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XPS Analysis on Nb–$SrTiO_3$ Thin Films Deposited with Pulsed Laser Ablation Technique

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Abstract

In order to increase an apparent dielectric constant of $SrTiO_3$ semiconductor ceramics, a grain boundary will be investigated more precisely. However, because there are many grain boundaries in ceramics, it is difficult to clarify their electrical properties. Therefore we have started to build up a model interface which consists of three-layer thin films (semiconductor: Nb–$SrTiO_3$/insulator: $SrTiO_3$/semiconductor: Nb-$SrTiO_3$) by pulsed laser ablation technique. During this process, we found that in a restricted experimental region Nb–$SrTiO_3$ thin films became semiconductors. In a non-restricted region, Nb–$SrTiO_3$ thin films became insulators. The Nb concentrations of these thin films were the same. However, in insulating Nb–$SrTiO_3$ films, the valence of Nb ion was 5+ (0·069 nm in an octahedral site) and in semiconducting Nb–$SrTiO_3$ thin films, the valence of Nb ion was 4+ (0074 nm in an octahedral site). This large ion radius distorted the TiO_6 octahedron, and therefore increased the vacancy of oxygen. The main peaks of O1s binding energy of the samples were almost the same. However, the shoulder peaks were 532·4 eV (semiconducting film), 531·2 eV (insulating film) and 531·4 eV (insulating film). The shoulder peaks were probably related to the oxygen near the oxygen vacancy. The oxygen of the shoulder peaks probably binds more tightly because of a distortion originating from many oxygen vacancies.

Keywords: films, interfaces, electrical conductivity, perovskites, varistors.

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1 Introduction

Recently, the miniaturization of electronic circuits, especially cellular phones, is in great demand. Take, for example, the decrease in the size of capacitors. In the 1980s capacitors were ordinarily 6 mm in diameter and 0·8 mm in thickness. By 1997 the smallest size was 1·0 mm in length, 0·5 mm in width and 0·5 mm in thickness.[1,2]

One of the problems arising from the miniaturization of capacitors increases the ratio of grain boundary volume to total grain volume. $SrTiO_3$ ceramics, which we use in our semiconductors, has an inherently high ratio. We therefore have a strong interest in the fundamental approach to researching grain boundary structure. To this end, we have started to build up a three-layer thin film (semiconductor-insulator-semiconductor)[3,4] model interface for $SrTiO_3$ ceramics, using the pulsed laser ablation technique.[5,6]

In this paper we describe how semiconducting Nb–$SrTiO_3$ thin films were built up and discuss why Nb-doped thin films are more conductive than SrTiO3 thin films.

2 Experimental

An ArF excimer laser at a wave length of 193 nm and a pulse width of 20 ns was operated at a repetition rate of 5 Hz. The laser fluence on the target was estimated to be about 4 J cm^{-2} in an irradiation area of $1\times2{\cdot}5\,mm^2$. The target was a stoichiometric, Nb 0·5 wt%–$SrTiO_3$. The substrates were polished with a conventional method. Thin films were deposited on $SrTiO_3$ (100) substrates by laser ablation. To investigate the effect of deposition conditions, the substrates were heated from 400 to 700°C. The deposition chamber was evacuated with

a turbomolecular pump to control the O_2 ambient pressure, which varied from 2×10^{-4} $3\cdot10^{-1}$ Torr.

Concentrations of Sr, Ti and Nb were measured by Secondary Ion Mass Spectroscopy (SIMS; Hitachi: IMA-3). Resistivity of these films was measured by two probe methods. DC voltage from 0 V to 10 V was applied to these thin films and the currents were measured (DC Voltage Source/pA meter; HP: 414011) after 1 min.

The valences of these thin films were measured by X-ray photoelectron spectroscopy (XPS; VG Scientific: VG-Microlab 320-D) method using Mg K_α as the X-ray source, and all spectra were referenced to the adventitious C 1s peak at 285·0 eV. Because the concentration of Nb was lower than those of Sr, Ti and O, the integration time for Nb 3d spectrum was multiplied by 16 compared to those of Sr, Ti and O.

3 Results and Discussion

3.1 The resistivity of thin films

It was noticed that the resistivity of Nb–$SrTiO_3$ thin films depended on the substrate temperature during deposition. Figure 1 shows the resistivity of these thin films. We found that there is a narrow region where Nb–$SrTiO_3$ was a semiconductor.

The substrate temperature strongly affected the resistivity. For example, the conductivity of the Nb–$SrTiO_3$ thin film deposited at 480°C was $1\cdot2\times10^3$ Ω m at room temperature while the films deposited at 440 and 650°C were more than $1\cdot0\times10^8$ Ω m at room temperature.

Additionally, the resistivity of $SrTiO_3$ thin films (Fig. 2) was measured. The resistivity of the $SrTiO_3$ thin film was $8\cdot0\times10^3$ Ω m at room temperature.

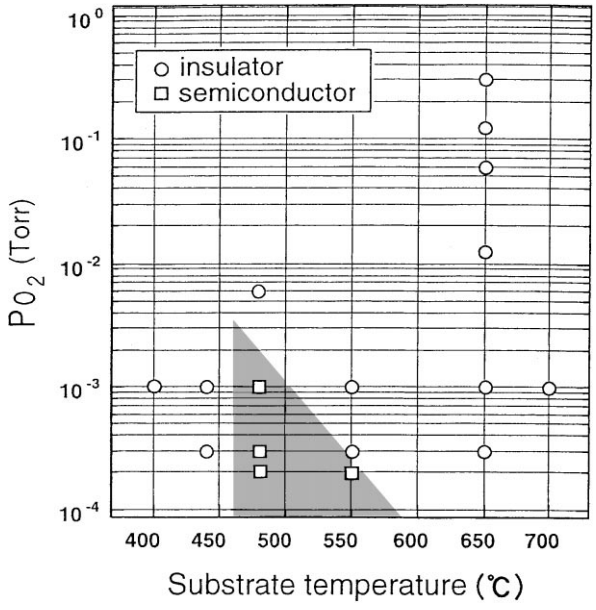

Fig. 1. Resistivity of Nb–$SrTiO_3$ thin films. This figure shows a region where fabricated thin films became semiconductors.

This revealed that the resistivity of the Nb–$SrTiO_3$ thin film was lower than that of the $SrTiO_3$ thin film, and therefore, that the presence of Nb decreases resistivity as well as oxygen vacancy.

3.2 Concentrations of Nb

Concentrations of Sr, Ti and Nb were measured by SIMS. Sr and Ti were constant, while Nb changed very little; Fig. 3 shows the Nb/Ti ratio of Nb–$SrTiO_3$ films deposited at the oxygen pressure of 3×10^{-4} Torr. The resistivity of these films also changed very little, showing that the resistivity was not directly affected by Nb concentration.

3.3 XPS analysis

3.3.1 Analysis of Nb

In Fig. 4, three Nb–$SrTiO_3$ thin films were measured. The substrate temperatures of the three samples were 480, 440, and 550°C, respectively. The sample (a) was a semiconductor and samples (b) and (c) were insulators. In samples (b) and (c)

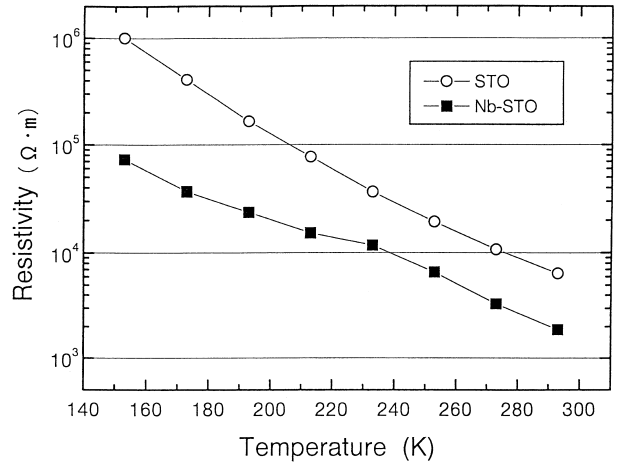

Fig. 2. Temperature dependence of resistivity of a Nb–$SrTiO_3$ thin film and a $SrTiO_3$ thin film. The fabricated condition was that the P_{O_2} was 3×10^{-4} Torr and the substrate temperature was 480°C.

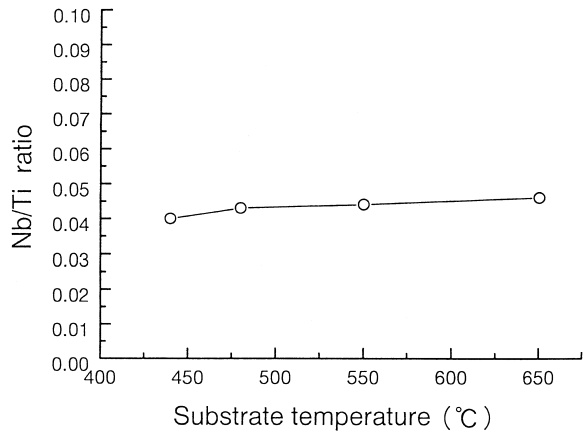

Fig. 3. Nb/Ti atomic ratios of the Nb–$SrTiO_3$ thin films were measured with SIMS. The abscissa was the substrate temperature when the films were fabricated.

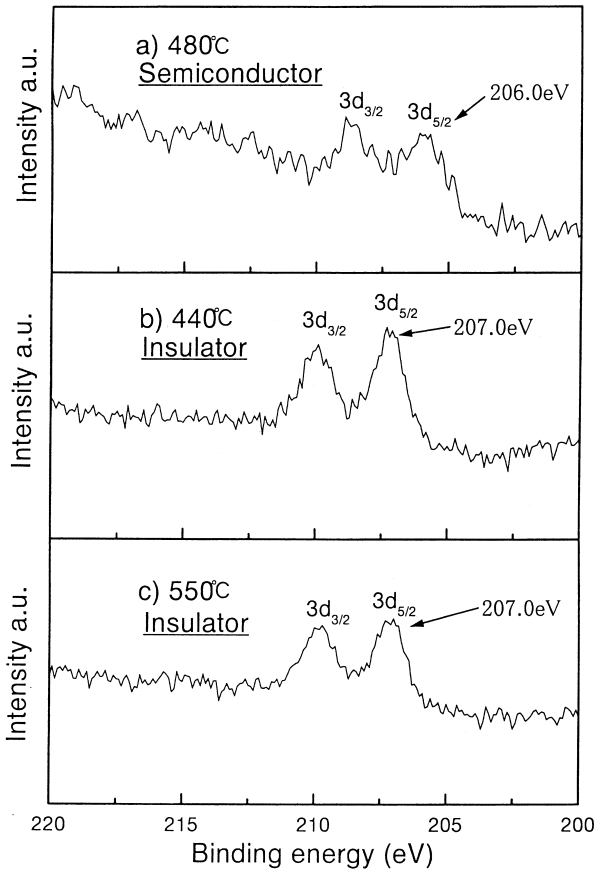

Fig. 4. XPS analysis of Nb ion on the Nb–$SrTiO_3$ thin films. All the samples were fabricated at the substrate temperatures of 480, 440, and 550°C, respectively. Sample (a) was a semiconductor and the other samples were insulators.

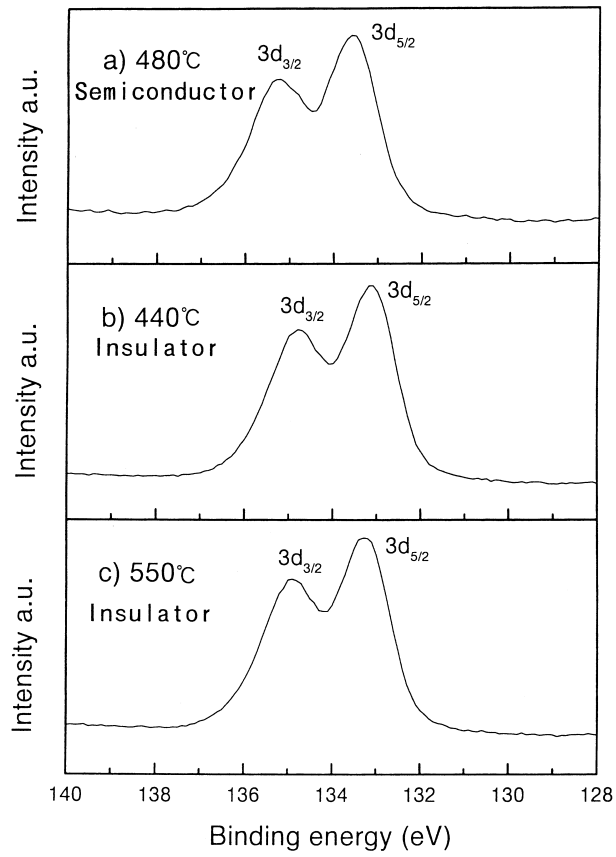

Fig. 5. XPS analysis of Nb ion on the Nb–$SrTiO_3$ thin films. All the samples were fabricated at the substrate temperatures of 480, 440, and 550°C, respectively. Sample (a) was a semiconductor and the other samples were insulators.

the positions of Nb $3d_{5/2}$ were both about 207·0 eV. They show that the valence of the Nb ion was 5+. However, in (a) the position of $3d_{5/2}$ shows a small chemical shift of about 1·0 eV. According to the literature,[7] binding energy decreases with the decrease of valence. When the valence of an Nb ion is 2+, the binding energy is under 204·7 eV. In this sample, the binding energy is about 206 eV. Therefore, the valence of Nb ion is not +5, it is probably 4+.

In an octahedral site, the ion radius of Nb ion is 0·069 nm (Nb5+) and 0.074 nm (Nb4+). Since the ion radius of Ti ion is 0·068 nm, the substitution of Nb4+ for Ti4+ distorts the TiO_6 octahedron and this probably releases the oxygen ion.

3.3.2 Analysis of Sr and Ti

The samples measured here were the same as mentioned in Fig. 4. Each of the samples had a binding energy of almost 133·0 eV (Fig. 5). Therefore, the valence of the Sr ions is 2+. In Fig. 6, the binding energy of these samples is almost 459·0 eV. Therefore, the valence of Ti ions is 4+.

3.3.3 Analysis of O

In Fig. 7, three Nb–$SrTiO_3$ thin films were measured. The substrate temperatures were 480, 440 and 550°C, respectively. The shapes of O1s spectra

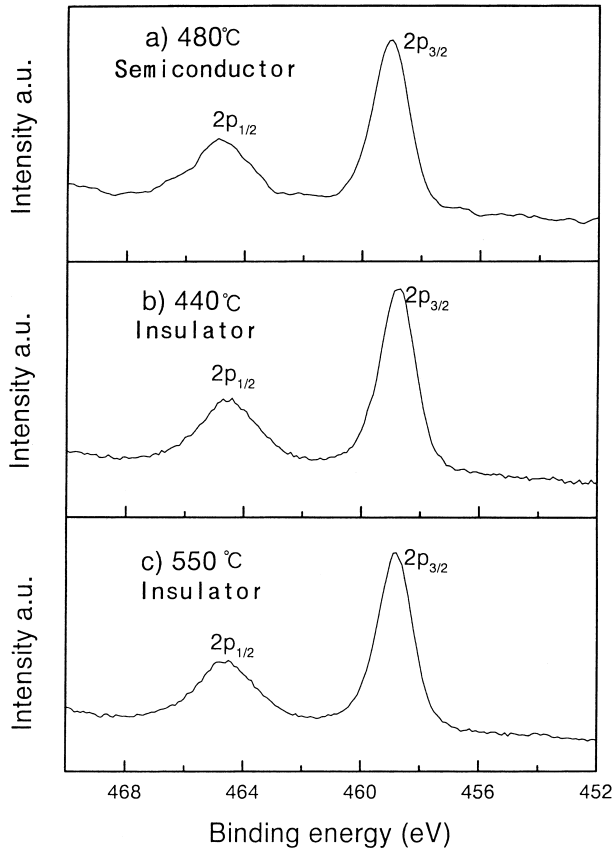

Fig. 6. XPS analysis of Nb ion on the Nb–$SrTiO_3$ thin films. All the samples were fabricated at the substrate temperatures of 480, 440, and 550°C, respectively. Sample (a) was a semiconductor and the other samples were insulators.

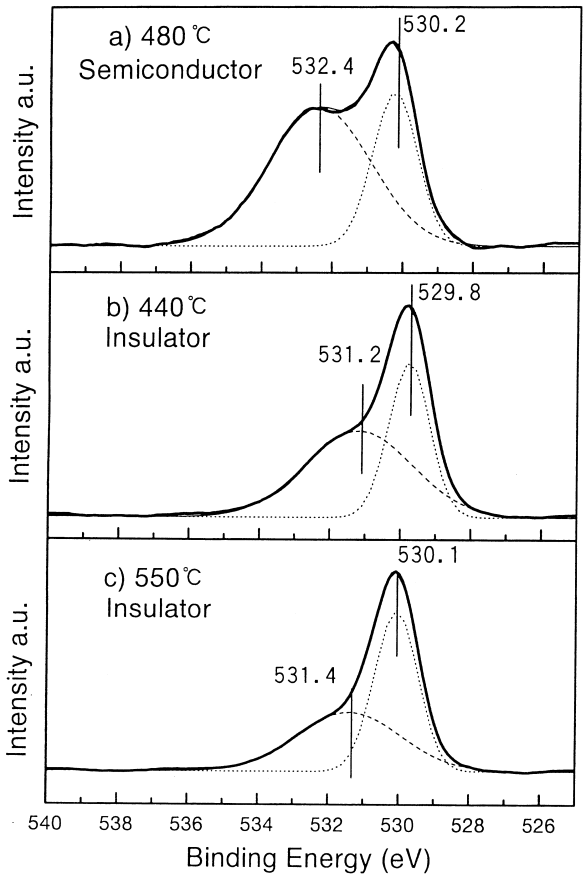

Fig. 7. XPS analysis of O ion on the Nb–$SrTiO_3$ thin films. The spectra were deconvoluted. All the samples were fabricated at the substrate temperatures of 480, 440, and 550°C, respectively. Sample (a) was a semiconductor and the other samples were insulators.

for these samples are quite different. The sample at 480°C has a higher shoulder peak than the other two. These three O1s peaks are deconvoluted. The binding energies of the main peak of O1s are almost the same; 530·2, 529·8, and 530·1 eV, respectively. However the binding energies of the shoulder peaks of the samples are different. The binding energy of the shoulder peak of the sample (a) is 532·4 eV, while the other two samples are 531·2 eV and 531·4 eV. The intensity of the sample (a) is higher than those of the other two samples. In a single crystal, the main peak of O1s is observed at near 529 eV,[8] but in these samples the main peaks are observed at near 530 eV. This is probably due to the difference in the structure between thin films and a single crystal. However, this cannot account for the difference between the shoulder peaks. The sample (a) is a semiconductor, and its concentration of oxygen vacancies are probably higher than that of an insulator, due to the binding energy of the oxygen close to the oxygen vacancy.

4 Conclusion

We have started to make three-layered thin film model interface, consisting of Nb–$SrTiO_3$ (Semiconductor)/$SrTiO_3$ (Insulator)/Nb–$SrTiO_3$ (Semiconductor)/$SrTiO_3$–substrate (100), with laser ablation technique.

In this process, the electrical properties of these thin films were carefully controlled in order to make the film a semiconductor. In the restricted experimental region a Nb–$SrTiO_3$ thin film became a semiconductor. In the other region, Nb–$SrTiO_3$ thin films became insulators.

The Nb concentrations of these thin films were the same. However, in insulating Nb–$SrTiO_3$ films the valence of Nb ion was 5+ (0·069 nm in an octahedral site) and in semiconducting Nb–$SrTiO_3$ thin film the valence of Nb ion was probably 4+ (0·074 nm in an octahedral site). This large ion radius distorts the TiO_6 octahedron and this probably releases the oxygen ion, making the sample more conductive.

The O1s binding energies of the samples were the same. However, the shoulder peaks of the O1s binding energies were 532·4 eV (semiconducting film), and 531·2 eV (insulating film) and 531·4 eV (insulating film). This difference was probably related to the binding energy of the oxygen close to the oxygen vacancy.

Acknowledgements

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References

1. Sumitomo Metal Electronics Devices Inc., Catalogue of dielectric resonators and high frequency devices, 1997.
2. Taiyo Yuden Co., *Electronics mount technology*, 1997, **13**(1), 36.
3. Glaister, R. M., The Institution of Electrical Engineers, 1961, **109**, Part B, Suppl. (22), 3634.
4. Yamaji, A. and Waku, S., *NTT kenkyuzituyoukahoukoku*, 1969, **18**(12), 3431.
5. Shibagaki, S. and Fukushima, K., *New Ceramics and Electronic Ceramics*, 1997, **6**, 56.
6. Fukushima, K. and Shibagaki, S., *Thin Solid Films*, 1998, **315**, 238.
7. Nefedov, V. L., Firsov, M. N. and Shaplygin, I. S., *J. Electron Spctrosc. Relat. Phenom.*, 1982, **26**, 65.
8. Fontaine, R., Caillat, R., Feve, L. and Guittet, M. J., *J. Electron Spectrosc. Relat. Phenom.*, 1977, **10**, 349.
9. Nagakar, P. V., Searson, P. C. and Gealy, F. D., *J. Appl. Phys.*, 1991, **69**(1), 459.