Thin Films and Coatings

MS.5.118
On the Huygens principle and crystallization of thin amorphous films according to “in situ” transmission electron microscopy data

A. Bagmut[1]

[1]National Technical University , Theoretic and Experimental Physics, Kharkov, Ukraine

agbagmut@mail.ru

On the basis of systematic electron diffraction and electron microscopy studies of species of crystallization of thin amorphous films on structural and morphological features, shared between the layered polymorphic crystallization [LPC], island polymorphic crystallization [IPC], dendrite polymorphic crystallization [DPC] and fluid-phase crystallization [FPC] [1,2]. This enabled to classify adequately a variety of crystallization processes in amorphous films.

The amorphous films were prepared by pulsed laser sputtering of rotating targets in vacuum and in oxygen atmosphere. Laser erosion plasma was deposited on the (001) surface of KCl crystals. Laser sputtering provided the formation of micro-babbles of sputtered substance in vapor-plasma flow, leading to the formation of micro-holes in the amorphous film. This allowed to analyze the spreading of crystallization line in the presence of barrier in the film. The films with thickness d ≈ 25-40 nm, transparent for an electron beam, were investigated. The obtained films were separated from the substrates in distilled water and placed on the micro grids for the electron microscopic investigations. Crystallization was initiated by local radiating influence of an electron beam on an amorphous film in a column of electron microscope ore by annealing of film in a muffle furnace on air. The film structure was investigated by electron diffraction methods and transmission electron microscopy. An example of LPC of amorphous film of HfO_2 is shown in figure 1a. The movement of crystallization line g - g' (dotted line in figure 1a and 1b) at velocity $v_т$ took place during crystal growth. This line corresponded to the geometrical area of interaction of amorphous phase, crystalline phase, and external environment (air or vacuum). One can describe the movement of g - g′ line as propagation of light wave front in accordance with Huygens principle. Based on the Huygens principle, each point of crystallization line should be considered as formation centers of “flat’ secondary crystals formed by several unit cells of crystalline lattice. The secondary crystals grow in directions, having acute angles with external normal to the crystallization line. Such crystals also have similar orientation coincident with crystals orientation (identical streaking in figure 1b). Practical implementations of the Huygens principle to the periodic reactions taking place in the condensed matter, were proved by Leduc Stefan in [3]. The movement of the crystallization line g-g' in the direction $v_т$ is a multiple of the unit cell size of the crystallized substance, and can be considered as a periodic process. Geometrical construction based on the Huygens principle, allowed to explain the diffraction of light and enveloping of various obstacles during light wave propagation. Such geometrical similarity is adaptable to the LPC mechanism and allows to understand the penetration of crystallization line into the geometrical shadow area formed by an obstacle (barrier h in figure 1b). Figure 1c and 1d illustrate the experimental confirmation of this idea. The holes h and h' serves as an obstacle to crystallization front propagation in the Cr_2O_3 amorphous film. TEM images shown in figure 1c and 1d, illustrate the propagation of crystalline phase, bypassing the hole h. The Cr_2O_3 single-crystalline layer is formed in the same orientation (zone axis [001] Cr_2O_3) behind the obstacle h (upper left corner in figure 1d). Such experimental investigations demonstrated the applicability of the Huygens principle to describe LPC of the amorphous films. One of the reasons for the implementation of a certain type of crystallization is the nature of the binding forces between the atoms of the elements. If dominated the covalent bonds, often the mechanism of LPC takes place. Metallic bond initiates the mechanism of IPC. In the case of LPC, the term “coherent” crystallization can be applied to the crystallization of thin film, as the single-crystal layer is provided by the same orientation (i.e. the “coherence”) of secondary nucleation centers. At the same time the LPC is an analog to the layer growth of the film on the substrate from the vapor phase (growth accordance to Frank and van der Merwe mechanism). As the result of the phase transformation on the mechanism of LPC, a crystalline film forms, where the dimensions of flat grains in the tangential direction by orders of magnitude are greater than its thickness. Island polymorphic crystallization is not a “coherent” crystallization. It is the analog of island film growth on the substrate from the vapor phase (growth accordance to Volmer and Weber mechanism). As the result of the phase transformation finely dispersed polycrystalline film is formed.

1. A. Bagmut, Technical Physics Letters 38 (2012), p. 488.
2. A. Bagmut, Functional Materials 19 (2012), p. 370.
3. S. Leduc, Théorie physico-chimique de la vie et générations spontaneés, Paris (1910), 202 p.

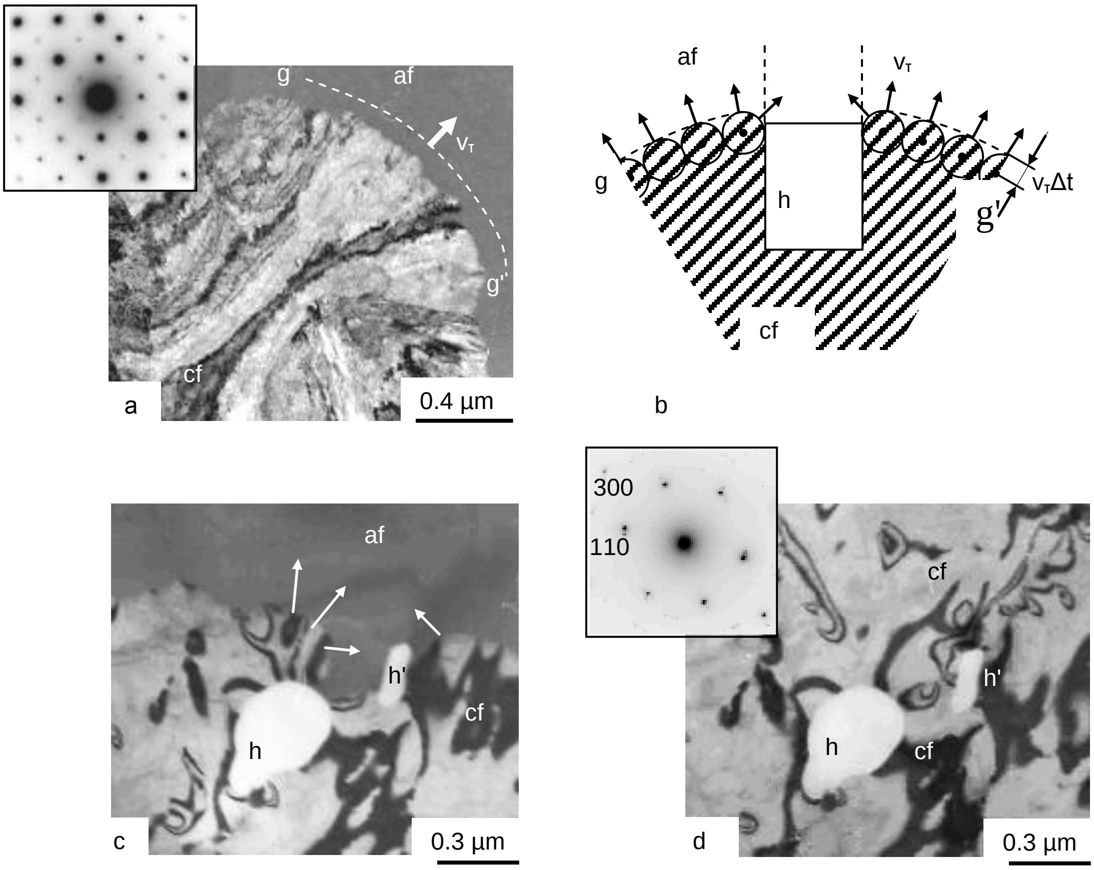

Figure 1. Layered polymorphic crystallization of amorphous films. a – crystallization of film of HfO_2 by annealing in a muffle furnace on air. b - the scheme of coherent crystallization, made by the analogy with the optical principle of Huygens. c, d - crystallization of amorphous film of Cr_2O_3 under the influence of the electron beam in vacuum. Crystallization line bypass the obstacles (holes h and h') by its moving. af - amorphous phase. cf - crystalline phase. The arrows indicate the direction of movement of the sections of the line of crystallization. In the upper left corner of the micrograph (a) and (d) the patterns of electron micro diffraction are shown (contrast is inverted).