Anisotropic Evaporation of ZnO Observed by In-situ Cs-Corrected High Resolution Transmission Electron Microscopy

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Group-III nitride and group-II oxide semiconductors have gained growing research interests owing to their direct bandgaps which span over energy ranges from ultraviolet to infrared. In particular, the wide bandgaps of AlN, GaN, and ZnO are potentially promising for the application to short-wavelength light emitting and high-power devices [1]. They usually possess hexagonal wurtzite (WZ) crystal structure and exhibit anisotropic properties in crystal growth, strain, thermal conductivity, etc., along the polar *c*-axis direction where the spontaneous polarization is induced. Particularly, zinc oxide (ZnO) nanoparticles and nanowires have been studied extensively for the application to diverse novel nanostructured devices [2]. It is well known that ZnO nanomaterials with the WZ crystal structure tend to grow preferentially along the polar *c*-axis orientation [3]. However, this anisotropic growth mechanism remains unclear due to difficulties in direct atomic-scale observations of dynamic processes. Understanding orientation-dependent growth (or evaporation) kinetics is essential to control growth morphology and sizes of ZnO nanomaterials.

To directly observe the atomic-scale dynamic evaporation processes of ZnO single crystals, here we design an in-situ high resolution transmission electron microscopy experiment at elevated temperatures in a Cs-corrected TEM (GRAND ARM 300 CF) and a high voltage electron microscope operated at 1.25 MV (ARM 1300S). FIB samples with clean and undamaged samples were prepared from a ZnO single crystal, and they were welded on DENSsolutions MEMS heating chip.

As the temperature increases to 150 °C, the edges of ZnO crystal show faceting along semi-polar {101} and polar (0001) planes. Above 300 °C, a fast evaporation process is dominant in the polar (0001) facet, accompanied by the formation of a liquid-like surface layer, while other non-polar {100} and semi-polar facets show ten times slower sublimation behaviour with dry and clean surfaces (**Fig.1: a - c**). The "liquid" layer forming at the polar surfaces tends to accelerate the transformation process (**Fig.1: d**), which is zinc-deficient as confirmed by EDS elemental mapping. The possible origin for the formation of the "liquid" layer is the higher surface energy of polar surfaces as predicted by the DFT calculations [4]. The anisotropic evaporation might be attributed to a lower desorption energy and resultant higher dissociation rate of zinc atoms compared to that of oxygen atoms. The observed thermodynamics behaviour gives new insights into understanding the anisotropic growth processes of ZnO nanostructures. An additional experiment using negative Cs imaging (NCSI) technique [5] shows this evaporation process at atomic scale with clearly resolving the zinc and oxygen columns in real time for the first time (**Fig. 2: a**). Dipole moments in unit cell can be measured unit cell by unit cell from the coordinates of Zn and O columns (**Fig. 2: c**). During evaporation, the lattice shows periodic distortion which is accompanied with the change of dipole moment (**Fig. 2: b**). It could be regarded as compensating the polar surface charge during the disappearance of top surface. Quantitative measurement of the dipole moments that change with time will be addressed in greater details.

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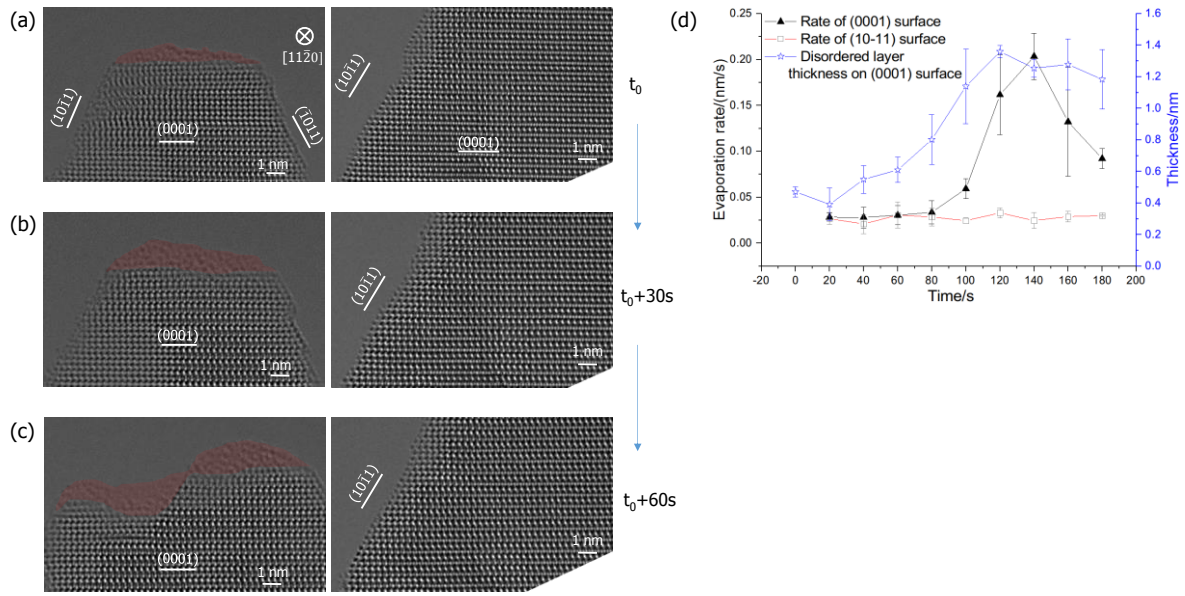

Fig. 1 Anisotropic evaporation of ZnO at 300℃: (a - c) (0001) surface forming an "liquid" surface layer on the top (highlighted by red). In contrast, the semi-polar {101} surface which remains dry exhibits a relatively slow and constant evaporation rate. (d) Plot of the evaporation rate as function of time. Comparing polar (0001) surface with semi-polar surface, the evaporation rate is almost up to 10 times higher.

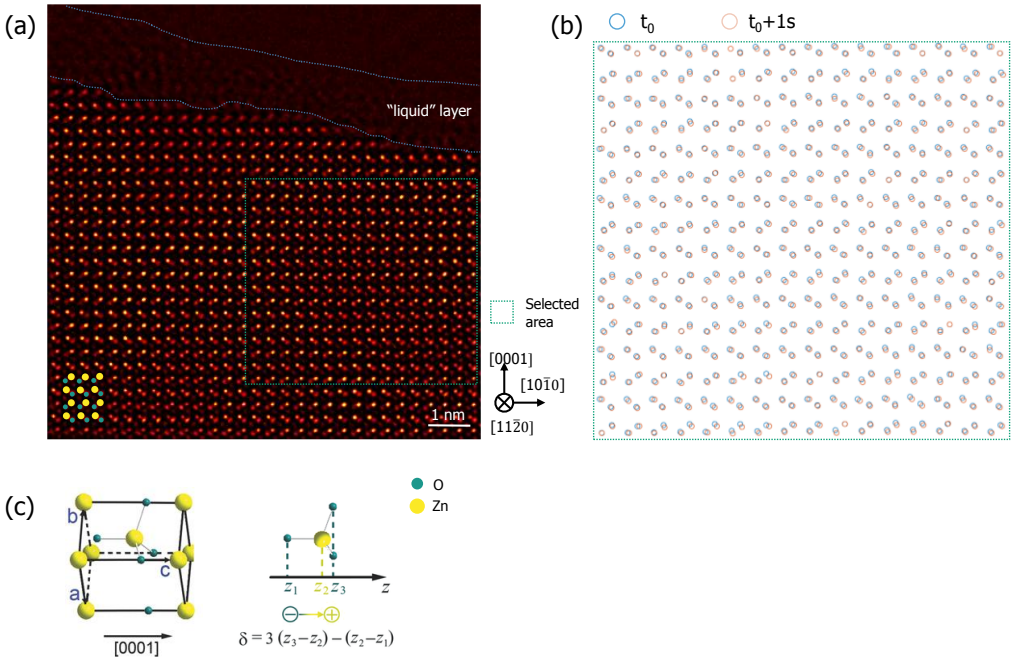

Fig. 2 (a) Snapshot of evaporation process of ZnO with NCSI technique showing the Zn and O columns. (b) Atom columns displacement within 1 second from selected area in (a). (c) Schematic of calculating dipole moment of wurtzite in projected view.