As-grown superconducting Mg-B films by single-target sputtering

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Abstract. In this work, preparation of as-grown superconducting films has been attempted on Si (111) and Si-N substrates by rf-magnetron sputtering in the atmosphere of Ar using a single target. The target of 5 mm thick Mg disc of 50mm in diameter on which 5×5×1 mm\(^3\) B chips were put, was used. In order to vary the composition of films, the number of B chips was adjusted. The substrate temperature \(T_d\) ranges from 230 to 250\(^\circ\)C and the Ar pressure \(P_{Ar}\) is around 2.00 Pa. According to the measurement of resistivity, superconducting transition is seen in films deposited from the target with 12 to 18 B chips. The \(T_c\) of films appreciably depends on the number of B chips. The highest \(T_c\) of ~24K was seen in films deposited from the target with 14 B chips. In films from the target with 12 B chips, the \(T_c\) is markedly reduced to 13 K. With increasing the number of B chips from 14 to 18, the maximum \(T_c\) gradually decreases to 19K. X-ray photoemission spectroscopy analysis of some films reveals that the ratio of B/Mg increases with the number of B chips.

1. Introduction

MgB\(_2\) has the potential use in both power and electronic device applications because of its high critical temperature. Especially in microelectronics high quality films with a longer coherence length than high-temperature oxide superconductors are required and much work on thin film synthesis has been done using techniques such as molecular-beam epitaxy [1], Laser ablation [2] and sputtering techniques [3]. Sputtering is one of the promising techniques for the production of practical thin films. A high-rate deposition system equipped with separate sputter guns of Mg and B targets [4] may be needed to prepare as-grown films, due to the high vapor pressure of Mg, the high sensitivity of Mg to oxygen, and the different sputtering yields of Mg and B. Though several workers tried to deposit films using a single target consisting of an Mg plate and B chips, most of as-grown films showed no superconductivity. Recently, we demonstrated as-grown superconducting films of MgB\(_2\) without post annealing treatments using a single target [5].

In this work, we have mainly investigated the effects of B chips of the target on the growth of MgB\(_2\). Relationships between transition temperature \(T_c\) of obtained films and deposition conditions.
such as the number of B chips, deposition temperature, substrate material and so on are given. Further, the systematic change of the B/Mg ratio with the number of B chips is shown for some films.

2. Experimental procedure

MgB$_2$ films were deposited on Si (111) and amorphous Si-N substrates in on-axis geometry by rf magnetron sputtering. A single target of Mg plate on which B chips were put, was used. The Mg plate is 50mmφ in diameter and 5 mm in thickness. The size of B chips is 5×5×1 mm$^3$. To obtain different films in composition, the number of B chips was basically adjusted and 12 to 18 B chips were symmetrically placed on the erosion area. Our sputtering apparatus has a liquid nitrogen vessel surrounding the substrate holder in order to suppress the incorporation of impurity gases such as O$_2$ and N$_2$ into films during deposition. The base pressure of the sputtering chamber is reduced down to 5.3×10$^{-5}$ Pa before the introduction of Ar into the chamber for sputtering. The argon pressure $P_a$ during sputtering was in the range of 1.33 to 4.0 Pa. The substrate temperature ranged from 180 to 300°C and was controlled to be constant. However, for some of the films the substrate temperature was varied during the course of deposition in order to make the composition change along the growth direction. After the pre-sputtering of 150 minutes, 100 to 1000 nm thick films were obtained by sputtering for 30 minutes.

The $T_c$ of films was measured by a standard four-probe resistance technique using a Si-diode thermometer. The film thickness was measured with a surface profiler (Dektak II). Crystal phases were analyzed by XRD (X-ray diffractometer) using Cu $K\alpha$ radiation. The composition ratios of B to Mg for some films are measured using X-ray photoemission spectroscopy (XPS).

3. Results and discussion

3.1. Preparation of films on Si(111) substrates

Previously, we reported the dependence of $T_c$ on substrate temperature $T_d$ and argon pressure $P_a$ for films of MgB$_2$ obtained using the present sputtering system under the conditions of 4 B chips with a size of 10×10×1 mm$^3$ and discharge power $P$=80 W. The optimum $T_d$ and $P_a$ are around 230°C and 2.0 Pa, respectively. Accordingly, B chips were cut into a small size and the dependence of the number of B chips on the $T_c$ was examined. Typical deposition conditions are illustrated in table 1. Here, the flow rate of Ar during sputtering ranges from 10 to 20 ccm. Figure 1 shows a typical single target where 18 B chips were symmetrically put on the Mg plate.

Table 1. Typical deposition conditions for MgB$_2$ films.

| Target                                      | 12 to 18 B chips(5×5×1 mm$^3$) on a 5 mm thick Mg plate of 50mmφ in diameter |
|---------------------------------------------|--------------------------------------------------------------------------------|
| Argon Pressure $P_a$ (Pa)                   | 2                                                                              |
| Target-Substrate Spacing (mm)               | 25                                                                             |
| Substrate Temperature $T_d$ (°C)            | 230                                                                            |
| Discharge Power $P$ (W)                     | 80                                                                             |
| Deposition Time (minute)                    | 30                                                                             |

Figure 1. Photograph of the present Mg-B target
Resistive transition curves of some of films deposited from the target with different numbers of B chips are given in figure 2. Here, depositions were carried out at applied rf power $P=80$W and $T_d=230^\circ$C. Although each film shows superconducting transition, its $T_c$ and normal-state resistivity $\rho_n$ are very different depending on the number of B chips. The film obtained from the target with 12 B chips exhibits resistive transition around 11 K and its $\rho_n$ is very low, $\sim 100 \, \mu\Omega\,\text{cm}$. With increasing the number of B chips to 14, the $T_c$ of obtained films appreciably increases to above 20K and the $\rho_n$ shows a marked increase. In the case of above 16 B chips, the $T_c$ is rather lowered. The relationship of $T_{c,\text{mid}}$ and $\rho_n$ of the films with the number of B chips is shown in figure 3. A film deposited at 20 B chips has high $\rho_n$ exceeding $\sim 3000 \, \mu\Omega\,\text{cm}$ and show no superconductivity. Clearly, the optimum number of B chips is around 14.

Figure 2. Resistivity vs. temperature curves.

Figure 3. Variation of $T_{c,\text{mid}}$ and $\rho_{40K}$ with the number of B chips. Here, $\rho_{40K}$ indicates the resistivity of films at 40K for $\rho_n$.

Figure 4. X-ray diffraction patterns of three films deposited from the target with 12, 14 and 16 B chips.
Figure 4 shows X-ray data on three representative films deposited at different numbers of B chips. In the film obtained at 12 B chips diffraction line peaks for Mg$_2$Si phase are observed. These peaks indicative of Mg$_2$Si are much reduced in films obtained at 14 and 16 B chips. Rather, there is a small line peak which may be connected with B phase. No line peaks for MgB$_2$ phase was seen in most of films. It is likely that the superconductivity of the present films is attributable to the growth of very fine grains of MgB$_2$ phase. According to our previous report, the Mg$_2$Si phase is observed in films deposited at $T_d$ between 190 and 230°C. The intensity of diffraction lines indicating the Mg$_2$Si phase has a decreasing tendency with increasing $T_d$. Namely, the amount of Mg in films decrease markedly with increasing $T_d$, because of higher vapor pressures of Mg at higher temperatures. The formation of Mg$_2$Si phase indicates that films obtained at 12 B chips have Mg-richer compositions. 14 B chips or higher may be required to grow the superconducting high-$T_c$ phase.

Figure 5 shows the XPS survey scan spectra for three films deposited from the target with 12, 16 and 18 B chips. The spectra were acquired after sputter cleaning for 5 min with Ar$^+$ ions of 3 keV. In the spectra, we observe distinct peaks from Mg, B, C and O. The atomic composition was obtained by the XPS semi-quantitative analysis with integrated intensities of these peaks. The surface contained carbon and oxygen decreased considerably after sputter cleaning for 5-10 minutes with Ar$^+$ ions of 3 keV. Surface precipitation of B atoms by preferential sputtering was notable after sputtering of above 30 minutes. In figure 6, the relative atomic ratios of B to Mg after sputter cleaning for 5 and 10 minutes are shown for the films with 12, 14, 16, 18 B chips. It is noticed that the B/Mg ratio is increased with the number of B chips. High-$T_c$ films deposited at 14 and 16 B chips show considerably Mg-richer, compositions, 1.5 -1.8.

3.2. Effects of substrate material and substrate temperature control
The Mg$_2$Si results from the reaction of Mg with Si substrate and may influence the growth of MgB$_2$ phase. In order to suppress the reaction of Mg with Si substrate, we have tested two methods. One is to prepare films on Si-N substrates at $T_d$ of 230 and 250°C. The other is to control substrate temperature during deposition. Namely, after initial deposition of 10 minutes at $T_d$ =280°C, 20 minutes deposition...
at $T_d=230^\circ \text{C}$ (Temp. Control 1) or 250$^\circ \text{C}$ (Temp. Control 2) follows. Usually at $T_d$ of 270 $^\circ \text{C}$ and higher, obtained films show very thin and have highly large volume fractions of B.

Figure 7 shows resistive transition curves of films deposited at 14 B chips. All of the films show transition about 21 K and exhibit about the same $T_c$ as films deposited on Si (111) substrate at constant $T_d$. However, the $\rho_n$ is highly reduced. Especially, by varying $T_d$ during deposition, films with small $\rho_n$ are obtained and the reaction with Si substrate seems to be suppressed. X-ray diffraction patterns of the two films are given in figure 8. X-ray diffraction line peaks indicative of the existence of the excessive Mg are observed and would be connected with XPS results suggesting Mg-richer compositions of high-$T_c$ films. It is probably that the reaction of Mg and Si (111) substrate is suppressed by a B layer which is initially formed by 10 minute deposition at 280$^\circ \text{C}$.

Figure 7. Resistivity vs. temperature curves for films deposited on Si-N substrates and deposited by varying $T_d$.

Figure 8. X-ray diffraction patterns of the two films deposited by varying $T_d$.

Figure 9. Relation between $T_{c,mid}$ and $\rho_{40K}$ for all films.
The relationship between $T_{c,\text{mid}}$ and $\rho_{40K}$ for all the films is given in figure 9. The $T_{c,\text{mid}}$ tends to increase with increasing $\rho_{40K}$ for films deposited on Si (111) and Si-N substrates. Around 1000 $\mu\Omega\cdot\text{cm}$ the $T_{c,\text{mid}}$ becomes maximum, 23K. In the case of films obtained by varying $T_d$ during sputtering, the dependence of $T_{c,\text{mid}}$ on $\rho_{40K}$ is somewhat different and higher values of $T_{c,\text{mid}}$ are seen even at low $\rho_{40K}$ of 10-100 $\mu\Omega\cdot\text{cm}$ where films on Si (111) and Si-N substrates show considerably lower $T_{c,\text{mid}}$. This result implies that films deposited on Si (111) substrates contain some products resulting from the reaction of Mg and Si. Although these products increase the resistivity of films, the maximum $T_c$ of films seems to be unchanged.

4. Summary
As-grown superconducting films on Si (111) and Si-N substrates by rf magnetron sputtering in an atmosphere of Ar from the single target consisting of an Mg plate and 12 to 18 B chips were prepared. The effects of the number of B chips on films were investigated. Further, the influence of substrate material and substrate temperature control on the growth of the high-$T_c$ phase was examined. The $T_c$ of films appreciably depends on the number of B chips. The highest $T_c$ of ~24K was seen in films deposited from the target with 14 B chips. X-ray photoemission spectroscopy analysis of films reveals that the ratio of B/Mg increases with the number of B chips and the present high-$T_c$ films have Mg-richer compositions. The reaction between Mg and Si for films on Si (111) substrates takes places and yields an increase of $\rho_n$. In order to get higher-$T_c$ films using our deposition system, the effects of residual impurity gas, the purity of target materials (Mg and B) and so on must be examined.

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