Formation and Electrical Properties of pn and n-p-n Structures on SrTiO₃ Single Crystal by CuO Diffusion and Excimer Laser Irradiation

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CuO 拡散とエキシマレーザー照射による SrTiO₃ 単結晶での pn 及び n-p-n 構造形成とその電気的性質

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N-type and p-type semiconducting regions were formed on an insulating SrTiO₃ single crystal by KrF excimer laser irradiation at non-treated and CuO-diffused surfaces, respectively. The n-type and p-type semiconductivity was confirmed using Hall coefficient measurement. The pn junction showed rectifying characteristics. An n-p-n structure was formed by laser-irradiation on a surface including a thin (1 µm in width) CuO-diffused layer. It shows nonlinear *I-V* characteristics with a nonlinear coefficient of 7, as observed in semiconducting SrTiO₃ ceramics with acceptor-diffused grain boundaries. This fabrication method was found to be effective for realizing the pn and n-p-n electrical properties at desired positions on insulating oxides.

[Received June 2, 1998; Accepted December 3, 1998]

Key-words: SrTiO₃ single crystal, KrF excimer laser irradiation, pn junction, n-p-n structure, CuO deposition, Nonlinear *I-V* characteristics

1. Introduction

Ceramic semiconductors are widely applied to electronic devices, such as positive temperature coefficient of resistance (PTCR) thermistors, varistors, boundary-layer (BL) capacitors, and gas sensors. The key function of these devices often originates from the unique characteristics of the grain boundary. For SrTiO₃-based BL capacitors, grains are made n-type semiconductive by donor doping or reduction in a low oxygen partial pressure and grain boundaries are made insulative or p-type semiconductive by diffusion of metal oxide flux (e.g., Bi₂O₃, PbO, CuO) painted on the surface.^{1)–4)} Sodium- or potassium-diffused SrTiO₃ BL capacitors also show nonlinear *I-V* characteristics in addition to a high permittivity.⁴⁾ In addition, direct utilization of interface properties, e.g., Pd/TiO₃ Schottky diodes⁵⁾ and CuO/ZnO heterocontacts⁶⁾ have been studied for application of gas sensor. If these grain boundary-derived properties can be realized in a limited area or at desired positions on oxide single crystals, application of these properties will be greatly extended in the field of microelectronic devices. Furthermore, it will aid the understanding of the precise role of interface properties of electronic ceramic devices.

Laser-induced processes on the surfaces of solids, including laser annealing, photochemical etching and laser ablation, have been topics of considerable interest. The laser ablation method is used for the production of a variety of functional thin films,^{7)–10)} laser etching is used for the fine circuit patterning of microelectronics. Also, excimer laser irradiation can modify electrical properties of insulating oxides.^{11),12)} In the case of SrTiO₃ single crystal, a drastic drop in resistance, from 10¹³ to 10⁴ Ω, was observed after KrF excimer laser irradiation with a fluence of 300 mJ/cm².¹²⁾ On the basis of Hall coefficient measurements and X-ray photoelectron spectroscopic (XPS) analysis, the lowering of resistivity was concluded to be n-type semiconductivity due to the generation of oxygen vacancies and free electrons.¹²⁾ The semiconducting-insulating-semicon-

ducting (n-i-n) structure was also formed on an insulating SrTiO₃ single crystal by KrF excimer laser irradiation onto the surface including a thin non-irradiated region with a width of about 1 µm.¹³⁾ Nonlinear current-voltage characteristics, with a nonlinear coefficient of 3–4, were observed for the n-i-n configuration.

In the present work, we attempted to form a pn semiconductor junction and an n-p-n structure on the surface of an insulating SrTiO₃ single crystal. The latter can be considered to be a quasi grain-boundary structure, i.e., a p-type semiconductive thin layer interposed between n-type regions. The p-type region was prepared by CuO deposition and annealing, and the n-type region was prepared by KrF excimer laser irradiation. In the present experiment, the KrF laser was used to irradiate a SrTiO₃ surface including both CuO-diffused and non-treated regions. Electrical properties of the p-type and n-type regions were examined by measuring the resistivity and Hall coefficient, and the interface properties were characterized by current (*I*)-voltage (*V*) measurements.

2. Experimental procedure

2.1 Sample preparation

The used SrTiO₃ in this study was commercially available single crystal (Shinko Ltd.) with a purity of 99.99%, surface roughness of 3 nm and size of 10×10×1 mm³. For pn junctions, a large area (3×3 mm²) of CuO film was deposited and annealed. The CuO film was deposited by RF sputtering at a gas pressure of 0.45 Pa using Ar gas with an RF power of 100 W. The deposition rate was 2.5 nm/min and the CuO film thickness was 150 nm.

The n-p-n structure was fabricated as follows; polymethyl-methacrylate (PMMA) solution was applied to the crystal by spin coating at 3000 rpm to form the photoresist. The thickness of the photoresist was controlled to be 100 nm after heat treatment at 170°C for 60 min. A 1 µm linewidth pattern was drawn using electron beam lithography (JEOL, JBX-5DII(U)) with a beam current of

Fig. 1. Fabrication process of pn and n-p-n structure on SrTiO₃ single crystal by CuO diffusion and excimer laser irradiation.

300 $\mu\text{C}/\text{cm}^2$. After deposition of the CuO film under the same conditions used for pn junction, the photo-resist was removed by stripping in boiled acetone.

The CuO-deposited SrTiO₃ was heated to 850°C at a rate of 3°C/min and annealed for 5h in air for CuO diffusion. KrF excimer laser with a wavelength of 248 nm (5.0 eV photon energy) was used to irradiate the SrTiO₃ surface including both the non-treated and CuO-diffused regions. Laser irradiation was performed with 20 pulses each 18 ns in duration with a repetition rate of 1 Hz at room temperature in air. The laser fluence was 300 mJ/cm². The fabrication process is summarized in Fig. 1.

For reference, polycrystalline SrTiO₃ specimens doped with 0 to 1.6 mol% CuO were prepared by sintering at 1400°C for 5h in air, with a heating rate of 5°C/min.

Phase identification was conducted with an X-ray diffractometer (Philips, PW1700) operated at a step width of 0.015°, and a scan speed of 1°/min between 10° and 80° (Cu K α). Lattice parameters of polycrystalline samples were calculated with a least-squares refinement program using five large peaks of SrTiO₃.

2.2 Observation of surface and chemical analysis of elements by EDX and XPS

Surface morphology was observed using a field-emission scanning electron microscope (Hitachi-4200). Chemical analysis was conducted on the surface using an energy-dispersive X-ray analyzer (EDX; HORIBA, EDAX 5770). Depth profile of chemical elements was measured by X-ray photoelectron spectroscopy (XPS; ULVAC-Phi, 5600), during which etching with 3 keV Ar ions X-rays of Mg K α was alternately repeated.

2.3 Electrical measurements

Electrodes of a size of 1 × 1 mm² were prepared by applying In-Ga alloy for n-type regions and Ag-In paste for p-type regions. The DC I - V characteristics were measured in the voltage range from 0.1 to 10 V at room temperature. Hall coefficient measurements were performed by the Van der Pauw method using four point Ag-In electrodes from 20 to 200°C, for polycrystalline SrTiO₃ doped with 1.6 mol% CuO (thickness of 0.6 mm), and CuO-diffused SrTiO₃ single crystals with and without laser irradiation. The measurement performed with a magnetic field of 0.31 Tesla, applied currents of 10 pA to 100 nA using equipment (BIO-RAD, HL5500PC) with a built-in electrometer (in-

putting impedance of 10¹⁵ Ω). For accurate estimation, ohmic check by measuring current-voltage relation, resistance check by permutation of electrode pairs, and inversion of magnetic field were conducted.

3. Results and discussion

The surface morphology of the same area of a CuO layer on SrTiO₃ (a) as-sputtered, (b) after annealing and (c) after KrF laser irradiation is shown in Fig. 2. Though the width of the as-sputtered CuO layer is 1 μm , it narrowed to about 0.7 μm and the shape of the edge became wavelike after annealing at 850°C for 5h. This shrinkage of CuO layer is caused by Cu diffusion from the surface into the SrTiO₃ lattice by the heat treatment. The CuO layer almost disappeared after KrF excimer laser irradiation. This indicates that the CuO layer was ablated by intense laser energy. In our previous report,¹²⁾ traces of local melting were observed as microcracks on the surface of SrTiO₃ single crystal irradiated with KrF excimer laser at the fluence of more than 200 mJ/cm². It is known that the melting temperature and the optical energy band gap of SrTiO₃ are 2080°C and 3.2 eV, respectively.¹⁴⁾ The melting temperature and the optical energy band gap of CuO are reported to be 1100°C and 1.35 eV, respectively.¹⁵⁾ Thereby, ablation of the CuO layer, which has a narrower band gap and a lower melting point than SrTiO₃, is feasible due to the photothermal effect.

Figure 3 shows the results of surface chemical analysis by EDX; (a) after annealing and (b) after KrF excimer laser irradiation, at the points (300 nm² area) located at 300 nm from the center of the CuO layer illustrated by white dots in Figs. 2 (b) and (c), respectively. The surface Cu-profile indicates that Cu diffused into the SrTiO₃ lattice during annealing. Figure 4 shows the Cu depth profile obtained by XPS for a CuO-diffused and laser-irradiated SrTiO₃ single crystal. For a measurement, a sample with CuO diffusion over a large area (3 × 3 mm²) was used and normalization for atoms of differing weights was not conducted. The depth of Cu diffusion was recognized to be approximately about 0.3 μm from the surface assuming an etching rate of 3 nm/min. The Cu concentration measured by EDX (Fig. 3) was smaller than that determined by XPS analysis (Fig. 4). This is assumed to be due to differences in the CuO-diffused area of samples and in the detectable

Fig. 2. Field-emission scanning electron micrographs of (a) as-sputtered CuO layer on SrTiO₃, (b) CuO layer after annealing, and (c) sample surface laser irradiation.

Fig. 3. Point-by-point chemical analysis (a) after annealing and (b) after KrF excimer laser irradiation, at the points indicated by dots in Fig. 1(b) and (c), respectively.

Fig. 4. Depth profile of elements in CuO-diffused and laser-irradiated SrTiO₃ single crystal.

Fig. 5. Lattice parameter vs. CuO content for Cu-doped SrTiO₃ polycrystals sintered at 1400°C.

Table 1. Resistivity, Hall Mobility and Carrier Density of SrTiO₃ Polycrystal and Single Crystal

Sample	Temperature	Resistivity (ρ)	Mobility (μ)	Carrier density
	°C	Ωcm	$\text{cm}^2/\text{volt-sec}$	hole/cm^3
(a) SrTiO ₃ (p.c.) doped with 1.6mol% CuO	150	1.00×10^4	0.54×10	1.2×10^{13}
(b) CuO/SrTiO ₃ (s.c.) annealed	50	5.63×10^2	3.32×10	3.4×10^{13}
	150	1.21×10^2	0.11×10	4.6×10^{16}
(c) CuO/SrTiO ₃ (s.c.) annealed and laser irradiated	50	1.35×10^2	2.44×10	4.6×10^{15}
	150	0.69×10^2	1.19×10	7.5×10^{17}
(d) SrTiO ₃ (s.c.) laser irradiated	20	0.2	0.54×10	5.4×10^{18} (electron)

*p.c.: polycrystal, s.c.: single crystal

† Annealing was performed at 850°C for 5h in air, and KrF excimer laser irradiation was performed at 300 mJ/cm² in air.

sensitivity of EDX and XPS, i.e., the detectable depth is 1 μm for EDX and 10 nm for XPS compared to the depth of 0.3 μm for Cu-diffused region.

The lattice parameter of the SrTiO₃ polycrystalline sample increased linearly with Cu content from 0 to 1.6 mol%, as shown in Fig. 5. This result is similar to the reported changes of lattice parameter in CuO-doped SrTiO₃ polycrystals.¹⁶⁾ From the result of identification of XRD peaks, it was concluded that other phase were not present. The ionic radius of Cu²⁺ is 0.087 nm at 6-coordinate, which is larger than that of Ti⁴⁺ (0.061 nm) but smaller than that of Sr²⁺ (0.132 nm; 12-coordinate).¹⁷⁾ From these ionic radii and the increased lattice parameter, it can be concluded that Ti⁴⁺ is substituted by Cu²⁺ in the SrTiO₃ lattice. For CuO-diffused SrTiO₃ single crystals, small CuO peaks and traces of Sr₄Ti₃O₁₀ peaks were recognized. However, the peaks were of an insignificant intensity, with relative intensities below 1 % of the SrTiO₃ (110) peaks. Furthermore, after laser irradiation, these peaks reduced in smaller intensity. Formation of an amorphous phase was not evident as inferred from unchanged baseline at low-angle diffraction. Therefore, it is certain that CuO is dissolved in SrTiO₃ single crystal during annealing. The CuO and other compounds left after annealing are assumed to be ablated by laser irradiation.

Table 1 shows resistivity, mobility and carrier density of SrTiO₃; (a) polycrystal doped with 1.6 mol% CuO, (b) CuO-diffused single crystal, (c) CuO-diffused and laser-irradiated single crystal, and (d) laser-irradiated single crystal. For measurements of (b) and (c), samples with CuO diffusion over a large area were used. The thickness of the surface semiconductive layer was assumed to be 0.3 μm for samples (b) to (d) from the Cu depth profile and the cross-sectional SEM photograph.¹²⁾ The major charge carrier was confirmed to be holes from the sign of the Hall coefficient for samples (a) to (c), including sample (a) at 50°C. Resistivity decreased and hole density increased in the order of (a) to (c), at 150°C.

It was reported that the doping of nickel produces p-type conduction in SrTiO₃ ceramics.¹⁸⁾ The report demonstrates an increase in conductivity with increasing Ni concentration up to 1.6 at% and with increasing oxygen partial pressure (P_{O_2}) in the high P_{O_2} region of 10^5 to 10^8 Pa. When Ti⁴⁺ of SrTiO₃ is substituted by the lower valency Cu²⁺, it is anticipated that the doped Cu²⁺ ions behave as acceptors. The substitution of Ti ions by Cu ions produces oxide ion

vacancies, $V_{\text{O}}^{\bullet\bullet}$, according to the reaction:

and oxygen atoms in gas phase would occupy the oxygen vacancies. This step leads to the formation of electron holes, $h^{\bullet}$:

For CuO-deposited SrTiO₃ single crystals, Cu²⁺ ions would diffuse into the SrTiO₃ lattice substituting for Ti⁴⁺ during annealing and behave as acceptors giving rise to an increase in hole density and the p-type conduction. In contrast, the n-type conduction of the laser-irradiated surface without CuO diffusion (sample (d) in Table 1) is due to the generation of oxygen vacancies and free electrons by photo-thermal and photo-excitation effects of excimer laser irradiation.¹²⁾ The reason for p-type conduction in CuO-diffused and laser-irradiated surfaces (sample (c)) is that the laser energy effective for the production of oxygen vacancies and electrons was lowered due to the energy dissipation by the ablation of the residual CuO layer.

Figure 6 shows the temperature dependence of resistivity and hole density for (a) CuO-diffused single crystal and

Fig. 6. Resistivity and hole density as a function of temperature for (a) CuO-diffused and (b) CuO-diffused and laser-irradiated SrTiO₃.

(b) CuO-diffused, laser-irradiated single crystal. According to the plot, the hole density was found to have an activation energy of 0.8 and 0.6 eV for samples (a) and (b), respectively. The doped Cu ions are found to act as acceptors at a deep level in the band gap of SrTiO₃. The higher hole density of sample (b) than sample (a) is assumed to be caused by frozen holes produced by an instantaneous temperature increase at laser irradiation.

A pn junction was formed on the surface of single crystal by excimer laser irradiation of both non-treated and CuO-diffused regions. The pn junction showed rectifying *I*-*V* characteristics, as shown in Fig. 7. Under reverse bias, a breakdown phenomenon was observed at 3.3 V. In the ideal model that is generally applied to pn semiconductor junctions, electric charge is transported by injected carriers that cross the interface barrier, and the current-voltage characteristics in forward bias can be represented in the following empirical form,¹⁹⁾

$$I \sim \exp\left(\frac{qV}{\eta kT}\right) \quad (3)$$

Fig. 7. Current-voltage characteristics of pn junction at 25°C.

Fig. 8. Natural logarithm of current vs. forward bias of the pn junction.

where the factor η equals 2 when the recombination current dominates and η equals 1 when the diffusion current dominates. Figure 8 shows the natural logarithm of current as a function of applied voltage under forward and reverse biases. In the present pn junction, the η value in forward bias was more than 10 at 1–3 V, which is much larger than that expected from the ideal model. In addition, voltage dependence of reverse current is larger than that in the model.

The departure from the ideal model to a larger η is known to be caused by the series resistance of component semiconductors or the interface states.¹⁹⁾ The former lowers the effective voltage applied to the junction interface. The latter is formed by extrinsic ionic charges or a large lattice mismatch at the interface. These states can act as generation-recombination centers, and the states with a high density often give rise to a leakage current from pn junction at low voltages. In the present junction, Cu diffusion along the surface reaches more than 0.5 μm from the edge of the CuO-deposited region as shown in Fig. 3. This means that acceptor concentration has a broad distribution around the interface and the width of interfacial region is large. In addition, the laser irradiation over the whole surface would give different instantaneous temperature increases for non-treated and CuO-diffused regions, which may cause some defects such as lattice mismatch at the interface. These would give a wide interfacial region with distributed interface states. Accordingly, the effect of interface states is assumed to be the main reason for the large difference from the ideal $\ln I$ -*V* relation. Such phenomena can often be observed in pn heterojunctions or metal-semiconductor junctions with adsorbates at the interface.^{20)–22)} The leakage current in reverse bias in the present system can be explained by the interface-state effect.¹⁹⁾

Figure 9 illustrates the electric-field dependence of current density, (a) laser-irradiated SrTiO₃ surface, i.e., n-type region, (b) CuO-diffused, laser-irradiated SrTiO₃ surface, i.e., p-type region and (c) CuO (1 μm layer)-diffused, laser-irradiated SrTiO₃ surface, i.e., n-p-n structure, where current and voltage were normalized by electrode

Fig. 9. The electric field dependence of current density: (a) laser-irradiated SrTiO₃ surface (n-type region), (b) CuO-diffused, laser-irradiated SrTiO₃ (p-type region) and (c) CuO (1 μm layer)-diffused, laser-irradiated SrTiO₃ surface (n-p-n structure).

length and distance between electrodes, respectively. In the plot, the n-type and p-type regions showed linear $\log I^*$ - $\log E$ relations with a slope of 1. Nonlinear I - V characteristics were observed for the n-p-n structure; the current, lower than that of p-type region at low voltages, increased markedly with increasing voltage and the increase became gradual at high voltages. The nonlinear coefficient α (defined as $\Delta \log I / \Delta \log V$) was 7 at 0.2–0.5 V/mm (0.3–0.7 V). This nonlinear behavior can be considered to be basically similar to that of the pn interface in forward bias, that is a lowering of diffusion potential at the negatively-biased pn interface by applied bias and an increase in carrier (electron) flow over the p-type region. The current at high voltages would be determined by the original resistance of the p-type and n-type regions.

The α value of 7 is larger than that observed for the n-i-n structure, which was formed by excimer laser irradiation of two regions separated by a non-irradiated region with a width of 1 μm .¹²⁾ For the n-i-n structure, the effect of lattice mismatch at the n-i interface seems to be larger than at the pn interface due to an instantaneous temperature increase occurring only at the irradiated region. This would give a broad potential barrier at the n-i interface and a smaller α value than that of n-p-n structure.

Non-ohmic I - V characteristics are reported for some ceramics with n-type semiconductive grains and insulating grain-boundaries. In ZnO-based varistors, grain-boundary potential barriers (double back-to-back Schottky barriers) are formed by excess oxygen ions in association with segregated dopant cations,²³⁾ and α values as high as 50 are achieved by electron tunneling through the barrier or abrupt barrier lowering above a threshold voltage.^{24),25)} The sodium- or potassium-diffused SrTiO₃ BL capacitors have α values of 10–20, which was interpreted to mean that diffused alkali ions segregated at grain boundaries and the acceptor ions act as electron traps leading to potential barriers.⁴⁾ TiO₂-based ceramics doped with Nb and Ba ions simultaneously showed the α values of 3–7.²⁶⁾ It was also interpreted as that the pentavalent cations create donors to raise the grain conductivity and divalent cations work as electron traps to form grain-boundary potential barriers. In the present n-p-n structure, the doped Cu ions act as electron traps to form a potential barrier layer. This n-p-n structure can be considered to have a similar electronic structure to the acceptor-segregated grain boundaries, although the width of the potential barrier layer is significantly larger than that of grain boundaries and further detailed investigation is required to investigate the conduction mechanism.

The present fabrication process, diffusion of a thin CuO layer and excimer laser irradiation, was found to be a promising method for the formation of pn junctions and n-p-n structures on an insulating oxide which exhibit nonlinear I - V properties similar to a grain boundary in semiconducting ceramics. The present method is believed to open up new possibilities for fundamental study on grain-boundary functions of semiconducting ceramics and also for applied research on microelectronic devices.

4. Conclusions

A pn semiconductor junction and n-p-n structure were formed on SrTiO₃ single crystal by KrF excimer laser irradiation. The laser was used to irradiate on both CuO-diffused and non-treated regions located adjacently for the

pn junction, and on a surface including a thin CuO (1 μm wide)-diffused layer for the n-p-n structure. Cu diffusion during annealing was confirmed to occur to a depth of approximately 0.3 μm , and the n-type and p-type semiconductivities were confirmed using Hall coefficient measurement. The mechanism for formation of thin p-type layer was concluded to be as follows: Cu²⁺ ions diffuse into the SrTiO₃ lattice substituting for Ti⁴⁺ during annealing and behave as acceptors giving rise an increase in hole density. The pn junction showed rectifying characteristics, and the n-p-n structure showed nonlinear I - V characteristics with a nonlinear coefficient of 7. The present fabrication process was found to be a promising method for the formation a pn junction and an n-p-n structure on an insulating oxide single crystal.

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