Nucleation and Crystal Growth of Zn$_{0.3}$In$_{1.4}$Sn$_{0.3}$O$_3$ (ZITO-30) Thin Films Studied by in-situ TEM

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Amorphous transparent oxide materials have been widely applied in various technologies, including UV detectors, fully transparent displays, integrated on-glass electronics, flexible electronics, and energy-conversion devices and systems [1]. Amorphous Zn$_{0.3}$In$_{1.4}$Sn$_{0.3}$O$_3$, in which 30% of the indium in the In$_2$O$_3$ structure is replaced by co-substitution of zinc and tin, (a-ZITO-30) is one kind of the transparent oxide materials. The a-ZITO-30 thin films grown by Pulsed Laser Deposition (PLD) at different temperatures have different structures with short-range and medium-range ordering [2]. This underscores the need to unravel the nucleation and growth processes of a-ZITO-30 thin films and to understand the role of dopants in this process.

In order to monitor the microstructure evolution of a-ZITO-30 thin films, in situ heating experiments have been carried out inside a transmission electron microscope (TEM) to directly observe the crystal nucleation and growth process in real time [3]. The thin and amorphous films were heated at a constant temperature, causing the amorphous-to-crystalline transition (Figure 1), as seen with the appearance of bend contours. Such contours are typical contrast features for crystalline films under strain. Based on the Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory [4], the kinetic crystal growth behavior of a-ZITO-30 thin film was also investigated. The deviation from JMAK theory (Figure 2. (a)) indicates that ZITO-30 thin films heterogeneously nucleate on the surface. The Avrami exponent derived from JMAK equation (Figure 2. (b)), as well as the large grain size distribution (Figure 2. (c)) calculated at a film thickness of about 50nm, agree with those predicted by a 2-D crystal growth mode. Furthermore, we studied the interface velocity, characteristic time and characteristic length for the nucleation process. When the holding temperature was raised from 355°C to 365°C, the interface velocity was found to increase from 0.46nm/s to 2.3nm/s. This suggests that energy barriers exist in the crystal growth system. With level-set simulation and inverse Wulff construction, nucleation mechanism as well as the anisotropic behavior of the system would be investigated. Combined with theoretical simulation, this in-situ TEM microstructural study will provide valuable insight for the design and synthesis of complex amorphous oxide semiconductor thin films with superior and unique optical, electrical, and thermal properties [5].

References:

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Figure 1. Selected images showing the process of 2-D crystal growth with heterogeneous nucleation at a constant temperature of 365°C. The processing time is inserted.

Figure 2. Transformed volume fraction versus transformed time, (a) in the whole process, (b) in the first 1500 seconds with fitting equation inserted, Avrami exponent of 1.5 indicates 2-D crystal growth mode. (c) Grain size distribution of ZITO-30 thin films after annealing, showing microscale grain size.