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Combined TEM-AFM studies of "transrotational" spherulites growing in amorphous films

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Abstract. Thin amorphous films of selenium and iron oxide were crystallized by local electron beam annealing. Two types of spherulite crystals grown (complicated by "transrotational" lattice ordering) were studied by transmission electron microscopy (TEM) and atomic force microscopy (AFM) techniques. The regularities of change in lattice orientations and imperfection along the crystals obtained by TEM are analyzed in parallel with AFM data for the film surface (relief) of the crystal and amorphous surrounding.

Introduction

Crystal growth in amorphous film can be accompanied by formation of rather well-known specific crystals — spherulites (with primarily azimuth lattice misorientations around axis normal to the film plane — "cylindrites", in fact) and less-known "transrotational" [1] crystals (with internal lattice bending round axis or axes lying in the film plane). In the present paper we study the "transrotational" spherulites having both 2 kinds of misorientaions, attained as result of nucleation and growth. We use transmission electron microscopy (TEM), primarily bend contour technique [2] with selected area electron diffraction, *in situ* studies (including video-records analysis) and high resolution electron microscopy (HREM), combined with atomic force microscopy (AFM) in a tapping mode and optical microinterferometry. Two different kinds of spherulites were produced by local electron beam annealing of amorphous films prepared by either vacuum condensation (Se with Te doping, 50–80 nm thick) or pyrolysis (Fe_2O_3, 20–30 nm thick) and separated from the substrate. Free-standing films placed on TEM grids were irradiated by electron beam inside the column of electron microscope.

Experimental

Complicated regular change in lattice orientations are indicated by regular bend contour patterns on the TEM images, Fig. 1a, 2a. The main features were presented earlier for both Se spherulites [3] and αFe_2O_3 [1]. In Se nucleus [001] of the hexagonal lattice originally is lying parallel to the film plane and finally it is oriented concentrically (indicated by bright arcs — extinction bend contours): spherulite consists primarily of radially elongated grains (fibers 100–500 nm width) which in its turn have strong orientational gradients $\sim 100^\circ/\mu$m (regular rotation of the unit cell round the axis oriented tangentially in the film plane). In αFe_2O_3 nucleus [001] is normal to the film plane, the strong orientational gradients are similar and have the same order of magnitude while grain morphology varies in complex manner. *In situ* TEM gives the magnitude of the crystal growth rate: $\sim 0.3\ \mu$m/s for Se, several times higher for perfect zones of αFe_2O_3 spherulite and lower for its concentric imperfect zones.

In the present combined studies, the interrelation of crystal lattice orientation and imperfection with the relief of the crystal surface is of prime interest. AFM has been used to visualize (and obtain corresponding data by profiling): the spherulite

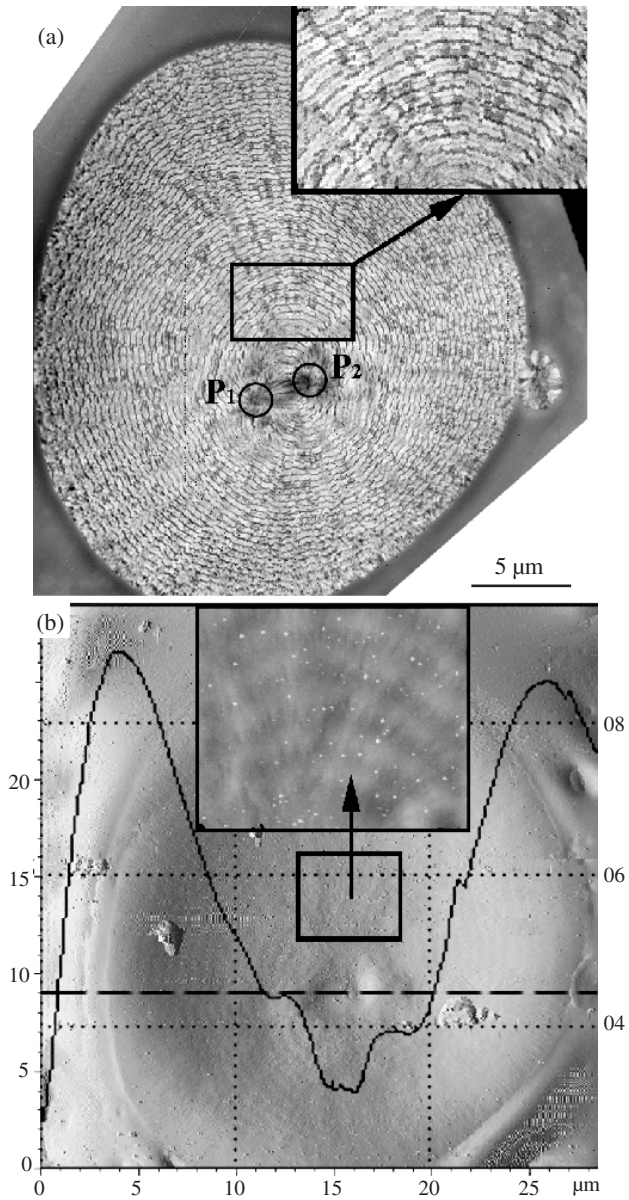

Fig. 1. Micrographs of Se spherulite in amorphous matrix with insets of higher magnification: TEM (a) indicating 60° rotation of the unit cell between adjacent dark lines, roughly traces of {100}, AFM (b) with a profile superimposed (measured along the dashed horisontal line).

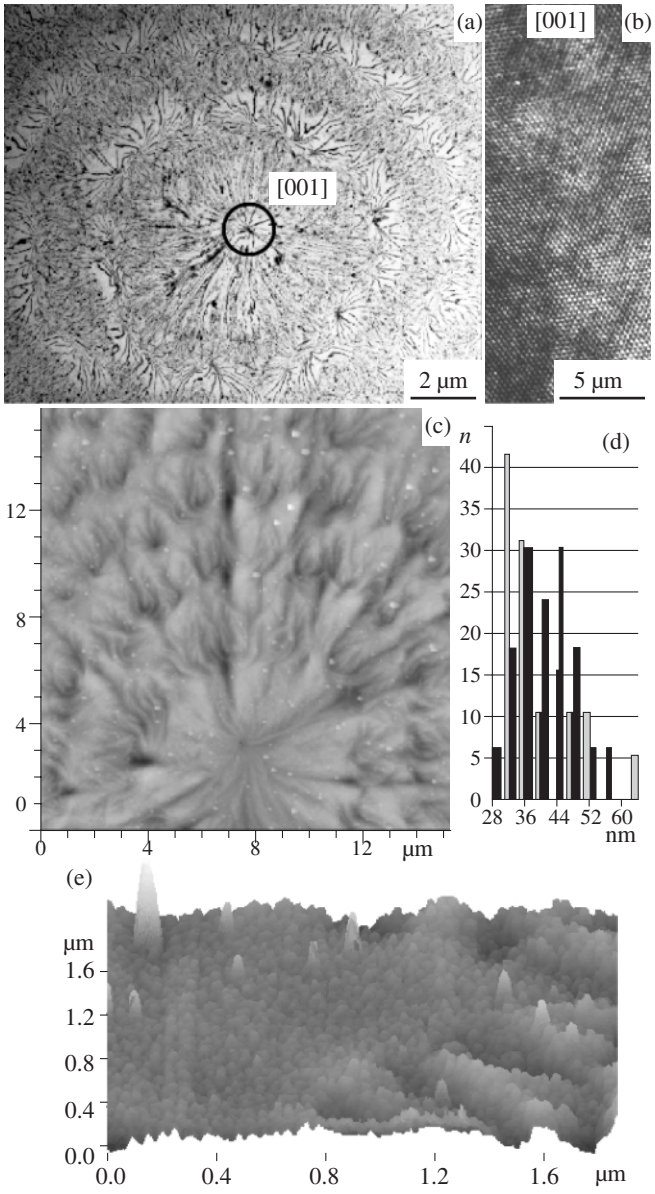

Fig. 2. Micrographs of αFe_2O_3 spherulites: TEM (a) indicating $\sim 90^\circ$ rotation of the unit cell between adjacent bright (perfect, almost single crystalline) and dark (imperfect) concentric zones (with [001] normal and parallel to the film plane, correspondingly), HREM of the spherulite centre (b), AFM (c), globular size histograms (d) for amorphous (gray) and crystal (black) film areas for AFM image of amorphous-crystalline (left-right) interface (e).

(Fig. 1b, 2c) and amorphous surrounding (Fig. 2d-e) including crystal growth front.

The macro relief of the crystal as a whole: usually Se spherulites (about 20–50 μm in diameter) have form of a hat, lying upside down with maximal deflection around 0.5–1 μm (as also reveled by microinterferometry), while Fe_2O_3 spherulites studied are almost flat.

The central region with 2 poles, separated by a distance about 3 μm (P_1, P_2, Fig. 1a) is studied for Se spherulite. Orientation [001] is almost normal to the film plane at the poles and is parallel to this plane in between where the crystal was nucleated (TEM data). It corresponds to AFM data: the poles are the lowest points of the crystal; an area including 2 poles has the form of a boat (width ~ 1.5 μm).

Micro relief of concentric zones for both spherulite types studied is similar in general (radial and tangential regularities revealed) but differs in details. Concentric zones of different orientations and imperfection revealed by TEM (Figs. 1a, 2a) are also seen in AFM, based on the variations in mean height (for Se, Fig. 1b, inset) and on the character of fibrous structure (especially distinct for Fe_2O_3, Fig. 2c). The last radial structure differs for two types of spherulites being more fine for Se. Both spherulites have radially elongated nodes and hollows of different character revealed by AFM on the scale below 1 μm, which needs further combined TEM-AFM studies.

AFM demonstrates the single feature for amorphous surrounding - globular (nodular) surface structure (globules of several dozens nm in diameter) which is inherited by crystallized area, Fig. 2(d-e). At the same time any facts of its influence on crystalline microstructure have not been found. HREM demonstrates (along with atomic resolution) additional contrast variations which can be considered as indications of some smaller nodes, sized several nm in plane, Fig. 2(b). HREM seems unsuitable for observations larger globules (nodes) in the crystals with varying lattice orientations.

AFM phase imaging mode made possible to visualize the cuneiform front of the Se spherulite.

Finally, probably most important observation for the amorphous-crystalline interface made for crystallization of αFe_2O_3 phase: there are strong variations in crystal height, probably associated with variations of lattice orientations, which should be taken into account for advanced models of crystal growth in amorphous films. Anyway it is evident, that simple concept: flat crystal growing along the inside of amorphous film, powered primarily by tensile stresses (caused by the density changes) in parallel with various imperfections at the crystal growth front, is inadequate.

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