Functional Materials 15, No.3 (2008)

Growth of crystals with bent crystalline lattice in amorphous semiconductor films

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Received February 15, 2008

Crystallization of amorphous films of gallium, indium and antimony chalkogenides (Sb_2S_3, In_2Se_3, Ga_2Te_3 and Sb_2Te_3) has been investigated to elucidate the crystallization character and to determine conditions favoring the growth of crystals with bent crystalline lattice. It has been found that the lattice bending of crystals formed during the crystallization of amorphous films under heating by electron beam in the electron microscope column is observed in crystals with orthorhombic and hexagonal lattices (Sb_2S_3 and Sb_2Te_3). The bending absolute magnitudes are larger in crystals with hexagonal lattice where they rich 160 grad/μm. The crystals with bent lattice appear mainly at fast heating of amorphous film when the rate of crystal growth in the film plane exceeds 1 μm/s. The crystal lattice bending increases as the amorphous film thickness diminishes. When heating slowly Sb_2S_3 films by electron beam, it has been revealed that at initial stages, very thin crystals with unbent lattice appear in the film subsurface layer; crystal lattice bending takes place during the crystal thickness increase.

Исследована кристаллизация аморфных пленок халькогенидов галлия, индия и сурьмы (Sb_2S_3, In_2Se_3, Ga_2Te_3 и Sb_2Te_3) с целью выяснения характера их кристаллизации и установления условий, способствующих росту кристаллов с изогнутой кристаллической решеткой. Установлено, что изгиб кристаллической решетки кристаллов, образующихся при кристаллизации аморфных пленок при их нагреве электронным пучком непосредственно в колонне электронного микроскопа, наблюдается в кристаллах с орторомбической и гексагональной решетками (Sb_2S_3 и Sb_2Te_3). Абсолютные значения изгиба больше в кристаллах с гексагональной решеткой, где они достигают 160 град/мкм. Кристаллы с изогнутой решеткой преимущественно возникают при быстром нагреве аморфной пленки, когда скорость роста кристаллов в плоскости пленки ≥1 мкм/с. Изгиб решетки кристаллов увеличивается с уменьшением толщины аморфной пленки. При медленном нагреве пленок Sb_2S_3 электронным пучком обнаружено, что сначала в приповерхностном слое пленки возникают очень тонкие кристаллы с неизогнутой решеткой; изгиб их кристаллической решетки происходит в процессе увеличения толщины кристаллов.

Dislocation-free crystals with monotonously bent crystalline lattice (up to 120 grad/μm) are formed during spherolitic crystallization of amorphous films of various materials [1–8]. However, the crystals themselves remain flat. The lattice bending has a character of elastic rotational distortion. The crystals with such bending of crystalline lattice are known as "transrotational" ones. The question about the growth cause of transrotational crystals in amorphous films remains unsolved to date.

In this work, crystallization of gallium, indium and antimony chalkogenides (Sb_2S_3, In_2Se_3, Ga_2Te_3, and Sb_2Te_3) amorphous films was studied by transmission electron microscopic methods to understand the crystallization character and to determine

the growth conditions of crystals with bent crystalline lattice. According to JCPDS data, antimony sulfide Sb_2S_3 has an orthorhombic lattice with periods: $a = 1.1229$ nm, $b = 1.1310$ nm and $c = 0.3839$ nm. In_2Se_3 has a hexagonal lattice, however, JCPDS data point to several In_2Se_3 modifications with hexagonal lattices but with different parameters. Ga_2Te_3 has a cubic lattice with $a = 0.5898$ nm. Sb_2Te_3 has a rhombohedral lattice which can be considered as a hexagonal layered structure with parameters: $a = 0.4262$ nm and $c = 3.045$ nm.

Amorphous films were prepared by thermal evaporating the appropriate substances of stoichiometric composition from a molybdenum boat in 10^{-3} Pa vacuum. A large current was passed through the boat at once to provide a sufficiently high evaporation rate and to prevent the material decomposition. The condensation was carried out onto (001) KCl surface at room temperature. The KCl crystals were placed at different distances from the evaporator to obtain the films of various thickness from ~10 nm to 50 nm in one experiment. The films were separated from crystal substrates by KCl dissolution in water and then placed onto copper gauzes. The local crystallization of separate areas of amorphous films was carried out in situ in the column of a PEM-125K electron microscope using electron beams of various intensity and focusing. To stop the growth process in order to study the structure of grown crystallites, the electron beam intensity was reduced. The growth rate was varied from 0.001 to 1 μm/s. The structural analysis was made by transmission electron microscopy using high-resolution mode. The local lattice bending $d\varphi/W$ ($d\varphi$ is the lattice rotation angle between hkl and $\bar{h}\bar{k}\bar{l}$ bent extinction contours; W, the distance between bent extinction contours) was determined according to [8] by analyzing the bent extinction contours in the crystallite images:

$$\frac{d\varphi}{W} = \frac{1}{R} = \frac{[1 + (d_{hk0}/d_{00l})^2]\lambda}{W d_{hk0}},$$

where R is the lattice curvature radius; d_{hk0} and d_{00l}, ($hk0$) and ($00l$) interplanar distances, respectively; λ, de Broglie wavelength for electrons.

Fig. 1 presents the electron microscopic image and electron diffraction pattern for a typical structure of the investigated amorphous films. A non-uniform contrast shaped as dark rounded spots (globules) of 100 nm in diameter is clearly observed in the image. Such contrast type may be caused by film heterogeneity either in thickness or in density. As it was found during the crystallization of the films, the globular structure may be inherited by crystalline film during crystallization or, in other cases, does not influence the crystal structure.

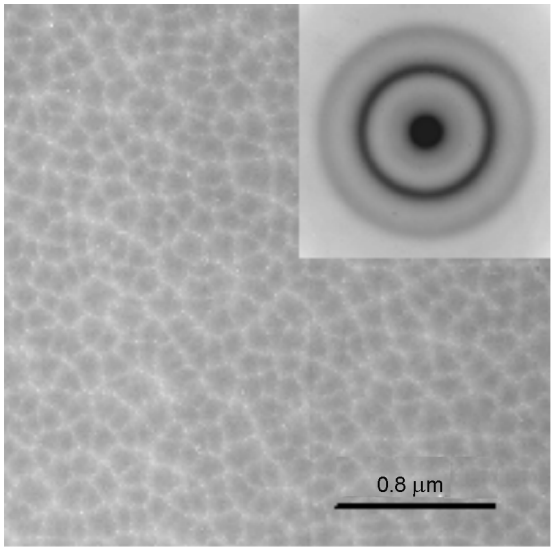

Fig. 1. Structure of Sb_2Te_3 amorphous film.

Let us consider some features of films crystallization for various semiconductor compounds.

During "in situ" investigations, it was revealed that the crystallization of antimony sulfide amorphous films occurs in two stages (Fig. 2). In the first stage, the excessive antimony is crystallized as a large amount of fine crystallites. The excess Sb in the film seems to be caused by partial decomposition of Sb_2S_3 during evaporation and, as a result, by the film depletion of sulfur being more volatile component. The number of Sb crystallites and their sizes do not change at a further heating of the film. In the second stage, Sb_2S_3 crystallites are formed in amorphous film at a higher electron beam intensity. The presence of Sb crystallites does not affect the propagation of Sb_2S_3 crystallization front. Moire images revealed on Sb crystallites in recrystallized areas of Sb_2S_3 film confirm their formation either on a film surface or in a thin subsurface layer. It was also found that the thinner Sb_2S_3 films are crystallized at a higher electron beam current density, moreover, the films of less than 10 nm thickness do not crystallize even at maximal electron beam current density attained without the aperture diaphragm of the second con-

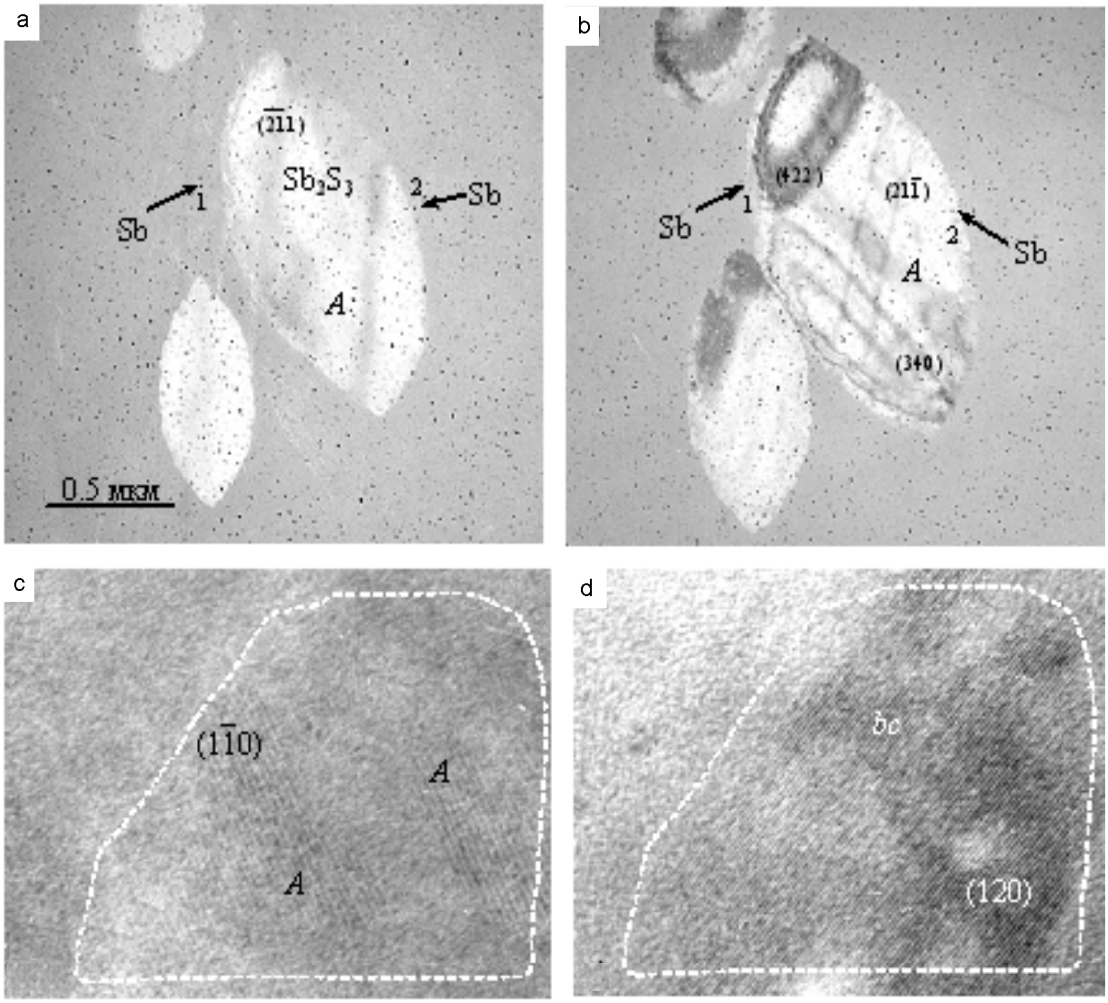

Fig. 2. Increasing curvature of Sb_2S_3 crystal lattice with increasing thickness at slow heating of the amorphous film.

denser. The difficulty of crystallization occurring at the film thickness decrease is in good correlation with the well-known dependence of the amorphous state stability increase on the condensed film thickness [9, 10]. At slow heating of amorphous film by electron beam and, accordingly, at small rates of crystal growth (0.001 μm/s in the film plane), very thin crystalline plates which thickness is significantly smaller than the film thickness appear instantaneously at first. Those have a very weak diffraction contrast. The extinction contours are rather wide or completely absent and, as a rule, only a single contour instead of the pair from similar planes is revealed. This fact indicates a slight crystal lattice bending. At further heating, the crystallite size in the film plane increases insignificantly, but they intergrow through the whole amorphous film thickness. As the crystalline plate thickness increases, the extinction contours become more narrow, the intercontour distances decreases, and the pairs of extinction contours from similar planes are observed simultaneously with contours from other plane systems. This clearly demonstrates the increase of the lattice bending. Figs. 2.a, b present two electron microscopic images obtained with 5 min interval from the same crystals grown in Sb_2S_3 amorphous film during slow heating. In Fig. 2a, very thin Sb_2S_3 crystals are observed. The local lattice curvature of crystal A calculated using the distance between the $(\bar{2}\,\bar{1}\,0)$ and $(21\bar{1})$ extinction contours is 2.9° per 1 μm. In Fig. 2b, the local lattice curvature calculated using the intercontour distance for the same pair of extinction contours is 9.5° per 1 μm. It is to note the fact that the lattice curvature is increased from the crystal center to its periphery. For ex-

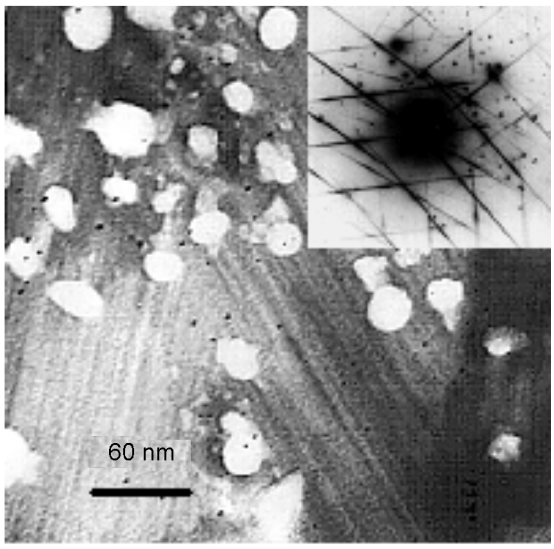

Fig. 3. Structure of a crystallized indium selenide film.

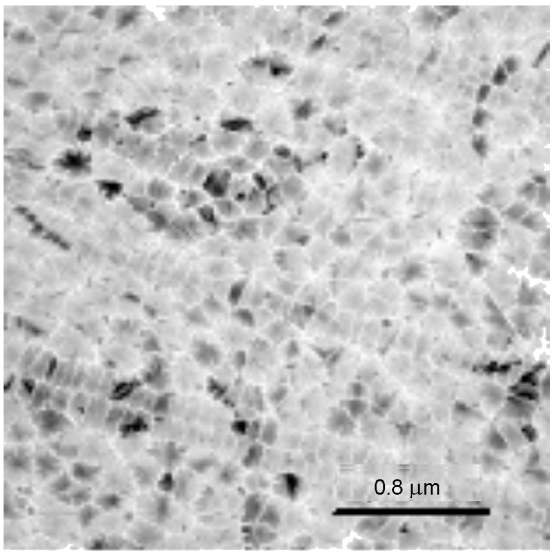

Fig. 4. Structure of a crystallized gallium telluride film.

ample, the lattice curvature in the area where the pair of (340) extinction contours is located is increased from 9.5° per 1 μm at the central part of the crystal to 19° per 1 μm at the crystal edge. Any morphological transformations are not observed in amorphous film surrounding the crystals. The relative change in the Sb_2S_3 film density in amorphous and crystalline states was estimated by the method described in [5]. To that end, the change in the distance between similar Sb crystallites (black points 1 and 2 in Fig. 2a,b) near Sb_2S_3 crystal during its thickness increase under intense electron beam exposure was measured. It was found that the relative increase of the substance density makes ~8 % at Sb_2S_3 amorphous film crystallization. Hence, it can be expected that the crystals in the film plane undergo tensile stresses. In spite of this fact, their crystalline lattice is bending. An increase of the crystalline lattice curvature at the crystal thickness increasing was observed during "in-situ" crystallization using the high-resolution electron microscopy mode. Figs. 2c, d show the images of the same film areas (enclosed by dotted line), obtained at different crystallization stages under electron beam exposure. In Fig.2 c, the (110) atomic planes are revealed within the crystalline plate (section A) corresponding to the pair of (110) bent extinction contours. The lattice curvature is changed as the crystalline area thickness increases, and the *bc* bent extinction contour is appeared in the plate image, where the (120) planes system comes up into reflecting position.

The electron microscopic image and microdiffraction pattern of indium selenide film are presented in Fig. 3. It is seen that the large crystallites of 1 μm size are formed during crystallization. These crystallites have a modulated structure, that is, they consist of a set of thin platelets, perhaps differing in chemical composition. A set of equilibrium semiconductor compounds similar in composition is known for the In–Se binary system: InSe, In_6Se_7, In_9Se_{11}, In_5Se_7, α-, β-, and γ-In_2Se_3. The most of those have hexagonal lattices with close parameters. Therefore, it is naturally to suppose that such modulated structures can be formed due to non-stoichiometry in amorphous films resulting from In_2Se_3 dissociation during evaporation.

Fig. 4 shows an electron microscopic image of a gallium telluride film crystallized under electron beam heating. The phase composition corresponds to the stoichiometric GaTe compound (monoclinic structure). This is in agreement with data from [11]. According to these data, Ga_2Te_3 compound is dissociated during evaporation:

$$2Ga_2Te_3 = 4GaTe + Te_2.$$

The structure of polycrystalline GaTe film inherits the amorphous film structure: GaTe crystallites are identical in shape and size to the amorphous film globules.

The crystallization of Sb_2Te_3 amorphous film starts with appearance of Sb crystal-

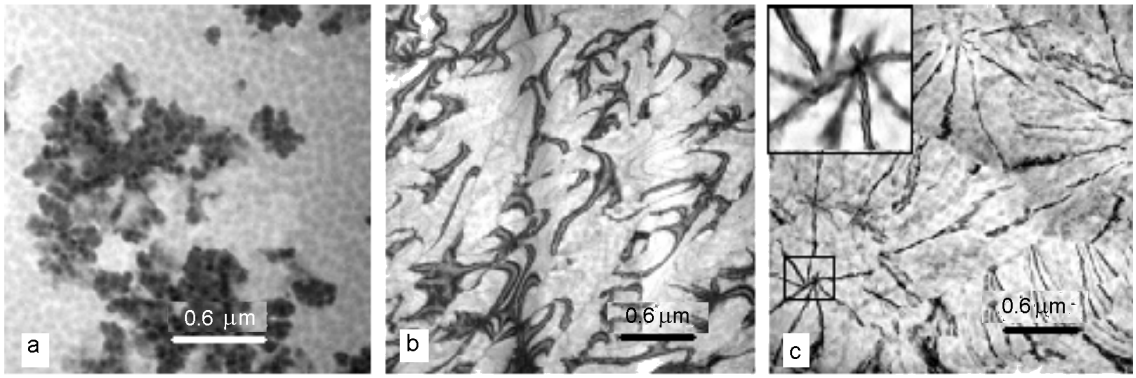

Fig. 5. Crystallization of an antimony telluride film at slow (a) and fast (b, c) heating. The Sb_2Te_3 film thickness 80 nm (a, b) and 20 nm (c).

lites in the film subsurface layer. Then the Sb_2Te_3 crystallization occurs. A dependence of the Sb_2Te_3 growth character on both the heating rate and the film thickness is revealed. At low heating rates, the crystallization proceeds in a manner similar to that of gallium telluride films (Fig. 5a): the Sb_2Te_3 crystallites are identical in shape and size to the amorphous film globules. As a result, a fine-crystalline structure is formed. At fast heating by electron beam, the Sb_2Te_3 spherolites with bent crystalline lattice are formed (Fig. 5b, c). The lattice bend of crystallites decreases as the film thickness rises. Electron microscopic images confirm this fact: the width of bent extinction contours becomes larger and the distances between them are also increased. In Figs. 5b and 5c, the twinned extinction contours are observed clearly. The lattice curvature calculated according to [8] is 30 to 100 grad/μm for 80 nm thick films and 100 to 160 grad/μm for films of 20 nm thickness.

Thus, the crystal lattice bend formed during crystallization of amorphous films being heated by electron beam in the electron microscope column is observed in crystals with orthorhombic and hexagonal lattices. The absolute curvature values are larger in crystals with hexagonal lattice where they rich 160 grad/μm. The crystals with bent lattice appear mainly at fast heating of amorphous film when the rate of crystal growth in the film plane exceeds 1 μm/s. The crystal bend increases at amorphous film thickness decrease. At slow heating of Sb_2S_3 films by electron beam, thin crystals with unbent lattice appear at initial stages in subsurface layer of the film; the crystal lattice bending occurs during the crystal thickness increase.

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Ріст кристалів з вигнутою кристалічною граткою в аморфних плівках напівпровідників

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Досліджено кристалізацію аморфних плівок халькогенідів галію, індію та стибію (Sb_2S_3, In_2Se_3, Ga_2Te_3 та Sb_2Te_3) з метою з'ясування характеру їхньої кристалізації та виявлення умов, що сприяють росту кристалів з вигнутою кристалічною граткою. Встановлено, що вигин кристалічної гратки кристалів, що утворюються при кристалізації аморфних плівок при їх нагріванні електронним променем безпосередньо у колоні електронного мікроскопа, спостерігається у кристалах з орторомбічною та гексагональною гратками (Sb_2S_3 та Sb_2Te_3). Абсолютні значення вигину є більшими у кристалах з гексагональною граткою, де вони досягають 160 град/мкм. Кристали з вигнутою граткою виникають переважно при швидкому нагріванні аморфної плівки, коли швидкість росту кристалів у площині плівки ≥1 мкм/с. Вигин гратки кристалів збільшується зі зменшенням товщини аморфної плівки. При повільному нагріванні плівок Sb_2S_3 електронним променем виявлено, що спочатку у приповерхневому шарі плівки виникають дуже тонкі кристали з невигнутою граткою; згинання їхньої кристалічної гратки відбувається у процесі збільшення товщини кристалів.