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Microstructures and superconducting properties of high performance MgB₂ thin films deposited from a high-purity, dense Mg-B target

G.Z. Li, M.A. Susner[†], S.D. Bohnenstiehl[‡], M.D. Sumption^{*}, and E.W. Collings

Center for Superconducting and Magnetic Materials, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH USA 43210

Abstract

High quality, *c*-axis oriented, MgB₂ thin films were successfully grown on 6H-SiC substrates using pulsed laser deposition (PLD) with subsequent *in situ* annealing. To obtain high purity films free from oxygen contamination, a dense Mg-B target was specially made from a high temperature, high pressure reaction of Mg and B to form large-grained (10~50 μm) MgB₂. Microstructural analysis via electron microscopy found that the resulting grains of the film were composed of ultrafine columnar grains of 19–30 nm. XRD analysis showed the MgB₂ films to be *c*-axis oriented; the *a*-axis and *c*-axis lattice parameters were determined to be 3.073 ± 0.005 Å and 3.528 ± 0.010 Å, respectively. The superconducting critical temperature, $T_{c,onset}$, increased monotonically as the annealing temperature was increased, varying from 25.2 K to 33.7 K. The superconducting critical current density as determined from magnetic measurements, J_{cm} , at 5 K, was 10^5 A/cm² at 7.8 T; at 20 K, 10^5 A/cm² was reached at 3.1 T. The transport and pinning properties of these films were compared to “powder-in-tube” (PIT) and “internal-infiltration” (AIMI) processed wires. Additionally, examination of the pinning mechanism showed that when scaled to the peak in the pinning curve, the films follow the grain boundary, or surface, pinning mechanism quite well, and are similar to the response seen for C doped PIT and AIMI strands, in contrast to the behavior seen in undoped PIT wires, in which deviations are seen at high *b* ($b = B/B_{c2}$). On the other hand, the magnitude of the pinning force was similar for the thin films and AIMI conductors, unlike the values from connectivity-suppressed PIT strands.

Keywords

Magnesium diboride; thin films; critical currents; flux pinning; pulsed laser deposition

^{*}Corresponding author to whom correspondence should be addressed.

[†]Now with Materials Science & Technology Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831, USA

[‡]Now with INRAD Optics, 181 Legrand Ave. Northvale, NJ 07647, USA

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1. Introduction

MgB₂, discovered to be superconducting in 2001 [1], has since been aggressively investigated both in terms of its fundamental properties and its promise for application. Over time, it has become clear that the main limitations of transport critical current density J_c , arise not from a weak pinning strength, but rather limitations in the upper critical field (B_{c2}) anisotropy γ , porosity and connectivity (see, e.g. the topical review of Collings *et al.* [2]). The critical aspects of connectivity, anisotropy and B_{c2} have been well described within the Eisterer's percolation model [3, 4]. However, separating these variables from one another is challenging. As shown by Susner [5], the contribution of anisotropy relative to porosity and connectivity is difficult to extract without a set of samples which have high connectivity and low porosity which can be compared directly to MgB₂ conductors. To facilitate a fundamental understanding of the structure-property relationships in MgB₂, thin films can be regarded as the ideal options as compared to bulks or wires, because anisotropy can be “decoupled” in highly textured films from the other parameters including connectivity. Therefore, the goal of this research was to prepare highly textured MgB₂ thin films with high purity and good connectivity, and to study the effects of anisotropy and connectivity on the superconducting properties of MgB₂, with reference to PIT and AIMI wires [6].

MgB₂ thin films can be produced using a variety of techniques [7–11], but one of the most used techniques has been pulsed laser deposition (PLD) [11–15]. Some representative examples include Kang *et al.* [11] who fabricated MgB₂ thin films by heat treating Mg with PLD-deposited B thin films, achieving a sharp superconducting transition at 39 K. Ferrando *et al.* [16] directly deposited MgB₂ thin films on MgO and Al₂O₃ substrates by PLD, obtaining samples with strong *c*-axis oriented films with $T_c \sim 38$ K and $B_{c2} \sim 22$ T at 15 K. Yates *et al.* [17] studied the oxygenation property in their PLD-made MgB₂ thin films. Patnaik *et al.* [18] also prepared MgB₂ films on SrTiO₃ substrates by PLD at room temperature and a post annealing in Mg vapor. In general, MgB₂ thin film growth is made difficult by the divergent melting points and vapor pressures of Mg and B, necessitating special approaches. Zhao *et al.* [12] deposited the Mg-B precursor films on Al₂O₃-R substrates from a MgB₂ target containing 15% pores. Then they capped a layer of Mg to compensate the Mg loss and annealed the samples either in the vacuum chamber (*in situ*) or in the tube furnace (*ex situ*). This “two-step” film fabrication route resulted in highly textured MgB₂ thin films (containing, however, a significant amount of MgO phase). Eom *et al.* [14] reported a accidental oxygen incorporation in one of their samples, showing abnormal B_{c2} enhancement. Matsumoto *et al.* [13] also observed oxygen contamination in their “two-step” *ex situ* PLD deposited MgB₂ thin films. They pointed out that precautions were ineffective because oxygen was mainly originated from the target. As illustrated in Figure 1, targets have been typically made using (i) compressed MgB₂ powders, either sintered or unsintered [19], (ii) a specially reacted combination of Mg and B precursor powders [12] or (iii) individual Mg and B precursor targets [11]. No matter the route employed, the main issues with traditional powder synthesis for targets were the oxide contamination from starting powders and the impurities attached on the porous surface within targets. Due to the small grain sizes of the powders, the resultant increase in surface

area allowed for likely oxide passivation on these surfaces, which contaminated the target before deposition was even started. It is clear that one of the simplest ways to reduce the oxide contamination of the target, and hence of the final film, would be to limit the initial surface area of the starting powder, i.e. to select coarse B and Mg precursors. An induction heating process developed by Bohnenstiehl [20] was used to manufacture a high density Mg-B target, whereby B and Mg were reacted at high temperatures to form under certain conditions a dense, large-grained two-phase mixture of Mg and MgB₂ with minimal oxygen impurity content.

In this paper, by using the specially-made target and two-step *in situ* PLD route, we have successfully deposited high purity, *c*-axis oriented MgB₂ thin films. The X-ray diffraction together with electron microscopy analysis found that the oxygen-free samples were composed of nano-sized MgB₂ columnar grains with *c*-axis perpendicular to the film surface. Such microstructures resulted in excellent superconducting properties by introducing a high density of flux pinning centers and very clean superconducting phases.

2. Experimental Procedures

Crystalline B powders (~60 mesh, 99%, Sigma Aldrich) and Mg turnings (99.98%, Alfa Aesar), with a nominal composition of Mg₃₅B₆₅, were melted and mixed by RF induction heating at 1500 °C for 10 min in Ar gas (10 MPa) in a specially instrumented autoclave [20]. The resulting ingot, around 2 cm in diameter, consisted of a two-phase mixture of MgB₂ (10–50 μm grain size) and Mg with infinitesimal oxygen incorporation. Electron probe microanalysis (EPMA) performed on a sample of the ingot, revealed the existence of stoichiometric MgB₂, Mg, and 0.5 at.% O [20], which was most likely due to unavoidable oxide adhesion on the sample surface. A section of this ingot was machined as the target.

The PLD system was produced by Neocera, Inc. The base pressure was 10⁻⁸–10⁻⁷ torr. A KrF excimer laser with maximum beam energy of 400 mJ /pulse was focused to a 5 mm² ellipse spot on the target. An above-mentioned Mg-B target and a Mg target have been used. The target-to-substrate distance was 35 mm. Instead of Al₂O₃, 6H-SiC was selected as the substrate. SiC substrate did not contain oxygen, thus preventing the formation of oxide secondary phases that were seen in MgB₂ thin films deposited on Al₂O₃ substrates [21]. Although SiC substrates reacted with MgB₂ at elevated temperatures, little second phase has been observed even at temperatures of up to 800 °C [21, 22]. During deposition, the substrate temperature was maintained at 300 °C, and a flux of high purity Ar gas with pressure of 75 torr was flowing through the chamber. The gas was 99.998% in purity and filtered via a Centorr Ti getter furnace and a mtorr MC1-902F in-line filter. The O₂ concentration in the post-processed Ar gas was below the resolution limit (i.e. < 1 ppm) of our instrument. The precursor film was deposited at a frequency of 10 Hz for 20,000 pulses, with effective growth rate was determined to be 0.065 Å/pulse. Then a thick layer of Mg was deposited onto the precursor film to compensate the Mg loss during annealing. Following the deposition, precursor films were annealed for 1–30 min in the vacuum chamber at temperatures of 550–750 °C in Ar atmosphere of 600 torr. After annealing, the samples were rapidly cooled down at a rate of 30–50 °C/min. Table I shows the annealing temperature, time, and resulting onset critical temperature, *T*_{*c,onset*}, of MgB₂ thin films.

X-ray Diffraction experiments were performed using a Rigaku SmartLab diffractometer with grazing incident diffraction (GID) in-plane and out-of-plane capability. This system utilized a Cu K_α X-ray sources ($\lambda = 1.5406 \text{ \AA}$) operating at a power of 2.2 kW. Scanning electron microscopy (SEM) were taken with a FEI/Philips Sirion Field Emission SEM. A FEI/Philips CM-200T instrument was the primarily used for TEM analysis. The TEM samples were prepared using a FEI Helios NanoLab 600 DualBeam or a FEI Nova NanoLab 600 DualBeam following the standard focused ion beam (FIB) milling procedure. Superconducting properties, including the temperature and field dependencies of the magnetization, M , were measured by using the AC susceptibility module (ACMS) in Quantum Design Model 6000 PPMS. Susceptibility was measured at 1 mT and 1000 Hz after a zero-field cool (ZFC) sequence was applied to the sample. The M - T curves at background fields of 0–14 T were measured. These data enabled the determination of $T_{c,onset}$ and a plot of $B_{c2}(T)$ curves. Magnetization (M - B) loops, taken with the magnetic field perpendicular to the film surface, were run using the DC extraction measurement on the ACMS option which used the ACMS accessory as a DC magnetometer. The magnetic field ramp rate was 13 mT/s. The magnetic J_c , J_{cm} , was calculated from the height of the hysteresis loop, M , using the expression $J_{cm} = 2 M / [w(1 - w/3l)]$, where l and w are the length and width of the film in meters, J_{cm} is in A/m² and M is in A/m.

3. Experimental Results and Discussion

3.1 Microstructural Analysis

Due to MgB₂ having a low X-ray scattering coefficient combined with the fact that the films were only 100–200 nm thick, grazing incidence diffraction (GID) was employed. Shown in Figure 2 are the diffraction profiles of sample C4, which is annealed at 700 °C for 10 min. The X-ray incident angle with respect to the film surface, ω , is 0.5°. As shown in Figure 2(a) the only visible non-substrate peaks in the out-of-plane scan are the (0001) and (0002) reflections from MgB₂, showing that the films are c -axis oriented. The inset shows the rocking curve around the MgB₂ (0002) reflection. The FWHM of this rocking curve is about 0.214°, comparable to FWHM reported for other PLD-deposited MgB₂ thin films [16]. Figure 2(b) shows the in-plane GID profile. Besides signals from residual silver paint for sample mounting and unreacted Mg, only the in-plane MgB₂ (10-10), (11-20) and (20-20) reflections are apparent, suggesting that although the films are c -axis oriented, the a -axis is randomly oriented in-plane. No oxide phases are observed by XRD, indicating a low level of oxygen contamination during the thin film synthesis. According to a careful peak-fitting of the highest order reflections, the lattice parameters of the hexagonal MgB₂ crystal lattice, a and c , are determined to be 3.073 ± 0.005 and $3.528 \pm 0.010 \text{ \AA}$, respectively.

Further characterization of MgB₂ thin films was performed via both SEM and TEM. Figure 3 shows the surface structure of sample C4. Here one can see fine grains, exhibiting sizes of less than 30 nm on average. The grain size does increase somewhat with annealing temperature, from $23.4 \pm 4.7 \text{ nm}$ at 550 °C to $27.3 \pm 2.8 \text{ nm}$ at 700 °C. Investigations of grain growth at longer annealing times were prevented by Mg loss whereby, as a result, the MgB₂ phase was lost. The cross-sectional structure of the sample C4 was examined by TEM in Figure 4. Figure 4(a) and (c) show the high magnification and low magnification views of

the sample respectively, with Figure 4(b) confirming the existence of MgB_2 phase. As shown in Figure (c), the thickness of MgB_2 thin film is around 230 nm. The MgB_2 film is firmly attached to the SiC substrate. A close look at the MgB_2 layer is shown in Figure 4(a), indicating columnar structure of MgB_2 grains. Apparent from the differing contrast of neighboring MgB_2 grains, we observe the grains to be 20–30 nm in width and about 230 nm in height, in accordance with the results observed by SEM. These columnar grains create a high density of grain boundaries along the film surface, important for flux pinning and critical current enhancement.

3.2 Magnetic and Transport Properties

Figure 5(a) illustrates the effect of annealing temperature on the $T_{c,onset}$ of MgB_2 thin films. All samples in this plot were *in situ* annealed at the designated temperatures for 10 min. Consequently, a higher annealing temperature leads to an improved $T_{c,onset}$. Increasing the annealing temperature from 550 °C to 750 °C caused $T_{c,onset}$ to increase from 25.2 K to 33.7 K. Sample C4 achieved a high $T_{c,onset}$ of 32.3 K. Our recent resistance versus temperature (R - T) measurements show that the superconducting transition of these high quality MgB_2 thin films is sharp, with temperature range, ΔT , equal to ~ 2 K. As shown in Table I, the same trend is observed for films annealed for 1 min or 30 min. However, longer annealing time is not preferred since it marginally broadens the superconducting transitions by resulting in a less homogeneous film. Figure 5(b) shows the $B_{c2}(T)$ characteristics of the same group of samples. It is seen that B_{c2} is significantly enhanced at all temperatures when the annealing temperature is raised up to 700 °C. The best performing sample, C4, achieves B_{c2} of 8.6 T at 20 K, which is about 1.9 times higher than that of the sample annealed at 550 °C. The extrapolated $B_{c2}(0\text{ K})$ for samples C1, C2, C3 and C4 are 19.8, 22.2, 21.7, 24.1 T, respectively.

The enhanced $T_{c,onset}$ and $B_{c2}(T)$ performance of MgB_2 thin films with increased annealing temperature is due to the improvement of crystallinity. After PLD deposition, the Mg-B precursor films are highly disordered, hence non-superconductive in most conditions. The annealing process provides adequate activation energy for atoms in the precursor films to rearrange their positions, in order to form ideal crystal structure, annihilate crystal defects and obtain an optimal stoichiometry in a localized region. This process can be better accomplished at higher temperatures. So the film annealed at 700 °C for 10 min achieves the highest T_{cs} and B_{c2} s. Nevertheless, the Mg volatility prevents MgB_2 from being stable if the annealing temperature is above 750 °C – the MgB_2 reflections for these samples are undetectable in the XRD, indicating Mg loss and decomposition of the MgB_2 phase. The T_{cs} of our MgB_2 thin films are then compared with results from other groups [8, 11]. However, because T_{cs} are determined by many factors such as deposition method, dopant, defect level and Mg/B stoichiometry, our comparison does not lead to a simple relationship between T_{cs} and lattice parameters in MgB_2 thin films.

It is noted that the $B_{c2}^{\parallel}(0\text{ K})$ of a defect-free MgB_2 single crystal is only about 16 T [23], much smaller than the $B_{c2}(0\text{ K})$ s of MgB_2 thin films. Moreover, the $B_{c2}(0\text{ K})$ of MgB_2 single crystals can be improved by introducing a moderate level of defects via C doping or proton irradiation [24–26]. This appears different from our observations in MgB_2 thin films,

but both relationships are valid due to difference in the defect density in samples. According to Gurevich *et al.* [2, 27], a moderate level of defects suppresses the electronic diffusivity, and thus consequently causes an enhanced B_{c2} . So $B_{c2}(0\text{ K})$ can be improved when defects are introduced in MgB_2 single crystals. However, the defect density should be within a certain range. An overdose of crystal defects, such as in MgB_2 thin films, is detrimental to the crystallinity and hence superconductivity, which as a result decreases T_c and B_{c2} . Therefore, in MgB_2 thin films high T_c s and B_{c2} s can be obtained through a proper improvement of crystallinity.

Not only high T_c , but also excellent J_{cm} has been achieved for our *in situ* PLD-made MgB_2 thin films. Figure 6(a) plots the field dependences of in-plane J_{cm} for the sample C4 at temperatures of 5–25 K. At 5 K, a J_{cm} of 10^5 A/cm^2 is achieved at 7.8 T. At 20 K, the J_{cm} of 10^5 A/cm^2 is reached at 3.1 T. Both results are comparable to the highest J_{cs} reported for MgB_2 thin films so far [8]. The $J_{cm}(B)$ characteristics are transformed into flux pinning force density curves in Figure 6(b) following the equation $F_p = J \times B$. The maximum pinning force density $F_{p,max}$ of the sample C4 reaches 29.3 GN/m^3 at 5 K, which is also among the best results for MgB_2 products [2].

For a better understanding of the pinning mechanisms and the structure-property relationship, sample C4 is compared with the state-of-the-art MgB_2 wires [4, 27–30] in terms of J_c and normalized pinning force density $F_p/F_{p,max}$ (Figure 7). In previous publications we have shown that the traditional powder-in-tube (PIT) wire is porous in microstructure, and hence does not have a good connectivity or a high J_c . Because C doping can improve B_{c2} while simultaneously reducing anisotropy, the J_{cs} of C-doped PIT wire are higher than those of undoped PIT wire. The infiltration process manages to obtain a dense MgB_2 wire with excellent connectivity [31], therefore the “advanced internal Mg infiltration (AIMI)” processed wire has an improved J_c as compared to PIT wires [32]. Our MgB_2 thin film has an extraordinary connectivity because the grains are close-packed and the sample is free from oxygen contamination. All the grains share the same *c*-axis orientation so that they appear highly isotropic when the magnetic field is applied perpendicular to the film surface and current flows within the film. Moreover, the nanosized grains provide a high density of grain boundaries, resulting strong flux pinning ability. All these features contribute to a high J_c . As a consequence, sample C4, even though undoped and having a moderate B_{c2} , achieves the highest J_{cs} in field of 0–6 T at 4.2 K among all types of MgB_2 samples shown.

Table II compares the $F_{p,max}$ as well as other related parameters between sample C4 and other MgB_2 in Figure 7(a). Here the maximum pinning force density $F_{p,max}$ represents the maximum of the F_p curve. The $F_{p,max}$ s for thin film, undoped PIT wire, C-doped PIT wire, and C-doped AIMI wire are 29.3, 7.7, 11.7 and 19.5 GN/m^3 respectively at 4.2 K. The MgB_2 thin film exhibits the highest $F_{p,max}$. According to Martinez [33], $F_{p,max}$ follows the relationship of $F_{p,max} \sim B_{c2}^2/D$, where D is the grain size. Hence we can see that the high $F_{p,max}$ of sample C4 is attributed to the fine grain size, good connectivity and low anisotropy. Figure 7(b) presents the normalized pinning force density $F_p/F_{p,max}$ as a function of normalized field $B/B(F_{p,max})$ for the above mentioned samples as well as a Kramer-Dew-Hughes prediction for grain boundary pinning [34, 35]. According to the grain boundary pinning function, the normalized pinning force density $F_p/F_{p,max} = [B/B(F_{p,max})]^{0.5} [1 -$

$B/B(F_{p,max})]^2$. Because grain boundary pinning is the dominant pinning mechanism for MgB_2 , all experimental data generally follow this relationship. However, due to low connectivity and high anisotropy, the undoped PIT wire shows a remarkable deviation from the theoretical predication, particularly at high fields. Carbon doping reduces the anisotropy to 2 [3, 7], which enables the high field pinning characteristics for C-doped PIT wire better satisfy the theory. For C-doped AIMI wire, its microstructure is further enhanced in term of density and connectivity. So it is seen that the $F_p/F_{p,max}$ curve for C-doped AIMI wire well meets the grain boundary pinning function. As shown in Table II, MgB_2 thin films have even smaller anisotropy and better connectivity (i.e. less oxygen contamination) than the C-doped AIMI wire. Nevertheless, the $F_p/F_{p,max}$ curve for the C-doped AIMI wire is comparable to that of the MgB_2 thin film..

4. Conclusions

High performance MgB_2 thin films have been successfully fabricated by *in situ* PLD deposition from a specially made Mg-B target with high purity and dense structure. The XRD and electron microscopy analysis showed that the films were highly *c*-axis textured. The MgB_2 grains were columnar in shape, with in plane dimensions of 20–30 nm. These films exhibited T_c s of up to 33.7 K. The J_{cm} s at 5 K, was 10^5 A/cm^2 at 7.8 T; at 20 K, 10^5 A/cm^2 was reached at 3.1 T. The maximum F_p s attained 29.3 GN/m^3 at 5 K, which were comparable to the best results reported in to date. The transport and pinning properties of these films were compared to “powder-in-tube” (PIT) and “internal-infiltration” (AIMI) processed wires. Additionally, examination of the pinning mechanism showed that when scaled to the peak in the pinning curve, the films follow the grain boundary, or surface, pinning mechanism quite well, and are similar to the response seen for C doped PIT and AIMI strands, in contrast to the behavior seen in undoped PIT wires, in which deviations are seen at high b ($b = B/B_{c2}$). On the other hand, the magnitude of the pinning force was similar for the thin films and AIMI conductors, unlike the values from connectivity-suppressed PIT strands.

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References

1. Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y, Akimitsu J. Superconductivity at 39 K in magnesium diboride. *Nature*. 2001; 410:63. [PubMed: 11242039]
2. Collings EW, Sumption MD, Bhatia M, Susner MA, Bohnenstiehl SD. Prospects for improving the intrinsic and extrinsic properties of magnesium diboride superconducting strands. *Supercond. Sci. Technol*. 2008; 21:103001.
3. Eisterer M, Zehetmayer M, Weber HW. Current percolation and anisotropy in polycrystalline MgB_2 . *Phys. Rev. Lett*. 2003; 90:247002. [PubMed: 12857216]
4. Li GZ, Zwayer JB, Kovacs CJ, Susner MA, Sumption MD, Rindfleisch M, Thong CJ, Tomsic M, Collings EW. Transport critical current densities and *n*-values of multifilamentary MgB_2 wires at various temperatures and magnetic fields. *IEEE Trans. Appl. Superconduct*. 2014; 24:6200105.

5. Susner, M. Ph.D dissertation. Columbus, OH, USA: Ohio State University; 2012. Influences of crystalline anisotropy, doping, porosity and connectivity on the critical current densities of superconducting magnesium diboride bulks, wires and thin films.
6. Li, GZ. Ph.D dissertation. Columbus, OH, USA: Ohio State University; 2015. Connectivity, doping and anisotropy in highly dense MgB₂.
7. Eisterer M, Krutzler C, Weber HW. Influence of the upper critical field anisotropy on the transport properties of polycrystalline MgB₂. *J Appl. Phys.* 2005; 98:033906.
8. Zeng X, Pogrebnnyakov AV, Kotcharov A, Jones JE, Xi XX, Lysczek EM, Redwing JM, Xu S, Li Q, Lettieri J, Schlom DG, Tian W, Pan X, Liu Z-K. In situ epitaxial MgB₂ thin films for superconducting electronics. *Nature Mater.* 2002; 1:1.
9. Yamamoto H, Tsukamoto A, Saitoh K, Okada M, Kitaguchi H. Relationship between flux pinning and microstructure in MgB₂ thin films with columnar grains formed by molecular beam epitaxy. *Appl. Phys. Lett.* 2007; 90:142516.
10. Kitaguchi H, Doi T. High-temperature and high-field performance of MgB₂ films with J_c of 10⁶ Acm⁻² (4.2 K, 4 T). *Supercond. Sci. Technol.* 2005; 18:489.
11. Kang WN, Kim HJ, Choi E-M, Jung CU, Lee S-I. MgB₂ superconducting thin films with a transition temperature of 39 kelvin. *Science.* 2001; 292:1521. [PubMed: 11303089]
12. Zhao Y, Ionescu M, Roussel M, Pan AV, Horvat J, Dou SX. Superconducting and microstructural properties of two types of MgB₂ films prepared by pulsed laser deposition. *IEEE Trans. Appl. Superconduct.* 2005; 15:3261.
13. Matsumoto A, Kobayashi Y, Takahashi K, Kumakura H, Kitaguchi H. MgB₂ Thin Films Fabricated by a Precursor and Post-annealing Method Have a High J_c in High Magnetic Fields. *Appl. Phys. Express.* 2008; 1:021702.
14. Eom CB, Lee MK, Choi JH, Belenky LJ, Song X, Cooley LD, Naus MT, Patnaik S, Jiang J, Rikel MO, Polyanskii AA, Gurevich A, Cai XY, Bu SD, Babcock SE, Hellstrom EE, Larbalestier DC, Rogado N, Regan KA, Hayward MA, He T, Slusky JS, Inumaru K, Haas M, Cava RJ. High critical current density and enhanced irreversibility field in superconducting MgB₂ thin films. *Nature.* 2001; 411:558. [PubMed: 11385563]
15. Kim J, Singh RK, Newman N, Rowell JM. Thermochemistry of MgB₂ thin film synthesis. *IEEE Trans. Appl. Superconduct.* 2003; 13:3238.
16. Ferrando V, Amoroso S, Bellingeri E, Bruzzese R, Manfrinetti P, Marrè D, Velotta R, Wang X, Ferdeghini C. Growth methods of *c*-axis oriented MgB₂ thin films by pulsed laser deposition. *Supercond. Sci. Technol.* 2003; 16:241.
17. Yates KA, Lackman Z, Kursumovic A, Burnell G, Stelmashenko NA, MacManus-Driscoll JL, Blamire MG. The effect of oxygenation on the superconducting properties of MgB₂ thin films. *Appl. Phys. Lett.* 2005; 86:022502.
18. Patnaik S, Cooley LD, Gurevich A, Polyanskii AA, Jiang J, Cai XY, Squitieri AA, Naus MT, Lee MK, Choi JH, Belenky LJ, Bu SD, Lettieri J, Song X, Schlom DG, Babcock SE, Eom CB, Hellstrom EE, Larbalestier DC. Electronic anisotropy, magnetic field-temperature phase diagram and their dependence on resistivity in *c*-axis oriented MgB₂ thin films. *Supercond. Sci. Technol.* 2001; 14:315.
19. Berenov A, Lockman Z, Qi X, MacManus-Driscoll JL, Bugoslavsky Y, Cohen LF, Jo M-H, Stelmashenko NA, Tsaneva VN, Kambara M, Hari B, Cardwell DA, Blamire MG. Growth of strongly biaxially aligned MgB₂ thin films on sapphire by post-annealing of amorphous precursors. *Appl. Phys. Lett.* 2001; 79:4001.
20. Bohnenstiehl, SD. Ph.D Thesis. The Ohio State University; 2012. Thermal Analysis, Phase Equilibria, and Superconducting Properties in MgB₂ and Carbon Doped MgB₂.
21. Bu SD, Kim DM, Choi JH, Giencke JE, Hellstrom EE, Larbalestier DC, Patnaik S, Cooley LD, Eom CB, Lettieri J, Schlom DG, Tian W, Pan XQ. Synthesis and properties of *c* axis oriented epitaxial MgB₂ thin films. *Appl. Phys. Lett.* 2002; 81:1851.
22. He T, Cava RJ, Rowell JM. Reactivity of MgB₂ with common substrate and electronic materials. *Appl. Phys. Lett.* 2002; 80:291.

23. Angst M, Puzniak R, Wisniewski A, Jun J, Kazakov SM, Karpinski J, Roos J, Keller H. Temperature and field dependence of the anisotropy of MgB_2 . *Phys. Rev. Lett.* 2002; 88:167004. [PubMed: 11955251]
24. Lee S, Masui T, Yamamoto A, Uchiyama H, Tajima S. Carbon-substituted MgB_2 single crystals. *Physica C.* 2003; 397:7.
25. Putti M, Vaglio R, Rowell JM. Radiation effects on MgB_2 : a review and a comparison with A15 superconductors. *Supercond. Sci. Technol.* 2008; 21:043001.
26. Zhong Y, Zhu H, Shaw LL, Ramprasad R. Ab initial computational studies of Mg vacancy diffusion in doped MgB_2 aimed at hydriding kinetics enhancement of the $\text{LiBH}_4 + \text{MgH}_2$ system. *J. Phys. Chem. C.* 2010; 114:21801.
27. Li GZ, Reddy KM, Zwyer JB, Kuldell MA, Susner MA, Yang Y, Sumption MD, Yue JJ, Rindfleisch M, Tomsic M, Thong CJ, Collings EW. Critical current density and current transfer length of multifilamentary MgB_2 strands of various design. *IEEE Trans. Appl. Superconduct.* 2013; 23:6200204.
28. Li GZ, Yang Y, Susner MA, Sumption MD, Collings EW. Critical current densities and n -values of MgB_2 strands over a wide range of temperatures and fields. *Supercond. Sci. Technol.* 2012; 25:025001.
29. Li GZ, Sumption MD, Zwyer JB, Susner MA, Rindfleisch M, Thong CJ, Tomsic M, Collings EW. Effects of carbon concentration and filament number on advanced internal Mg infiltration processed MgB_2 strands. *Supercond. Sci. Technol.* 2013; 26:095007.
30. Li GZ, Sumption MD, Rindfleisch MA, Thong CJ, Tomsic MJ, Collings EW. Enhanced higher temperature (20–30 K) transport properties and irreversibility field in nano- Dy_2O_3 doped advanced internal Mg infiltration processed MgB_2 composites. *Appl. Phys. Lett.* 2014; 105:112603.
31. Li GZ, Sumption MD, Collings EW. Kinetic analysis of MgB_2 layer formation in advanced internal Mg infiltration (AIMI) processed MgB_2 wires. *Acta Mater.* 2015; 96:66.
32. Li GZ, Sumption MD, Susner MA, Yang Y, Reddy KM, Rindfleisch M, Tomsic M, Thong CJ, Collings EW. The critical current density of advanced internal-Mg-diffusion-processed MgB_2 wires. *Supercond. Sci. Technol.* 2012; 25:115023.
33. Martinez M, Mikheenko P, Martinez-Lopez M, Millan A, Bevan A, Abell JS. Flux pinning force in bulk MgB_2 with variable grain size. *Phys. Rev. B.* 2007; 75:134515.
34. Dew-Hughes D. Flux pinning mechanisms in type II superconductors. *Philos. Mag.* 1974; 30:293.
35. Kramer EJ. Scaling laws for flux pinning in hard superconductors. *J Appl. Phys.* 1973; 30:293.

Highlights

1. To obtain high purity films free from oxygen contamination, a dense Mg-B target was specially made from a high temperature, high pressure reaction of Mg and B to form large-grained (10~50 μm) MgB_2 .
2. Microstructural analysis via electron microscopy found that the resulting grains of the film were composed of ultrafine columnar grains of 19–30 nm. The superconducting critical current density as determined from magnetic measurements, J_{cm} , at 5 K, was 10^5 A/cm^2 at 7.8 T; at 20 K, 10^5 A/cm^2 was reached at 3.1 T.
3. The transport and pinning properties of these films were compared to “powder-in-tube” (PIT) and “internal-infiltration” (AIMI) processed wires. Additionally, examination of the pinning mechanism showed that when scaled to the peak in the pinning curve, the films follow the grain boundary, or surface, pinning mechanism quite well, and are similar to the response seen for C doped PIT and AIMI strands, in contrast to the behavior seen in undoped PIT wires, in which deviations are seen at high b ($b = B/B_{c2}$). On the other hand, the magnitude of the pinning force was similar for the thin films and AIMI conductors, unlike the values from connectivity-suppressed PIT strands.

Figure 1.
Various PLD synthesis routes of MgB₂ thin films.

Figure 2. XRD data for the sample C4. a) Out-of-plane GID XRD showing c -axis peaks from MgB_2 . Inset: the rocking curves around the MgB_2 (0002) reflection. b) In-plane GID XRD showing peak reflections from MgB_2 , Mg (from the cap layer) and Ag (from the Ag paste used to fix the substrate to the substrate holder).

Figure 3.
SEM picture of the plane-view of sample C4, showing end view of columnar grains.

Figure 4.

TEM micrographs of sample C4. (a) High magnification, bright field TEM showing the columnar MgB₂ grains, with (b) corresponding diffraction patterns. (Note: the yellow dashed lattice indicates SiC diffraction patterns and the white indexes indicate MgB₂ diffraction patterns) (c) Low magnification TEM image illustrating the general microstructure of the thin film (the top right part is vacuum).

Figure 5.

a) Evolution of $T_{c,onset}$ as a function of annealing temperature (Note: all samples were *in situ* annealed for 10 min. b) Temperature dependencies of B_{c2} for samples C1, C2, C3 and C4, annealed at different temperatures from 550 to 700 °C for 10 min.

Figure 6. Field dependence of (a) magnetic critical current density, J_{cm} , and (b) bulk pinning force density, F_p , for sample C4 at temperatures 5–25 K.

Figure 7.

A comparison of (a) $J_c(B)$ curves and (b) normalized pinning force density, $F_p/F_{p,max}$, between the MgB₂ thin film, an undoped powder-in-tube (PIT) type MgB₂ wire, a C-doped PIT wire, and a C-doped infiltration-processed (AIMI) MgB₂ wire. Note: in (b), a grain boundary pinning function based on Kramer-Dew-Hughes relationship is added for comparison.

Table I

Annealing temperature, time and $T_{c,onsets}$ for MgB₂ thin films.*

Sample Name	$T_{c,onsets}$, K	Annealing Temperature, °C	Annealing Time, min
A	< 5	-	0
B1	25.3	550	1
B2	NA	600	1
B3	29.5	650	1
B4	30.4	700	1
C1	25.2	550	10
C2	28.2	600	10
C3	30.1	650	10
C4	32.3	700	10
C5	33.7	750	10
D1	28.3	550	30
D2	29.1	600	30
D3	29.4	650	30
D4	33.4	700	30

* All samples are 3 mm × 3 mm in dimension except sample C4. XRD analysis was performed on sample C4 (3 mm × 10 mm in size).

Table II

Comparison between MgB₂ thin film C4 and different kinds of MgB₂ wires.

Sample type	undoped thin film	undoped PIT wire	C-doped PIT wire	C-doped AIMI wire
B_{c2} , T (4.2 K)	20 *	3–15	15–30	15–30
anisotropy, γ	~ 1 **	5	2	2
grain morphology	columnar	platelet	platelet	platelet
texture	highly textured	randomly oriented	randomly oriented	randomly oriented
grain size D, nm	20–30 in width 230 in height	50–100 in thickness 200–300 in width	50–100 in thickness 200–300 in width	50–100 in thickness 200–300 in width
porosity	no	$\sim 25\%$	$\sim 25\%$	no
connectivity	good	bad	bad	good
$F_{p,max}$, GN/m ³ (4.2 K)	29.3	7.7	11.7	19.5

* extrapolated data from Figure 5(b).

** The anisotropy here means the anisotropy of B_{c2} within the MgB₂ thin film plane, for the purpose of J_c consideration.