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XAFS study of crystallization process of PLD-deposited $SrZrO_3$ thin films

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Introduction

Room-temperature PLD and post-annealing process (RT-PLD) for oxide thin film fabrication is studied. In this process, as-deposited thin films are amorphous and are epitaxially crystallized by post-annealing in air. It has to be noted that epitaxial crystallization in the post-annealing process is very rapid and the epitaxial crystallization temperature of $SrZrO_3$ in this process is 540 C, which is significantly lower than that of the high temperature PLD (HT-PLD). Furthermore, it is found that the epitaxial $SrZrO_3$ thin films on MgO(001) substrates fabricated by the RT-PLD have different structural properties from those by the conventional PLD (HT-PLD): lattice strain is different and columnar structure is not very obvious compared to HT-PLD.

In this work, XAFS spectra of the $SrZrO_3$(SZO) thin films are analyzed to investigate the change in the local structure in post-annealing.

Experimental

Fluorescence EXAFS spectra of the Sr and Zr K-edges have been obtained by a Lytle type ionization chamber at PF 9C and PF-AR NW10A. The thin film specimens on single crystalline substrates were rotated during the measurements and the substrate was fixed at a certain angle to exclude diffractions of the MgO substrate. In order to investigate the influence of substrate, SZO thin films fabricated on fused silica wafers have also been studied. EXAFS data have been analyzed by REX2000 combined with FEFF 8.

Results and discussion

In-situ XRD measurements of the post-annealing process of $SrZrO_3$ thin films on fused silica substrates have revealed that the crystallization occurs at about 500 degree C and the rearrangement of the cations is very slow to form crystalline grains. It is interesting that the crystallization temperature is comparable to that on the single crystalline substrate. The *in-situ* measurements have revealed that secondary phase is grown above 620 degree C. The secondary phase is identified as ZrO_2 nanocrystals around the $SrZrO_3$ grains, which have been observed by high-resolution electron microscopy.

In our former XAFS studies, it has been found that configuration (CN, bond length) of the oxygen atoms around Sr in as-deposited thin film is clearly different from that in post-annealed SZO thin films of RT-PLD process, while almost no difference is found around Zr.

The radial structure functions obtained from Zr and Sr EXAFS spectra clearly shows the as-deposited thin films have no long range order but the coordination numbers of the cations are found to be comparable to those of crystalline specimens. Zr-O inter-atomic distances obtained by one shell fitting of the first peak are not very different among all specimens. On the other hand, Sr-O inter-atomic distance is different from each other. For the crystalline specimens, three-shell fittings (N=4, 4, 4) give the best fitting results (Fig. (a)), while the best fitting results have been obtained by one-shell fitting (N=12) in as-deposited thin film. For comparison, an amorphous thin film, which is post-annealed at 450C for 10 hours, has also been investigated. For this specimen, the best fitting result is obtained by two-shell fitting (N=8 and 4) (Fig. (b)). These results suggest that the coordination of oxygen ions bound to a Sr cation changes slightly below crystallization temperature to make the ZrO_6 octahedron tilt to form orthorhombic $SrZrO_3$ structure.

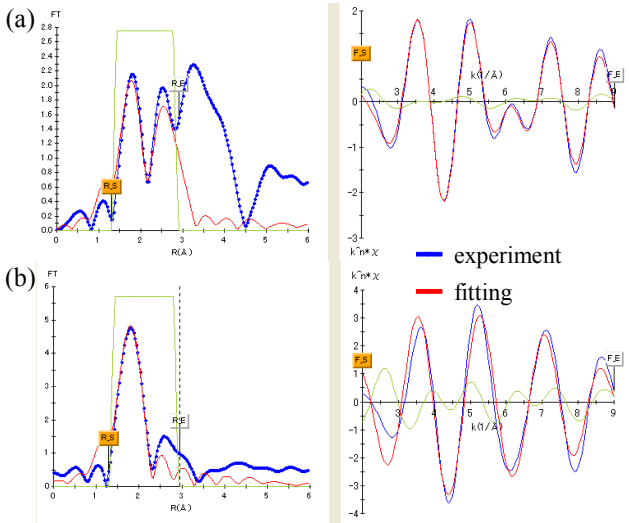

Figure: Curve fitting results of the radial structure function and the $k^3\chi$ spectra for Sr-O bond (R= 1.289-2.945 Å) at the Sr K edge of HT-PLD SZY thin film(a) and RT-PLD SZO thin film post-annealed at 450C(b).

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