Self-Organized Solid-State Epitaxy of PZT Thin Films by Chemical Solution Deposition

The film–substrate interface is critical for crystal growth via solid-state epitaxy. We have elucidated the local structure and crystallization mechanism of amorphous phase $PbZr_xTi_{1-x}O_3$ (x = 0.3) thin films deposited onto $SrTiO_3$ (001) single-crystal substrates by chemical solution deposition. The amorphous phase involves a short-range order of $(Ti/Zr)O_6$ octahedra and Pb-O. The first unit cells of the film have already crystallized with a cube-on-cube epitaxial relationship with the substrate.

Chemical solution deposition (CSD) is a thin film growth technique with several advantages over gas-phase processes, such as excellent composition transferability from mixed raw materials to thin films, simple facilities, and low cost. We have studied metal-organic deposition as the simplest CSD. This process involves the following steps: metal-organic precursors with long-chain organic ligands were dissolved in an organic solution, and coated by spraying, dipping, or spin coating. These were then dried to remove solvents, decomposed into an amorphous oxide thin film as a precursor, and heated to crystallize. In this CSD process, it is important to establish the structure and bonding states of amorphous oxide thin films, and the interface structure between the film and substrate, immediately after decomposition. However, the initial stage of the crystal growth mechanism using chemical solvents has not been elucidated because crystal growth cannot be monitored in real time.

Figure 1 shows the (a) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and (b) annular bright field STEM (ABF-STEM) images of the amorphous PbZrxTi1-xO3 (PZT) thin film after pyrolysis at 350 °C, which is considerably lower than the crystallization temperature of 650 °C [1]. The first Pb-O layer of PZT crystallized coherently, while the second Pb-O layer showed a weaker contrast.

These results correspond to a situation in which the first Pb-O layer widely covers the $SrTiO_3$ surface, while the second layer covers it locally, and the interplane distance increased. Figure 1(b) shows the incorporation of atoms in the second Pb-O layer.

Figure 2(a) shows the Ti-L_3 electron energy loss near-edge structures (ELNES) of the amorphous phase, interface layer, tetragonal phase, and rhombohedral phase of PZT thin films [1]. The pyrolyzed films show ligand field splitting under O_h local symmetry, that is, the TiO_6 octahedron coordination structure already exists in the pyrolyzed

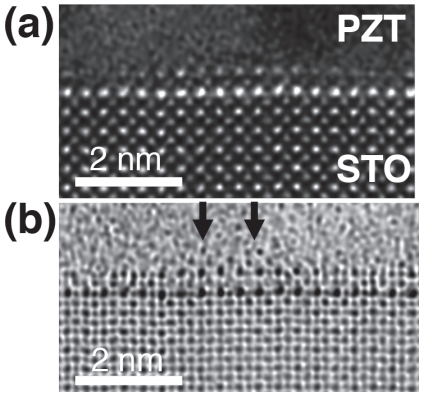

Fig. 1 (a) HAADF- and (b) ABF-STEM images of the amorphous PZT thin film. Arrows point out just incorporating atoms on the second Pb-O layer.

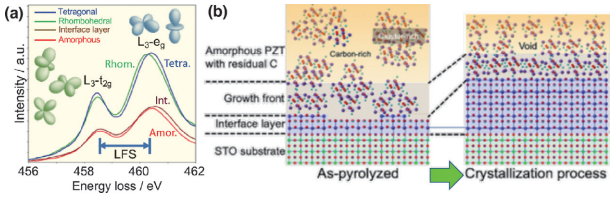

Fig. 2 (a) Ti-L_3 ELNES of amorphous phase, interface layer, tetragonal phase, and rhombohedral phase of PZT thin films. (b) Schematic model of the crystallization process of the amorphous PZT thin film.

PZT thin film, which is apparently an amorphous phase, as shown in Fig. 1. These results indicate that the amorphous PZT thin film has a short-range order and was incorporated into the crystalline films via interface layers as self-organized nucleation sites (Fig.2(b)).

The present study demonstrates that the interface layer and short-range order in amorphous films are among the essential factors governing the solid-state epitaxy of oxides by CSD.

References

[1] T. Kiguchi, T. Shimizu, T. Shiraishi, and T. J. Konno, J. Ceram. Soc. Jpn. **128**, 501 (2020).

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