Anomalous dielectric and optical properties in perovskite-type artificial superlattices

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Abstract

Perovskite-type BaTiO$_3$/SrTiO$_3$ (BTO/STO) artificial superlattices were fabricated by molecular beam epitaxy process and their dielectric properties and refractive indices were measured. A large leakage current was observed in the films on Nb-doped STO substrate. Dielectric permittivity was therefore measured using planer interdigital electrodes. Fine planer electrodes were necessary to reduce the penetration of electric flux into the substrate. Interdigital electrodes were formed by electron-beam lithography. Dielectric permittivity of superlattices along the film surface was determined using electromagnetic field analysis. It was found that the dielectric permittivity of the BTO/STO superlattice with the period of 10 unit cells showed a maximum value above 30,000, which was almost independent from frequency up to 110 MHz. The refractive index of superlattices measured with a spectroscopic ellipsometer also showed the highest value when the period was 10 unit cells. This indicated that the structure of superlattices affected not only the ionic polarization but also the electric polarization. The origin of anomalous properties observed in superlattices may be interpreted by the strains induced into the film.

Keywords: Artificial superlattice; Perovskite compound; Dielectric property; Ellipsometry; Interdigital electrodes; Electromagnetic field analysis

1. Introduction

Artificial superlattices of oxide materials have been attracting the interests of material scientists because the superlattices have the potential to show unknown properties or to drastically improve material properties. Oxides with perovskite-type structure exhibit various properties, such as ferroelectricity, superconductivity and so on, therefore, the perovskite-type artificial superlattices seem to be one of the most interesting systems in the research of the oxide superlattices. Some research groups have succeeded in fabricating perovskite type artificial superlattices [1–5]. An anomaly of dielectric properties in BaTiO$_3$/SrTiO$_3$ (BTO/STO) superlattice was pointed out by Tabata et al. [3] and Nam et al. [4]. However, the dielectric properties of BTO/STO superlattices are still not very reliable because superlattices made in an ultra-high vacuum system usually show high-leakage currents. Optical properties of oxide superlattices are also attractive research topic. Ellipsometry is a powerful technique to determine the thickness and the refractive index of thin films. This technique has been applied to semiconductor superlattices. However, ellipsometric measurements of oxide superlattices have not been done so far. Ellipsometry of oxide superlattices is extremely difficult because they are ultra-thin transparent films whose refractive index is very close to that of the substrate.

In this study, we have fabricated BTO/STO artificial superlattices by a computer-controlled automatic molecular beam epitaxy (MBE) apparatus. Dielectric properties of the superlattices were measured using interdigital electrodes, and their refractive indices were determined by means of a spectroscopic ellipsometer modified for the measurements of ultra-thin transparent films. Results of this study revealed that the superlattices with the period of 10 unit cells showed anomaly high dielectric permittivity and refractive index.

2. Experimental procedure

2.1. Fabrication of superlattices

The superlattices were fabricated on STO(001) single crystals by MBE method shown in Fig. 1. Barium
and strontium metals were evaporated from the Knudsen cells, and titanium metal was evaporated from an electron-beam gun. The superlattices were prepared at 600 °C at a pressure of 10⁻⁶ Torr being irradiated by electron cyclotron resonance plasma on the surfaces of the growing films. The deposition sequence was controlled by three computers.

The structure of BTO/STO superlattices is represented by a formula \((\text{BTO})_m/\text{(STO)}_m\), where the subscript \(m\) indicates the period of layers \((m = 1, 10, 20, \text{and } 40)\). The total thickness of the multilayered films was fixed at 80 unit cells of the primitive perovskite lattice.

Crystallographic orientation and crystallinity of the BTO/STO superlattices were analyzed by reflection high-energy electron diffraction (RHEED) and X-ray diffraction (XRD).

2.2. Dielectric measurements

Dielectric properties of oxide superlattices are usually measured using conductive oxide films as a bottom electrode because superlattices cannot be grown on metals. We first used conductive Nb-doped STO single crystals as a bottom electrode but reliable results could not be obtained because of large leakage currents. The leakage was caused by the diffusion of Nb into superlattices. To solve this problem, we employed planar interdigital electrodes on the superlattices deposited on pure STO single crystals.

Interdigital electrodes were formed by the electron-beam lithography technique and the lift-off method. The thickness of Au-sputtered electrodes was approximately 60 nm, and the resistance of interdigital electrodes was \(7.4 \times 10^{-6} \Omega \text{ cm}\).

The capacitance and the complex admittance of superlattices were measured with an impedance analyzer (Agilent, 4294A). For accurate measurement of impedance at a wide frequency range, a four-terminal pair configuration was employed, and open/short/load calibration was performed using an impedance standard substrate (Cascade Microtech).

We used commercial high-frequency planer analysis software (Sonnet em) to calculate the complex admittance of the superlattices with an interdigital electrode because conventional theory proposed by Farnell et al. [6] cannot be applied to ultra-thin films like superlattices. A microphotograph of the interdigital electrodes and a model for the analysis are shown in Fig. 2. The software calculates the \(s\)-parameters and admittance between the ports 1 and 2.

2.3. Ellipsometry

A rotating-analyzer type spectroscopic ellipsometer (Mizojiri, DVA-36VWS) was used to determine the refractive indices of superlattices. Polarized light from 350 to 850 nm was provided from a Xe lamp (75 W) through a computer-controlled monochrometer and an optical fiber. The incident angle was varied from 58 to 77°. Experimental errors in the ellipsometric measurements are theoretically proportional to \((\sin \Delta)^{-1}\) [7]. Measurements on transparent materials are usually difficult because they sometimes give \(\Delta < 10°\). In this case, a compensator (a quarter-wave retarder) was inserted after the polarizer to reduce the experimental errors. The refractive indices of thin films were calculated using the three-phase model (ambient-thin films-substrate). In the analysis, the superlattices were...
regarded as uniform thin films along the thickness. The Marquardt method was employed to determine the complex refractive index of thin films from ellipsometric parameters measured at different incident angles.

3. Results and discussion

3.1. Structure of superlattices

Fig. 3 shows a streak pattern of RHEED observed during the deposition. The trace of specular intensity of RHEED during the deposition of BTO/STO superlattice is shown in

![Image](image1.png)

Electric resistivity of Pt electrode: $7.4 \times 10^{-6} \, \Omega \cdot \text{cm}$

Fig. 2. (a) Microphotograph of interdigital electrode and (b) a model for electromagnetic field analysis.

Fig. 4. Trace of specular intensity of RHEED observed during the deposition of superlattice.

Fig. 5 shows XRD profiles of superlattices. The simulation of XRD profile was done using the supercell model developed by ourselves [8]. The observed profiles agreed well with simulation, indicating fabrication of the superlattices with designed structures.

3.2. Dielectric and optical properties

The optimum electrode size was first determined using electromagnetic field analysis. In the measurement with interdigital electrodes, the electric flux penetrates into the substrate if the thickness of films is too thin and the space of the interdigital electrodes is too wide. The degree of the penetration could be evaluated by comparing admittance of substrate ($Y_s$) and that of film with substrate ($Y_f$). The $Y_s$ and $Y_f$ were calculated using the electromagnetic field analysis by assuming that the permittivity of STO substrate was 310, the thickness and permittivity of film were 30 nm and 1000, respectively. A parameter $\Delta Y$,
defined as $\Delta Y = (Y_t - Y_s)/Y_s$, is shown in Fig. 6 as a function of the width of the digits in an interdigital electrode. It is obvious that the $\Delta Y$ increased with decreasing size of electrode. In order to reduce the penetration of electric flux into the substrate and to accurately determine the dielectric permittivity of films, we selected the width of 5 $\mu$m.

Fig. 7 shows capacitance of BTO/STO superlattices as a function of frequency measured using interdigital electrodes. It was found that the capacitance was highly dependent on the stacking period of superlattices. The (BTO)$_{10}$/(STO)$_{10}$ superlattice showed anomaly high capacitance in comparison with other superlattices. It should also be noted that the capacitance less depended on the frequency up to 110 MHz, which is important for high frequency applications. The dielectric loss tangents (tan $\delta$) of all superlattices were less than 1% in whole frequency range. This indicates that planer interdigital electrodes overcame the problem of high-leakage currents. Fig. 8 shows dielectric permittivity of superlattices determined from the capacitance and the electromagnetic field analysis. The permittivity shows a maximum value over 30,000 at the periodicity of 10 unit cell.

The superlattice has an anisotropic structure. It is therefore important to understand that the high permittivity is obtained whether along the stacking direction or perpendicular to it. We have calculated the admittance change due to the change of dielectric permittivity along the stacking direction, and found that the admittance is independent from it. This indicated that the admittance measured is determined by the permittivity of superlattices perpendicular to the stacking direction.

The refractive index of the BTO/STO superlattices determined by the ellipsometry was shown in Fig. 9 as function of light wavelength. The refractive index decreased with increasing wavelength for all specimens. It was found that the refractive index of (BTO)$_{10}$/(STO)$_{10}$ is higher than other specimens. This result is well consistent with that of dielectric measurement. The dielectric permittivity at low frequencies may be determined by the ionic polarization while the refractive index is determined by the electric polarization. The similar behavior of the dielectric permittivity and the refractive index is very interesting phenomenon. The stacking structure in superlattices affects not only the ionic motion but also on the electronic structure or chemical bonding nature in the superlattice.
The origin of the high dielectric permittivity and refractive index in superlattices with the periodicity of 10 unit cells has not been clearly understood at present but the authors are considering that the strain induced in the films may play important role to determine the properties. Structural models of normal epitaxial films and superlattices are shown in Fig. 10. Strains are induced in epitaxial films due to the lattice matching to the substrate, however, they are relaxed as the thickness of the film increases. This is the case of BaTiO₃ and (Ba,Sr)TiO₃ films in Fig. 10. However, in the case of the superlattices, strains are periodically induced in the films and cannot be relaxed as the thickness increases. The strains induced in the film plane enlarge the lattice parameter along the film thickness, giving rise to the artificial ferroelectricity. This ferroelectricity may be the reason of high permittivity and refractive index.

4. Conclusion

The MBE process to fabricate perovskite-type superlattices was established. The XRD analysis indicated that the structure of superlattices prepared in this study consisted with that designed. The dielectric permittivity of BTO/STO superlattices along the film plane depended on the stacking period of superlattices. The superlattices with the period of 10 unit cells of perovskite structure showed a maximum permittivity above 30,000, which was almost independent of frequency up to 110 MHz. The refractive index of superlattices measure with a spectroscopic ellipsometer also showed the highest value when the period was 10 unit cells. This indicated that the structure of superlattice affected not only the ionic polarization but also electric polarization. The origin of anomalous properties observed in superlattices may be interpreted by the strains induced into the film.

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