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TEM AND TED INVESTIGATION OF Ag/PbTe THIN FILM BILAYERS

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Morphology and phase structure of Ag/PbTe thin film bilayers were investigated. This system was of particular interest because of interfacial reaction observed previously in an analogous Ag/SnTe system. Reaction products due to the interdiffusion of Ag with the substrate were determined as well as their orientations. They are discussed in view of the reaction products' structural relations to the PbTe.

1. Introduction

In modern semiconductor devices, thin metal layers are used as barrier layers or as contact surfaces. At the metal – semiconductor interface, a reactive interdiffusion may occur and its products can effect the electrical characteristics [1]. $A_{IV}B_{VI}$ semiconductors are composed of one fourth group element of the periodic system and of one sixth group element. They are of NaCl or slightly distorted NaCl structure, can be deposited in the form of oriented thin films in a simple way and are interesting for infrared technologies (gap of 2000 to 12000 nm). Due to the electronic structure of some of these compounds and their structural similarity, as well as relatively small differences in unit-cell parameters, ternary compounds can be prepared of $A_{IV}B_{VI(x)}C_{VI(1-x)}$ composition with the possibility of varying the energy gap and even obtaining the zero gap value by varying the stoichiometry [2]. $SnSe_xTe_{1-x}$ is an example of such a compound. Extensive studies of epitaxial growth on metal chalkogenides, isostructural to $A_{IV}B_{VI}$ compounds, but with predominantly ionic bonding character, have been carried out (e.g. Ref. 3). This study complements them with some information about the Ag growth on another binary system with predominantly covalent substrate.

Ag thin films of different thickness were deposited onto (001) PbTe (FCC, $a = 0.644$ nm [4] at various substrate temperatures (T_S). Transmission electron microscopy (TEM) and diffraction (TED) supplemented by energy dispersive X-ray analysis (EDAX) were used to analyse these Ag/PbTe bilayers. Ag growth modes, interdiffusive reaction products and their orientations towards the substrate were determined and discussed.

2. Sample preparation

Ag/PbTe thin film bilayers were prepared by vacuum evaporation of PbTe, approximately 30 nm thick, onto freshly cleaved (001) KCl, at the substrate temperature of 370 K. In this way, (001) oriented PbTe was obtained. Thin Ag film, of 7 to 20 nm, was deposited onto the (001) PbTe surfaces during the same vacuum cycle at three main substrate temperatures (T_S) of 370, 470 and 550 K. Some bi- layers were also prepared with Ag deposited at intermediate temperatures. Ag was evaporated from Mo crucibles. The layer thickness was monitored by the quartz microbalance. Ag/PbTe bilayers were floated of the KCl crystals and picked up by standard ($\phi = 3$ mm) copper grids for TEM and TED analysis.

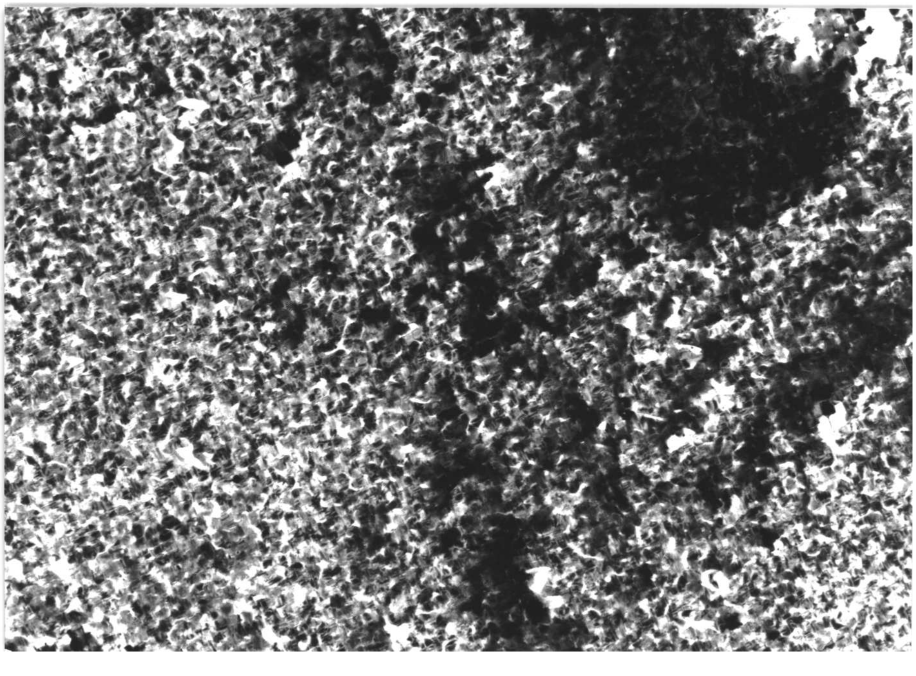

Fig. 1. 7 nm of Ag *deposited onto* PbTe*; magnification 54000×.*

3. Experimental and results

Main phenomena observed at deposition of Ag (7 to 20 nm) onto (001) PbTe can be summarized as follows: at $T_S \leq 370$ K, Ag layers were virtually continuous, substrate coverages were close to 100 %. Between 370 K$\leq T_S \leq 470$ K, growth of Ag became increasingly discontinuous, and for the same nominal thickness of deposited Ag, coverages were decreasing with increasing T_S. At 470 K, Ag grew in the form of small polyhedral crystallites on the PbTe surface (for any nominal deposition thickness investigated). At $T_S \geq 470$ K, TED showed additional reflection spots due to Ag_2Te, which means that in this range of substrate temperatures Ag growth was accompanied by chemical reaction with the substrate.

3.1. Continuous Ag layers

Thin Ag film of 7 nm on the PbTe substrate forms a continuous layer of microcrystalline nature (Fig. 1). The corresponding diffraction image (Fig. 2) gives the following orientation of these microcrystallites relative to the substrate:

$$[110]\ \mathrm{Ag} \parallel [100]\ \mathrm{PbTe} \tag{1a}$$
$$(001)\ \mathrm{Ag} \parallel (001)\ \mathrm{PbTe} \tag{1b}$$

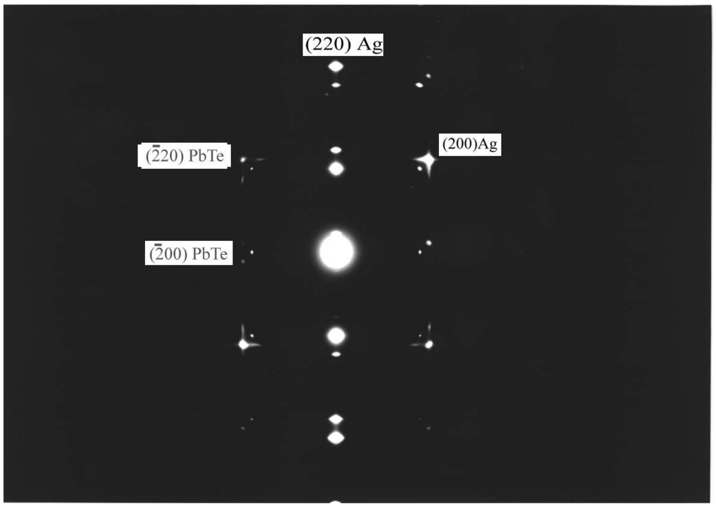

Fig. 2. Diffraction image of an area of the layer shown in Fig. 1.

Prolongation of (200) Ag reflection spots in $< 110 >$ directions suggests a high proportion of microtwins in Ag subgrains (Fig. 2). Morphology of the samples did not change with increasing thickness of Ag deposit. However, TED of thicker Ag layers (20 nm) showed less twinning and additional reflection spots due to the double diffraction.

3.2. *Discontinuous Ag layers*

As already pointed out, at $T_S \geq 470$ K, Ag grew in isolated, polyhedrally shaped crystalline grains. Irrespective of Ag deposition thickness (7 to 20 nm), surface density of these grains and their average linear dimensions were determined by TEM as $(4.5 \pm 0.5) \times 10^9$ cm^{-2} and about 150 nm, respectively. One can conclude that in this temperature range Ag grew mainly in the z direction (perpendicular to the surface of the substrate).

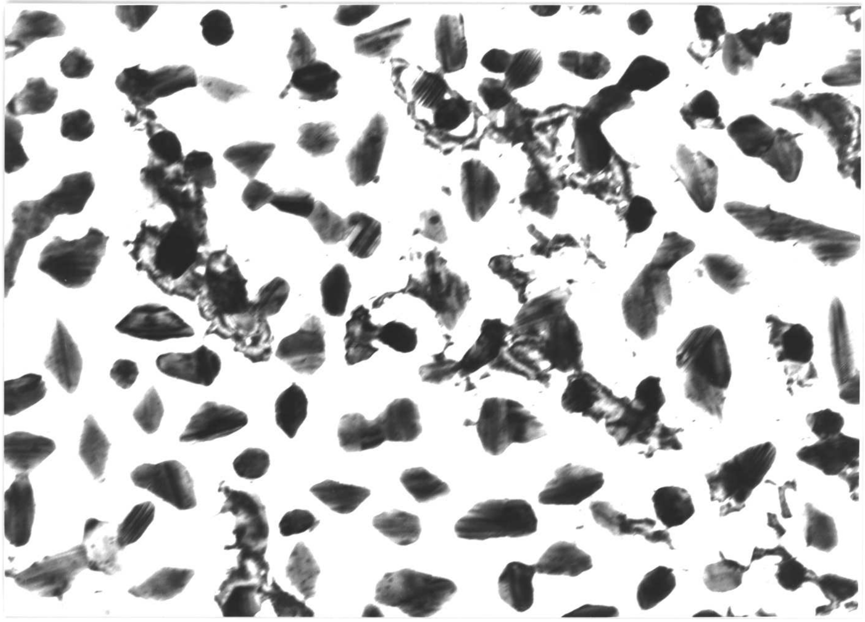

Fig. 3. Nominally 10 nm thick discontinuous layer of Ag *on* PbTe*; magnification 64000×.*

Nominally, 10 nm of Ag was deposited onto PbTe at $T_S = 470$ K (Fig. 3). Striped contrast observable in some grains is due to the planar defects. TED investigation of the same sample showed that orientation (1a, 1b) was still predominant in most Ag grains in spite of their differing shapes.

TED of this sample also showed additional reflection spots which appeared in te zone [001] PbTe, approximately at the positions of forbidden $\{100\}$ PbTe reflections (Fig. 4, extremely overexposed to make additional reflections visible). This may be interpreted as a first sign of Ag - PbTe reaction during Ag growth.

3.3. *Ag - PbTe reaction*

The additional reflection spots, first observed at $T_S = 470$ K intensified at higher T_S, while Ag reflections diminished. Also, new reflections appeared which could be ascribed to the same new phase in different orientations (Figs. 5 and 6).

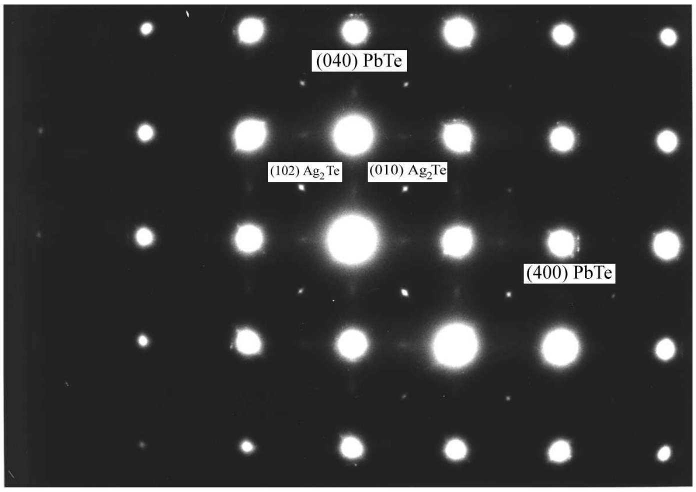

Fig. 4. Diffraction image of an area in Fig. 3; overexposed, to make weak additional reflections visible.

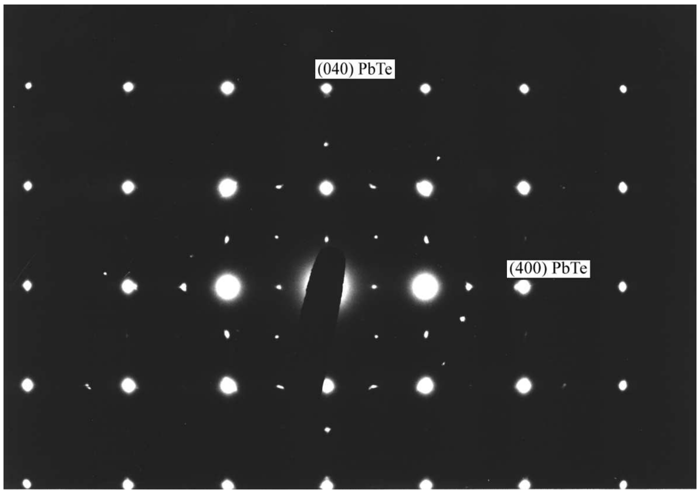

Fig. 5. Diffraction image of Ag/PbTe *layer prepared at* $T_S = 550$ K.

On the basis of the diffraction images, the new phase was identified as β-Ag_2Te, (monoclinic, $a = 0.809$ nm, $b = 0.448$ nm, $c = 0.896$ nm, $\beta = 123.3°$ [4]), the low-temperature phase of Ag_2Te. This suggests that at $T_S \geq 470$ K, as had already been established for Ag/SnTe system [5], Ag growth is accompanied by the following reaction:

$$2\mathrm{Ag} + \mathrm{PbTe} \rightarrow \mathrm{Ag_2Te} + \mathrm{Pb}. \qquad (2)$$

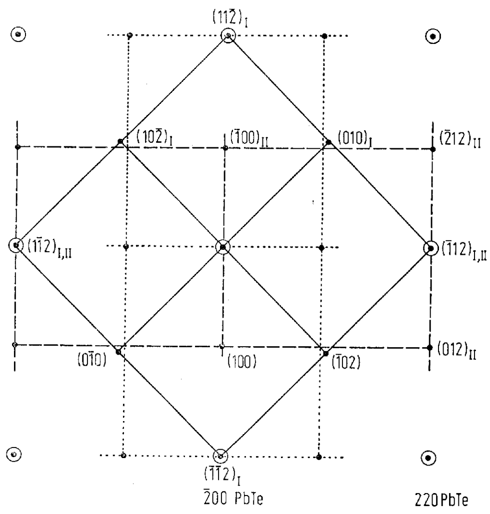

Fig. 6. Reconstruction of diffraction image shown in Fig. 5.

However, no domain microstructure, characteristic of low-temperature monoclinic β-Ag_2Te, was observed in the vicinity of Ag grains as in Ag/SnTe system. It appeared only after intense electron-beam-induced heating of the sample inside the electron microscope.

Additional confirmation about the reactive Ag growth, as described by Eq. (2), was obtained by repeated heating and cooling of the Ag/PbTe bilayer with monoclinic domains already formed on heating stage inside the electron microscope (Figs. 7a–f).

Monoclinic domains were repeatedly disappearing and reappearing as sample temperature was passing through 420 K, i.e. the temperature of the phase transition between the two phases of Ag_2Te. The first step is shown in Fig. 7. While the original and final diffraction images were equivalent and showed β-Ag_2Te reflections, the diffraction image of the sample heated over 420 K (Fig. 7d) seemed to show PbTe reflections only. As already mentioned, the phase transition of Ag_2Te occurs at 420 K from monoclinic β-Ag_2Te to cubic α-Ag_2Te (FCC, $a = 0.657$ nm [4]). This means that in the diffraction image of the sample heated over the transition temperature, α-Ag_2Te reflections were also present, but could not be distinguished from the PbTe reflections due to the isostructurality and small difference (2%) in the lattice parameters of α-Ag_2Te and PbTe.

Further evidence for the described Ag growth mode was derived from some diffraction images of reacted Ag/PbTe bilayers, where also PbO was found (tetragonal, $a = 0.397$ nm, $c = 0.502$ nm [4]) (Fig. 8). It is possible that it appeared due to Pb that outdiffused onto the sample surface according to Eq. (2). Large dark agglomerates, non-transparent to TEM or TED, could be produced on the surface of reacted bilayers by electron beam heating. It was established by EDAX that they consisted mainly of Pb (Fig. 9).

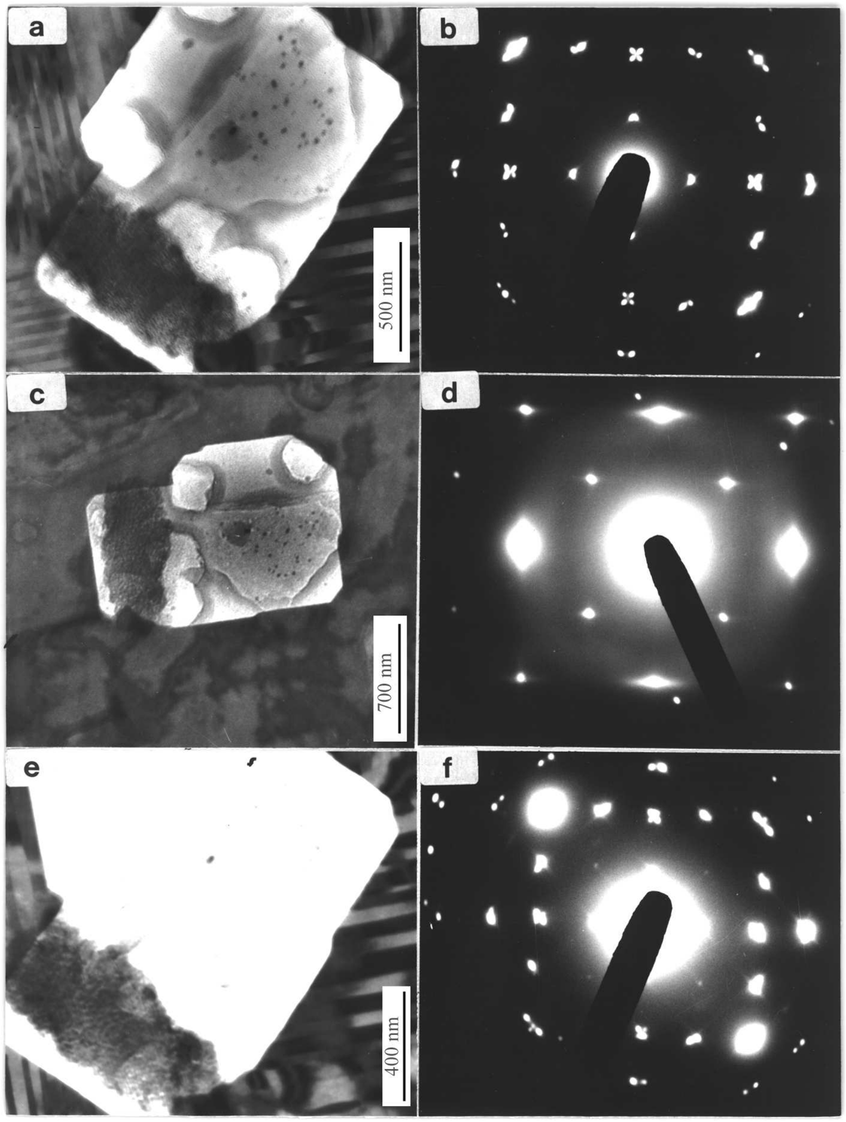

Fig. 7. (a) Monoclinic domains of Ag_2Te, *(b) corresponding diffraction image, (c) the same sample heated to over 420* K, *(d) corresponding diffraction image, (e) bright field image of the same area after cooling the sample below 420* K, *(f) corresponding diffraction image.*

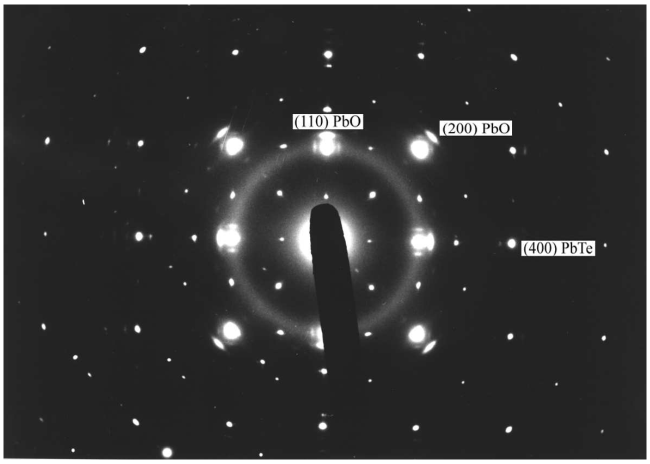

Fig. 8. Diffraction image of reacted Ag/PbTe *bilayer with* PbO *reflexions.*

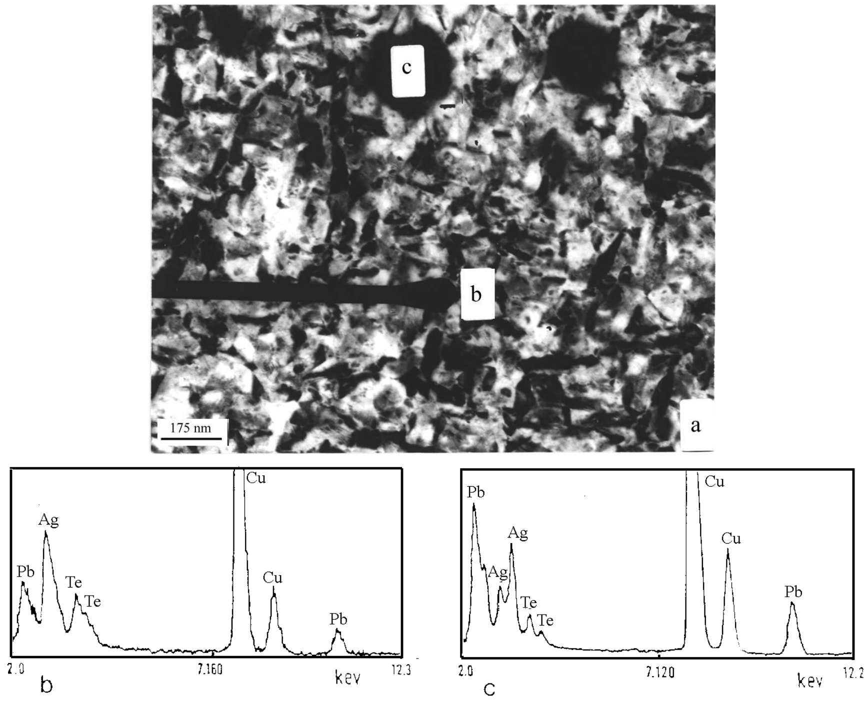

Fig. 9. (a) Non-transparent agglomerate on the surface of reacted Ag/PbTe *bilayer, heated by electron beam, (b) EDAX analysis of the sample surface in the vicinity of the agglomerate and (c) of the agglomerate.*

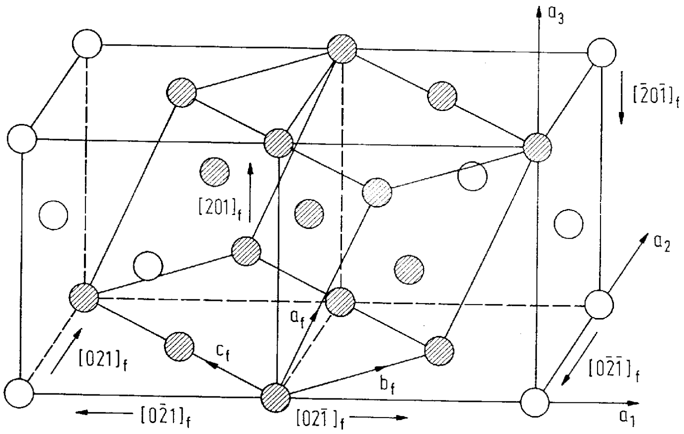

Fig. 10. Unit cells of α-Ag_2Te *and* β-Ag_2Te*; only* Te *sublattices are shown.*

4. Discussion and conclusions

Different Ag deposit microstructures obtained at $T_S = 370$ K and $T_S = 470$ K, respectively, could be due to the increased mobility of Ag atoms and microagglomerates at higher substrate temperatures.

Epitaxial orientation of Ag on PbTe, Eqs. (1a) and (1b) was also observed in Ag/SnTe system [5] and is an example of the so called "45° orientation", frequently observed at epitaxial growths of cubic phases on cubic substrates, with unit cell parameters ratio close to $\sqrt{2}$. This ratio is approximately 1.5 for Ag/PbTe system.

Reaction enthalpy E per atom for the reaction (2) is about 0.17 eV/atom, which satisfies the Brillson's semiempirical criterion for reactions in thin films ($E < 0.5$ eV) [6, 7]. As already mentioned, high-temperature α-Ag_2Te and PbTe, more precisely, their Te sublattices, are isostructural. Ag in α-Ag_2Te is randomly distributed [8]. At the phase transition α-Ag_2Te→ β-Ag_2Te (or vice versa), Te sublattice is only slightly distorted. In β-Ag_2Te, Ag is ordered, predominantly inside tetrahedral interstitions [8]. The relation between the monoclinic and cubic unit cells of β-Ag_2Te and α-Ag_2Te can be described by (see Fig. 10):

$$\left.\begin{vmatrix} a \\ b \\ c \end{vmatrix}\right|_{\beta} \approx \begin{Vmatrix} 0.5 & -0.5 & 1 \\ 0.5 & 0.5 & 0 \\ -1 & 1 & 0 \end{Vmatrix} \cdot \left.\begin{vmatrix} a_1 \\ a_2 \\ a_3 \end{vmatrix}\right|_{\alpha} \tag{3}$$

Because of the small differences in unit cell parameters between α-Ag_2Te and PbTe, Eq. (3) also describes orientational relationship between β-Ag_2Te and PbTe.

TED showed intense Ag_2Te formation at $T_S \geq 470$ K. At these temperatures, α-Ag_2Te is stable. Due to structural relationship between PbTe and α-Ag_2Te, only the cations are rearranged while the Te sublattice remains virtually unchanged. It was expected that upon cooling the sample bellow the transition temperature (420 K), monoclinic domains would appear in 3 equivalent orientations, $[201]_\beta$ parallel to each of the 3 $< 001 >$ PbTe as in the Ag/SnTe system [5]. This would also be consistent with the TED data (Fig. 5). Possible reason for the appearance of the domains only after some external disturbance (e.g. heating during TEM) may be the small misfit (2%) at the topotactical growth of β-Ag_2Te oriented towards PbTe according to (3). Only Ag atoms may rearrange to their positions of the β phase during the transition from the α to the β phase, while the structure as a whole remains pseudocubic (and possibly metastable). In the Ag/SnTe system, this phenomenon is not observed since corresponding misfit between β-Ag_2Te and SnTe amounts to nearly 5%.

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TEM– I TED–ISTRAŽIVANJA TANKIH DVOSLOJEVA Ag/PbTe

Istraživala se je morfologija i fazna struktura tankih dvoslojeva Ag/PbTe. Taj je sustav posebno zanimljiv zbog graničnih reakcija koje su se ranije opazile u sličnom sustavu Ag/SnTe. Odredili su se reakcijski produkti koji nastaju uzajamnom difuzijom Ag i podloge kao i njihove orijentacije, te raspravljaju strukturni odnosi s PbTe.