

光電子分光と X 線吸収分光によるペロブスカイト型 Ti 酸化物薄膜の 強誘電性の安定性の研究

Investigation of Ferroelectric Stability of Perovskite Ti-oxide Thin Films by PES and XAS

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Ferroelectric thin films are promising for miniaturization of integrated microelectronic devices. However, there exist the suppression of ferroelectricity in perovskite oxides thin films, and understanding size effects and polarization instability in thin-film ferroelectrics is of fundamental importance and crucial in their future applications. Here, we fabricate high-orientated epitaxial $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin films on Nb-doped SrTiO_3 (100) substrates by the pulsed laser deposition, and report the resonant photoemission spectroscopy spectra in the valence band region as a function of film thickness at RT and 12K. Our results demonstrate that 2nm $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin film is still ferroelectric, but ferroelectricity vanishes in 1.2 nm thin film, which open a new route to explore the fundamental limits of the ferroelectric materials.

強誘電性を示す薄膜は、集積マイクロエレクトロニクスデバイスの小型化にとって、有望な物質である。しかし、ペロブスカイト型の酸化物薄膜では強誘電性が抑制されてしまう。そのため、強誘電体薄膜におけるサイズ効果や分極の不安定性を理解することは、その将来の応用にとって非常に重要である。ここで我々は、パルスレーザー堆積法により Nb をドープした SrTiO_3 (100) 上に $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ の高配向エピタキシャル薄膜を作製し、薄膜の厚さを関数として室温と 12 K で測定した価電子帯の共鳴光電子分光の結果を報告する。我々の結果は 2nm の厚さの $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ 薄膜はまだ強誘電性を示すが、1.2nm の厚さの薄膜では強誘電性が消えていることを示している。この結果は、強誘電物質の臨界サイズの探求への新たな道筋を開くものである。

Ferroelectric compounds with the perovskite ABO_3 structure, especially in thin film form, have attracted considerable attention due to their promising potential applications as materials in ferroelectric random-access memories and metal-oxide semiconductor field-effect transistors.^{1,2} In these applications, a crucial challenge is how small the ferroelectric material can maintain a stable switchable remnant polarization. As previously reported by experimental investigations and theoretical calculations, a degradation of ferroelectric properties was observed with decreasing the film thickness or particle size.^{3,4} It is generally believed that there exists a critical size on the order of several tens to hundreds of angstroms depending on materials below which a spontaneous electric polarization will disappear. Such behavior will make ferroelectrics useless below this size for applications, therefore, it should be essential to find a reasonable fundamental understanding of what happens at this shutoff. In many experimental investigations of ferroelectric thin films and small particles, a degradation of the ferroelectric properties was observed. Tybell and co-workers showed that a stable polarization still exist in $Pb(Zr_xTi_{1-x})O_3$ film with thickness of 40 Å or less.⁵ First principles calculations indicated that $BaTiO_3$ thin films between two metallic $SrRuO_3$ electrodes lose their ferroelectric properties below a critical thickness of 2.4 nm.⁶ However, it's very difficult to find the accurate critical thickness by conventional electric measurements due to a large leakage current. In this work, we have employed resonant photoemission spectroscopy (RPES) to address issue.

We fabricated highly-orientated epitaxial $Ba_{0.5}Sr_{0.5}TiO_3$ thin films with various

thicknesses on Nb-doped $SrTiO_3$ (100) substrates by the pulsed laser deposition, and report the RPES spectra in the valence-band region as a function of film thickness at RT and 12K. Nb-doping was used to avoid charging effects in the RPES measurements. As shown in Fig. 1, XRD peaks were observed only from BSTO (00 l) and STO ($h00$), which indicates that BSTO film are strongly oriented in the (00 l) planes.

Figure 2 shows the Ti $L_{2,3}$ near-edge XAS spectrum of 3 nm BSTO film.

Figure 3 shows typical RPES spectra of 3 nm BSTO film at $h\nu = 466$ eV. The results indicate that the valence-band spectra have two main features A (at bonding energies 4-5.5 eV) and B (6-9 eV), corresponding to the O 2 p nonbonding and O 2 p -Ti 3 d bonding states, respectively. Comparing the spectra of the ferroelectric phase (at 12 K) and the paraelectric phase (at 300K), there are marked differences in the intensities of the features A and B, indicating a change in the

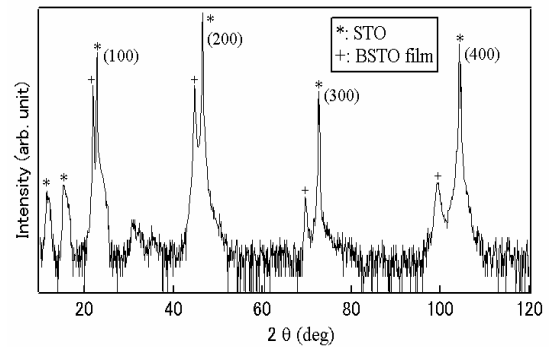


Fig.1 XRD patterns of 200nm BSTO film

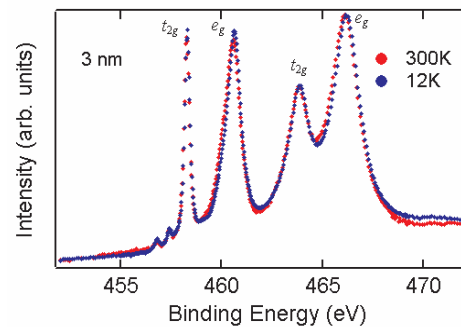


Fig.2 XAS spectra of 3 nm BSTO film taken at room temperature and 12 K.

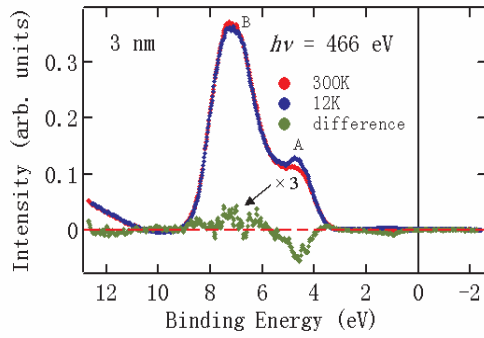


Fig.3 RPES spectra in the valence band region of 3 nm BSTO film at RT and 12K

Strontium Titanate thin film and its photoemission spectra. 2005, in preparation.

Ti $3d$ -O $2p$ hybridization before and after the phase transition.

We also measured the RPES spectra in the valence-band region of other three BSTO film samples with thicknesses of 200nm, 2nm and 1.2nm at 466 eV. Our results demonstrate that 2nm $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin film is still ferroelectric, but ferroelectricity vanishes in the 1.2 nm film. The present method opens a new route to explore the fundamental limits of the ferroelectric materials

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Papers and patents

1. Ferroelectric Stability of Ultrathin Barium Strontium Titanate Film by in Situ Resonant Photoemission Spectra. 2005, in preparation.
2. Preparation of highly-oriented Barium