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CONFERENCE.
AMORPHOUS, VITREOUS, AND POROUS SEMICONDUCTORS

Electron Microscopy Study of a Chalcogenide-Based Polycrystalline Condensate Microstructure: The Effect of Composition and Thickness on Internal Lattice Bending

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Abstract—The grain microstructure of polycrystalline structures formed in thin amorphous Ge–Te, Tl–Se, and Cd–Te condensates has been studied using transmission electron microscopy. Pronounced internal lattice bending (up to 200 deg/μm) is detected in fine-grain structure crystallites using the bend extinction contour method. The effect of the initial film thickness and composition on the internal bending of the lattice grain is investigated. © *2005 Pleiades Publishing, Inc.*

1. INTRODUCTION

The internal lattice bending in microcrystals that grow in an amorphous phase was detected in, and has been studied since, the 1980s [1, 2]. To date, many materials and compounds of various chemical types, whose thin films exhibit this effect, are known. Crystals with pronounced internal bending of their structure were identified and found to form in thin (up to 100 nm) amorphous chalcogenide (Se and Te) foils, metals and alloys (Re, Co–Pd, and Cu–Te), metal oxides (Fe_2O_3 and Cr_2O_3), and semiconductors (Ge–Te, Sb–S, Sb–Se, and Ge–Sb_2Se_3). Judging from the accumulated data (see [3] for more detail), the internal lattice bending mechanism is general and independent of the material; instead, the mechanism results from a material's initial state in the form of a thin film of an amorphous material.

Previously, a corresponding hypothesis was suggested that described the formation of strong transrotational (a term introduced in [3]) bending of the lattice as a consequence of compensation of the stresses that arise during surface nucleation in a thin amorphous film [4]. Figure 1 schematically shows the growth model of such a crystal.

Earlier [2, 3, 5], crystals with strongly bent lattice were mainly studied using rather large crystallites (~1 μm or larger) grown in thin amorphous films. The effect of the film thickness [6] and composition [7] on the internal bending was established in such films. In this paper, we consider the results of studying polycrystalline formations with grain sizes of up to 0.8 μm. The current interest in the internal bending of polycrystal grains is caused by the wide application of polycrystalline (including thin-film) materials. However, there are no data related to the effect of internal bending in fine grains on polycrystalline material properties. Such have not been undertaken because the patterns of bend extinction contours in small grains are much less informative (zone-axis patterns are often absent) and the indexing of individual contours is very complicated.

2. EXPERIMENTAL

Thin amorphous films were grown by thermal sputtering in vacuum at a residual pressure of 10^{-3} Pa using a VUP-4 setup. The films were deposited onto a freshly cleaved mica surface coated with a thin amorphous carbon layer (to prevent epitaxial growth). In order to study the effect of composition and thickness on the internal lattice bending in crystals growing in films, we obtained condensates of variable (along a single direction) composition and/or with a thickness gradient (along the perpendicular direction) (Fig. 2). The film component concentrations were varied by sputtering materials from two crucibles placed at opposite sub-

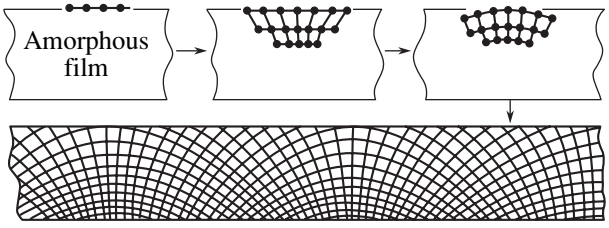

Fig. 1. Schematic diagram of the formation and growth of a crystal with strong internal lattice bending due to surface nucleation. The lines indicate lattice planes (about one line per ten planes); the bending is magnified about tenfold.

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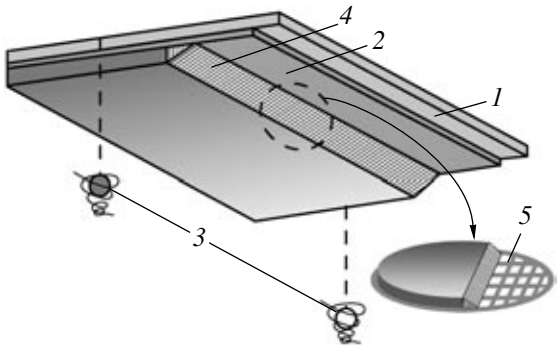

Fig. 2. Geometric layout of the growth of thin amorphous films: (*1*) substrate, (*2*) amorphous carbon layer, (*3*) crucibles with material, (*4*) thin amorphous film with thickness and composition gradients (shaded), and (*5*) a free film region, with thickness and composition gradients, placed on the electron microscopy grid.

strate edges. The thickness gradient was attained due to intentional substrate shielding, which was selected so that the entire thickness range (from 10 to 100 nm for various films) could be studied within a ~100-μm single cell of the electron microscopy grid (mesh 200). The deposition scheme is shown in Fig. 2.

After deposition, the amorphous films were separated from the substrate under surface tension forces in distilled water and placed onto a copper grid in preparation for electron microscopy studies (Fig. 2, *5*). Then, observations using a transmission electron microscope were carried out at accelerating voltages of 80–200 kV using bright- and dark-field imaging and selected-area diffraction.

The structural features of the growing crystals were studied by analyzing the patterns of bend extinction contours [8]. In particular, the internal lattice bending $\theta \approx 1/R$ [1] was determined according to the distance N between pair contours (hkl and $\bar{h}\bar{k}\bar{l}$) using the known formula $R = Nd/\lambda$ (corresponding to formulas from [9]), where R is the radius of the internal lattice bending, d is the interplane spacing of the set of planes corresponding to the contours, and λ is the electron beam wavelength. In fact, the local characteristic of the internal bending (lattice bending about the axis lying in the film plane) was determined in areas 0.1–0.01 μm in size. In most cases, the contours were indexed by comparison of bright- and the dark-field electron microscopy images of the same area of the sample under study [10].

In order to determine the distribution of sputtered materials over the film surface and, hence, the film composition, a calculation method formulated by Vekshinskiĭ [11] was used. By applying this technique, codes were developed on the basis of the MatLab 5.3 software that allowed estimation of the material distribution over a film surface of binary composition.

3. MAIN EXPERIMENTAL RESULTS AND THEIR ANALYSIS

3.1. Cd–Te Films

Films in the form of a Cd–Te binary system were prepared in a Te concentration range of 35–75%. The film thickness was varied from 15 to 60 nm. Due to spontaneous crystallization (at room temperature and immediately after deposition), the films were completely crystallized and represented polycrystalline tellurium (of hexagonal structure). The grain size varied from 0.1 to 0.5 μm.

The patterns of the bend extinction contours in images of tellurium crystal grains indicate preferential bending of the lattice planes about the axes lying in the film plane. The grains contained a rather large number of defects, especially in the thick film region, and their crystallographic orientations had appreciable differences (different diffraction contrasts, see Fig. 3). There were a small number of grains possessing the most appropriate contours for bending measurements (up to 10% from the total number of crystallites).

A numerical analysis of the crystallite lattice bending showed that its value varies from 20 to 200 deg/μm depending on the film thickness at the point of crystallite formation. Based on similar results from our previous studies (where this fact was unambiguously confirmed for larger crystals and grains), we can state that internal lattice bending in the grains is more probable than bending of the grain as a whole. This circumstance also holds in relation to the discussions in the next sections of the paper. A threefold decrease in the film thickness increased the internal bending of the grain lattice almost tenfold. In this case, the dependence was nonlinear; one of the possible approximations is shown in Fig. 3. Micrographs of crystallized film areas in the regions of corresponding thicknesses are also shown.

3.2. Ge–Te Films

Binary films of variable Ge–Te composition (50–80 at % of Ge) were grown in an amorphous state. The films were crystallized using the electron beam in the transmission electron microscope column. In the film region with a rather low germanium content (50–60 at %), single large (up to 5 μm) rhombohedral tellurium crystals grew under the beam. The crystals featured a high defect density and a complex system of bend contours.

The film regions with higher Ge contents were crystallized and segregated hexagonal tellurium grains from 0.03 to 0.4 μm in size appeared. As analysis of the negatives obtained using the electron microscope detected more than 50 grains with appropriate contours for measuring the internal lattice bending (crystals with pronounced pairs of bend contours, indicated by the circles in Fig. 4, were selected). It is noteworthy that the relative fraction of crystals that can be studied using the bend contour method is small. Apparently, this circum-

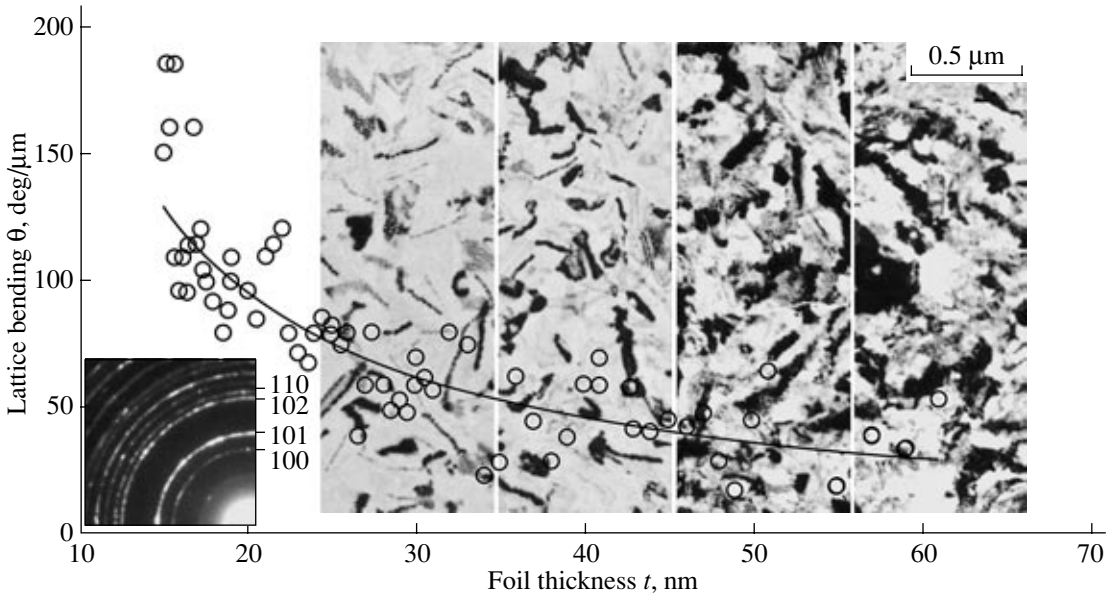

Fig. 3. Micrographs of Cd–Te film regions of various thicknesses and the dependence of the internal lattice bending on the film thickness. The inset shows the typical diffraction pattern and ring indices.

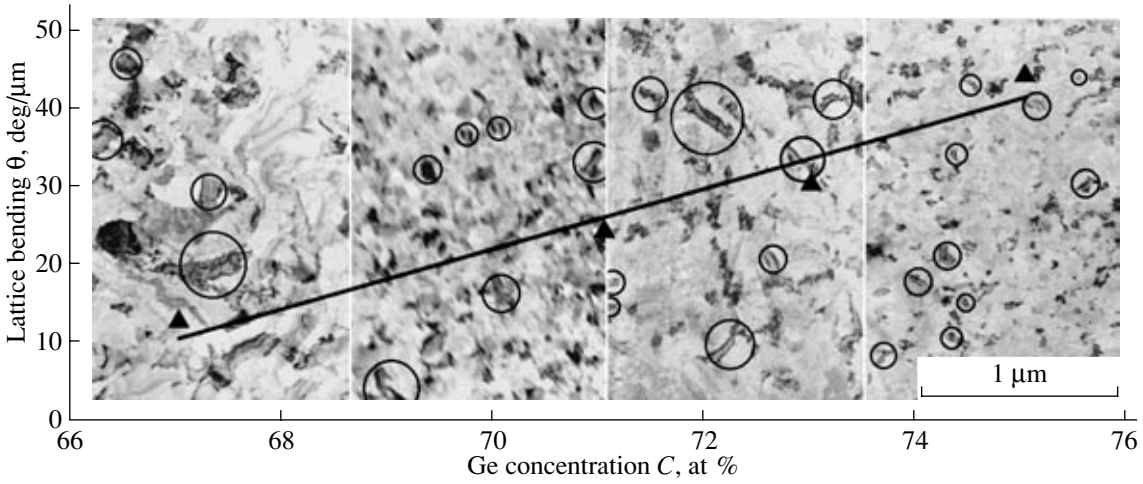

Fig. 4. Micrographs of the polycrystalline Te formations in a Ge–Te film with varying germanium content and the dependence of the internal bending of the grain lattice on the germanium content.

stance is due to the high total defect density in the grains, as well as their varied lattice orientation. In order to determine the internal bending, the distances between the most intense pair contours (corresponding to the {101} and {110} lattice planes) were measured in the negatives.

An analysis of the experimental data showed that the Ge content significantly affects the internal bending of lattice grains in the polycrystals used in the measurements. In particular, an 8% increase in the germanium content (from 67 to 75%) resulted in a fourfold increase in the internal bending (from 12 to 45 deg/μm, see Fig. 4). In this case, the dependence was close to being linear.

3.3. Tl–Se Films

Films of variable Tl–Se composition, with their Tl content ranging from 30 to 70 at %, were grown. The film regions with the highest Tl content experienced the most crystallization, which was initiated immediately after the film deposition and separation of the tetragonal tallium selenide phase. In regions with a lower Tl content, crystallization was slower, which allowed in situ studies of the crystals while they were being grown

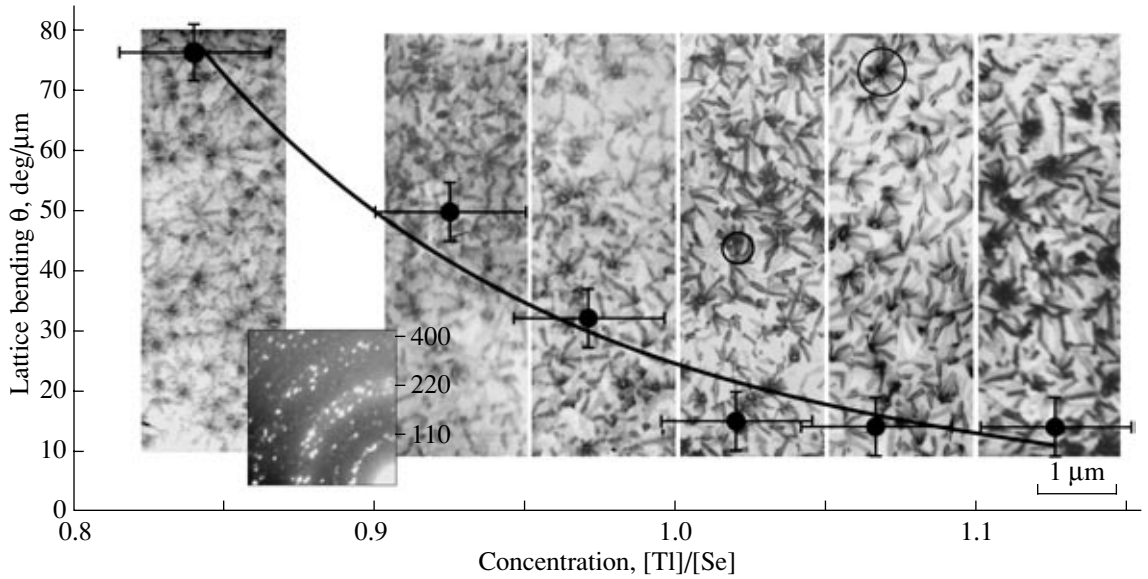

Fig. 5. Micrographs of polycrystalline TlSe film areas with varying composition and the dependence of the internal bending of the grain lattice on the film composition. Examples of grains with the [001] orientation normal to the film surface are indicated by the circles. The inset shows the typical diffraction pattern and ring indices.

(at a rate of ~1 μm/s) in the amorphous film (by varying the electron beam focusing directly in the electron microscope column).

Crystals with various morphologies were observed: fractal structures, a fine-grain polycrystalline structure (with a grain size of 0.3–0.8 μm), and spherulite-like structures. The dominant orientations were [001] (Fig. 5), [010], and [111]. Since this study is devoted to lattice bending in polycrystalline structures, hereafter, we consider only this type of structure. Polycrystalline formations in the Tl–Se condensates featured a much lower defect density in comparison with the Ge–Te and Cd–Te films. The patterns of bend extinction contours and the contours themselves were more distinct; zone-axis patterns of crossed bend contours were often observed. The number of grains with contour patterns appropriate for study was large; indeed, the measurements could be carried out for almost every grain, since they represented almost perfect single crystals. These measurements were facilitated by the rather close grain orientations as well as larger (than in the other films described above) crystallite sizes.

The internal bending in an aged polycrystalline film structure was as large as 80 deg/μm (measured, using the bend extinction contour method, by the brightest contours). A profound effect of the film composition on the internal bending of the grain lattice was detected, which is illustrated in Fig. 5 by the curve and micrographs. It is also worth noting that the shown approximation is not unique. For example, in the regions to the right and left of the composition [Tl]/[Se] = 1, the dependence can be approximated by straight lines. In this case, the bending rate varies by a factor of 4 as this composition changes. Generally, the results unambiguously suggest that an increase in the selenium content in the film in this composition range results in an increase in the internal bending of the TlSe grain lattice.

4. CONCLUSIONS

Electron microscopy of the polycrystalline formations in thin amorphous films based on certain chalcogenides allows to make the following conclusions.

(i) The bend contour technique allows determination of the internal lattice bending in a polycrystalline film even at grain sizes of fractions of a micrometer.

(ii) In the grains of Te and TlSe polycrystals growing in thin amorphous films consisting of binary Cd–Te, Ge–Te, and Tl–Se systems, internal lattice bending as great as 200 deg/μm (Cd–Te film) was detected using the bend extinction contour method.

(iii) As in the large grains and crystals studied previously, the film thickness and composition significantly affect the internal bending of the lattice planes in fine-crystalline condensates. In this case, the experimentally measured dependences are qualitatively close to similar dependences obtained for coarse-grained films [12] and isolated crystals in an amorphous environment.

(iv) The effect of the composition was detected in the Tl–Se and Ge–Te films. In the Ge–Te films, an increase in the Ge content by ~10% results in a fourfold increase in the internal bending of the tellurium grain lattice. In the Tl–Se condensates, a slightly smaller increase in the Se content causes a more than sevenfold increase in the internal bending of the TlSe crystal lattice. A similar pattern for the effect of the initial amorphous film composition on internal lattice bending was

earlier observed for separately growing crystallites, e.g., Se in thin condensates representing a Se–Te binary system [7].

(v) In the Cd–Te condensates, lattice bending in the polycrystalline grains increases almost tenfold as the film thickness decreases by a factor of 3. In this case, the dependence obtained is nonlinear: the lattice bending significantly increases in thinner film regions. This dependence is understandable, since larger degrees of elastic bending are attainable in thin films than in thick ones.

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