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Electron Microscopy Investigation of the Influence of Thickness on Crystal Growth in Amorphous Films of Selenium and Antimony Compounds

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Growth of crystals of selenium, antimony selenide and antimony sulfide with the unusual type of imperfection (a strong internal bending of the crystal lattice) in amorphous films has been studied *in situ* by transmission electron microscopy. Based on the bending extinction contours, the structure peculiarities of crystals have been investigated.

INTRODUCTION

The state of thin amorphous films is non-equilibrium. Crystallization accompanied by the formation of defect crystals is one of the consequences of this non-equilibrium. Under some conditions (the influence of the electron beam in an electron microscope), one can directly observe *in situ* the growth of an unusually ordered crystal (which is free of dislocations for some substances). The lattice of such a crystal is formed with continuous monotonic bending (up to 120° per micrometre) around the axis in the film plane [1]. The crystal remains plane (Fig. 1) [2]. It is clear from the general concepts that for such a geometry of lattice internal bending, the maximally possible lattice elastic distortions in the surface layers can be realized at the stronger lattice bending with the film thickness decreasing. Consequently, one can expect the formation of a stronger internal bending of the lattice when thinner films are crystallized.

In this work the formation of defect crystals with the internal bending of the lattice in amorphous films of antimony selenide, antimony sulfide and selenium with a variable thickness has been studied *in situ.* The purpose of the investigation was to find the influence of film thickness on the formation of unusual imperfection of the growing crystal.

EXPERIMENTAL

Amorphous films were prepared by the method of vacuum thermal deposition. The deposition was carried out on the substrate of fresh-cleaved mica at room temperature. To exclude non-controlled factors, the influence of the thickness of Se, $Sb2Se_3$ and Sb_2S_3 films on their crystallization was investigated on one film with the special geometry of deposition leading to the formation of the strong gradient of films thickness, rather than on different films of different thickness. Various ways differing by the mutual position of the crucible, substrate and shadow mask were tested. The scheme at which the flat metallic plate 0.5 μm thick was closely adjacent to the substrate was the most successful. For the corresponding choice of the mutual position of the crucible and substrate, the metallic plate formed a sufficiently narrow shadow on the latter. As a result, after the film was removed from the substrate and placed on the electron microscope grid, the film thickness varied from ~10 nm (the maximal value) down to practically zero within one cell of the electron-microscope grid (50-100 (Am) (Fig. 2).

The structure of the initial films, their crystallization as the result of heating and the structure peculiarities of the crystallized regions were studied by electron microscopes JEM-200 CX'and TESLA BS-613. Local crystallization of individual regions was conducted by the action of the electronic beam of various focusing and intensity in the column of the electron microscope. It has been found earlier [2] that the degree of bending of the lattice of a growing crystal depends on the growth rate and reaches the maximal values in the range of 0.5-1 μm/s. In this work, the crystallization rate in the majority of experiments was maintained constant within this range. The structure investigations were carried out further at the defocused beam with the decreased intensity to exclude the additional crystallization during the investigations.

To determine the degree of bending of the crystal lattice of growing crystals, the method of bending extinction contours developed earlier [3] was used. Formulae connecting the positions of the bending contours on the electron microscopic image of the crystal with the bending parameters of the crystal or its lattice and with the parameters of the unit cell are the basis of the method. When the lattice is strongly bent, the bending contours are usually situated by couples of the lines corresponding to the reflections from the *(hkl)* planes with opposite signs, and the local values of the radius of curvature and the lattice disorientation can be found from the distance between the lines [3]. Large re-orientations of the lattice, integral values of the lattice curvature or small disorientation at the very strong bending can be determined through the angle between the indexed axes of the bands of the reflecting planes - the places of crossing of the bending contours (Fig. 3b). The brightest bending contours on the dark-field image often exhibit the fine structure consisting of a set of additional maxima, through the distance between which we found the crystal thickness [4].

RESULTS AND DISCUSSION

In the amorphous films obtained, both the large crystals or ribbons with the preferred direction of growth from the thicker part of the film to thinner one and back and the chains of individual crystals were grown. The thickness of the crystals varied from the almost maximal one of ~100 nm down to the minimal one of ~10 nm (amorphous films at the

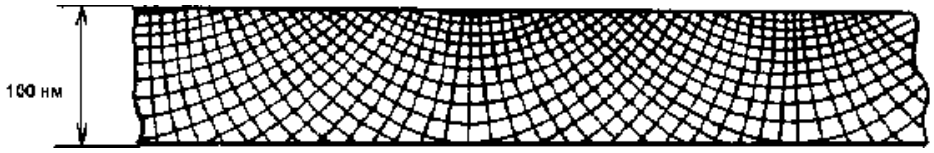

Figure 1. Model of the internal bending of the crystal lattice planes for a crystal grown in a thin amorphous film [2]. Two systems of planes (one line per ~20 planes) are schematically shown in the cross-section of the film, their bending is strongly exaggerated for visualization.

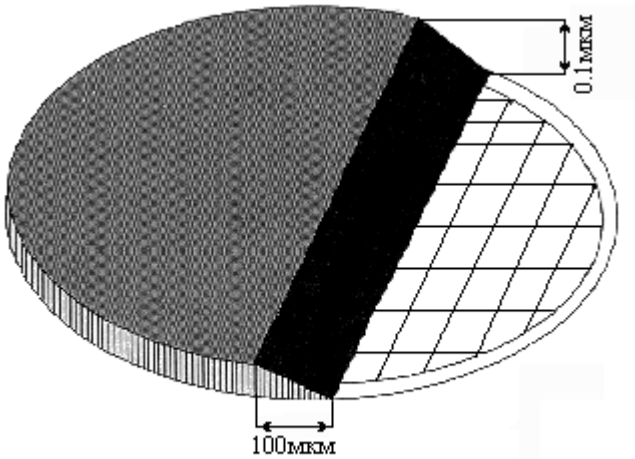

Figure 2. Schematic image of the electron microscopic grid and thin film on it with the strong thickness gradient at the film edge.

thickness less than ~10 nm are very stable and could not be usually crystallized by the electron beam). The following similar regularities were observed in all the situations investigated:

1. The degree of the internal bending of the crystal lattice abruptly increases, on the average by an order of magnitude, with the thickness decreasing (from 100 nm down to 10-15 nm). If these changes are characterized by the radius of curvature of the crystal lattice, they correspond, on average, to the decrease of the bending radius from 10-20 urn down to 1-2 μm (the bending radius of 1 μm corresponds to the lattice bending of ~57° per 1 μm of the crystal length).

2. The density of the boundaries of blocks and the irregularity of bending are increased with the film thickness decreasing.

3. The rate of the crystal growth decreases to the complete stop of crystallization with the film thickness decreasing (at the constant intensity of the electron beam).

The first two regularities are illustrated by the crystallized regions in ah antimony selenide film (Fig. 3). Figure 3a illustrates a couple of bright parallel lines - bending

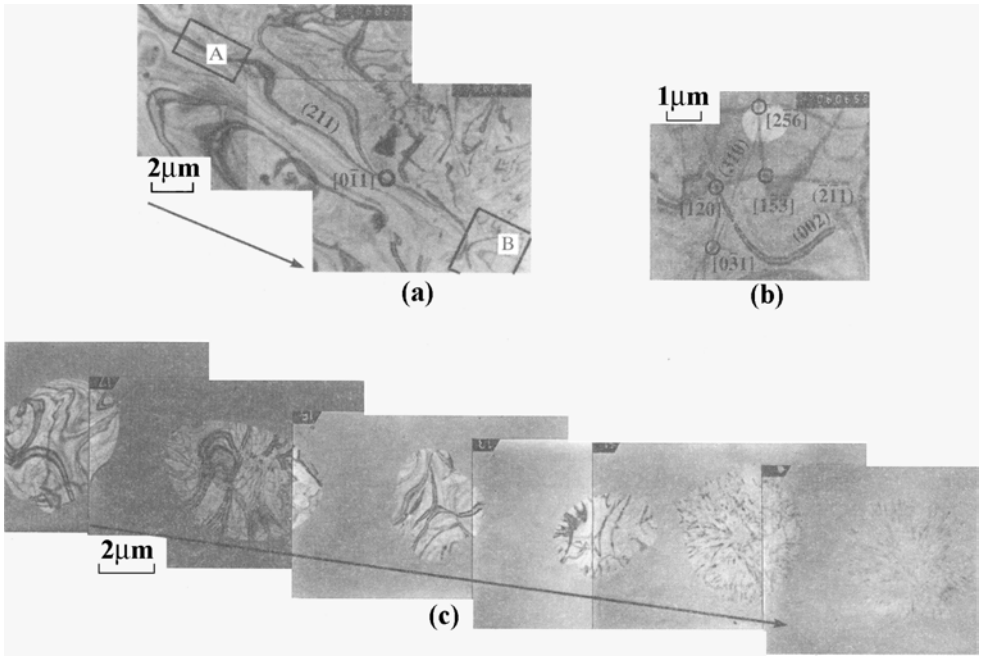

Figure 3. Microphotographs of the Sb_2Se_3 film: the fragment crystallized in the direction from A to B (o), expanded image of the thinnest part of it (b) and a series of patterns of subsequently grown crystals (c). Arrows show the direction of decreasing the crystal thickness and increasing the degree of the lattice bending; some bending contours and axes of bands of reflecting planes are indexed.

contours directed to the thickness gradient. Their identification by the indexed microdiffraction pattern and dark-field images [4] allows one to attribute to them the indices corresponding to the reflections from the (211) planes. In the region A, where the thickness is 59 nm, the bending radius, which is determined by the distance between the contours of this couple, is 17 μm (this corresponds to the bending of the crystal lattice of ~3° per 1 μm). To the left and above this place, the bending is smaller in the thicker part of the film. During the crystal growth from the thick part of the crystal to the thin one, the distances between the contours of the considered couple of the bending contours (and, consequently, the radius of curvature of the lattice) decreased monotonously. The couple of the bending contours at the thickness of 16 nm in region *B,* which corresponds to the reflections from the (211) planes, merged into the common contour. To calculate the lattice bending, the calculations of the angular disorientation between the axes of the plane bands corresponding to neighboring axes band pictures (Fig. 3b) were used. The calculation of the degree of the lattice bending in this region gives the values lying in the range of 19-29° per 1 μm with the same tendency of increasing the internal bending of the lattice for thinner regions. So, when the crystal grows from a thick part of the amorphous film to a thin one, the bending of the crystal lattice constantly increases.

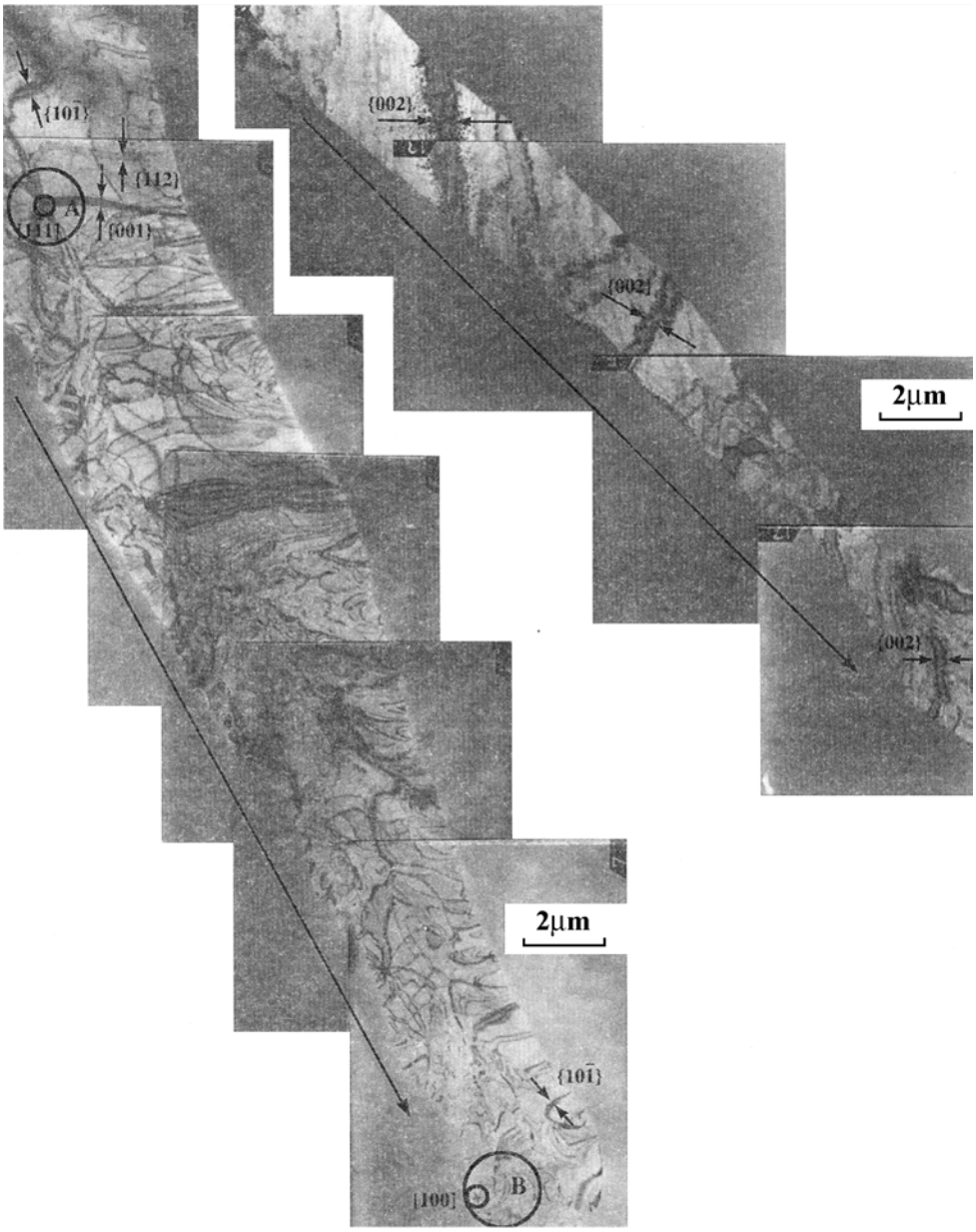

Figure 4. A series of electron microscopic images of fragments of Se *(a)* and 85283 *(b)* amorphous films crystallized in the form of a ribbon. Arrows show the direction of the preferred growth, decrease of the film thickness, and increase of the bending degree of the crystal lattice.

Analogous results are observed when individual crystals are subsequently grown in neighboring regions of different thickness. An example of the chain of crystals demon-

strating the change of the degree of the lattice bending more than one order of magnitude is shown in Fig. 3c. The calculation of the radius of curvature of the lattice using the brightest bending contours shows that it changes from 12 μm down to 0.4 μm. Figure 3c also illustrates an increase of the density of grain boundaries and blocks as the film thickness decreases. It is indicated by an increase of the number of the bending contours undergoing shifts, distortions and splitting.

Figure 4a illustrates similar regularities for a selenium crystalline ribbon 35 μm long grown also in the direction of decreasing the film thickness. In region A, the bending radius of the crystal lattice is ~10 μm and the thickness is 70-80 nm. In region B, the bending radius is ~1 μm and the thickness is ~10 nm. It is seen that the degree of bending of the crystal lattice increases by an order of magnitude as the crystal film thickness decreases by an order of magnitude. A microphotograph of the crystal ribbon of antimony sulfide (Sb_2S_3) is shown in Fig. *4b*. The bending radius of the lattice decreases with the crystal thickness decreasing from 35 down to 9 μm.

All three regularities presented at the beginning of this section are clear. The most important regularity - an increase of the degree of bending of the crystal lattice with decreasing the film thickness - is quite predictable from the energy viewpoint. It is also clear when assuming the constantly acting mechanism of the lattice bending of the crystal growing in an amorphous film. The appearance of grain boundaries, mosaic blocks and an increase of the intensity of block formation with decreasing thickness of the crystallized film can be explained by the fact that the values of elastic stresses related to the elastic internal bending of the crystal lattice are close to the limiting value of elasticity of the material. Their possible random local and (or) regular exceeding due to the changes in the reorientation of the crystal lattice on the growth front (the factor of anisotropy of elastic features of the crystals of selenium, antimony sulfide and antimony selenide comes into effect), which are more frequent in the thin part of the film, leads to the plastic deformation with the removal of excessive stresses and with the formation of grain boundaries and blocks. The decrease of the crystallization rate down to a complete stop with the film thickness decreasing corresponds to the well-known regularity of increasing the stability of the amorphous state as the thickness of condensed films decreases [5, 6]. For the films placed on a substrate, this regularity is explained by the action of tension stresses appearing in condensates under cooling after the deposition on a substrate [7]. The smaller the film thickness (at the unchanged temperatures of the substrates), the greater these stresses. This factor can exist, maybe to a smaller degree, in our case for films without a substrate. Tension stresses of such a nature can result in the increase of the degree of bending of the crystal lattice on the one hand and of the formation of blocks with decreasing the film thickness on the other hand.

CONCLUSIONS

Amorphous films with the strong thickness gradient have been obtained using the special scheme of deposition. Such a film geometry allows one to study *in situ* the influence of the thickness on crystallization.

It has been found that when the crystals are grown in selenium, antimony selenide and antimony sulfide amorphous films, the degree of the internal bending of their crystal lattice

substantially increases (on the average, by an order of magnitude) up to the values of~60° per 1 μm and more with the thickness decreasing in the range of 100-10 nm, the density of the grain boundaries also noticeably increases.

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