1. Introduction

In the SrTiO₃ base sintered body doped with Bi and Nb, Nb ion substitutes for Ti in the SrTiO₃ perovskite structure. Bi ion, however, is not soluble in SrTiO₃ and segregates at the grain boundary. Bi- and Nb-added SrTiO₃ ceramics show the nonlinear voltage–current characteristics or so-called varistor characteristics. The varistor characteristics are known to be grain-boundary-induced characteristics and have been studied widely. Introducing the varistor characteristics into a thin film might produce future microelectronic devices. Epitaxial film usually has homogeneous crystal orientations both along and perpendicular to the substrate, but exhibits different microstructures, i.e., single crystal or polycrystalline. The epitaxially grown film might be made a model system for the varistor by means of introducing a foreign atom or controlling the crystal orientation.

The varistor characteristics in oxide thin films have been reported for ZnO, BaTiO₃, and SrTiO₃. These varistor characteristics were obtained by postannealing of the semiconductive ZnO or BaTiO₃ films with the deposition of foreign metal atoms, i.e., Bi or Mn. The processes were multiple and highly complicated. To date, a single process for realizing the varistor characteristics in thin film by means of introducing foreign atoms with a nonsoluble nature into the grain boundary. Bi- and Nb-added SrTiO₃ ceramics are known to be grain-boundary-induced characteristics and have been studied widely. This study is also to make a model system for the varistor by means of introducing a foreign atom or controlling the crystal orientation.

2. Experimental procedure

2.1 Fabrication of Nb-doped or Bi, Nb co-added SrTiO₃ thin films

The Nb-doped SrTiO₃ film (Nb–SrTiO₃) and Bi and Nb co-added SrTiO₃ film (Bi, Nb–SrTiO₃) were fabricated on the (001) MgO substrate using a vertical-type cold-wall MOCVD apparatus. A MgO single-crystal block (Mira-Crystal, Tateho Chemical) was used as a substrate. Since MgO is sensitive to humidity and carbon dioxide, the MgO substrate was prepared by cleavage of the MgO block. Ti(O-i-C₃H₇), Nb(O-C₂H₅)i, and Bi(DPM)₃ were used as the starting materials. Their vaporizing conditions are listed in Table 1. The basic MOCVD deposition procedure was described in a previous paper. Deposition conditions used in this study are listed in Table 2.

2.2 Characterization of the films

A wavelength-dispersion-type X-ray-fluorescence apparatus (WDS: PW2404, Philips, The Netherlands) was used to determine the composition and the thickness of the obtained films. Phase analysis, lattice spacing determination and in-plane crystal orientation measurement were conducted using the X-ray diffraction apparatus (XRD: X’Pert-MPD, Philips, The Netherlands). The lattice spacing measurement along the direction perpendicular to the substrate was conducted by normal ω-2θ diffraction. The in-plane lattice constant was calculated from the lattice spacing value measured from the asymmetric incident diffraction. Microstructures of the films were observed using the field-emission type scanning electron microscopy apparatus (FE-SEM: S–800, Hitachi, Japan), the atomic force microscopy apparatus (AFM: NanoScope, Digital Instrument, U.S.A.) Voltage-current characteristics and electrical resistivity
were measured using a four-probe measurement system with a tungsten probe (236, 195 A and 705, Keithley, U.S.A.).

Table 1. Starting Materials and Vaporizing Conditions

<table>
<thead>
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<th>starting materials</th>
<th>vaporizing conditions</th>
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<tr>
<td></td>
<td>temperature / °C</td>
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<tr>
<td>Sr(C1H3O2)2(C1H8N2)2</td>
<td>122.0</td>
</tr>
<tr>
<td>TiO(i-C1H12)</td>
<td>28</td>
</tr>
<tr>
<td>NbO(i-C1H12)</td>
<td>75</td>
</tr>
<tr>
<td>Bi(C1H6O2)2</td>
<td>145</td>
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</table>

Table 2. Deposition Conditions of Thin Films by MOCVD

<table>
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<tr>
<th>deposition temperature / °C</th>
<th>total gas flow rate / sccm</th>
<th>reactor pressure / Pa</th>
<th>oxygen partial pressure / Pa</th>
<th>heating and cooling rate / °C·min⁻¹</th>
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<tr>
<td>500-800</td>
<td>500</td>
<td>6.6×10²</td>
<td>2.6×10²</td>
<td>10</td>
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</tbody>
</table>

3. Results and discussion

3.1 Characteristics and electrical properties of the Nb-doped SrTiO₃ thin film

Figure 1(a) shows the XRD pattern of the Nb-SrTiO₃ thin film deposited at 800°C for 300 min on the (001) MgO substrate. The composition of the film was found to be Sr:Ti:Nb=54.5:42.7:2.8 (molar ratio) by WDS. The main phases of the deposited film are the (001) and (110) orientations of SrTiO₃. This result corresponded to that for the SrₓTi₁₋ₓO₃ thin film with x=0.4-0.6 deposited on (001) MgO, which showed (001) and (011) crystal orientation. In the case of x<0.4, (001)-oriented film was obtained. In Fig. 1(a), the phase with (001) orientation was epitaxially grown on MgO with a cube-on-cube arrangement. The films deposited at 700 and 800°C show a similar nature.

Figure 2 shows the effect of Nb addition on the two-direction lattice parameters. The lattice parameter perpendicular to the substrate was measured by ω-2θ diffraction, and the in-plane lattice parameter was calculated using the values of (204) and (024) lattice spacing obtained by the asymmetric reflection scanning. All films plotted in Fig. 2 have an almost constant Sr composition of 56-57 mol%. With increasing Nb content in the range of 1.6 to 4.1 mol%, the lattice parameters also increase. The extrapolated value of the lattice parameter at Nb content to be 0 mol% corresponds roughly to the bulk lattice parameter. The lattice parameters are almost constant with Nb addition of more than 4.1 mol%. The cubic root values of the lattice volume of Nb-SrTiO₃ thin film changed linearly with the Nb content in the range of 1.6 to 4.1 mol%, the cubic root of the lattice volume was fit with the calculated slope in which the Nb⁴⁺ ion substituted for the Ti⁴⁺ ion instead of the Nb⁵⁺ substitution. We observed the same tendency in the Nb-doped BaTiO₃ thin films deposited on (001) MgO substrates.

In Fig. 2, the Nb-SrTiO₃ films have higher lattice parameter values perpendicular to the substrate than along the substrate surface. The Nb-doped SrTiO₃ bulk ceramics shows the cubic crystal system at room temperature. The different lattice parameter values for the thin film are caused by the thermal expansion coefficient (TEC) difference between Nb-SrTiO₃ film and MgO substrate. The TEC value of SrTiO₃ is thought to be 11.7×10⁻⁶ K⁻¹ and that of MgO to be 12.8×10⁻⁶ K⁻¹. Since the TEC value of thin film is smaller than that of the substrate, Nb-SrTiO₃ film receives in-plane compressive stress from the MgO substrate during cooling, which deforms the crystal system of Nb-SrTiO₃ from cubic to tetragonal.

The voltage-current characteristics of the Nb-SrTiO₃ thin film showed a good linear relationship. This means that the Nb-SrTiO₃ film had a semiconductive nature, and there...
was no parasitic barrier at the thin film-electrode interface in the four-probe measurement. Figure 3 shows the change of electrical resistivity of Nb–SrTiO₃ thin films on the (001) MgO substrate as a function of the Nb content. The Nb–SrTiO₃ thin film exhibited a semiconductive nature with the Nb addition ranging between 1.6 and 3.5 mol% in this study. The minimum electrical resistivity value was 0.11 Ω·cm at 2.8 mol% Nb addition. The minimum resistivity value in Nb-doped SrTiO₃ ceramics is three orders higher compared with that in the thin film. The amount of Nb addition for achieving the minimum resistivity in ceramics is less than 1 mol%. As described above, the substitution of Nb⁴⁺ for Ti⁴⁺ in Nb–SrTiO₃ should not produce a controlled valence-type semiconductor. Added Nb ions initially substitute for the Ti⁴⁺ as a valence of 4+. This might be caused by the in-plane compressive stress in the film from the MgO substrate. With adding Nb ion of more than 1.6 mol%, Nb might act as a valence-controlling ion. The precise mechanism for forming a semiconductive thin film of Nb–SrTiO₃ is not yet clear.

The Nb–SrTiO₃ films deposited on the (001) MgO substrate at 500 and 600°C did not exhibit a semiconductive nature. The films deposited at 700 and 800°C exhibited semiconductor characteristics. Non-semiconductive films showed low crystallinity. Controlling the crystallinity might be important for realizing thin films with good semiconductive characteristics.

### 3.2 Characteristics and electrical properties of the Bi, Nb co-added SrTiO₃ thin film

Bi metal and its oxide have low melting and boiling temperatures. Measurements of the Bi presence in the Bi₂O₃ film deposited on the 0.5 mass% Nb-doped (001) SrTiO₃ substrate showed a decrease in the amount of Bi with increasing deposition temperature. At 800°C, no Bi was detected on the substrate surface. The deposition temperature of 700°C was chosen for the Bi and Nb co-added SrTiO₃ (Bi, Nb–SrTiO₃) thin film. Figure 1(b) shows the XRD pattern of the film deposited at 700°C for 300 min under the Bi carrier gas flow rate of 10 sccm. The Bi, Nb–SrTiO₃ film shows (001) and (110) SrTiO₃ peaks and a weak Bi₂O₃ peak. This is the same tendency as observed for Nb–SrTiO₃ (Fig. 1(a)). An XPS depth profile measurement of the Bi, Nb–SrTiO₃ film deposited on LaAlO₃ substrate revealed at less than 0.5 at.% of Nb was present in the film. The Bi₂O₃ indicated in Fig. 1(b) might be deposited only on the film surface. A quantitative value for Bi in the film could not be detected by WDS. The composition of the film was Sr:Ti:Nb = 57.2:38.0:4.8 (molar ratio). The Bi, Nb–SrTiO₃ film showed almost the same composition and in-plane orientation (cube-on-cube epitaxial growth on (001) MgO).

Figure 4 shows the change of lattice parameter and electrical resistivity of Bi, Nb–SrTiO₃ thin films (Sr:Ti:Nb = 57.2–59.7:35.9–38.4:4.4–5.0 (molar ratio), Bi = not detected) deposited on the (001) MgO substrate as a function of the carrier gas flow rate of the Bi vaporizer. The procedure and the peaks used for the measurement of the lattice constants were the same as in Fig. 2. A small amount of Bi addition increases both lattice parameters of the Bi, Nb–SrTiO₃ films. The lattice parameter change is, however, constant under a Bi carrier gas flow rate of more than 8 sccm. The electrical resistivity is also constant with this Bi carrier gas flow rate. Comparing the electrical resistivity value and Nb concentration in Fig. 4(b) and in Fig. 3, the effective concentration of Nb to realize the semiconductor characteristics is somewhat different but the resistivity value is almost the same. This means that the Bi concentration in the film was too low to affect the resistivity, or that Bi did not exist in the film.

Figure 5 shows the voltage–current characteristics of the Bi, Nb–SrTiO₃ thin film deposited on (001) MgO at 700°C for 180 min under a Bi carrier gas flow rate of 10 sccm and Bi vaporizer pressure of 39 kPa. The voltage–current shows a linear relationship. Introducing the Bi simultaneously with Nb did not lead to the successful realization of the nonlinear relationship like that of the varistor.
3.3 Varistor characteristics in the Bi, Nb-added SrTiO₃ thin film deposited on the (001) MgO substrate with a SrO seed layer

In general, the varistor characteristics are governed by the existence of the barrier of the carrier transmission at the grain boundary. Considering the result discussed in the previous section, introducing the Bi atom into the grain boundary of the epitaxially grown Nb–SrTiO₃ film was unsuccessful. This is why the grain boundary in epitaxially grown Nb–SrTiO₃ might be a small angle boundary or coincidence boundary, and very clean. It is necessary to introduce a large angle boundary and an obvious grain boundary, i.e., a columnar structure. We observed that a very thin buffer layer, i.e., TiO₂ (0.5 nm) or SrO (1–2 nm), at the boundary between the target film and the substrate changed the film’s nature markedly in the film with SrTiO₃/buffer layer/YSZ/Si structure deposited by PLD. The SrTiO₃ thin film was also grown with a cube-on-cube nature on the (001) MgO substrate by MOCVD, and the TiO thin layer might be present at the boundary. Therefore, we attempted to introduce an island (Volmer-Weber)-type very thin SrO seed layer on the MgO substrate surface. SrO thin film was formed on the (001) MgO substrate for 15 min. The estimated average film thickness of the SrO seed layer was ~2 nm. To avoid the reaction of SrO with humidity or carbon dioxide, the deposition of Bi, Nb-SrTiO₃ was conducted without removing the SrO film. The carrier gas flow rate and pressure of the Bi vaporizer were 8 sccm and 39 kPa, respectively. Other conditions were the same as those in Tables 1 and 2.

XRD patterns of the Bi, Nb–SrTiO₃/SrO/(001) MgO structured film were the same as those in Fig. 1(a). No Bi₂O₃ peak was detected because of the high Bi vaporizer pressure compared with that in Fig. 1(b). The composition of this film was Sr:Ti:Nb = 58.6:37.4:4.0 (molar ratio), and Bi was not detected. The pole figure measurement revealed that the in-plane orientation of the (001)-oriented Nb–SrTiO₃ phase had two types of domains, both with (001) MgO substrate, i.e., a 45° rotated arrangement (dominant) and a cube-on-cube arrangement (minor). The surface of the SrO-seeded Bi–Nb–SrTiO₃ thin film was very flat and a small number of hill-like shapes of 300 nm in diameter was observed. The cross-sectional observation of the film revealed no obvious grain boundary structure.

Figure 6 shows the voltage–current characteristics of the film. The solid line was drawn by linear regression based on the low voltage (current) region. Compared with Fig. 5, the nonlinear property is obtained in SrO-seeded Bi–Nb–SrTiO₃ thin film. Since there is no obvious microstructure difference between with and without the SrO seeding layer, the nonlinear voltage–current characteristics might occur due to the co-existence of two types of grains.

Figure 7 shows the TEM micrograph of the cross section of the SrO-seeded Bi–Nb–SrTiO₃ thin film and corresponding schematic drawings. The grain boundary between the cube-on-cube growth grain and the 45° rotated grain might act to produce nonlinear properties. Since we did not fabricate SrO-seeded film grown without Bi, the role of the Bi in this film was not clear. However, if we could introduce a significant amount of Bi into this film, more distinct varistor characteristics would be obtained.

4. Conclusion

Nb-doped semiconductive SrTiO₃ films were successively grown on (001) MgO substrate. The (001)-oriented SrTiO₃ phase was grown epitaxially with a cube-on-cube structure in relation to the MgO substrate. The film exhibited a semiconductive nature with low electrical resistivity (0.11 Ω·cm) that is three orders of magnitude lower than that in bulk ceramics by adding a much higher Nb addition (1.6–3.5 mol%). Most of the added Nb is thought to substitute for the Ti⁴⁺ as valence 4 +, as suggested by the dependency of the cell volume change. Substituted Nb⁺⁺ may not act as a valence control ion; only the remaining part of Nb makes the thin film semiconductive. By introducing the Bi and Nb simultaneously into the SrTiO₃ film, epitaxially grown Bi–Nb co-added SrTiO₃ film was obtained. The lattice parameter was somewhat changed with the addition of Bi, but
the amount of Bi content was undetectable. The addition of Bi did not produce the thin film with nonlinear electrical resistivity. Introducing a SrO seed layer on the (001) MgO substrate produced two kinds of in-plane orientations, i.e., 45° rotated and cube-on-cube grain. The SrO-seeded Bi, Nb co-added SrTiO3 film exhibited weak nonlinear voltage-current (varistor) properties.

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References