STRUCTURE OF ZnO THIN FILMS DOPED WITH RARE EARTH COMPOUNDS

V. Koleshko, A. Gulay, A. Shevchenok, T. Kuznetsova, V. Gulay Belarusian National Technical University, Minsk, Belarus

Zinc oxide thin films doped with rare earth compounds (rare earth oxides and fluorides) up to the 1–4 mass % concentration were produced by the ion-beam sputtering of the ceramic targets of the stoichiometric composition. The thin film surface morphology of the nanometer scale thickness was studied by the atomic force microscopy (AFM) with the use of the NT-206 microscope (Microtestmashiny Co., Belarus) equipped with MicroMasch Co. (Russia) standard silicon probes. The probe edge radius is 10 μ m, the vertical resolution is 0.2 nm, and the horizontal resolution is 2 nm.

For the ZnO-YF₃ (1mass %) thin films deposited for 6–10 min, the surface roughness is 0.1 - 0.5 nm in the field of $1.5 \times 1.5 \mu$ m. The AFM surface relief image made in the topographical mode contains noise interference in the form of parallel horizontal breakups and bands placed diagonally at regular intervals as seen in Fig. 1. Distinguished grain boundaries are not observed at that because the grain structure has no time to be formed at this stage of the thin film growth. Dark rounded islands consisted of 20 nm sized clusters against a light background substrate can be revealed in the image made in the "Torsion" mode.





An increase of the deposition time to 60 min results in the formation of a thin polycrystalline film with the obvious grain structure. The film surface roughness is 1.3 nm in the field of $1.3 \times 1.3 \,\mu$ m as shown in Fig. 2. A two-phase structure is revealed in the tapping mode, i.e. dark rounded grains 20 nm in diameter and light grains about 50 nm in diameter are observed. Light grain boundaries are clearly defined, grains are round shaped. Dark grains are located, at a rule, in the triple nodes of the light grain boundaries, i.e. in the cavities. Their quantitative content, area distribution and contrast against the rest of surface allow us to assume in the grain yttrium containing phase.



Figure 2 – The AFM surface image of the thin film deposited for 60 min at right angles:
(a) 2D image made in the tapping mode, scan field is 1.6×1.6 µm;
(b) 3D image made in the topographical mode, scan field is 1.3×1.3 µm.

A thin film crystallite development degree depends on both the deposition time and the angle between the flow of material deposited and the substrate surface. So, the thin film surface roughness is nearly halved (from 1.3 nm to 0.6 nm in the $1.3 \times 1.3 \mu m$ field) if the deposition angle decreases from 90° to 30°. Grains of the light phase are observed in the image made in the "Torsion" mode as shown in Fig. 3. The grain length is twice as much as the grain width. In the image made in the topographical mode grain boundaries have no clear outline.



Figure 3 – The AFM surface image of the thin film deposited for 60 min in the tapping mode: (a) at right deposition angles, scan field is $0.5 \times 0.5 \ \mu m$; (b) the deposition angle is 30°, scan field is $1.2 \times 1.2 \ \mu m$.

The film texture can be revealed when the texture axis is placed diagonally against the AFM scan direction as shown in Fig. 4. The grain elongation direction is defined by the sequential surface scanning in concurrent orthogonal directions. At the scanning along the texture direction, grain boundaries are reveals only in the topographical mode while at the scanning across the texture direction, grain boundaries are reveals in the AFM "Torsion" mode to be in agreement with the operation principle of lateral forces in this mode.



Figure 4 – The AFM surface image of the thin film deposited for 60 min at right angles:
(a) 3D image made in the topographical mode, scan field is 1.2×1.2 μm;
(b) 2D image made in the tapping mode, scan field is 0.8×0.8 μm, texture is placed at an angle of 45° to the scan direction.

Comparing a surface morphology of thin films obtained at different deposition times, the following can be noted. Rounded dark islands ("Torsion" mode) are observed in all films equal in nearly equal amounts to be nearly equal in size at that. Apparently, this is a containing rare-earth element phase which is the first to be crystallized on the substrate. But number of yttrium-containing islands distributed over the surface differs insignificantly for the 1 mass % and 4 mass % YF_3 concentration. Rare earth compounds may be assumed to serve as additional zinc oxide crystallization centers at the thin film formation.

The research into the structure of zinc oxide thin films is of a considerable interest for the fabrication of sensors of various physical parameters, specifically gas concentration sensors. Adsorption and diffusion rate is dependent on the grain size and grain boundary development in the thin film to define finally operation behavior of gas sensors based on zinc oxide thin films.