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Crystallization of amorphous BST thin films grown on MgO(100) by R.F Magnetron Sputtering : An *in-situ* Synchrotron X-ray Scattering Study

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I. INTRODUCTION

$(Ba_xSr_{1-x})TiO_3$ (BST) has been heavily studied for applications in giga-bit level dynamic random access memories (DRAM). In applications for microelectronic devices, thin BST crystalline films are desirable. Recently many growth techniques, such as R.F. magnetron sputtering, laser ablation, chemical vapor deposition, and sol-gel method, are developed to obtain BST films of high dielectric constant that have better contact with metal electrodes. Crystalline BST films are usually obtained only at high substrate temperatures. The inter-layer formed at the interface and rather rough surface morphology resulting from the high growth temperature have serious effects on the dielectric constant and leakage current. An alternative approach is to grow crysralline BST films by so called solid phase epitaxy, that is, to growth amorphous BST films at room temperature, and to make crystalline film by post-annealing process. The purpose of this study is to understand the crystallization process of an amorphous BST thin film by an *in-situ* annealing experiments using Synchrotron X-ray Scattering.

II. EXPERIMENTAL SET UP

The BST thin films were grown in amorphous form on single MgO(100) substrates by R.F. magnetron sputtering technique at room temperature. The Films were prepared for various thickness, 350Å, 650Å and 6500Å. The film composition was estimated to be about $(Ba_{0.5}Sr_{0.5})TiO_3$ from the X-ray diffraction profile of the target material. The composition of a thin film is usually very close to the target in R.F. sputtering methods. The *in-situ* synchrotron x-ray experiments were carried out at beamline 3C2 at Pohang Light Source (PLS). The incident x-rays were focused by a toroidal mirror, and monochromatized by a double bounce Si(111) crystals. A series of x-ray scattering profiles were measured during real time annealing of the amorphous films.

III. RESULTS AND DISCUSSION

Figure1 shows the reflectivity curves, and the powder scattering profiles of BST thin films measured at each temperature. The crystallization of the BST films was clearly demonstrated on each sample. The details, however, were quite different from sample to sample. For all the samples, a peak from an intermediate phase, which we believe to be a metastable pyrochlore-like phase, was generated close to the MgO(002) peak at ~600℃. It disappeared at higher temperature as the sample transform to the crystalline perovskite phase. We suspect that the metastable pyrochlore-like phase was nucleated near the interface region, since the x-ray reflectivity curve indicates that the interface became rather rough as the intermediate phase occurred.

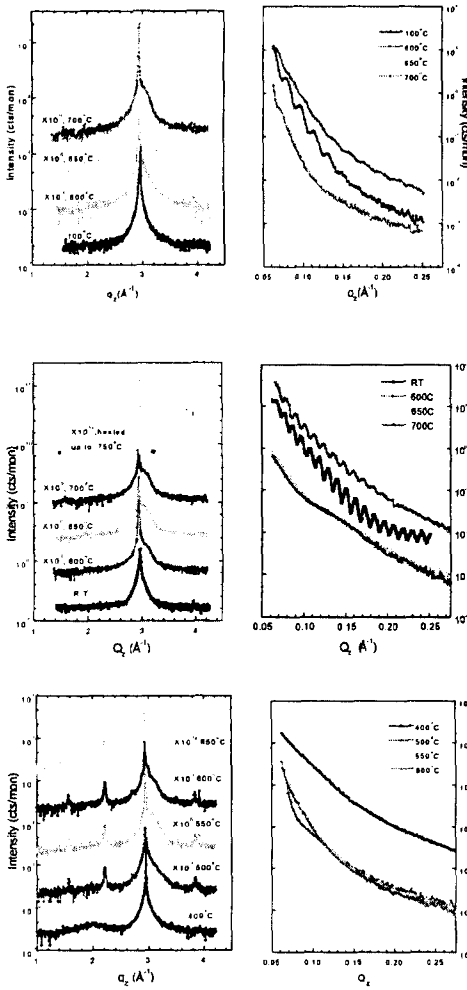
In 650Å thick film, the crystal peak appeared at 750℃ with the <100> preferred orientation, which was proved by the BST (001) crystal peak. However in 6500Å thick film, all allowed BST crystal peaks appeared at 500℃. It was clear that the 6500Å thick film was powder crystals with random orientation. This was rather different from the crystallization of PZT in which the crystals were nucleated from the interface, and became single crystalline. We believe that BST crystals were nucleated in the bulk of the film away from the interface.

Figure 2 shows that the crystallization temeperature decreased monotonically with increasing the film thickness, while the intermediate phase were nucleated roughly at the same temperature. To explain this, we assume that the films were composed of two regions. One is a near interface region, the other one is a near surface region. This model is shown in Fig.3. In the near interface region, the substrate field is dominant and less sensitive to the film thickness. But in the near surface region, the effect of the substrate filed is dependent on the film thickness. Using this model, we might explain the above results. A pyrochlore-like phase was nucleated near the interface region, thus it was strongly influenced by the substrate field, and generated at nearly same temperature for all the samples. The crystal nucleation was occurred away from the interface, therefore the nucleation temperature and the alignment of the crystalline axis depended on the film thickness. For the thin film, the substrate filed was still important in the near surface region, while in the case of thick film it was not. This is the reason why the crystallization temperature and the orientation depended on the film thickness.

Finally, we compared the *in-situ* results with the results obtained in a rapid thermal annealing(RTA) process performed at 800℃ in a furnace for 650Å and 6500Å thick films. The peak shape was almost the same. Therefore we believe that RTA process follows the similar trace as the *in-situ* result.

IV. CONCLUSION

In summary, we have studied the crystallization process of amorphous BST thin films by synchrotron x-ray scattering measurements. The pyrochlore-like phase generated in the near interface region, thus the peak was relatively insensitive to the film thickness. The crystal was nucleated in the near surface region therefore the orientation and nucleation temperature were dependent on the film thickness. Specially, when the film thickness is less than 1000Å, the substrate field affected the orientation of nucleation. Thus preferred orientation was appeared.



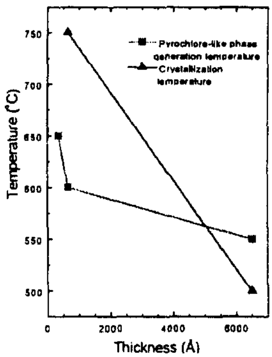


Figure 2. Crystallization and pyrochlore-like phase generation temperature as a function of the film thickness.

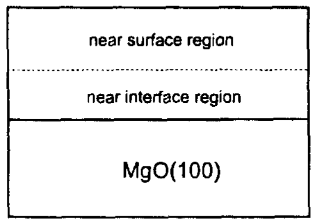


Figure 3. Proposed film model composed of two regions.

Figure 1. The powder scattering profiles and reflectivity curves of (a) 350Å, (b) 650Å, and (c) 6500Å thick film.