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Heteroepitaxial growth and characterization of (001)$Ba_xSr_{1-x}TiO_3$/(001)$YBa_2Cu_3O_y$ ferroelectric thin films on (100)MgO substrate

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Highly polarizable $Ba_xSr_{1-x}TiO_3$ (x=0~1) thin films have been grown heteroepitaxially by the ArF excimer laser ablation method. They were characterized by XRD, RHEED, FTIR, *C-V* and UV spectroscopic measurements, and x-dependent properties were studied systematically.

1. INTRODUCTION

$SrTiO_3$ (STO) and $BaTiO_3$ (BTO) are the perovskite ferroelectristics well studied so far. Particularly, STO is the incipient ferroelectristic, which exhibits nonhysteretic P-E curve even at low temperatures. Owing to those characteristic features, they are expected to be the most promising materials for use to the micro-size thin film capacitor in the next generation Si-ULSIs[1]. In addition, they are potential candidates as the gate insulator capable of inducing a number of sheet carriers by at least a couple of decades higher than the conventional SiO_2. Namely, they can bring about a field-effect-modulation in the order of $10^{14}/cm^2$. Actually, STO has been employed as a gate insulator of the oxide superconductor field effect transistors (Al/STO/YBCO MISFETs)[2].

The dielectricity of ferroelectric, however, reveals strong temperature dependency. For instance, the dielectric constant ε *vs* T curve has a steep hump and, at a specific temperature "T_{peak}", the dielectric constant ε has its maximum value. The "T_{peak}" is called a Curie temperature of ferroelectristics expect for STO, and its value differs from material to material: T_{peak} of STO is ~30K and BTO has T_{peak} of ~500K[3]. However, these specific temperatures T_{peak} do not always meet the condition device requests. In the case of YBCO MISFET, despite of the optimum temperature 30K for STO gate insulator, the device is designed for use at the liquid nitrogen temperature 77K, being significantly disparate temperature. Because of this mismatching, the actual application could not bring its ability to the full.

To remove this obstacle, we have investigated the quaternary $Ba_xSr_{1-x}TiO_3$ (BSTO) thin films. This solid-solution system is substantially beneficial for adjustment of its high dielectricity at arbitrary temperatures only by setting the molar ratio "x". In the present work, an attempt has been done in preparing the epitaxial BSTO films by the ArF excimer laser deposition method and systematically characterizing them.

2.EXPERIMENTAL

The laser ablation targets BSTO were prepared from starting materials of $SrCO_3$, TiO_2 and $BaCO_3$. They were mixed by wet-milling and fired at 1000°C for 6 hours, and this process was repeated 3 times. The targets were classified into two groups: One is stoichiometric ($Ti/(Ba_x+Sr_{1-x})=1$) and the other is nonstoichiometric ($Ti/(Ba_x+Sr_{1-x})=1.1$). The powder thus prepared were pressed in a metal bin and installed in the deposition chamber. The BSTO deposition was carried out at 660°C in O_2 atmosphere of 40Pa. The laser pulse duration, rate and energy were 10ns, 10Hz and $1.4J/cm^2$, respectively. Grown BSTO films were 200nm thick.

Three types of BSTO films were prepared, depending on the underlying layer condition. They were i) (101)BSTO/(111)Pt/(100)MgO, ii) (001)BSTO/(001)YBCO/(100)MgO, and iii) (101) BSTO/(100)MgO. The nonstoichiometric targets were used for the type iii) films, whose composition was previously known to be closer to the stoichiometric one[4]. For types of i) and iii), we tentatively labeled as (101)BSTO, but it is not certain if the film orients to (101) or (110) directions. The films iii) were used for transmittance measurements from which the optical energy gap was deduced. On top of films i) and ii), we deposited Cr counter electrodes ($\sim 7.5\times10^{-4}mm^2$) and *C-V* measurements (at 1MHz) were done on these MIM' capacitors.

3. RESULTS AND DISCUSSION

An example of the observed RHEED (25 keV) pattern is given in Fig.1, showing a net pattern from (100)BSTO. This figure indicates epitaxial growth owing to good lattice matching between (100)BSTO and (001)YBCO.

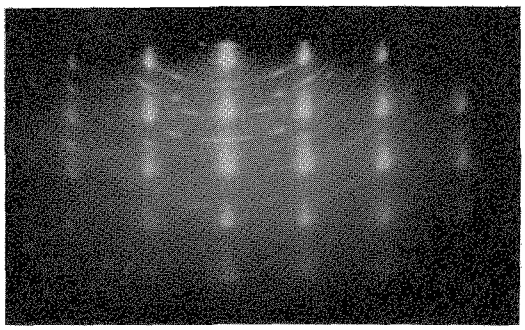

Figure 1. RHEED pattern of BSTO/YBCO/MgO multilayer. An acceleration energy was 25keV.

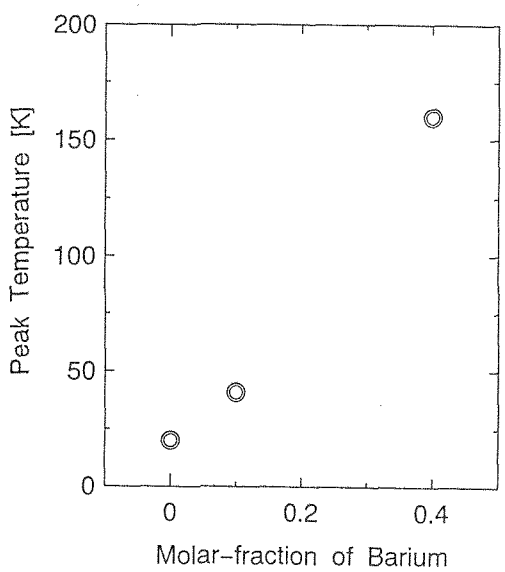

Figure 2. Temperature, Tpeak, of BSTO films *vs* Ba content

The temperature for the peak static dielectric constant ε of BSTO was obtained from *C-V* measurement. Measurements were done with temperatures T_M varied from 300 K to 4.2 K. The peak temperatures are plotted in Fig.2 as a function of molar-fraction of Ba. As seen in this figure, the peak temperature rises up with the addition of Ba. This characteristic is very close to that reported from the ceramic bulk[5].

The FTIR absorption spectra of BSTO thin films are shown in Fig.3. Measurements were carried out in the reflection mode. Absorption peaks are clearly seen in all spectra. These peaks are due to resonance with the longitudinal optic (LO) phonon modes. With the addition of Ba, the absorption peak shifted very clearly to lower wavenumber and became broader. The reason for the former may be due to the change of the atomic weight. Ba (137.3) is heavier than Sr (87.62). In that case, the more Ba content, the heavier the mass of BSTO. As a result, lattice oscillation becomes slower and resonant wavenumber decreases.

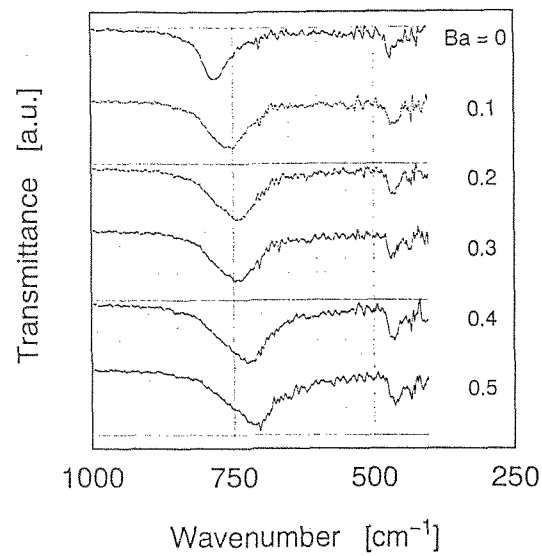

Figure 3. FTIR absorption spectra from BSTO thin films. Measurements were made in the reflection mode.

The optical band-gap energy of BSTO thin films at absorptivity α=10000cm^{-1} is plotted in Fig.4 as a function of the molar fraction of Ba. This figure suggests that the optical band-gap energy higher than 3eV (for $x \leq 0.4$) can

allow us to use these films as a MIS gate insulators.

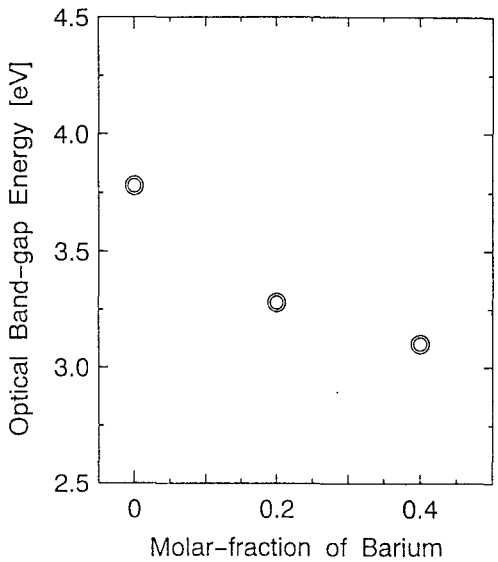

Figure 4. Optical band-gap of BSTO thin films. They were obtained at absorptivity α = 10000cm^{-1}.

The lattice constants deduced from XRD patterns of targets and grown films are plotted in Fig.5 against the Ba content. Particular interests in this figure are twofold: One is the film lattice parameter which roughly obeys Vegard's law and the other is rather complicated crystallinity of the target materials. As to the latter we refer to the supplemental data of Fig. 6 which discloses the coexistence of dominant STO and BTO together with the several intermediate BSTOs as minor phases. Namely, the significant phase-separation develops on the target powder sintered at as high as 1000°C. Those facts seem to partly account the broadening of FTIR peaks with increasing Ba content as shown in Fig.3. Although XRD peak from BSTO film is single-hump, the BSTO solid-solution might be likely to phase-separate even at the growth temperature 660°C. The FTIR peak broadening might be a sign of instability of BSTO quaternary system.

By the way, BTO crystal, differed from the cubic STO, has the tetragonal structure at room temperature. In consequence, their solid-solution BSTO is thought to change its crystal structure depending on the composition. According to the

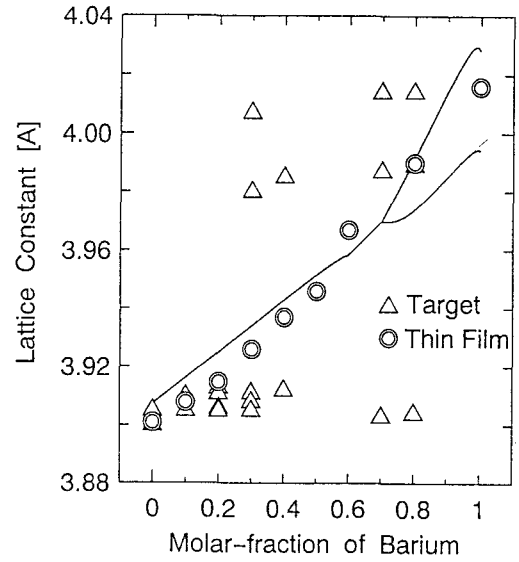

Figure 5. Lattice constants of the BSTO targets and the BSTO thin films.

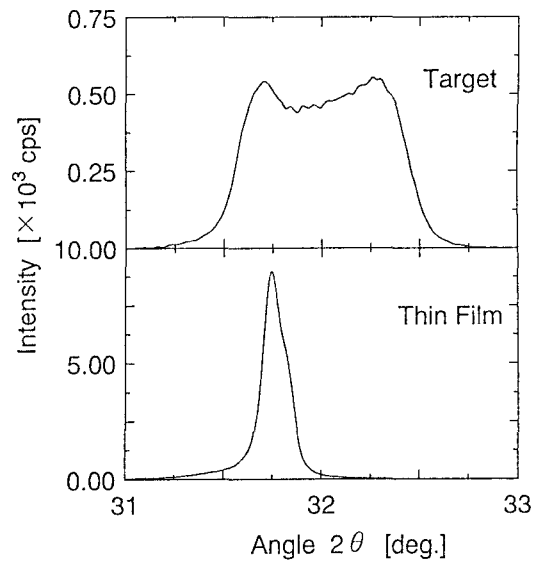

Figure 6. XRD patterns of $Ba_{0.5}Sr_{0.5}TiO_3$.

ceramic data [6], the tetragonal phase develops for x>0.7 as shown by solid curves in Fig.5. Unfortunately, however, we could not

discriminate the XRD patterns of grown films with x values below and above 0.7. This is because our specimens were (101)BSTO epitaxial films and we did measurements by θ-2θ mode which can not reflect the inplane lattice parameter. In the present case, all that we obtained is the mean value of a- and c-axes parameters, which just locates between a- and c-axes parameters of ceramic sample in Fig.5.

4. CONCLUSIONS

BSTO quaternary epitaxially films were grown by the ArF excimer laser ablation method and characterized from crystallographic, dielectric and optical point of view. Success was obtained in controlling the temperature of peak ε value, but degradation of crystallinity developed in the quaternary systems. Lower temperature growth and/or superlattice structure may be the solution for the remaining problem.

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