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Increase in the in-field critical current density of MgB$_2$ thin films by high-temperature post-annealing

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We propose a novel fabrication technique based on the formation of a Nb protective layer on a MgB$_2$ thin film and high-temperature post-annealing to increase the critical current density ($J_c$) of MgB$_2$ films under an external magnetic field. Analyses of the crystal structure and the composition of the processed MgB$_2$ films confirmed the suppression of the evaporation and oxidation of Mg by high-temperature annealing above 550 °C. The MgB$_2$ film annealed at 650 °C exhibited a $J_c$ of 1.62 MA cm$^{-2}$ under 5 T, which is the highest reported value for MgB$_2$ films, wires, and bulk samples to date.© 2021 The Japan Society of Applied Physics

The critical temperature ($T_c$) of magnesium diboride (MgB$_2$) is 39 K, higher than that of conventional metallic superconductors, such as Nb–Ti and Nb$_3$Sn. This enables the liquid-helium-free operation of MgB$_2$ at 20 K with a suitable cryocooler or liquid-hydrogen cooling. There have been extensive studies to optimize the characteristics of MgB$_2$ as an alternative to conventional metallic superconductors for applications in liquid-helium-free and low-cost superconducting wires. An important potential application of MgB$_2$ is in superconducting magnets for magnetic resonance imaging systems that are widely used for noninvasive biological imaging.

Powder-in-tube (PIT) techniques, involving in situ, ex situ, and internal magnesium diffusion processes, have been extensively explored for the convenient fabrication of superconducting wires. However, PIT techniques are based on powder sintering that results in not only a low filling factor, but also the formation of MgO between adjacent MgB$_2$ grains, which hinders the flow of the superconducting current. Consequently, the critical current density ($J_c$) of MgB$_2$ wires at 20 K is lower than that of Nb–Ti wires at 4.2 K. The preparation of MgB$_2$ has been explored using thin-film deposition techniques under vacuum, such as pulsed laser deposition, molecular beam epitaxy, electron beam evaporation (EBE), hybrid physical-chemical vapor deposition (HPCVD), radio frequency magnetron sputtering, and reactive evaporation. The synthesis of MgB$_2$ under vacuum results in a high relative density and suppresses the oxidation of Mg; thus, there is an increase in the superconductivity. The $J_c$ of MgB$_2$ thin films is generally more than ten times higher than that of PIT-processed wires in practice. HPCVD can be utilized to fabricate high-quality MgB$_2$ films that exhibit a self-field $J_c$ of approximately 100 MA cm$^{-2}$ at 20 K. However, the $J_c$ of these films decreases drastically to approximately 0.5 MA cm$^{-2}$, which is similar to that of PIT-processed MgB$_2$ wires under a magnetic field of 1.5 T. It is necessary to optimize the $J_c$ characteristics of MgB$_2$ films under magnetic fields at 20 K to facilitate large-scale engineering applications.

In one of our previous studies, we demonstrated the effects of in situ annealing under ultrahigh vacuum (<4 × 10$^{-7}$ Pa) on MgB$_2$ thin films that were grown by EBE at a low substrate temperature of 280 °C. The film that was annealed at 550 °C for 100 h exhibited a $T_c$ of 36.7 K and an in-field $J_c$ of 0.64 MA cm$^{-2}$ at 20 K under 5 T. The $T_c$ of the film was comparable to that of PIT-processed MgB$_2$ wires. However, the in-field $J_c$ of the film was several times higher than that of as-grown MgB$_2$ films and several tens of times higher than that of PIT-processed MgB$_2$ wires. These results suggested that high-temperature annealing above 550 °C can increase the in-field $J_c$ of MgB$_2$ thin films. However, high-temperature annealing also promotes the diffusion, evaporation, and oxidation of Mg in MgB$_2$, thereby decreasing $T_c$ and $J_c$.

It is considered that the fabrication of a suitable protective layer on the MgB$_2$ film can effectively prevent the degradation of this film during high-temperature annealing. The protective layer must not react with MgB$_2$ during post-annealing. It should also possess a high conductivity in the low-temperature range at which the MgB$_2$ wire is operated, so that a current flows into the copper stabilization layer, which passes through the protective layer, during the quenching of the MgB$_2$ wire. This study demonstrates the use of Nb as a protective layer during the high-temperature annealing of MgB$_2$ at 650 °C. Nb is commonly used as sheath material for PIT-processed MgB$_2$ wires, and it has been reported that Nb sheaths hardly degrade the superconductivity of MgB$_2$ at annealing temperatures below 700 °C. The results showed that the Nb protective layer facilitated the post-annealing of MgB$_2$ thin films at 650 °C. This resulted in the optimization of the $J_c$–B characteristics of the MgB$_2$ thin films, and the annealed film exhibited a high $J_c$ of 1.62 MA cm$^{-2}$ at 20 K under 5 T.

The MgB$_2$ thin film was fabricated on a single-crystalline Si substrate (20 mm × 20 mm × 0.5 mm) by EBE. The base pressure of the EBE chamber was less than 6.2 × 10$^{-6}$ Pa. The substrate was heated at 270 °C using a halogen lamp heater during the deposition in the EBE chamber. The raw materials for the fabrication of the MgB$_2$ thin films were a...
block of Mg (99.9%) and granular B (99.5%). The flux rates of Mg and B were independently controlled using two quartz crystal monitors, and the deposition rate of MgB$_2$ was 0.6 nm s$^{-1}$. The chemical composition was quantitatively determined by inductively coupled plasma-optical emission spectrometry. The crystalline phases in the films were determined using $\theta$–2$\theta$ X-ray diffraction (XRD). The measurements of $J_c$ (at 20 K under various external magnetic fields up to 6 T) and $T_c$ were performed by a four-probe method using a physical property measurement system (Quantum Design, Inc., California, USA). The applied magnetic field was perpendicular to the film surfaces. The cross-sectional microstructures and the elemental mappings of the films were obtained by bright-field scanning transmission electron microscopy (BF-STEM) and energy-dispersive X-ray spectroscopy (EDS), respectively.

A 5 nm thick Nb layer was fabricated using an arc plasma gun in the EBE chamber after the fabrication of the MgB$_2$ film. The Nb layer prevented the oxidation of Mg during the transfer. The sample was taken out from the EBE chamber into the atmosphere and placed in a sputtering chamber. Additionally, a 3 $\mu$m thick Nb layer was prepared to protect the MgB$_2$ thin films during post-annealing. The post-annealing was performed after the deposition of the layers in a furnace at 450 °C, 550 °C, and 650 °C for 1 h in an atmosphere of Ar+$\text{H}_2$ (3%) at approximately 100 Pa. Subsequently, the crystal structures, the microstructures, and the elemental mappings were obtained for the samples; additionally, the values of $J_c$ and $T_c$ were measured. The chemical composition of the MgB$_2$ thin film before annealing was Mg:B = 1:1.97, which was similar to the stoichiometric composition of MgB$_2$.

Figure 1 shows the XRD patterns of the MgB$_2$ thin films under various post-annealing conditions. The presence of Nb (110) and MgB$_2$ (002) peaks in the XRD pattern of the nonannealed films revealed the formation of c-axis oriented MgB$_2$ thin films. The intensity of the XRD peaks of MgB$_2$ was low owing to the deposition of the Nb protective layer on the MgB$_2$ thin films. When the annealing temperature was increased, there was an expansion of the region where Mg diffused in the B layer. A small amount of diffusion of Mg into the Nb layer was also observed; however, the amount of diffusion did not increase, even when the temperature was increased. This indicated that the Nb layer effectively suppressed the evaporation of Mg. The B distribution images revealed the presence of the B signal at the Nb/MgB$_2$ boundary decreased in the region where the O signal was observed. This suggested the formation of an ultrathin MgO layer at the Nb/MgB$_2$ boundary. There was no evidence of oxidation in the MgB$_2$ layer, apart from the presence of this ultrathin MgO layer.

Figure 2 shows cross-sectional BF-STEM images and the EDS elemental mappings (Nb, Mg, B, and O) in the annealed samples (450 °C, 550 °C, and 650 °C) comprising the Nb/MgB$_2$/B/Si layers and EDS line profile of Mg. Each layer was clearly visible in the BF-STEM images. The thicknesses of the B, MgB$_2$, and Nb layers were determined to be 88 nm, 193 nm, and 3 $\mu$m, respectively, using the BF-STEM images. The sizes of the columnar grains of MgB$_2$, which were observed in the MgB$_2$ layers, did not change with the annealing temperature. The average grain size was determined to be 36.8 nm using the cross-sectional STEM images. The results of the EDS elemental mappings indicated that the diffusion of Nb into the MgB$_2$ layers did not occur under any annealing condition in this study. However, a diffusion of Mg from the MgB$_2$ layers into the B layers was observed. The EDS line profile in Fig. 2(d) shows a more detailed distribution of Mg at each annealing temperature. When the annealing temperature was increased, there was an expansion of the region where Mg diffused in the B layer. A small amount of diffusion of Mg into the Nb layer was also observed; however, the amount of diffusion did not increase, even when the temperature was increased. This indicated that the Nb layer effectively suppressed the evaporation of Mg. The B distribution images revealed the presence of the B signal not only in the MgB$_2$ and B layers but also in the Nb layer. This was attributed to the overlapping of the characteristic X-rays that were emitted from the B and Nb layers (0.1833 keV for the B K$_\alpha$ line and 0.1717 and 0.1718 keV for Nb M-lines), and we considered that there was no diffusion of B into the Nb layers. In fact, Nb sheaths in the PIT-processed MgB$_2$ wires work well, even after heat treatment at 650 °C. A clear O signal from the natural oxide film of Si was observed at the B/Si interface of the sample that was annealed at 450 °C. This sample also exhibited a weak background O signal that was spread over all layers. The sample that was annealed at 650 °C exhibited the presence of a strong O signal at the Nb/MgB$_2$ boundary, in addition to the O signal from the natural oxide film of Si. The intensity of the B signal at the Nb/MgB$_2$ boundary decreased in the region where the O signal was observed. This suggested the formation of an ultrathin MgO layer at the Nb/MgB$_2$ boundary. There was no evidence of oxidation in the MgB$_2$ layer, apart from the presence of this ultrathin MgO layer. Therefore, the Nb layer effectively protected the MgB$_2$ layer from the effect of oxygen.

Figure 3 shows the temperature dependence of the resistivity of the MgB$_2$ thin films under various annealing conditions. The sample that was annealed at 450 °C exhibited the presence of a strong O signal at the Nb/MgB$_2$ boundary, in addition to the O signal from the natural oxide film of Si. The intensity of the B signal at the Nb/MgB$_2$ boundary decreased in the region where the O signal was observed. This suggested the formation of an ultrathin MgO layer at the Nb/MgB$_2$ boundary. Therefore, the Nb layer effectively protected the MgB$_2$ layer from the effect of oxygen.

![Fig. 1](https://example.com/fig1.png)

**Fig. 1.** (Color online) XRD patterns for the nonannealed and annealed (450 °C, 550 °C, and 650 °C) MgB$_2$ thin films.
The resistivities of the annealed samples in the normal state were lower than the actual resistivities owing to the additional current flowing through the Nb protective layer that was not deposited on the nonannealed sample. The onset and the zero-resistivity $T_c$ for the nonannealed sample were 35.5 K and 34.9 K, respectively. The zero-resistivity $T_c$ for the films that were annealed at 450 °C, 550 °C, and 650 °C were 36.3, 36.8, and 37.5 K, respectively. The increase in the $T_c$ with the increase in the annealing temperature was attributed to the increase in the crystallinity of the MgB$_2$ layers after annealing, as proven by the XRD analysis. The $T_c$ of the film that was annealed at 650 °C increased by 2.6 K as compared to that of the nonannealed film and was equivalent to that of the PIT-processed wires. The transition widths (onset $T_c$–zero-resistivity $T_c$) of the samples that were annealed at 450 °C, 550 °C, and 650 °C were 0.3, 1.0, and 0.8 K, respectively. As shown by the XRD patterns in Fig. 1, high-temperature annealing improved the crystallinity. However, the MgB$_2$ thin film consisted of nonuniform grains with an average grain size of about 36.8 nm, as shown in the STEM image in Fig. 2, and the degree of improvement in crystallinity is also expected to vary with each grain. Thus, the increase in the transition widths at high annealing temperatures ($\geq 550$ °C) was attributed to the distribution of the $T_c$ in the MgB$_2$ layer owing to the nonuniform increase in the crystallinity after annealing.

Figure 4 shows the dependence of the $J_c$ of the MgB$_2$ films at 20 K on the magnetic fields under various annealing conditions. The results for the EBE-prepared MgB$_2$ film that was annealed in vacuum, the PIT-processed MgB$_2$ wire, and the HPCVD-prepared MgB$_2$ film are also plotted in the figure to facilitate comparison. In all data, the magnetic fields were applied perpendicular to the film surfaces. The $J_c$ of the nonannealed MgB$_2$ film in a self-magnetic field (1.65 MA cm$^{-2}$) was almost identical to that of the MgB$_2$ films that were annealed at 450 °C and 550 °C in the present experiment. There was a decrease in the $J_c$ of the Thin MgB$_2$ layers after annealing at high temperatures (> 550 °C) was attributed to the distribution of the $T_c$ in the MgB$_2$ layer owing to the nonuniform increase in the crystallinity after annealing.

Figure 4 shows the dependence of the $J_c$ of the MgB$_2$ films at 20 K on the magnetic fields under various annealing conditions. The results for the EBE-prepared MgB$_2$ film that was annealed in vacuum, the PIT-processed MgB$_2$ wire, and the HPCVD-prepared MgB$_2$ film are also plotted in the figure to facilitate comparison. In all data, the magnetic fields were applied perpendicular to the film surfaces. The $J_c$ of the nonannealed MgB$_2$ film in a self-magnetic field (1.65 MA cm$^{-2}$) was almost identical to that of the MgB$_2$ films that were annealed at 450 °C and 550 °C in the present experiment. There was a decrease in the $J_c$ of the MgB$_2$ fil
nonannealed film to 0.18 MA cm$^{-2}$, which was approximately 90% lower than that in the self-magnetic field under a magnetic field of 5 T. The decrease in the $J_c$ of the annealed sample under a magnetic field of 5 T was approximately 40%, which was significantly lower than that of the non-annealed sample. The MgB$_2$ film that was annealed at 650 °C exhibited a $J_c$ of 1.62 MA cm$^{-2}$ at 20 K under 5 T. This was not only more than 2.5 times higher than the previous highest $J_c$ of 0.64 MA cm$^{-2}$ for the EBE-prepared MgB$_2$ films that were annealed at 550 °C in vacuum\(^{12}\) but also more than 100 times higher than the $J_c$ for the PIT-processed wires.\(^{13}\)

The results of our study demonstrated that high-temperature annealing and the Nb protective layer significantly increased the $J_c$ of the EBE-prepared MgB$_2$ thin films under high magnetic fields. The reasons for the high $J_c$ can be explained as follows. The values of $T_c$ and $J_c$ in a self-magnetic field for the EBE-prepared films in this study were lower than those for HPCVD-prepared films. This was attributed to the smaller grains in the EBE-prepared films as compared to those in HPCVD-prepared films and the formation of a thin MgO wall with a thickness of several nanometers around each grain in the EBE films.\(^{12}\)

Furthermore, the cross-sectional area of the superconducting channels was only a few tens of percent of that in an ideal superconducting material. The MgO around the grains acted as pinning centers and increased the $J_c$ under high magnetic fields.\(^{15}\) To increase $J_c$ under an external magnetic field, it is necessary to increase the crystallinity of MgB$_2$ inside the small grains and improve $T_c$ without forming MgO. Although high-temperature annealing above 550 °C is effective in improving $T_c$, it is considered to be difficult owing to the oxidation and evaporation of Mg. However, the deposition of a $3 \mu$m thick Nb protective layer in this study effectively prevented the oxidation and evaporation of Mg at high annealing temperatures. The annealing improved $T_c$ and facilitated flux-pinning in the grain boundaries without inducing a deterioration in the superconductivity. Thus, there was an increase in the $J_c$ of the thin films under magnetic fields. The results of the study indicated that the performance of the fabricated MgB$_2$ films under external magnetic fields was optimized by simple post-annealing.

To summarize, we deposited a Nb protective layer on the MgB$_2$ thin films to suppress the evaporation and oxidation of Mg. Furthermore, the effects of the post-annealing treatment on the $J_c$ and $T_c$ of the MgB$_2$ films were examined. The fabrication of the Nb protective layer and the annealing at 450 °C, 550 °C, and 650 °C resulted in an increase in the $T_c$ and $J_c$ of the MgB$_2$ films. The film that was annealed at 650 °C exhibited a $J_c$ of 1.62 MA cm$^{-2}$ at 20 K under 5 T, which was more than 100 times higher than the $J_c$ of PIT-processed wires. The results confirmed the efficacy of the fabrication technique in this study for the realization of MgB$_2$-based conductors for practical superconducting applications at 20 K under external magnetic fields.

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