New deposition method of MgB$_2$ thin film with thermal evaporation of Mg and sputtering of B

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Abstract

We are now developing a new in situ deposition process for MgB$_2$ film as a candidate method to mass-produce MgB$_2$ thin film superconducting tape. In the new method, a MgB$_2$ film is deposited on a heated metal substrate by a hybrid deposition method, which consists of thermal evaporation of magnesium and sputtering of boron. By using the hybrid deposition method, the substrate temperature can raise from 250 to 350 $^\circ$C, while its fluctuation is kept less than 1 $^\circ$C, which will improve the quality and reproducibility of MgB$_2$ film in mass production. The $I_c$ of MgB$_2$ film deposited by the hybrid deposition method at 20 K and self-field was more than 30,000 A mm$^{-2}$, which was better than the results reported by the two-step in situ process using DC sputtering and 830 $^\circ$C high-temperature post annealing [1] or by the as-grown deposition using sputtering targets of Mg and B [2]. Although we obtained better $I_c$ than other deposition methods that use sputtering process, the $I_c$ is still lower than the value we obtained by using a co-evaporation method with electron beam (EB). We investigated the film structure and $I_c$–$B$–$T$ properties of the film made by the hybrid deposition method and compared them with those of the film made by co-evaporation. From the analysis results, we think the reasons for the lower $I_c$ are the larger amount of heterogeneous phases such as magnesium oxides in the film and the amorphous B phase under the MgB$_2$. We expect to improve the the crystal qualities and superconductivities of the MgB$_2$ film deposited by the new method by removing impurities in Ar gas during sputtering and thinning the B amorphous phase by increasing the Mg deposition rate in the initial stage of deposition.

1. Introduction

Magnesium diboride (MgB$_2$) is a promising material for liquid-helium-free superconducting applications, such as magnetic resonance imaging (MRI) scanners [3, 4], wind turbines [5], energy storages [6], and aircraft components [7], operating at 10–20 K by conduction cooling or liquid-hydrogen cooling. Applied as superconductor wire, MgB$_2$ has advantages such as low cost, low weight, a simple crystal structure, and chemical composition, low anisotropy of superconductivity [8, 9], and long coherence length [10, 11].

MgB$_2$ can be produced by various techniques, but the most common is powder-in-tube (PIT). In PIT, MgB$_2$ superconducting wires are produced by filling a high-melting-point metal tube with MgB$_2$ powder or a mixed powder of Mg and B, drawing the tube into a wire, and heating it to synthesize a MgB$_2$ core in the wire. A MgB$_2$ superconducting wire produced by PIT has already been commercialized, and the number of superconducting applications using MgB$_2$ has dramatically increased in recent years [12].

Another approach to produce MgB$_2$ is using thin-film deposition. MgB$_2$ films deposited by thin-film processes (e.g., hybrid physical–chemical vapor deposition (HPCVD) [13], molecular beam epitaxy (MBE) [14], and electron beam (EB) evaporation [15, 16]) have high critical current density $I_c$ ($>$10$^6$ A mm$^{-2}$ at 4.2 K and
self-field). We also have developed 10 μm-thick MgB2 films on copper substrates (plates and tapes) by using co-evaporation of B and Mg, which uses EB evaporation for B and thermal evaporation from the effusion cell for Mg, and obtained high \( J_c \), which suggest that MgB2 film is a promising candidate for next-generation superconducting tape conductors and coils [17, 18].

The next step in our research is to make the MgB2 film on a long tape. To do this, we have to establish a deposition process suitable for a reel-to-reel machine. Figure 1 shows a schematic view of the reel-to-reel machine used to make a long MgB2 thin film superconducting tape. In this machine, a long MgB2 thin film superconducting tape is made by depositing Mg and B on the heated long tape substrate passed between reels while taking up the substrate. We have to arrange several Mg and B evaporation sources in line or in a matrix and precisely control their deposition conditions (e.g., deposition rate, thickness uniformity, and substrate temperature) for a long time and over a wide area to completely deposit MgB2 film on the tape. Especially, the quality of superconductivities of MgB2 thin film strongly depends on the substrate temperature. Therefore, the substrate temperature must be kept stable during deposition to obtain good reproducibility in mass production.

However, controlling the substrate temperature in the EB deposition of B for a long duration in mass production is not easy because high-temperature radiant heat from a high melting-point-material B evaporation source easily fluctuates due to the melting condition and residual quantity of B in the source. In addition, EB is not suitable for mass production due to the relatively poor stability of the B deposition rate.

Among the several thin-film deposition processes, the sputtering method is one of the most suitable for mass production because it has lower radiant heat to the substrate than EB and its deposition rate has excellent stability and high uniformity in a large deposition area. Previous studies have reported MgB2 films deposited by the two-step in situ process that uses DC sputtering and 830 °C high-temperature post annealing [1] or by the as-grown deposition that uses sputtering targets of Mg and B [2]. However, the two-step in situ process must be carried out post-annealing in a sealed box filled with saturated Mg vapor and thus is not suitable for manufacturing a long wire or tape in the reel-to-reel system. On the other hand, the as-grown sputtering process is suitable for manufacturing a long wire in reel-to-reel system but needs a very high Mg deposition rate. The Mg particle from the sputtering source has difficulty adsorbing on the heated substrate and re-evaporates easily, because it has higher kinetic energy (10 ~ 100 eV) than thermal evaporation and high vapor pressure.

To overcome these drawbacks, we have developed a new deposition method for MgB2 film by replacing the EB source of boron with a B sputtering target while keeping the thermal evaporation of Mg as it was. The planer structure of the B sputtering target easily offers us a stable and uniform deposition rate of B in a large deposition area in the reel-to-reel system. Also, because the B sputtering target is cooled by water and the input RF power to the Ar plasma is constant during the deposition, the radiant heat from the B target is stable, and thus fluctuation of the substrate temperature is negligible. The kinetic energy of Mg particles thermally evaporated from a cell with low kinetic energy (0.1 ~ 0.2 eV) and thus adsorb on the heated substrate more easily than the sputtered Mg particles.

2. Experimental methods

A schematic view of the co-evaporation system we used in our previous work [17] is shown in figure 2. The deposition chamber was evacuated to less than \( 5 \times 10^{-6} \) Pa by a turbo molecular pump (TMP) and cryo-pump.
The copper substrates were mounted on the substrate holder, which was set just in front of a heater heated up to 250 °C. Boron was evaporated from a hearth liner of the EB evaporation system, while magnesium was thermally evaporated from an effusion cell. To test the new deposition method, we remodeled the deposition chamber by replacing the EB hearth liner as the B source with a sputtering target while keeping the effusion cell of Mg as it was. A schematic view of the new hybrid deposition system is shown in figure 3. The sputtering target had a diameter of 50.8 mm and discharge power of 200 W. The Ar gas pressure during deposition was 0.4 Pa. The radiant heat from the B sputtering target is lower and more stable than that from the EB hearth liner of B. Moreover, the deposition rate was stable and uniform in the larger deposition area.
Table 1. Deposition conditions of MgB$_2$ films.

| Sample name | Substrate temperature (°C) | Mg deposition rate [Å s$^{-1}$] | B deposition rate [Å s$^{-1}$] | Post-annealed temperature (°C) | Post-annealed time [h] |
|-------------|---------------------------|---------------------------------|-------------------------------|-------------------------------|----------------------|
| 360–6       | 360                       | 6                               | 1.5                           | 360                           | 1                    |
| 360–8       | 360                       | 8                               | 1.5                           | 360                           | 1                    |
| 390–8       | 390                       | 8                               | 1.5                           | 360                           | 1                    |
| 390–10      | 390                       | 10                              | 1.5                           | 360                           | 1                    |
| 420–8       | 420                       | 8                               | 1.5                           | 360                           | 1                    |
| 420–10      | 420                       | 10                              | 1.5                           | 360                           | 1                    |

To obtain MgB$_2$ film, the Mg and B particles need to adsorb on the substrate for a while to react because the reaction speed of MgB$_2$ is relatively slow. The kinetic energy of particles from a sputtering source is higher (10 $\sim$ 100 eV) than that of particles from the effusion cell (0.1 $\sim$ 0.2 eV). In addition, Mg is a material that has high vapor pressure. Thus, the Mg particles from the sputtering target hardly adsorb on the heated substrate and more easily desorb from the substrate than the particles from the effusion cell. For these reasons, we continue to use the effusion cell for Mg evaporation in the new method.

By using the new hybrid deposition system that consists of B sputtering and Mg thermal evaporation, we could raise the substrate temperature to promote the reaction of Mg and B. We raised the substrate temperature from 250 °C to 360 °C $\sim$ 420 °C for increasing the reaction speed of Mg and B on the substrate. The deposition conditions of MgB$_2$ films deposited by the new hybrid deposition method are shown in table 1. The substrate temperature was changed from 360 to 420 °C, and the Mg deposition rate was changed from 6 to 10 Å s$^{-1}$. The B deposition rate was 1.5 Å s$^{-1}$. The samples were post-annealed at 360 °C for 1 h. To prevent a reaction between the Cu substrate and Mg particles at a substrate temperature higher than 300 °C[19], we deposited a 200-nm-thick Ti barrier film on the Cu substrate. The Ti barrier film was deposited by another sputtering machine.

The deposited films were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES), x-ray Diffraction (XRD), scanning transmission electron microscope (STEM) or TEM, and energy-dispersive x-ray spectroscopy (STEM-EDX) and electron diffraction (ED). ICP-AES was used to check Mg content of MgB$_2$ film. Cross-sectional SEM or STEM was used to determine the thickness and observe the micro-structure of the film. Cross-sectional STEM-EDX was used to investigate element distribution, and ED was used to check the crystal structure of the film. The magnetic susceptibility of the film was measured with a superconducting quantum interference device (SQUID) flux meter to determine the critical temperature $T_c$.

The critical current density $J_c$ was determined by four-probe resistance measurement. The current was fed by a solder bonded directly on the MgB$_2$ film. The $J_c$–$B$–$T$ properties of the samples were measured in a temperature range of 5 to 20 K and in an external-magnetic-field range of 0 to 10 T. The sample was cooled by a jet of helium gas (evaporated from liquid He), and its temperature was controlled by a heater attached behind the sample holder. The voltage criterion used for determining $J_c$ was $1 \mu$V cm$^{-1}$ at $J_c > 10^4$ A mm$^{-2}$. At $J_c < 10^4$ A mm$^{-2}$, $J_c$ at the inflection point of the $J$–$V$ curve was determined in order to avoid overestimating $J_c$ due to low shunt resistance of the copper substrate.

3. Results

Figure 4 shows the fluctuations of substrate temperature during deposition in the previous co-evaporation system using EB and the new hybrid deposition system using sputtering. The fluctuations of substrate temperatures in the co-evaporation system and new hybrid deposition system were 9 and 1 °C, respectively. The superconductivities of MgB$_2$ film strongly depend on the substrate temperature, so the substrate temperature needs to be kept stable during deposition to obtain good reproducibility in mass production. Although the allowable substrate temperature fluctuation that can maintain the superconducting properties of MgB$_2$ film has not been clarified, the $T_c$ of MgB$_2$ film changes by about 1 K when the substrate temperature changes by about 10 °C[20]. Therefore, it is highly possible that the substrate temperature fluctuation in the new hybrid deposition system has almost no effect on the superconducting properties. Thus, the fluctuations of substrate temperatures in the new hybrid deposition method seem to be small enough to use it for mass production.

To investigate proper deposition conditions, we made several films by changing the substrate temperature from 360 to 420 °C, and Mg deposition from 6 to 10 Å s$^{-1}$. The composition ratios (B/Mg) of MgB$_2$ films measured by ICP-AES are shown in figure 5. The caption of a sample number means (substrate temperature at degree centigrade–deposition rate at Å s$^{-1}$). As shown in figure 5, the composition ratios of samples (360–6), (390–8), and (420–10) were 1.98, 2.02, and 2.05, respectively, which are close to the stoichiometric composition of MgB$_2$. 

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The $T_c$ of samples $\langle 360-6 \rangle$, $\langle 390-8 \rangle$, and $\langle 420-10 \rangle$ are shown in table 2. The $T_c$ of sample $\langle 360-6 \rangle$ was 23 K. However, samples $\langle 390-8 \rangle$ and $\langle 420-10 \rangle$ did not show superconductivity.

The XRD spectrum of the sample $\langle 360-6 \rangle$, $\langle 390-8 \rangle$ and $\langle 420-10 \rangle$ are shown in figure 6. As shown in figure 6, the MgB$_2$ peak was not found in the spectra of all the samples, and their crystal qualities were low. In addition, the MgCu$_2$ and CuTi peaks were found in the XRD spectrum of the samples $\langle 390-8 \rangle$ and $\langle 420-10 \rangle$.

$J_c$–$B$–$T$ properties of the $\langle 360-6 \rangle$ MgB$_2$ films when the magnetic field was applied (i) perpendicular to the film (B $\perp$ film) and (ii) parallel to the film (B $\parallel$ film) are shown in figure 7. In cases (i) and (ii), the $J_c$ at 20 K and self-field (0 T) was 31,000 A mm$^{-2}$. The $J_c$ at 20 K and self-field was 4,000 A mm$^{-2}$ for the film deposited by the two-step in situ process [1] and 9,000 A mm$^{-2}$ for the film deposited by the as-grown sputtering process using Mg and B targets[2]. Thus, the MgB$_2$ film deposited by the new deposition method has $J_c$ at 20 K and self-field superior to those of the MgB$_2$ film deposited by the two-step in situ process or as-grown sputtering process.

Next, we analyzed the film structure of sample $\langle 360-6 \rangle$, cross-sectional BF-STEM images of which are shown in figure 8. The sample consists of an amorphous phase on a Ti barrier film and a columnar crystal structure phase at the top. The thicknesses of the Ti barrier film, amorphous phase, and columnar crystal structure phase were 0.20, 0.18, and 0.47 $\mu$m, respectively.

### Table 2. $T_c$ of MgB$_2$ films deposited by the new hybrid deposition method.

| $T_c$ [K] | $\langle 360-6 \rangle$ | $\langle 390-8 \rangle$ | $\langle 420-10 \rangle$ |
|----------|-------------------|----------------|------------------|
|          | 23                | —              | —                |

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**Figure 4.** Comparison of fluctuation of substrate temperature during deposition by EB evaporation and new hybrid deposition method.

**Figure 5.** Composition ratios (B/Mg) of MgB$_2$ films measured by ICP-AES.
Cross-sectional STEM-EDX images of the sample (360–6) are shown in figure 9. At the bottom of the Ti barrier film, the copper diffused into the Ti film but not onto the Ti film. Thus, the 200-nm-thick Ti barrier film prevented the reaction between Mg and Cu at 360 °C. The samples (390–8) and (420–10) did not show superconductivity. In addition, the MgCu₂ and CuTi peaks were found in the XRD spectrum of the samples (390–8) and (420–10) as shown figure 6. We think the cause was a heterogeneous phase such as CuMg₂ forming.
due to the reaction between Mg and Cu, which reacted with the Ti barrier film and diffused from the Cu substrate onto the Ti film when the substrate temperatures were 390 and 420 °C, which are higher than that of the sample (360–6) (360 °C). It has been reported that Cu starts to diffuse from the Cu substrate onto the 1-μm-thick Ti film surface when substrate temperature is 430 °C [21]. The substrate temperatures of samples (390–8) and (420–10) were 390 and 420 °C, respectively, slightly lower than 430 °C, but the Ti barrier film of these samples was one-fifth as think as the Ti film in the previous report (0.20 versus 1.0 μm). Thus, Cu was likely to diffuse from the Cu substrate onto the Ti barrier film surface. As for the MgB2 films deposited on Cu substrates, it has been reported that MgCu2 peaks appeared in their XRD spectrum and their superconducting properties were degraded when their substrate temperature were raised [22]. In the report, one of the reasons for the deterioration of superconducting properties of the MgB2 films was the increase of MgCu2 impurity phases due to temperature rise of substrate, and we believe the reason that samples (390–8) and (420–10) did not show superconductivity was the same. The oxygen exists near the top of Ti barrier film because the film was deposited at the other sputtering machine in advance and surface oxidation occurred before the MgB2 deposition. From figures 9(2) and (3), the magnesium and boron are evenly distributed in the film, but the phases with higher boron and less magnesium concentration exist on the Ti barrier film, and the positions of these phases correspond to the positions of the amorphous phase in figure 8. The amorphous phase is richer in B than stoichiometric MgB2. In the initial stage of the MgB2 deposition, Mg particles tend to re-evaporate from the heated substrate before reacting with B, and B particles sputtered from the target by argon ions preferentially adhered to the Ti barrier film. Moreover, the B particles formed the amorphous B phase. Columnar crystal structure phases with higher Mg concentration than the amorphous phase exist on the amorphous phase. Figure 10 shows an electron beam diffraction pattern from the phase. It coincides well with the calculated electron diffraction pattern from MgB2 crystal. Therefore, the columnar crystal structure phases are the columnar MgB2 crystals. In addition, the columnar phases with higher oxygen and lower magnesium

![Figure 9](image-url)
concentration exist at the grain boundaries of the columnar MgB₂ crystals shown in figures 9(3) and (4). Moreover, the positions of these phases are consistent as shown in figures 9(3) and (6), which show the elemental distribution of Mg and O. Thus, the columnar phases at the grain boundaries of the columnar MgB₂ crystals are the columnar magnesium oxides. The columnar MgB₂ crystals and magnesium oxides become larger closer to the film surface. The film has the columnar grain boundaries with high oxygen concentration, which are similar to the structure of films deposited by the co-evaporation system under relatively higher residual moisture vapor pressure [18].

To investigate the film structure in more detail, we made samples cut in parallel with the substrate by ion milling. The positions of plane sampling, (A), (B), and (C), are shown in figure 11. Figure 12 shows the planar BF-TEM images of the samples taken from locations shown in figure 11. The positions of (A), (B), and (C) are near the amorphous boron phase surface, directly above the amorphous boron phase, and near the MgB₂ film surface, respectively. In (A), no crystals are observed, and black spots are observed in the amorphous boron phase that are considered to be cores of crystallization of MgB₂. In (B), MgB₂ crystals appear just above the...
amorphous boron phase and magnesium oxides surround them. The MgB$_2$ crystals and magnesium oxides become larger in (C) where the sampling position becomes closer to the film surface. This is consistent with figure 9. We think the mechanism for the formation of columnar magnesium oxides is as follows. First, the magnesium oxides were formed around the nuclei of MgB$_2$ crystals formed just above the boron amorphous phase. After that, the MgB$_2$ crystals grew into a columnar shape along the c axis, and magnesium oxides also grew into a cylindrical shape due to the surrounding MgB$_2$ columnar structure. We previously reported a similar phenomenon with the MgB$_2$ film deposited in the chamber with residual moisture [18]. In the MgB$_2$ film deposited in the chamber with residual moisture, MgB$_2$ crystals also appear just above the substrate and surrounding magnesium oxides, and the MgB$_2$ crystals and magnesium oxides become larger as the sampling position becomes closer to the film surface. Therefore, we think the mechanism for the formation of MgB$_2$ film in the new hybrid deposition method using sputtering of B and thermal evaporation of Mg is basically the same as that in the co-evaporation of B and Mg.

4. Discussion

Although we obtained better $J_c$ at 20 K and self-field than other deposition methods that use the sputtering process, the $J_c$ is still lower than the value we had obtained by using the co-evaporation method with EB and the effusion cell. Figure 13 compares $J_c$–B–T properties deposited by (a) co-evaporation and (b) new hybrid deposition method when the magnetic field was applied (i) perpendicular to the film ($B \perp$ film) and (ii) parallel to the film ($B \parallel$ film).

Figure 12. Planar BF-TEM images of the samples taken from locations shown in figure 11. (A) near the amorphous boron phase surface, (B) directly above the amorphous boron phase, and (C) near MgB$_2$ film surface.

Figure 13. $J_c$–B–T properties of the MgB$_2$ films deposited by (a) co-evaporation and (b) new hybrid deposition method when the magnetic field was applied (i) perpendicular to the film ($B \perp$ film) and (ii) parallel to the film ($B \parallel$ film).
(a) co-evaporation at 20 K and 5 T but only 380 A mm\(^{-2}\) for the MgB\(_2\) film deposited by (b) the new hybrid deposition method at 20 K and 1 T.

As for the MgB\(_2\) film deposited by (a) co-evaporation, the slope of the \(J_c-B\) curves are steeper in case (i) than in case (ii). On the other hand, the MgB\(_2\) film deposited by (b) the new hybrid deposition method has steeper \(J_c-B\) curves in case (ii) than in case (i).

To discuss the differences of these \(J_c-B-T\) properties, \(B_{irr}\) (irreversible magnetic field) values of the film were compared. \(J_c-B-T\) curves around \(I_c=0\) of the MgB\(_2\) film in cases (i) [perpendicular to the film] and (ii) [parallel to the film] are shown in figure 14. \(B_{irr}\) can be determined from the magnetic field at \(I_c=0\). The \(J_c\) of the MgB\(_2\) film deposited by (a) co-evaporation usually becomes larger in case (ii) \(B_{//}\) than in case (i) \(B_{\perp}\) as the magnetic field becomes larger [17]. This depends on the lower \(B_{irr}\) at \(B_{\perp}\) than \(B_{irr}\) at \(B_{//}\). This anisotropy comes from the anisotropy of \(B_{c2}\) (upper critical magnetic field) of the MgB\(_2\) crystal, which is higher in the \(ab\)-plane \(\left(\text{B}_{//}\right)\) and lower along the c-axis \(\left(\text{B}_{\perp}\right)\) [23, 24].

On the other hand, \(B_{irr}\) of the MgB\(_2\) film deposited by (b) the new hybrid deposition method becomes larger in case (i) \(B_{\perp}\) than in case (ii) \(B_{//}\). Cross-sectional STEM-EDX images near the surface of the MgB\(_2\) films deposited by (a) co-evaporation is shown in figure 15. In figure 15, magnesium and boron are evenly distributed in the film. In addition, since this analysis was carried out one year after the film was formed, the film surface was oxidized, and oxygen was concentrated on the film surface. However, oxygen in the MgB\(_2\) films deposited by (a) co-evaporation was not detected under the surface and the film didn’t have cylindrical magnesium oxides surrounding the MgB\(_2\) columnar structure phase. We believe the differences in \(B_{irr}\) are due to the larger amount of cylindrical magnesium oxides which the film deposited by (b) the new hybrid deposition method had. A schematic diagram of the MgB\(_2\) film deposited by (b) the new hybrid deposition method is shown in figure 16. In case (i) \(\text{B}_{\perp}\), although the flow of superconducting current in the film is disturbed by the cylindrical magnesium oxides, the cylindrical magnesium oxides act as effective pinning centers and improve \(B_{irr}\) and \(J_c\) at high magnetic fields by making the \(J_c-B\) curves less steep. In case (ii) \(\text{B}_{//}\), cylindrical magnesium oxides did not act as effective pinning centers. In addition, the flow of superconducting current in the film is disturbed by the cylindrical magnesium oxides.

We think the reason for lower \(T_c\) and \(J_c\) of the MgB\(_2\) film deposited by the new deposition method is the larger amount of heterogeneous phases such as magnesium oxides as shown in figures 9 and 12. The specifications of MgB\(_2\) films are shown in table 3. As shown in table 3, the basal partial pressures of \(\text{O}_2\) and \(\text{H}_2\) of (b) the new hybrid deposition method were equivalent to that of (a) co-evaporation, and the film deposited by (a) co-evaporation didn’t have magnesium oxides. Since magnesium and oxygen react even at a low temperature of 200 °C [25], we believe the substrate temperature of (b) the new hybrid deposition method higher than that of (a) co-evaporation was not related to the forming magnesium oxides in the film. So, we think the magnesium oxides between columnar MgB\(_2\) crystals were formed by the reaction of Mg with oxygen or moisture in Ar gas. Various measures are taken in the sputtering process to remove impurities from the process gas and deposition chamber. For example, highly pure Ar gas is used for sputtering of magnetic thin film on hard disk drives to prevent heterogeneous phase formation. We believe the crystal qualities and superconductivities of the MgB\(_2\) film deposited by the new method will be improved if more impurities in Ar gas are removed.

![Diagram](image_url)
Figure 15. Cross-sectional EDX images near the surface of the MgB$_2$ film deposited by (a) co-evaporation: (1) ADF-STEM image and EDX images of (2) B, (3) Mg, and (4) O.

Figure 16. Schematic diagram of the MgB$_2$ film deposited by new method: conditions (i) $B \perp$ film and (ii) $B \parallel$ film.
Table 3. Specifications of MgB₂ films.

| Condition                        | (a) Co-evaporation | (b) New hybrid deposition method |
|----------------------------------|--------------------|----------------------------------|
| Substrate temperature [°C]       | 250                | 360                              |
| Basal vacuum degree [Pa]         | 3.4 × 10⁻⁵         | 3.2 × 10⁻⁵                       |
| Basal partial pressure of O₂ [Pa]| 6.03 × 10⁻⁷        | 5.92 × 10⁻⁷                      |
| Basal partial pressure of H₂O [Pa]| 5.91 × 10⁻⁶        | 5.74 × 10⁻⁶                      |

Another reason for lower \( J_c \) is the boron amorphous phase. As shown in figures 9 and 10, the MgB₂ film deposited by the new hybrid method has a relatively thick boron amorphous phase on the Ti barrier film. The MgB₂ film deposited by co-evaporation with EB did not have the boron amorphous phase [17, 18]. The re-evaporation rate of Mg particles from the substrate surface rapidly increases and the stay time of the Mg particles on the substrate rapidly decreases as the substrate temperature become higher because Mg has high vapor pressure. Therefore, in the initial stage of deposition, B particles had difficulty reacting with Mg particles in the new hybrid deposition method because the stay times of B and Mg particles on the substrate were shorter than that in co-evaporation. The B particles that did not react with Mg particles adhered to the substrate because the vapor pressure is low. On the other hand, the Mg particles that did not react with B particles easily re-evaporated from the substrate due to the high vapor pressure. We believe the B amorphous phase was formed in this way. Thus, the \( J_c \) of the film deposited by new method will be improved by increasing the Mg deposition rate in the initial stage of deposition and thinning the B amorphous phase.

5. Conclusion

MgB₂ films were deposited on a Cu substrate by a new hybrid deposition method. The fluctuations of substrate temperatures in the new method were 1/9 of that in a co-evaporation process using electron beam (EB) (1 versus 9 °C). Thus, the fluctuations in the new method seem to be small enough to obtain good reproducibility in mass production.

The \( J_c \) of the MgB₂ films deposited by the new hybrid deposition method when the magnetic field was applied (i) [perpendicular to the film (B⊥film)] and (ii) [parallel to the film (B∥film)] were 31,000 A mm⁻² at 20 K and self-field (0 T). These \( J_c \) are better than the results obtained by the two-step in situ process using DC sputtering and 830 °C high-temperature post annealing [1] or by the as-grown deposition using sputtering targets of Mg and B [2].

Although we obtained better \( J_c \) at 20 K and self-field than other deposition methods that use the sputtering process, the \( J_c \) is still lower than the value we had obtained by using a co-evaporation method with EB. We think the reasons for lower \( T_c \) and \( J_c \) of the MgB₂ film deposited by the new hybrid deposition method are the large amount of heterogeneous phases such as magnesium oxides in the film and the amorphous B phase under the MgB₂. We believe the crystal qualities and superconductivities of the MgB₂ film deposited by the new hybrid deposition method will be improved by removing impurities in Ar gas and thinning the B amorphous phase by increasing the Mg deposition rate in the initial stage of deposition.

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