Combined AFM-TEM studies of amorphous-crystalline transformation and interface in thin films of Se and Fe$_2$O$_3$

V Yu Kolosov$^1$, C L Schwamm$^1$, R V Gainutdinov$^2$, A L Tolstikhina$^2$

$^1$ Physics Dept., Ural State Economic University, 8 Marta Str. 62, 620219 Ekaterinburg, Russia
$^2$ Institute of Crystallography RAS, Leninskii prospekt 59, 119333 Moscow, Russia

E-mail: VladKol@usue.ru

Abstract. Thin amorphous films of selenium and iron oxide were crystallized by local electron beam annealing. Two types of spherulite-like 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.

1. 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” spherulite-like crystals having both two kinds of misorientations, attained as result of nucleation and growth. We use transmission electron microscopy (TEM), primarily bend contour [2] technique [3] with selected area electron diffraction, in situ studies and high resolution electron microscopy (HREM), combined with non-contact atomic force microscopy (AFM) and optical microinterferometry to study and correlate internal crystal microstructure and corresponding relief of its surface. Our approach is aimed on combined studies of isolated or selected micro crystal/grain/area by these two different techniques without destruction of a sample (thus making it available for the cycles of search of suitable crystals, estimates and further studies). It differs from other papers devoted to combination of TEM and AFM methods that anyway are all rather rare and unique [e.g., 4-7]. Two different kinds of spherulite-like crystals 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$_2$O$_3$, 20-30 nm thick). Free-standing films (separated from the substrate in distilled water and placed on TEM grids) were irradiated by more or less focused electron beam inside the column of electron microscope to initiate the crystal growth in a chosen area.

2. Experimental
Complicated regular change in lattice orientations are indicated by regular bend contour patterns on the TEM images, Fig. 1, 2. The main features were presented earlier for both Se spherulites [8, 9] and αFe$_2$O$_3$ [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 $\alpha$Fe$_2$O$_3$ 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 $\alpha$Fe$_2$O$_3$ spherulite and lower for its concentric imperfect zones.

**Figure 1.** Micrographs of Se spherulite in amorphous matrix: TEM indicating $60^\circ$ rotation of the unit cell between adjacent dark lines, roughly traces of $\{100\}$, AFM with concentric zones of different relief and crystal profile along O-O' (superimposed).

**Figure 2.** $\alpha$Fe$_2$O$_3$ spherulite in amorphous matrix: AFM with superimposed profile along O-O' (a), TEM with superimposed scheme of [001] axis orientation (made for central O-O' cross-section of thin-film crystal) (b), HREM of the crystal center with [001] zone-axis pattern.

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 spherulites (Fig. 1, 2) and amorphous surrounding (Fig. 2, 5) 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, Fig. 1, right (as also revealed by microinterferometry, fig. 3), while Fe$_2$O$_3$ spherulites studied are almost flat.

**Figure 3.** Group of Se crystals: AFM (a) and microinterferometry (b) images.

The central region with 2 poles, separated by a distance about 3 µm (P$_1$, P$_2$, Fig. 1) 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 1, 2) are also seen in AFM, based on the variations in mean height (for Se, Fig. 1) and on the character of fibrous structure (especially distinct for Fe$_2$O$_3$, Fig. 2). The 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 precise TEM-AFM studies.

Some fine relief perturbations of αFe$_2$O$_3$ crystals presented at the fig. 4 also require additional studies and interpretation: firstly the depression is usually observed in the crystal center where nucleation takes place (Fig. 4b), secondly there are specific regular surface “turbulent” disturbances that look like an “eye” (Fig. 4d).

**Figure 4.** Some interesting details of αFe$_2$O$_3$ crystal AFM image (a): central part with a depression in the centre (b), periphery (c) with an “eye” (d).

AFM demonstrates the single feature for amorphous surrounding - globular (nodular) surface structure (globules of several dozens nm in diameter). The similar globular surface structure is also observed for crystallized area which thus can be described as being inherited by crystallized area, Fig. 5 a, b. 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 (along with atomic resolution) which can be considered as indications of some smaller nodes, sized several nm in plane, Fig. 2. Anyway such HREM data are not sufficient to look for larger globules (nodes) revealed by AFM for the surface of these transrotational crystals.

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

![Graph](image.png)

**Figure 5.** AFM of amorphous-crystalline interface in Fe₂O₃ film (a), globular size histograms for amorphous and crystalline film areas (b).

Finally, probably most important observation for the amorphous-crystalline interface made for crystallization of αFe₂O₃ phase: there are strong variations in crystal height (Fig. 5, a), probably associated with regular variations of lattice orientations observed, which should be taken into account for advanced models of crystal growth in amorphous films. Anyway it is evident, that simple concept: crystal are growing along the inside of flat amorphous film, powered primarily by tensile stresses (caused by the density changes), is inadequate.

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