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Clean epitaxial MgB_2 films fabricated by the *ex situ* annealing of chemical vapour deposition-grown B films in Mg vapour

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Abstract
Low residual resistivity in superconducting thin films is required for their applications in radio frequency (RF) cavities. Here we report on clean epitaxial MgB_2 films fabricated by the *ex situ* annealing of B films, grown by chemical vapour deposition, in Mg vapour. The films show sharp superconducting transitions at about 40 K and a high residual resistivity ratio of about 10. The result indicates that a clean precursor B film and a contamination-free annealing procedure are important for a viable MgB_2 film fabrication process for RF cavity applications.

1. Introduction

The 40 K superconductor MgB_2 has great potential for applications such as Josephson junctions and digital circuits [1], high field magnets for magnetic resonance imaging (MRI) systems [2], and superconducting radio frequency (RF) cavities [3]. High quality MgB_2 films are critical for electronic applications, and are promising for high field magnets in the form of coated conductors and for RF cavities by coating the interior cavity wall. Extensive research has been devoted to the deposition of MgB_2 films using different approaches, including *ex situ* high-temperature annealing in Mg vapour [4–12], *in situ* annealing at intermediate temperatures [13–18], and *in situ* deposition at low temperature in low Mg vapour pressures [19–21] or at high temperature in high Mg vapour pressures [22–24]. Among these techniques, hybrid physical–chemical vapour deposition (HPCVD) has been the most effective technique, which generates high magnesium vapour pressures necessary for phase stability and provides a clean environment for the growth of high purity MgB_2 films [22]. The pure MgB_2 films grown by HPCVD show high T_c over 40 K and normal-state resistivity as low as 0.1 $\mu\Omega$ cm [25]. The low resistivity value, in combination with the relatively large energy gap, leads to a low BCS surface resistance, making MgB_2 a promising superconductor beyond Nb for RF cavities [3]. For fabricating MgB_2 films on large and complex surfaces such as an RF cavity, the two-step *ex situ* annealing approach may be an easier-to-implement solution among various deposition techniques [3]. However, so far the properties of the MgB_2 films made by *ex situ* annealing have not been as good as those in the *in situ* HPCVD films, with the highest residual resistivity ratio RRR (RRR $\equiv \rho(300\ \mathrm{K})/\rho(42\ \mathrm{K})$) values $\sim 3^5$ as compared to over 80 in HPCVD films [25]. In this work, we present high quality MgB_2 films (from 1 to 10 μm in thickness) fabricated by *ex situ* annealing B films, grown by chemical vapour deposition (CVD), in Mg vapour, which show high T_c of $\sim$40 K and RRR of $\sim$10.

2. Experiments

In the two-step *ex situ* annealing technique for MgB_2 films, a B or Mg–B mixture precursor film is annealed in Mg

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vapour at 700–950 °C to react with Mg and form the MgB_2 phase. The precursor film can be deposited by pulsed laser deposition [4, 5], electron-beam evaporation [6, 7], thermal evaporation [8], magnetron sputtering [9, 10], screen printing [11], or CVD [12]. Because the high Mg vapour pressure generated by heating Mg bulk in an enclosure allows annealing at high temperatures, MgB_2 films grown by this approach show good superconducting properties with $T_c \sim 39$ K and J_c exceeding 10^7 A cm^{-2} at zero field [4, 5, 12]. In our work, precursor B films were deposited on (0001) 6H-SiC substrates by CVD using precursor gas of 5% B_2H_6 in H_2, which ensured that the B films were of high purity. The B film was then wrapped with Nb foil and sealed in a low-carbon steel tube with high purity magnesium (99.99%) pellets wrapped in a separate Nb foil. The tube was sealed in Ar atmosphere in a glove box with a pressure slightly higher than 1 atm. The normal sintering procedure included a fast heating to 840–900 °C in 30 min, followed by holding at that temperature for 30 min to 6 h depending on the boron film thickness, and then quench cooling to room temperature in 10 min. A piece of quartz was also placed in the low-carbon steel tube, which was found to be very effective in preventing Mg from depositing on the film surface during cooling. When changing from B to MgB_2, the film experienced a volume expansion of about 200%. For example, a B film of ~1.5 μm results in a MgB_2 film of ~3 μm after the reaction.

The film thicknesses for the samples in this work were determined from the cross-section SEM images of the fractured samples. X-ray diffraction measurements were performed using a Philips X'Pert Pro MRD 4-circle diffractometer with Cu Kα radiation. The resistivity measurements were performed using a van der Pauw geometry over the temperature range of 30–300 K. Critical current densities were determined from the magnetization measurement and estimated from the hysteresis loops using the Bean critical state model with the magnetic field applied perpendicular to the surface of the films.

3. Results and discussion

Typical x-ray diffraction (XRD) spectra for a 3 μm thick MgB_2 film grown on a (0001) 6H-SiC substrate are shown in figure 1. The θ–2θ scan in figure 1(a) reveals strong 000ℓ reflections from MgB_2 besides the substrate peaks, indicating that the film consists predominantly of c-axis oriented MgB_2. There are also weak peaks in the spectrum that do not belong to MgB_2 and are difficult to identify. They could be from the B-rich Mg–B phases due to incomplete reaction of B with Mg or from other foreign phases resulting from the annealing process. The intensities of these peaks are low, indicating that the amount of these foreign phase materials is small. The ω-scan in figure 1(b) shows a full width at half maximum (FWHM) of 0.94° for the MgB_2 0002 peak, further confirming the excellent c-axis orientation of the film. Figure 1(c) presents the ϕ scan of the $10\bar{1}1$ peak of the film. In this scan $\phi = 0^o$ corresponds to when the in-plane component of the diffraction vector is aligned parallel to the $[10\bar{1}1]$ in-plane direction of the SiC substrate. It reveals the presence of a six-fold symmetry for the MgB_2 film and a 'hexagon-on-hexagon' epitaxial growth

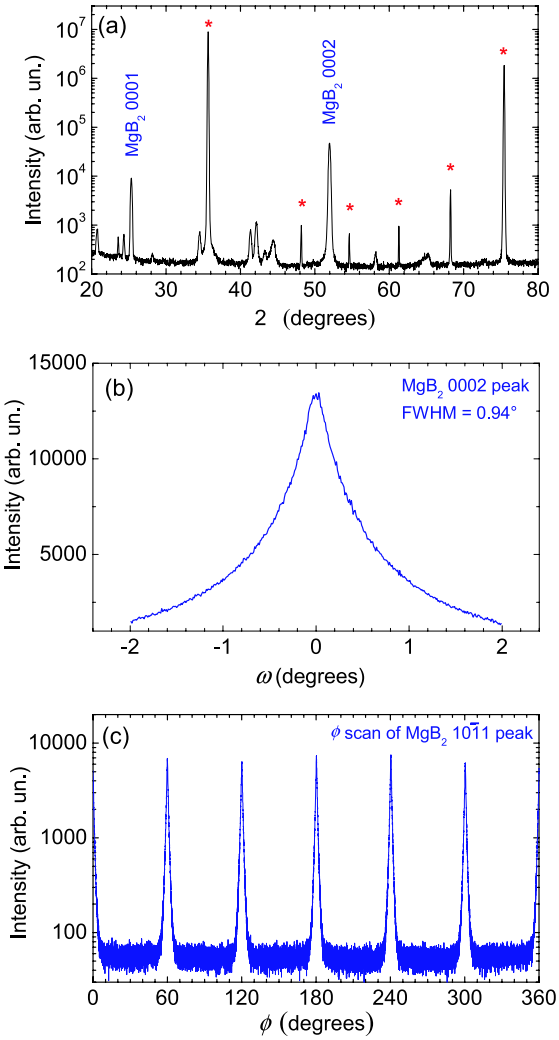

Figure 1. XRD spectra for a 3 μm thick MgB_2 film on (0001) 6H-SiC substrate. (a) θ–2θ scan. Substrate peaks are marked with asterisks (∗); (b) ω-scan of the MgB_2 0002 peak; and (c) ϕ scan at $\chi = 37.44°$ of the $10\bar{1}1$ MgB_2 peak. $\chi = 90°$ aligns the diffraction vector to be perpendicular to the plane of the substrate. $\phi = 0°$ corresponds to when the in-plane component of the diffraction vector is aligned parallel to the [1011] in-plane direction of the substrate. (This figure is in colour only in the electronic version)

on the (0001) 6H-SiC substrate. The existence of the small amount of foreign phases does not seem to affect appreciably the epitaxial quality of the MgB_2 film, possibly because they are scattered at the surface or grain boundaries.

Figure 2 shows scanning electron microscopy (SEM) images of a 3 μm thick MgB_2 film. The surface image, shown in figure 2(a), indicates that the film is composed of densely packed grains of about a half micrometre in size. The cross sectional image is shown in figure 2(b). The film is dense except for the large voids occasionally seen in some parts of the film. Energy-dispersive x-ray spectroscopy (EDX) analysis of different spots on the cross section of the film in figure 2(b) indicates that Mg has diffused through the entire thickness of the film to react with B and any incompletely reacted phases are in minute amount beyond detection. We rely on the cross sectional image, combined with XRD, to ensure that the film

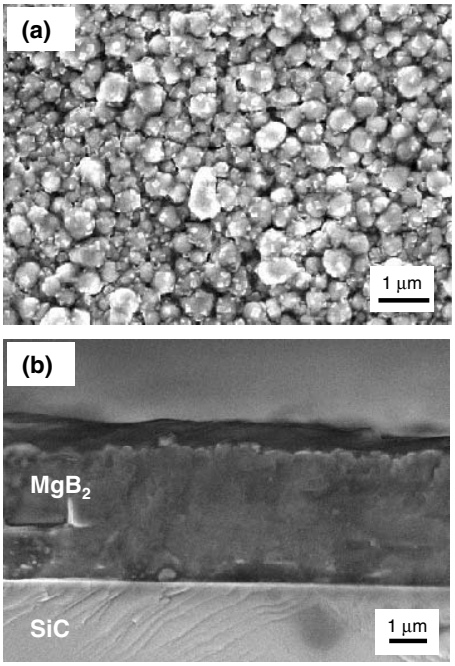

Figure 2. SEM images of (a) the surface and (b) the cross section for a 3 μm thick MgB_2 film.

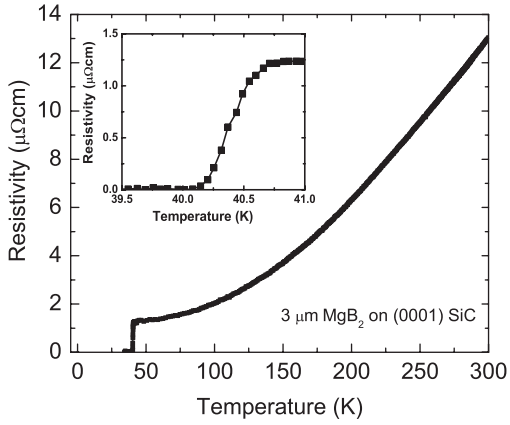

Figure 3. Resistivity versus temperature plot for the 3 μm thick MgB_2 film.

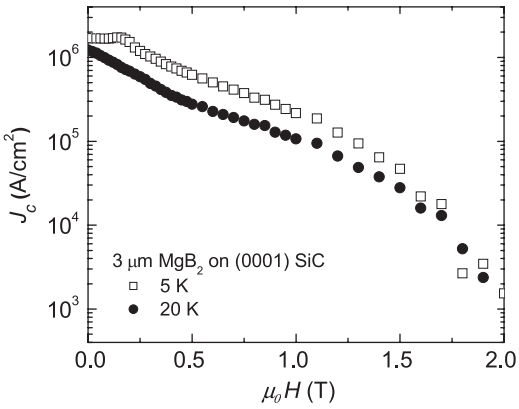

Figure 4. Critical current density versus applied magnetic field for the 3 μm thick MgB_2 film at 5 and 20 K.

is fully reacted to form the MgB_2 phase under the annealing conditions used. Incompletely reacted films show contrast in brightness in different layers in the cross sectional SEM image, and some show MgB_4 peaks in XRD. In those cases, the uncertainty in MgB_2 layer thickness in the incompletely reacted films can lead to uncertainty in the resistivity and critical current density values. EDX studies also show the existence of small amounts of Si in the films, suggesting that some reaction with the SiC substrate took place during the annealing. This reaction is likely to be the reason of difficulties in obtaining superconducting films thinner than 200 nm. In this paper, only results from films of 1 μm or thicker are presented. Research is underway to study MgB_2 films on other substrates where reaction does not occur.

Figure 3 is the resistivity versus temperature plot for the 3 μm thick film. It shows a sharp superconducting transition at 40 K and a low residual resistivity of 1.25 $\mu\Omega$ cm. The low resistivity value is comparable to values reported in clean HPCVD MgB_2 thin films. The RRR for this film is over 10, which is much higher than values previously reported in the literature for MgB_2 films fabricated by the *ex situ* annealing method [4–12]. The high T_c, low resistivity, and high RRR indicate the cleanness and good connectivity of the film.

The critical current density J_c under different applied magnetic fields perpendicular to the film surface, measured by the magnetization hysteresis loops using the Bean model, for the 3 μm thick film is shown in figure 4. At self field, the measured value of J_c is 1.7×10^6 A cm^{-2} at 5 K and 1.2×10^6 A cm^{-2} at 20 K. The low temperature, low field result is lower than the actual value in the film because the flux jumps at these conditions reduce the connectivity between the grains in the film. The rapid drop of J_c in magnetic field is due to the lack of pinning in the film, another indication of the cleanness and crystallinity of the film.

For coated-conductor applications, it is necessary to deposit thick MgB_2 films in order to maximize the superconductor fraction in the wire or tape and enhance the engineering critical current density. We have made MgB_2 films of various thicknesses using the two-step annealing process and the resistivity versus temperature plots of 1, 3, 7.5 and 10 μm thick films are shown in figure 5. The transition remains sharp for all the films with an average of 0.3 K, and T_c ranges from 39.5 to 40.7 K. It is interesting to note that T_c in thinner films are higher than the bulk value, similar to the epitaxial HPCVD films, where it is attributed to the epitaxial tensile strain [26]. The two-step annealing process is different from the *in situ* HPCVD and the coalescence strain is absent in the present films. It is possible that the larger thermal expansion coefficient in MgB_2 (5.5×10^{-6} K^{-1} at room temperature) than in SiC (3.0×10^{-6} K^{-1} at room temperature) causes tensile strain in the films during the cooling from the annealing temperature, leading to the higher T_c [26]. When the films become thicker, this effect is less important, and the T_c value is similar to the bulk in the 10 μm thick film. The residual resistivity of the film ranges from 1.15 to 1.75 $\mu\Omega$ cm. The slight increase in resistivity with thickness may be due to more

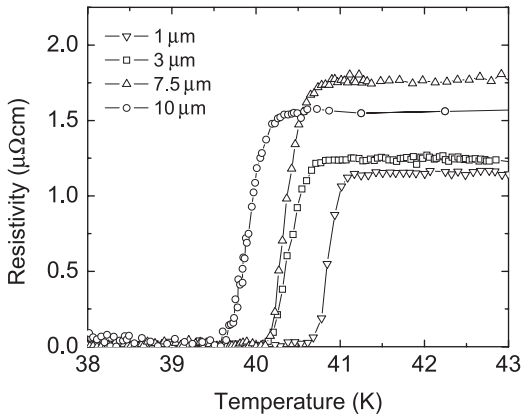

Figure 5. Resistivity versus temperature plots for 1, 3, 7.5 and 10 μm thick MgB_2 films.

cracks in the thicker films. This is also reflected in J_c, which drops to 3×10^5 A cm^{-2} in the 10 μm film. Such drop is absent in *in situ* HPCVD thick films [27]. Further work is underway to prevent cracking in thicker films.

4. Conclusion

In summary, we have succeeded in fabricating clean MgB_2 films by annealing CVD-deposited B films in Mg vapour. The CVD deposition results in very clean B films, while the annealing in carbon steel tube and caps in Ar atmosphere reduces chances of contamination. The films have high T_c of ~40 K, low residual resistivity of less than 2 $\mu\Omega$ cm, and high self-field J_c. The films are dense except that voids, likely formed during the reaction process, exist in the film. The density of voids or cracks increases with film thickness. The results demonstrate that the *ex situ* deposition method can produce clean MgB_2 films with superior superconducting properties close to the films fabricated by the *in situ* HPCVD method, which is significant for applications such as MgB_2 superconducting cavities and coated-conductor wires and tapes.

Acknowledgments

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