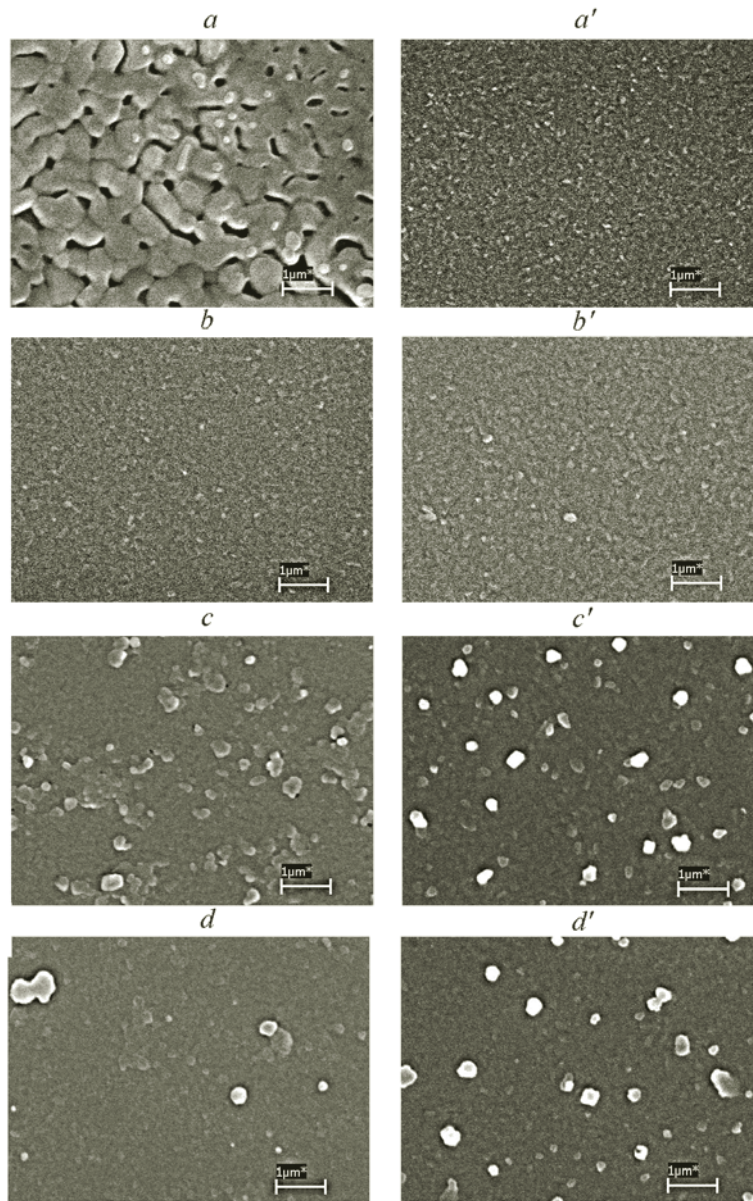


Fig. 1. Microphotographs of PbTe films on glass substrates before (a, a') and after steady thermal processing at $T_{\text{ann}} = 300$ (b, b'), 350 (c, c'), and 400°C (d, d'); $T_{\text{sub}} = 60$ (a–d) and 90°C (a'–d').

Figure 2 shows the reflection spectra of these films. The spectrum for the original film with $T_{\text{sub}} = 60^\circ\text{C}$ contains a series of bands with minima at $\nu_{\text{min}} \approx 990, 1360, \text{ and } 3480 \text{ cm}^{-1}$ (curve 1'). After thermal processing of this film at $T_{\text{ann}} = 300^\circ\text{C}$, a red shift of the minimum of the high frequency band to $\nu_{\text{min}} \approx 3160 \text{ cm}^{-1}$, together with an increase in its intensity and in its steepness on the low-frequency edge (curve 2'), is observed, while the intensities of the low-frequency bands decrease and their positions change negligibly. When T_{ann} is increased to 350°C, the minimum of the high-frequency band shifts to the blue to $\nu_{\text{min}} \approx 4200 \text{ cm}^{-1}$ (curve 3'), and for $T_{\text{ann}} = 400^\circ\text{C}$ it again undergoes a redward shift to $\nu_{\text{min}} \approx 3950 \text{ cm}^{-1}$ (curve 4'). At the same time, there is a substantial increase in the intensity of the bands with $\nu_{\text{min}} \approx 990$ and 1360 cm^{-1} . Similar "spectroscopic" behavior with initial annealing is typical of the films with $T_{\text{sub}} = 90^\circ\text{C}$ but it is less distinct (cf. curves 1, 1' and 2, 2'). Here, also, there is a decrease in the intensity of the low-frequency bands. But on going from $T_{\text{ann}} = 350$ to 400°C there is a shift in the high-frequency band to the blue from $\nu_{\text{min}} \approx 5290$ to 5390 cm^{-1} , not to the red as for the film with $T_{\text{sub}} = 60^\circ\text{C}$ (cf. curves 3, 3' and 4, 4').

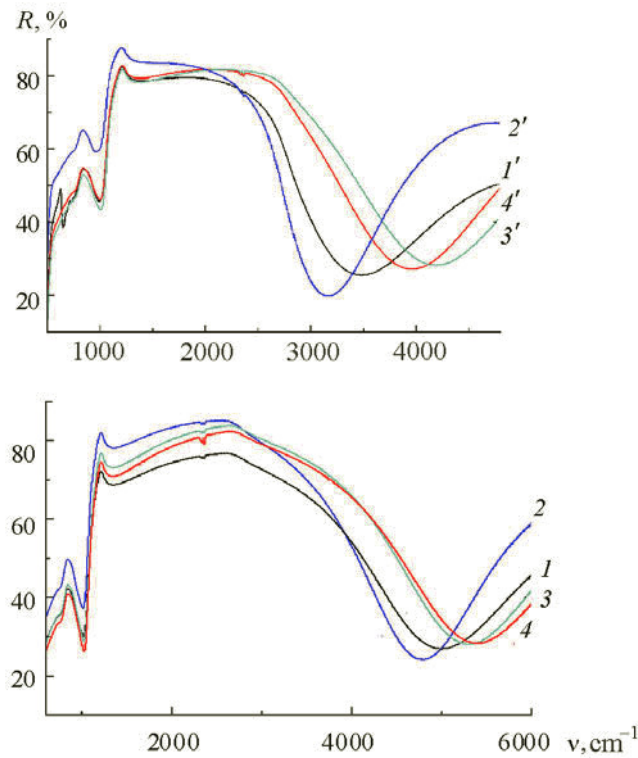


Fig. 2. Reflection spectra of PbTe films on glass substrates before (1, 1') and after thermal processing at $T_{\text{ann}} = 300$ (2, 2'), 350 (3, 3'), and 400°C (4, 4'); $T_{\text{sub}} = 60$ (1'–4') and 90°C (1–4).

The rather large thicknesses of these films and the predominance of lead in them (which ensures an excess of electrons [5]) means that their characteristics can be compared with bulk samples of *n*-type PbTe. It has been shown [6] that annealing of the latter in a dry oxygen atmosphere for 4 h at a pressure of 300 Torr with $T_{\text{ann}} = 300^\circ\text{C}$ is accompanied by the appearance of a small fraction of PbO_2 , while annealing at $T_{\text{ann}} = 400^\circ\text{C}$ for 48 h yields a substantial concentration of PbTeO_3 . The absence of clear signs of oxide phases in our case can be attributed mainly to the short annealing times. Nevertheless, there should be some concentration of defects associated with impurity oxygen, at least at the edges of the crystalline granules near the film surface. If we assume that the bands with $\nu_{\text{min}} \approx 990$ and 1360 cm^{-1} are caused by impurity oxygen [7], then, according to spectra 1, 1' and 2, 2' of Fig. 2, initial annealing leads to a drop in its concentration. Given the increased steepness of the red edge of the high-frequency reflection band, which is caused by interband transitions, and the greater homogeneity of the film surface (cf. Fig. 1a and a' and Fig. 1b and b'), its crystal structure becomes more perfect. This fact can be related to healing of structural deformation defects. With further increases in T_{ann} the surface structure of the films will be determined by the competition between the increase in the concentration of deformation defects owing to the mismatch of the coefficients of linear thermal expansion of the film ($19.80 \cdot 10^{-6} \text{ K}^{-1}$ [8]) and the substrate ($6 \cdot 10^{-6} \text{ K}^{-1}$ [9]) at $\sim 27^\circ\text{C}$, and the healing of these defects.

Conclusions. Short-term annealing in air of *n*-type PbTe films can be used to control the position of the interband absorption edge and its steepness and, thereby, the perfection of the crystal structure of the film.

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