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Electrical Properties of Low Temperature Sintered $SrTiO_3$ Varistor

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The effects of SiO_2 and MnO addition on the sinterability and the electrical properties of 0.4 mol% Nb-doped $SrTiO_3$ varistor were investigated. The SiO_2 content was fixed at 0.3 mol% and the MnO content varied from 0 to 1.0 mol%. With 0.3 mol% SiO_2 and 0.3 mol% MnO addition, optimum density was obtained by sintering at 1200°C without excess liquid phase. Impedance spectroscopy was performed on the sintered specimens with 0.3 mol% SiO_2 and various MnO contents. It was found that the resistivities of grains was increased with increasing MnO content. The dielectric constant was measured to be above 50000 in the specimen with 0.3~1.0 mol% Mn content. The non-linear coefficient increased substantially with MnO addition, and it varied from 1 to 9 depending on the MnO content.

Key words : $SrTiO_3$, Varistor, Non-linear coefficient

I. Introduction

$SrTiO_3$ is one of the most important electroceramic materials.[1,2] Recently, the varistor characteristics of $SrTiO_3$ have been found.[3] Since the dielectric constant of $SrTiO_3$ is by two or three orders larger than that of ZnO varistor, a $SrTiO^3$ varistor shows a large surge capability and a sharp pulse response.[4-6] It can also be used as multifunctional components (MFC) like varistor-capacitor.

Since high temperature (>1400°C) is required in the firing process to manufacture $SrTiO_3$ varistor, it is difficult to fabricate mutilayer chip.[7,8] In order to realize $SrTiO_3$-based multilayer chip varistor, many studies have been carried out to lower the firing temperature, and there are several reports on the lowering sintering temperature with various additives, such as lithium salts.[9-11] Noi et al. reported that it is possible to make the $SrTiO_3$-based multilayer chip varistor using sintering additives, $5MnO \cdot 3SiO_2 \cdot 2TiO_2$ and annealing method which enables to insulate grain boundaries.[12]

In this study, we used annealing after fired in reducing atmosphere with additives as MnO and SiO_2 to fabricate low temperature sintered $SrTiO_3$-based varistors. To investigate the effect of MnO addition on the sinterability and the electrical properties of low-temperature sintered $SrTiO_3$, MnO content was varied from 0 to 1.0 mol%, in which Nb_2O_5 content and SiO_2 content were fixed to be 0.4 mol%, 0.3 mol% respectively. Secondary ion mass spectroscopy (SIMS) analysis and electron paramagnetic resonance (EPR) was also carried out to ensure the profile of MnO and electronic state.

II. Experimental Procedure

Ceramic specimens were prepared by a conventional mixed-oxide route, starting from 1 mol of $SrCO_3$, 1 mol of TiO_2, and 0.004 mol of Nb_2O_5. Powder mixtures were wet-milled for 24 h and then completely dried at 150°C. After dried, powders were calcined at 1100°C for 2 h. After calcination, 0.3 mol% SiO_2 and 0~1.0 mol% MnO were added to the calcined powders. The powder mixtures were remilled for 24 h. Each specimen was pressed under 100 MPa into a disk-shape of 10 mm in diameter and 1.2 mm in thickness and fired at 1150, 1200 and 1250°C for 4 h in a reducing atmosphere (90% N_2+10% H_2). The sintered specimens were annealed at 700, 900, and 1100°C for 1 h in air.

The dielectric properties and impedance of the specimens were measured with Ag-electrode by an impedance/gain-phase analyzer (4194A, Hewlett-Packard, USA). *I-V* characteristics was employed by a high voltage source measurement unit (237, Keithley, USA). After carefully polished and chemically etched, the microstructures of the specimens were observed by scanning electron microscopy (SEM) (S-2100, Hitachi, Japan). The diffusion profiles of Mn and Si ions in the specimen were obtained by SIMS (7200, PHI, USA). The electronic states of Mn ions were estimated by EPR spectrum (ESP-300S, Bruker, USA). The EPR spectrum of the specimen was measured at room temperature using the microwave frequency, 9.77 GHz.

III. Results and Discussion

1. Microstructure

Fig. 1 shows the relative density of sintered specimen as a function of MnO content and sintering temperature. When specimens were sintered at 1200°C with 0.3 and 0.6 mol% MnO, the relative densities of sintered specimens were found to be above 94%. Fig. 2 shows the microstruc-

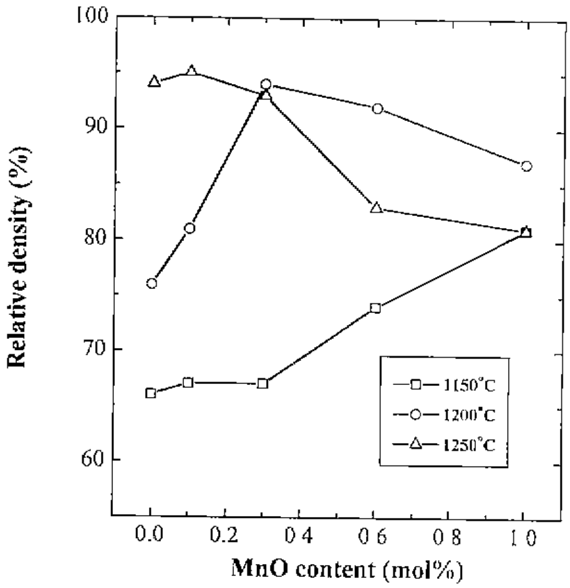

Fig. 1. Relative density of $SrTiO_3$ with different MnO content and sintering temperature.

tures of sintered specimens with different MnO content. The Variation of the grain size with respect to the MnO content is given in Table 1. An abnormal grain growth was observed with 1.0 mol% MnO due to a excess liquid phase, which is produced by TiO2-SiO2-MnO reaction.

2. SIMS analysis and EPR spectrum

SIMS analysis was employed to ensure the distribution of Mn ions in the specimens and performed in the area of 70 μm × 70 μm (Fig. 3). To remove any contamination at the surfaces, the surfaces of specimens were sputtered in the chamber of SIMS instrument. Mn and Si ions maps in Fig. 3 show inhomogeneous distribution of Mn and Si throughout the specimen.

Fig. 4 shows the EPR spectrum of 0.4 mol% Nb-doped $SrTiO_3$ sintered at 1200°C with the addition of 0.3 mol% MnO and 0.3 mol% SiO_2. Since most of the data were obtained at room temperature, it could be determined whether the electronic states of Mn ions were 2 or 4 from the EPR spectrum. The g value and |A| were found to be

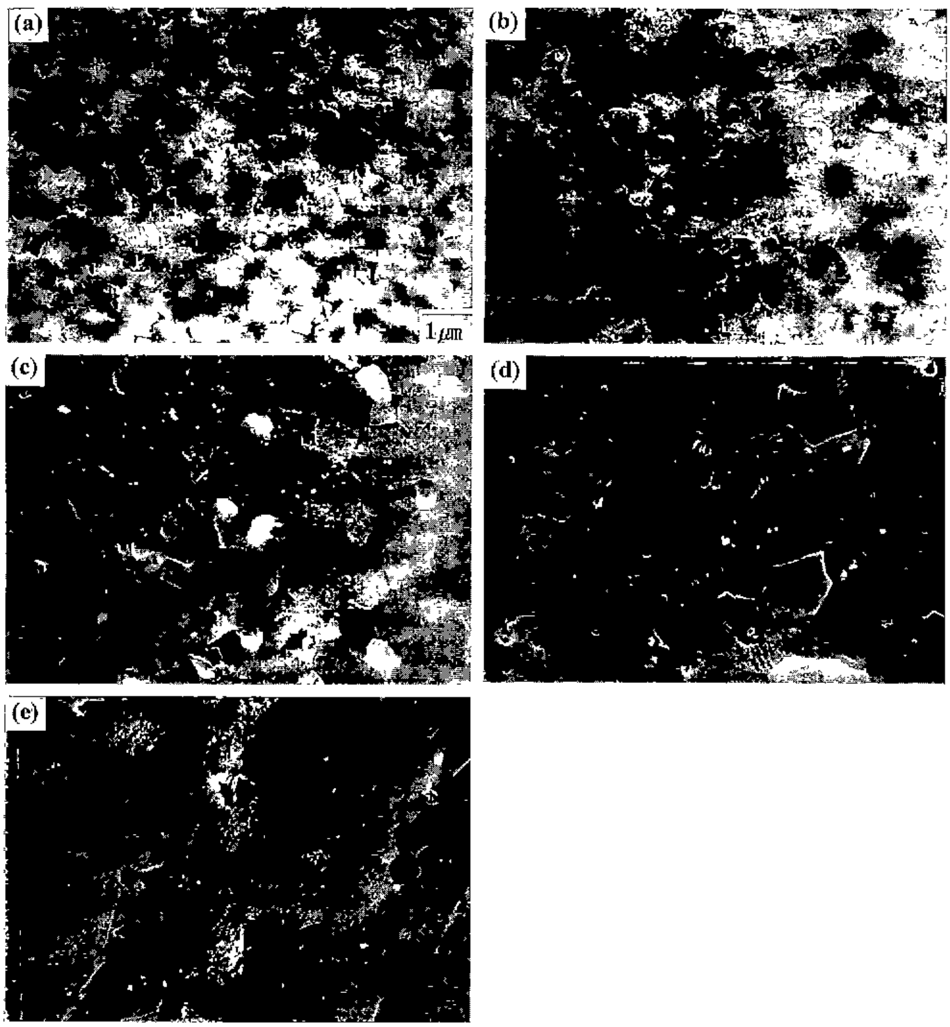

Fig. 2. SEM micrographs of $SrTiO_3$ sintered at 1200°C with different MnO content: (a) 0 mol%, (b) 0.1 mol%, (c) 0.3 mol%, (d) 0.6 mol% and (e) 1.0 mol%.

Table 1. Grain Size, Dielectric Constant, Dielectric Loss and Non-linear Coeffcient of $SrTiO_3$ Sintered at 1200°C with Different MnO Content and Annealing Temperature

MnO content (mol %)	Re-annealing temperature (°C)	Average grain size (μm)	Dielectric constant (K)*	Dielectric loss (%)*	Non-linear coeffcient
0	700 900 1100	0.7	1000 900 500	22.7 15.2 28.6	1.0 1.2 1.1
0.1	700 900 1100	0.4	45000 2500 1000	11.5 11.0 7.2	1.2 1.4 1.0
0.3	700 900 1000	2.4	6000 73000 2500	9.5 5.3 2.3	7.2 8.3 1.2
0.6	700 900 1100	3.3	70000 73000 2500	8.7 6.8 8.6	6.3 7.9 1.1
1.0	700 900 1100	5.2	95000 65000 2700	7.8 10.3 2.5	6.1 2.2 1.2

*Measured at 25°C, 1 kHz, 1 V_{rms}

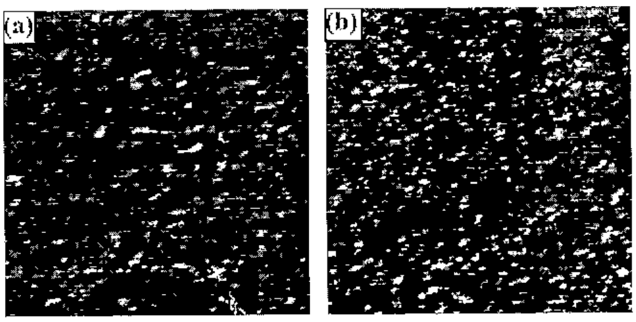

Fig. 3. SIMS micrographs of $SrTiO_3$ with 0.3 mol% MnO and 0.3 mol% SiO_2. Images are taken from a 70×70 mm^2 area: (a) Mn ion and (b) Si ion.

2.0067 and 82×10^{-4} cm^{-1} respectively. It was reported that the valence of Mn was 2 in the case that the g value was above 2.[13] Serway *et al.* also observed that the g value and |A| of Mn ions which substitute Ti ions in reduced $SrTiO_3$ specimen were 2.0036 and 82.6×10^{-4} cm^{-1}, respectively.[14]

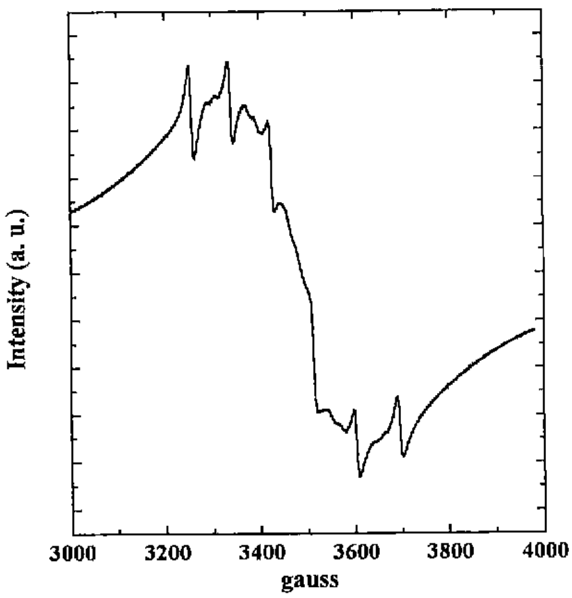

Fig. 4. EPR Spectrum of $SrTiO_3$ with 0.3 mol% MnO and 0.3 mol% SiO_2 and 0.4 mol% Nb_2O_5.

3. Electrical properties

It was found that the dielectric constant increases with the MnO content (Table 1). The dielectric constant was increased with the densification and the grain size. It is generally known that the dielectric constant of a grain boundary barrier layer capacitor increases with the median grain size.[15]

Fig. 5 shows the non-linear coefficients of the specimens annealed at the various temperatures. The non-linear coefficients of the 900°C annealed specimens are relatively higher than those of 700 and 1100°C anneled samples. The specimen added with 0.3 mol% MnO and annealed at 900°C exhibited the maximum non-linear coeffcient, about 9. The specimen annealed at 1100°C did not show the non-ohmic behavior. It was also observed that the non-linear coefficient of the specimen is more vigorously changed by the variation of the MnO content (Fig. 6).

Impedance spectroscopy is employed to investigate the effects of MnO addition and annealing temperature on the resistances of the grain and the grain boundaries. The measurements were carried out at 450°C, because at below 400°C, the resistances of specimens were too high to obtain any measurable values. As shown in Fig. 7 the low-frequency arc represents a contribution from the grain boundaries, while the high frequency arc does that from grains. A commercial fitting program (Boukamp's Equ-

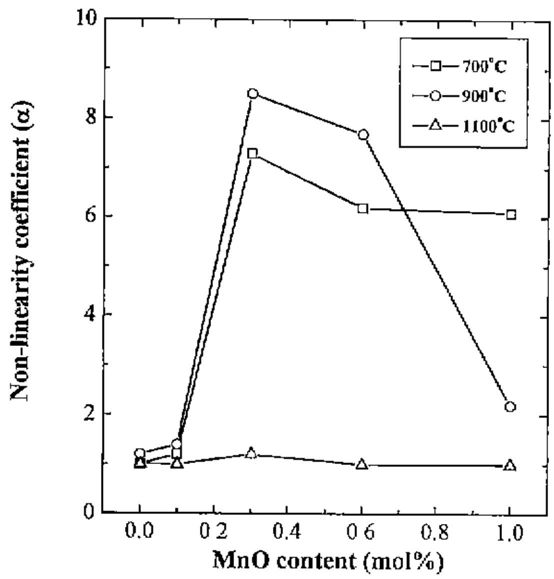

Fig. 5. Non-linear coeffcients of $SrTiO_3$ sintered at 1200°C with different MnO content and annealing temperature.

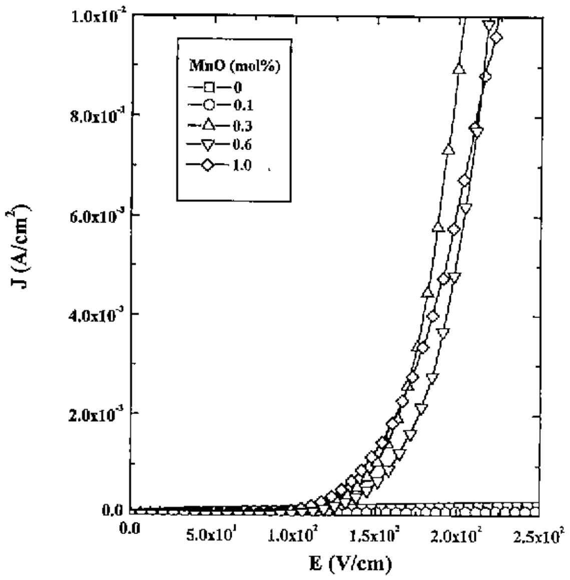

Fig. 6. *I-V* characteristics of 900°C Annealed $SrTiO_3$ sintered at 1200°C with different MnO content.

vert.pas program) was used to obtain more precise values of resistivities. According to the fitting results, the resistivities of the grain boundaries of the specimens annealed at 700, 900, and 1100°C were 64, 1061, and 3820 Ωcm, respectively.

The resistivities of the grains and the grain boundaries of 900°C annealed specimens as a function of the MnO content were listed in Table 2. The complex impedance plots of 0 and 0.1 mol% Mn-doped specimens can not be separated to the two semicircles. However, when MnO was doped above 0.3 mol%, it was possible to obtain the separated values. Based on the measurable values obtained, it was found that the resistivities of the grains

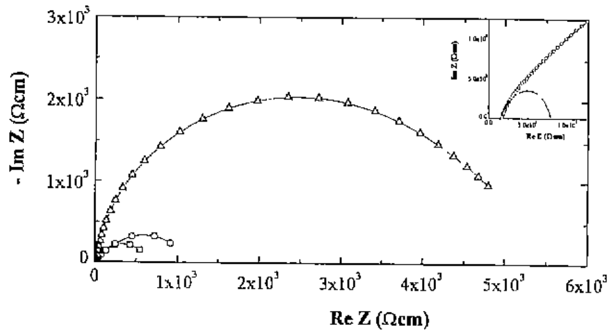

Fig. 7. Complex impedance plots of 700, 900, and 1100°C annealed $SrTiO_3$ with 0.4 mol% Nb_2O_5, 0.3 mol% MnO and 0.3 mol% SiO_2: □, 700°C; ○, 900oC; △, 1100°C (measured at 450°C)

Table 2. The Resistivities of Grains and Grain Boundaries of 900°C Annealed Specimens Sintered at 1200°C as a Function of MnO Content (measured at 450°C)

MnO content (mol %)	Resistivity (Ωcm)	
	Grain	Grain Boundary
0	-*	32000
0.1	-*	29000
0.3	60	1100
0.6	150	2100
1.0	170	8400

*Not measured.

and the grain boundaries are increased with the MnO content (Table 2). Mn^{-2} replacing Ti ion would result in negatively charged defects which were compensated by positively charged oxygen vacancies or holes. The electrons produced by substituting Nb ion for Ti ions were preferentially "trapped" on these sites.[16] Thus, with increasing the amount of substituted Ti site with Mn, the donor concentration was decreased and the resistivities of the bulks increased. This is consistent with the results obtained from the measured impedances of the specimens as listed in Table 2. Since the smaller donor concentration indicated that the grain boundaries possessed the higher Schottky barrier height, the donor concentration of grain decreased and the potential barrier height increased with increasing MnO content.[17] In the case of ZnO varistors, it was suggested that by the addition of MnO, the Schottky barrier height and the non-linear coefficient increased.[18] From the results of *I-V* characteristics as a function of the MnO content, the non-linear coefficients were increased with the MnO content. However, the precise relation of the potential barrier height and the non-ohmic behavior were not confirmed in this study. Further study is required to understand this phenomenon.

IV. Conclusion

The effects of MnO addition on the sinterability and the electrical properties of $SrTiO_3$ with fixed SiO_2 and Nb_2O_5 contents were investigated. At 1200°C, the sinterability increased with the MnO content up to 0.6 mol%. With higher addition, however, the density decreased due to the formation of excess liquid phase. The non-linear coeffcient of the specimens were highly influenced by the MnO addition, and it was about 8 for the specimen with 0.3 mol% MnO content. From the EPR measurement, it was found that Mn ions substituted the Ti ions in the lattice.

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