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Low Temperature Preparation of High-Tc Superconducting Thin Films by Reactive Sputtering Using N_2O Gas

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Superconducting $Gd_1Ba_2Cu_3O_{7-x}$ thin films have been prepared by rf magnetron sputtering using N_2O gas. N_2O dissolved into OI, N_2 and N_2^+ in the plasma. For N_2O, the c-axis is preferentially oriented perpendicular to the (100)MgO substrate at the substrate temperature above 585 °C. the epitaxial temperature can be decreased when N_2O gas is used instead of O_2 as sputtering gas mixture. The onset temperature was 90 K. But the width of superconducting transition was broad and Tc(R=0) was 53K. N atoms existed in the films prepared by N_2O.

1. INTRODUCTION

On the applications of high·temperature superconducting oxide thin films to electronic devices, high quality thin films must be fabricated on semiconductors and insulators. In earlier works, high temperature annealing (>800 °C) in an oxygen atmosphere after the film deposition was required superconductivity. Integration of superconductor and semiconductor devices, however, becomes difficult because of the increase of surface roughness, inter-diffusion between the thin film and the substrate, and cracks in the film caused by this treatment. Moreover, in case of preparing the superconducting thin films on semiconductor devices, such a high temperature annealing damages these devices. Therefore, low temperature processes are indispensable to fabricate the high-Tc superconducting devices, hybrid of semiconductor devices and so on.

The challenge to low temperature process has been carried out in various methods such as sputtering[1], pulsed laser evaporation[2], e-beam co-evaporation[3] and molecular-beam epitaxy[4]. From those results, it is confirmed that the "reactive" oxygen is effective to prepare the superconducting thin films at low substrate temperature deposition. The methods for low temperature film preparation are classified as follows; (1) High partial pressure of oxygen gas around the substrate is used. (2) Oxygen gas is excited by dc discharge[2], rf discharge, microwave[4], electron-cyclotron-resonance (ECR)[5] and laser. (3) Ozone (O_3)[6] or dinitrogen monoxide (N_2O)[7] gas is used instead of oxygen gas.

We have investigated the "in situ", low temperature preparation of the superconducting thin films by sputtering. N_2O gas can be dissociated easily and dissolves into reactive atomic oxygen and nitrogen molecule. We expected that this oxygen is more effective to reduce the process temperature. In this paper, we report the results of preparation of superconducting $Gd_1Ba_2Cu_3O_{7-x}$(GBCO) thin films by reactive sputtering using N_2O gas.

2. EXPERIMENTAL

GBCO thin films were prepared on MgO(100) single-crystal substrates by rf planar magnetron sputtering using a mixture of Ar and N_2O for sputtering gas. The ratio of N_2O to Ar was varied from 1:4 to 1:1. For investigation of effect of N_2O, we also curried out the experiment using Ar-O_2 gas mixture. Sputtering target was complex oxide of Gd-Ba-Cu with a 1:2:4.5 ratio. The sputtering conditions are listed in Table 1. The substrate temperature was determined by measuring the surface temperature of a reference MgO substrate on a stainless-steel holder using a two-wavelength infrared radiation thermometer. The deposition rate was about 4-6 nm/min, and sputtering time was 30 min. After the deposition, oxygen gas was subsequently introduced into the sputtering chamber and the substrate was quickly cooled down to room temperature.

The film composition was determined by electron-probe microanalysis(EPMA) and the distribution of each element of the film compounds was measured by secondary ion mass spectrometry(SIMS). The crystal structures were examined by x-ray diffraction and resistivities of the films were measured with a standard dc four-probe method. In order to study the plasma state of sputtering gas during deposition, we observed the optical emission spectra(OES) from the plasma between target and substrate.

Table I. Sputtering conditions.

Target	$Gd_1Ba_2Cu_{4.5}O_x$ (diam. 100 nm)
Substrate	MgO (100) single crystal
Sputtering gas	Ar/N_2O (1:1-4:1), Ar/O_2 (1:1-4:1)
Total pressure	0.4 Pa
Substrate temperature	520-630 ^{o}C
rf power	150 W
Growth rate	4-6 nm/min

3. RESULTS and DISCUSSION

A typical OES from plasma of Ar and N_2O is shown in Fig. 1 (a). The gas flow ratio of Ar to N_2O was 3:2 and the other sputtering conditions were fixed to those listed in Table 1. For comparison, the OES from that of Ar and O_2 is also shown Fig. 1 (b), whose ratio is 3:2. In comparison with these two OES data, the many sharp emission lines between 300 and 400 nm and the three broad band signals corresponding to N_2 or N_2^+ were observed in case of Ar and N_2O. 777 nm peak is the emission of OI. This peak intensity for Ar-N_2O mixture was smaller than that for Ar-O_2 mixture. The O_2^+ emission lines of N_2O were little observed. We found out that N_2O gas was dissociated and dissolved into OI, N_2 and N_2^+.

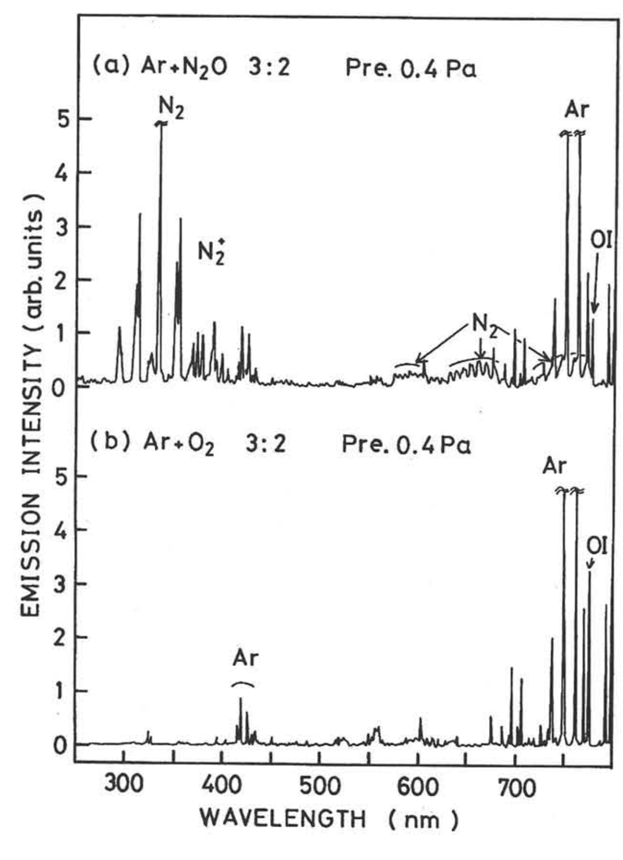

Fig. 1. Optical emission spectra of (a)Ar+N_2O and (b)Ar+O_2 plasma.

The film compositions prepared by Ar and N_2O depend on gas flow ratio of Ar to N_2O as shown in Fig. 2. The atomic ratios of Ba/Gd and Cu/Gd decreased as the N_2O gas pressure increased. But, the ratio of Cu/Ba did not changed. When the ratio of Ar to N_2O was 3:2, the film composition matched to nearly stoichiometory. In this figure, we show the result obtained by Ar and O_2. The difference between two kinds of sputtering gases was negligible nevertheless plasma emission intensity ratios of argon and oxygen were dissimilar between two sputtering gas mixtures.

The x-ray diffraction patterns of films depend on the substrate temperature. Fig. 3 shows these dependence of the peak intensities of (005), (200) and (103) reflections. The gas flow ratio of 3:2 was set for both Ar to N_2O and Ar to O_2. In case of Ar and N_2O, (00n) peaks were appeared at the substrate temperature up to 570 °C. Especially, for substrate temperature above 585 °C, no peaks were observed except (00n) peaks. In this temperature region, the c-axis of the films was preferentially oriented perpendicular to the (100)MgO substrate. At the substrate temperature below 570 °C, the other peaks appeared. The films had polycrystalline structure. At the temperature region from 520 to 570 °C, (200) peak appeared and (103) peak appeared below 545 °C. Thus the crystal structure of the films are very sensitive to substrate temperature. This tendency was similar to that in case of Ar and O_2. For Ar and O_2, however, (00n) peaks were not observed below 610 °C. We found out that the epitaxial temperature can be decreased when N_2O gas is used instead of O_2 as sputtering gas mixture.

Temperature dependence of resistivity for the films prepared by Ar:N_2O sputtering gas at substrate temperature of 610 °C is shown in Fig. 4. The onset temperature was 90 K, but the width of the transition was broad and zero resistance was achieved below 53 K. The critical current density of this films was about 1×10^5 A/cm^2 at 40 K.

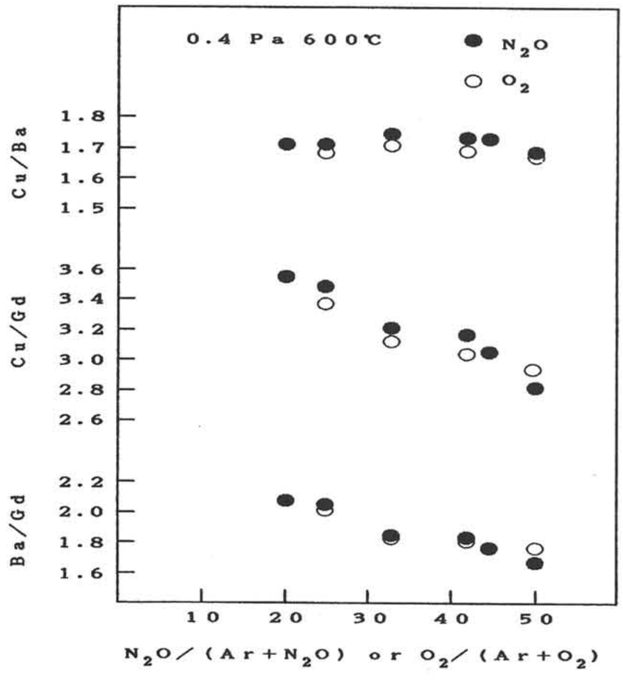

Fig. 2. Ba/Gd, Cu/Gd and Cu/Ba atomic ratios for various partial pressure.

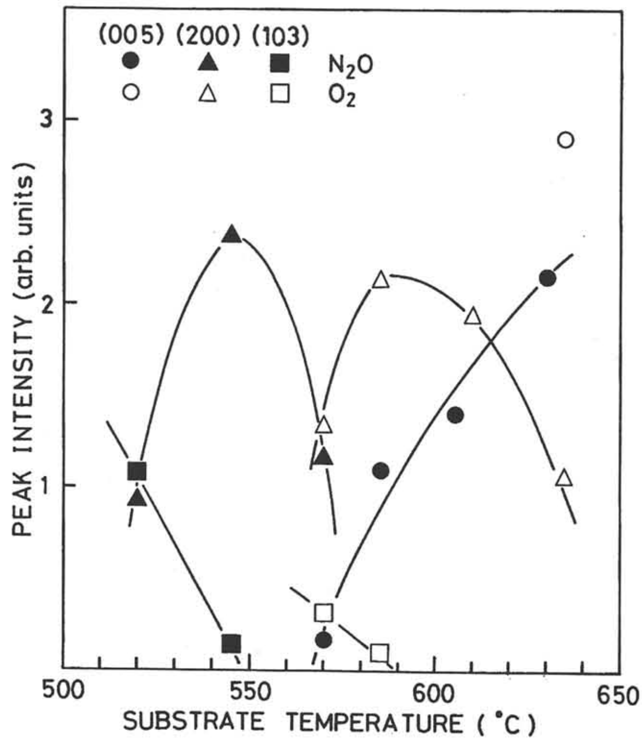

Fig. 3. Substrate temperature dependence of x-ray diffraction intensities of (005), (200) and (103).

As the Tc(R=0) was low in spite of high preferential orientation of the c-axis, we examined the contamination of the films by SIMS. Fig. 5 shows the depth profiles of Gd, Ba, Cu, O and N atoms. Because of weak sensitivity of N in SIMS measurement, we could obtain N spectra from the measurement of the signal for N+Cs. The depth distributions of Gd, Ba, Cu and O atoms were very uniform through the film. N atoms existed in the films though its concentration couldn't be estimated exactly. And N near the surface was rich comparing with the interface. We consider that the existence of N in the film is one of reasons for lowering the zero resistance temperature.

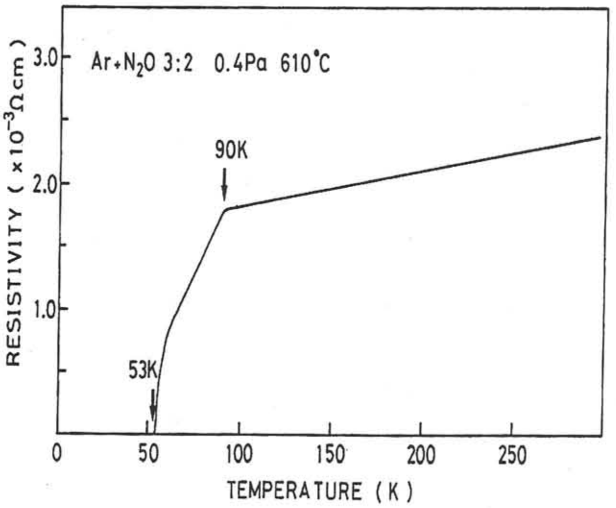

Fig. 4. Temperature dependence of resistivity for GBCO film prepared by Ar and N_2O.

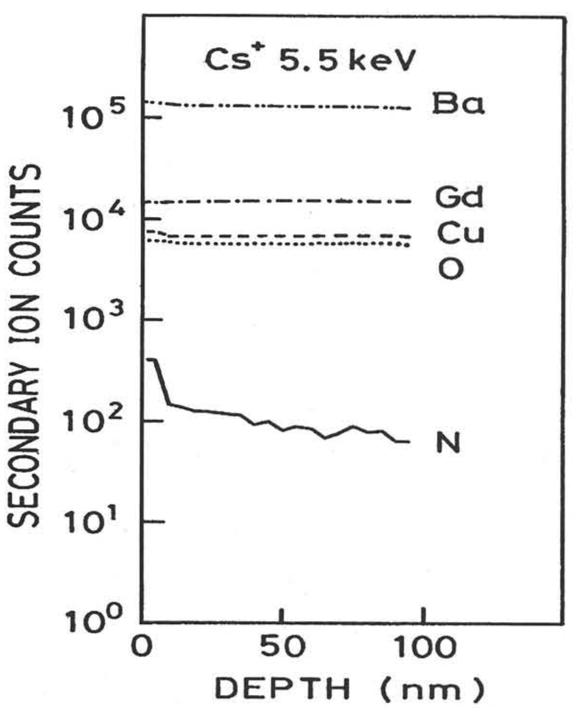

Fig. 5. Elemental depth profile measured by SIMS.

4. SUMMARY

We tried to prepare the high-Tc superconducting thin films by reactive sputtering using N_2O in order to reduce the process temperature. The epitaxial temperature was able to lower by use of N_2O in comparison with that of O_2. The film obtained by N_2O was superconducting with an onset temperature at 90 K, but exhibited a broad superconductive transition and zero resistance was realized below 53 K. It was found that N atoms existed in the films by SIMS. This existence is probably responsible for the poor superconductivity.

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