Preparation of Semiconductive Epitaxial BaTiO₃ Thin Film and its Electrical Properties

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半導性エピタキシャル BaTiO₃ 薄膜の合成とその電気的性質

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Submicron semiconductive epitaxial BaTiO₃ thin film was prepared on (100)MgO substrate. An epitaxially grown BaTiO₃ film prepared by MOCVD was coated with ethanol solution of LaCl₃ and heated under a reducing atmosphere at 800–1200°C. The resistivity was less than 1 Ω·cm and the carrier concentration was in the order of 10¹⁸ cm⁻³. The film was n-type semiconductor and the resistivity increased abruptly with the increase in temperature above 600°C in air because of the decrease of the carrier concentration.

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1. Introduction

Semiconductive BaTiO₃ ceramic has some outstanding electric properties, for example, the positive temperature coefficient of resistivity (PTCR) and high apparent dielectric constant by barrier layer (BL) capacitor.¹⁾ Semiconductive BaTiO₃ is easily prepared by doping of rare-earth element or post-annealing under a reducing atmosphere.²⁾ It has become apparent that these properties originate from grain boundaries and interfaces of the grains in the sintered body.³⁾

A lot of attempts to prepare the film having these excellent properties have been done.^{4)–8)} Some researchers have been reported the preparation of relatively thick semiconductive BaTiO₃ film more than 100 μm in thickness.^{4),5)} These films show PTCR character. However, there are only a few reports for the preparation of semiconductive films below and nearly 1 μm in thickness by adding some additives.^{7),8)} These films were prepared by sputtering and showed the relative high resistivity in the order of 100 Ω·cm, which is more than 10 times as high as that of sintered ceramics.

We have been prepared dielectric BaTiO₃ film with less than 1 μm in thickness by CVD.⁹⁾ The present paper describes the first success for the preparation of the semiconductive BaTiO₃ thin films with less than 1 μm in thickness, the resistivity of which was less than 1 Ω·cm comparable to that of BaTiO₃ ceramics. Moreover, some electrical properties of this film were also investigated.

2. Experimental

BaTiO₃ films about 0.7–1 μm in thickness were prepared by metal organic chemical vapor deposition (MOCVD). The preparation method was almost the same as that of the already reported one.⁹⁾ Barium

β-diketonate [bis(dipivaloylmethanato) barium, Ba(DPM)₂], titanium iso-propoxide [Ti(O·i-C₃H₇)₄] and O₂ were used as the starting materials. BaTiO₃ films were prepared at 730°C under the total gas pressure of 530 Pa. (100)MgO single crystal with the dimensions of 10×10×0.5 mm³ was used as a substrate because of its excellent chemical stability. Semiconductive film was not obtained from the BaTiO₃ films prepared on Pt/SiO₂/Si and fused silica substrates because these films reacted with the substrates during the post-annealing.

Semiconductive BaTiO₃ film was prepared by the following method; The surface of dielectric BaTiO₃ film was coated with ethanol solution of LaCl₃ (0.0005 mol/l). After that, this film was post-annealed under a reducing atmosphere of H₂/N₂=5/95 or in air at 800–1350°C for 2h with the heating and cooling rates of 200°C/h. Some samples were annealed only under a reducing atmosphere without the coat of ethanol solution of LaCl₃.

Barium and titanium contents in BaTiO₃ film were measured by inductively coupled plasma (ICP) and energy-dispersed spectroscopy (EDS) attached to scanning electron microscopy (SEM). The constituent phase and the orientation of the film were identified by X-ray diffraction (XRD). The microstructure was observed by SEM. Resistivity and carrier concentration were measured by using Van der Pauw's method from room temperature to 800°C under various oxygen partial pressures (*p*_{O₂}).¹⁰⁾ The advantage of this method is that it is not affected by the shape of the sample. Pt wires were mounted as electrodes at four corners of a sample by In–Ga electrodes. On the other hand, Pt paste was used instead of In–Ga for the measurement above room temperature. However, it has been known that BaTiO₃ ceramics do not have ohmic contact with Pt electrode.

In fact, non-linear V - I character was observed below 1 V by using Pt electrodes. Therefore, the resistivity above ± 5 V was used as the resistivity of the film.

3. Results and discussion

3.1 Preparation of semiconductive BaTiO₃ film

Figure 1 shows the electrical resistivity at room temperature as a function of post-annealing temperature from 800 to 1200°C. The presence of La element in the film was ascertained by ICP for the film coated with LaCl₃. However, the measurement of La content in this film is difficult because of a small amount of total La in the film and some other techniques are under investigation. The color of BaTiO₃ film changed from transparent to grayish by this treatment. Semiconductive BaTiO₃ film was obtained even at 800°C. This results agreed with the distance data of the reduced region in BaTiO₃ sintered body under a reducing atmosphere at 800°C.¹¹⁾ The film coated with LaCl₃ had low resistivity compared to uncoated one by the heat treatment at 800 and 1000°C. Moreover, the resistivity decreased with increasing annealing temperature for the film coated with LaCl₃. This tendency was also observed for the film uncoated with LaCl₃ and heated at 800 and 1000°C. On the other hand, BaTiO₃ film heated at 1200°C in air did not show semiconductive character even though the surface of the film was coated with LaCl₃. This result is different from that of ceramics which become semiconductive heated in air with the addition of La element.¹²⁾

The reaction phase between BaTiO₃ film and MgO substrate, BaMg₆Ti₆O₁₉, was detected by XRD for the heat-treated film irrespective of the addition of LaCl₃. XRD peak intensity ratio of (107) reflection of BaMg₆Ti₆O₁₉ to (200) one of BaTiO₃ for the film coated with LaCl₃ increased abruptly above 1200°C. Moreover, this film was not semiconductor and its surface became rough. This result shows that the film and the substrate react vigorously above 1200°C. Judging from these result, the resistivity of the film coated with LaCl₃ and heated at 1200°C under a reducing atmosphere is the lowest one within

Fig. 1. Resistivity of the film at room temperature as a function of the post-annealing temperature. (●) LaCl₃ uncoated, (○) LaCl₃ coated.

Fig. 2. SEM micrographs of the semiconductive BaTiO₃ film.

the limit of the present study, i.e., less than 1 Ω·cm. This value was compatible to that of ceramics.¹³⁾ Therefore, in the following section, the property of this film was investigated.

Other reflections without ($h00$) of BaTiO₃ were not appeared on XRD pattern together with that of the substrate by this heat treatment. Moreover, the rocking curve of (200) reflection was almost the same. These result show that the quality of the orientation of this film almost unchanged by this treatment. Figure 2 shows the SEM micrographs of the semiconductive BaTiO₃ film annealed at 1200°C under a reducing atmosphere. Smooth surface and the columnar structure were remained by this heat treatment. As a result, this treatment did not change the crystallinity and microstructure of the film.

3.2 Electrical properties of semiconductive BaTiO₃ film

The resistivity of the film heated at 1200°C under a reducing atmosphere was less than 1 Ω·cm at room temperature and the carrier was electron, so that this film was n-type semiconductor. The carrier concentration and the mobility at room temperature were in the order of 10¹⁸ cm⁻³ and 10⁰ cm²·V⁻¹·s⁻¹, respectively. These were almost the same orders as the reported ones for the sintering body and the single crystal of semiconductive BaTiO₃.^{14),15)} Figure 3 shows the V - I character at room temperature, where In-Ga was used as electrodes. Good linearity was observed up to 100 V, which shows the ohmic relation.

Fig. 3. V - I character of semiconductive BaTiO₃ film.

Fig. 4. Resistivity change of semiconductive BaTiO₃ film with the temperature.

(○) in air, (●) under p_{O_2} of 10^{-10} Pa

Fig. 5. Carrier concentration and mobility as a function of resistivity for the film heated in air shown in Fig. 4.

Figure 4 shows the changes of the resistivity with temperature up to 800°C in air and under p_{O_2} of 10^{-10} Pa. Pt paste was used as electrodes. In air, the resistivity slightly decreased with the increase in temperature below 500°C. However, it gradually increased with temperatures above 500°C, and rapidly above 650°C. Moreover, the film heated to 800°C maintained this high resistivity even at room temperature, more than 1000 $\Omega \cdot \text{cm}$. On the other hands, under p_{O_2} of 10^{-10} Pa, the resistivity was scarcely changed with temperatures below 800°C. Therefore the increase of the resistivity of the film heated in air is considered to be attributed to the oxidation of the film.

Figure 5 shows the carrier concentration and the mobility as a function of the resistivity for the same film heated in air in Fig. 4. The mobility was almost constant against the resistivity. However, the carrier concentration decreased with the increase of the resistivity. This result shows that the temperature dependence of the resistivity in Fig. 4 is due to the change of the carrier concentration. Moreover, the carrier concentration changed with the oxidation as shown in Fig. 5.

The facts that BaTiO₃ film heated in air did not show semiconductive character even though the surface of the dielectric film was coated with LaCl₃, and the carrier concentration of semiconductive film coated with LaCl₃ decreased by the heat treatment in air shown in Fig. 5 mean that main carrier was not considered to be generated by the substitution of La element. Oxygen vacancy is considered to be one of the possibility of the origin of the conductive carrier, electron. At that time the resistivity is considered to be unchanged under p_{O_2} of 10^{-10} Pa even at 800°C as shown in Fig. 4 because the vacancy is still remained and carrier concentration is enough to conduction. The conduction mechanism of this semiconductive film is under investigation.

4. Conclusion

Submicron semiconductive epitaxial BaTiO₃ thin film prepared on (100)MgO substrate was successfully prepared. This dielectric film was heated at 1200°C under a reducing atmosphere after the surface of the film was coated with the ethanol solution of LaCl₃. The film was n-type semiconductor and the conductive carrier was made from the oxygen vacancy. The resistivity and the carrier concentration were less than 1 $\Omega \cdot \text{cm}$ and in the order of 10^{18} cm^{-3} , respectively. The resistivity abruptly increased with the increase in temperature above 600°C in air, which was originated from the decrease of the carrier concentration.

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