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High quality MgB_2 thick films and large-area films fabricated by hybrid physical–chemical vapor deposition with a pocket heater

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Abstract
A hybrid physical–chemical vapor deposition process using a pocket heater was developed for the growth of high quality epitaxial large-area MgB_2 thin films and *c*-axis textured MgB_2 thick films. This technique is able to independently control the substrate and Mg source temperatures and maintain sufficient Mg overpressure to ensure phase stability. The two-inch large-area MgB_2 thin films showed uniform superconducting properties with the superconducting transition temperature T_c of about 40 K, residual resistivity ratio (RRR) of about 10, and critical current density J_c of about 10^7 A cm^{-2} (0 T, 5 K). The thick films ($\sim$10 μm) on sapphire substrates showed a maximum T_c of 40 K and RRR of 15, and a J_c of 1.6×10^6 A cm^{-2} at low applied magnetic fields even at 20 K. High quality thick films also have been obtained on metal substrates.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The 40 K superconductor MgB_2 has received great attention due to its potential in applications such as Josephson junctions and digital circuits [1], magnetic resonance imaging (MRI) magnets [2], and superconducting radio frequency (RF) cavities [3]. Various thin film deposition techniques have been developed that will allow this new superconductor to be used in the above applications [4–17]. Among these techniques, hybrid physical–chemical vapor deposition (HPCVD) has been the most effective one for the growth of small-area thin films, which generates high magnesium vapor pressures necessary for phase stability and provides a clean environment for the growth of high purity MgB_2 films [12].

For superconducting coated conductor applications [18, 19], 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. Very recently, Lamborn *et al* developed an impinging-jet HPCVD technique for the growth of thick films, which is modified from the original HPCVD configuration [20]. In this geometry, the Mg source and substrate temperatures are controlled independently and a water-cooled gas inlet for diborane (B_2H_6) is used to suppress the thermal decomposition of B_2H_6 and minimize upstream B_2H_6 depletion. A high growth rate of more than 100 μm h^{-1} was achieved using this technique and MgB_2 films up to 10 μm grown by this technique showed good superconducting properties. Although the impinging-jet HPCVD has demonstrated high quality in thick MgB_2 films, for practical applications such as superconducting coated conductors and

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superconducting RF cavities, techniques capable of depositing thick and large-area MgB_2 films need to be developed.

The most successful deposition technique so far for the growth of large-area MgB_2 thin films is the reactive evaporation technique reported by Moeckly and Ruby [13]. It utilizes a pocket heater with a rotating substrate holder spinning at several hundreds rotation per minute (rpm). The substrate is exposed to the chamber via an opening in the heater during about a third of one rotation cycle, when boron is deposited by e-beam evaporation. When the substrate spins inside of the pocket heater where a high Mg vapor pressure is provided by an independently heated Mg source, the boron layer reacts with Mg to form MgB_2. The cycle repeats itself for the deposition of thicker films. With a boron deposition rate of 0.1 nm s^{-1}, Moeckly and Ruby reported high quality, large-area MgB_2 films of over 500 nm in thickness with a T_c value of 38–39 K and residual resistivity ratio (RRR) value of about 4 [13].

In this work, we report high quality thick and large-area MgB_2 films grown by HPCVD using a pocket heater the same as that used in the reactive evaporation technique. The films as thick as 10 μm show T_c of about 40 K, RRR of 15 and J_c of 1.6×10^6 A cm^{-2} at zero field and 20 K. The technique combines the advantages of a pocket heater in growing large-area and thick films with those of HPCVD for growing clean MgB_2 films.

2. Experiments

Figure 1 presents a schematic of the HPCVD setup using a pocket heater. The pocket heater was provided by Superconductor Technologies Inc., and the details of the reactive evaporation deposition of MgB_2 films using a similar pocket heater have been described in [13]. In our work, instead of e-beam evaporation for boron layer deposition, we used chemical vapor deposition (CVD) for the growth of the boron layer. The mixture of 5% diborane (B_2H_6) in ultra high purity (UHP) H_2 was used as the boron source. UHP H_2 was used as the carrier gas which ensured an oxygen-free atmosphere in the chamber so that very clean MgB_2 film can be achieved. Before deposition, the chamber was first pumped to below 10^{-2} Torr and then purged for 10 min with UHP H_2. The substrate and the Mg source were independently heated to about 620 °C and 720 °C, respectively, in 3–8 Torr UHP H_2. The substrate holder was rotating at 120 rpm. A B_2H_6 in H_2 mixture gas was then introduced into the chamber and through a radiation shielded gas tube to the front of the opening on the pocket heater. For large-area film deposition, a shower-type gas tube was used to deliver the B_2H_6 uniformly to the substrates, and for small-area film deposition a simple vertical gas tube was used. Once the B_2H_6 gas began to flow, the cycles of consecutive boron layer deposition and reaction with Mg started. The deposition rate depends on the B_2H_6 flow rate. For large-area thin films 40 sccm B_2H_6 mixture was used, leading to a deposition rate of 0.5 nm s^{-1}, and for thick films 150 sccm B_2H_6 was used with a deposition rate of 3.7 nm s^{-1}. The film growth was terminated by switching off the B_2H_6 mixture gas before the Mg in the Mg source was completely evaporated. The substrate heater was then turned off to allow cooling under the H_2 carrier gas and the Mg source heater temperature was adjusted to be approximately 100 °C higher than the substrate temperature to maintain a constant overpressure of Mg vapor. When the substrate temperature was lower than 500 °C, the Mg source heater was turned off and allowed to cool under an UHP H_2 flow.

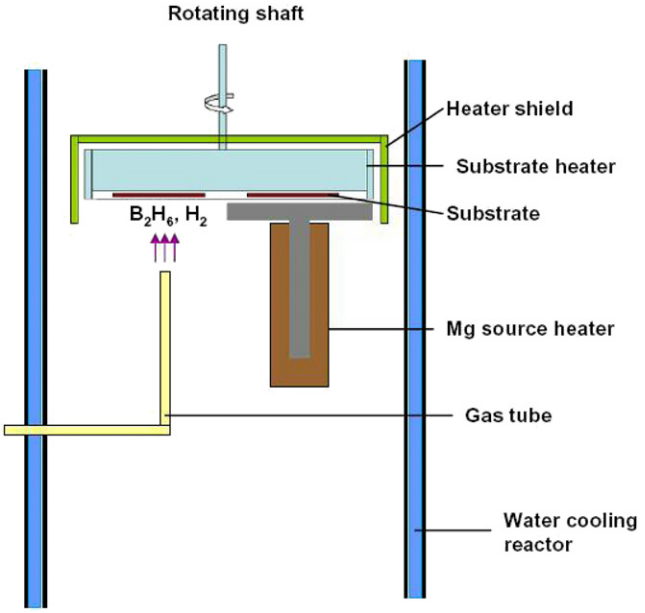

Figure 1. Schematic of the HPCVD setup using a pocket heater.

Compared to the reactive evaporation deposition of MgB_2 films by Moeckly and Ruby [13], our HPCVD process operates in 3–8 Torr hydrogen atmosphere instead of the high vacuum environment for reactive evaporation, and the substrate temperature is higher (620 °C as compared to of 400–600 °C for reactive evaporation). To reduce the heating of the vacuum chamber and the B_2H_6 gas delivering tube due to the high hydrogen pressure, thermal shielding for the heater and the gas tube was installed.

3. Results and discussion

3.1. Large-area films

The pocket heater used in this work can accommodate three 2 inch diameter wafers. Figure 2(a) shows x-ray diffraction (XRD) θ–2θ scan of a 400 nm-thick 2 inch MgB_2 film grown on a (0001) sapphire substrate. Apart from the substrate peaks, the only peaks observed arise from the (000l) reflections of MgB_2, indicating that a phase-pure MgB_2 film with the c-axis normal to the film surface is obtained. The ω-scan in the inset to figure 2(a) shows a full width at half maximum (FWHM) of 0.76° for the MgB_2 0002 peak, further confirming the excellent c-axis orientation of the film. Figure 2(b) presents the ϕ scan of the $10\bar{1}1$ peak of the film. A six-fold symmetry characteristic of a (000l)-oriented MgB_2 film with in-plane epitaxy is observed. Very weak peaks at 30° $\pm$ n60° (where n is an integer) in this figure indicate that there are trace amount of grains that are rotated by 30° with respect to the majority of grains [12]. The epitaxial relationship of MgB_2 films on c-sapphire is $[10\bar{1}1]MgB_2 \parallel [11\bar{2}0]Al_2O_3$, that is, the

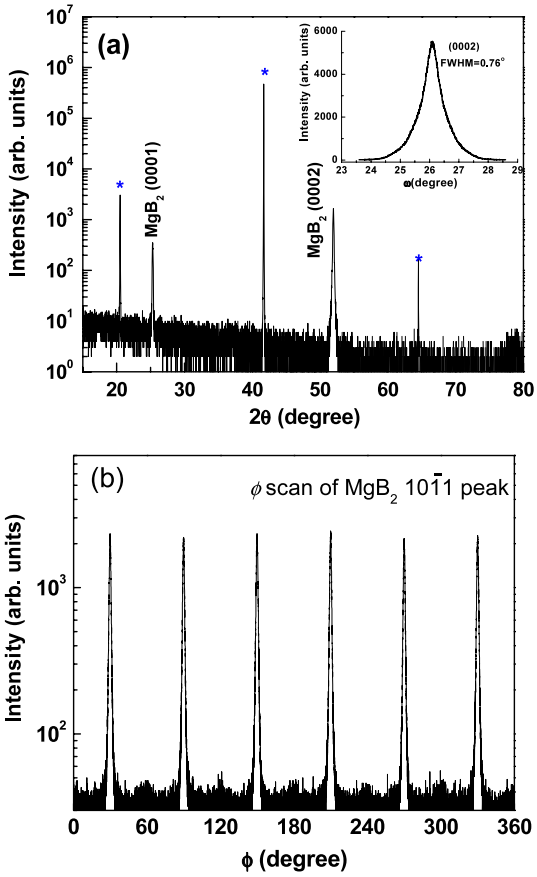

Figure 2. XRD patterns for a 400 nm 2 inch MgB_2 film on (0001) sapphire substrate. Substrate peaks are marked with asterisks. (a) θ–2θ scan and (b) ϕ scan of the $10\bar{1}1 MgB_2$ peak. The inset to (a) is the rocking curve of MgB_2 (0002) reflection.

hexagonal MgB_2 lattice is rotated by 30° to match the hexagonal lattice of sapphire.

The large-area MgB_2 thin films fabricated by the pocket heater HPCVD technique have smooth surface. When measured by atomic force microscopy over a 5 μm × 5μm area, the root-mean-square roughness of the 400 nm-thick 2 inch MgB_2 thin film on Al_2O_3(0001) was about 3.6 nm.

The large-area MgB_2 films show good and uniform superconducting properties. Figure 3(a) shows the resistivity versus temperature curve for a 400 nm-thick MgB_2 film with a 5 × 5 mm^2 area cut from the center of a 2 inch MgB_2 film. The film has a high T_c of 40.2 K, a low residual resistivity of 1.01 $\mu\Omega$ cm, and a high RRR of 9.8. These properties are similar to those observed in standard HPCVD films [21]. Such excellent properties are obtained uniformly across the 2 inch area film. Figure 3(b) shows the zero resistance superconducting transition temperature T_c and RRR for a series of 5 × 5 mm^2 films cut from different positions of the 2 inch film. The T_c is in the range of 39.9–40.2 K and the RRR is in the range of 8.8–10, indicating a very uniform clean film with good connectivity. The higher T_c and RRR values than in films fabricated by reactive evaporation [13] may be due to the reducing hydrogen atmosphere during the deposition and the higher deposition temperature.

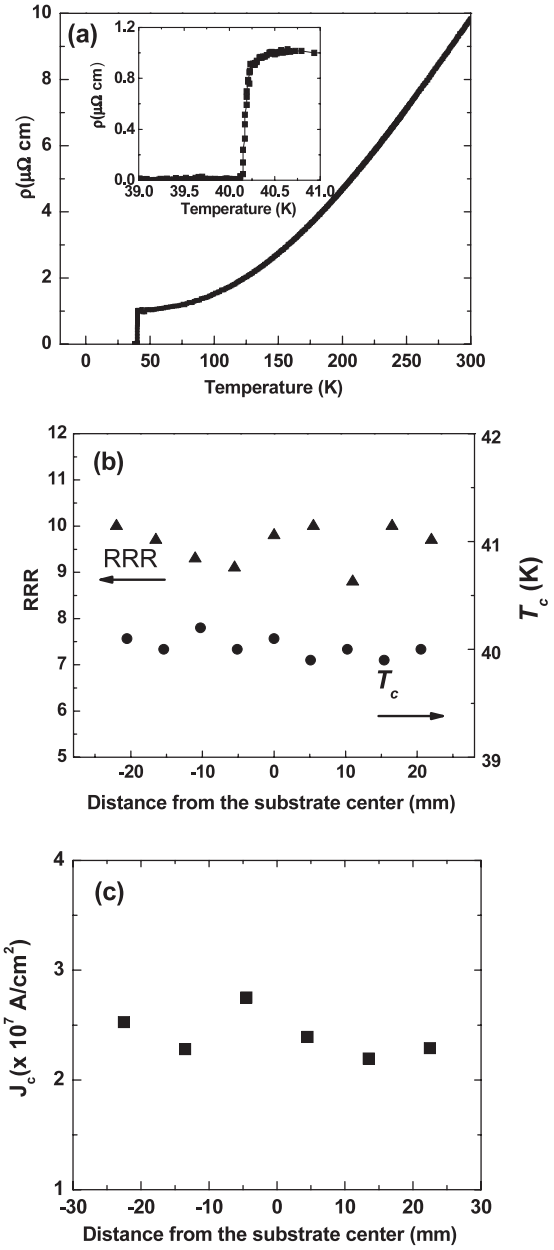

Figure 3. (a) Resistivity versus temperature curve for a 400 nm-thick 2 inch MgB_2 films on *c*-sapphire substrate. Inset shows details near the superconducting transition. (b) T_c^{zero} and RRR and (c) J_c (0 T and 5 K) of the 2 inch film as a function of the location on the film.

Critical current density J_c was measured by magnetization and estimated from the hysteresis loops using the Bean critical state model with the magnetic field applied perpendicular to the surface of the films. Figure 3(c) shows the J_c distribution at different points on the 2 inch film, varying between 2.28 × 10^7 A cm^{-2} and 2.75 × 10^7 A cm^{-2} at 0 T and 5 K, another indication of the uniform properties of the film.

3.2. Thick films

Thick MgB_2 films grown by HPCVD using the pocket heater also show high quality. Figure 4(a) shows a surface scanning electron microscopy (SEM) image of a thick MgB_2 film on

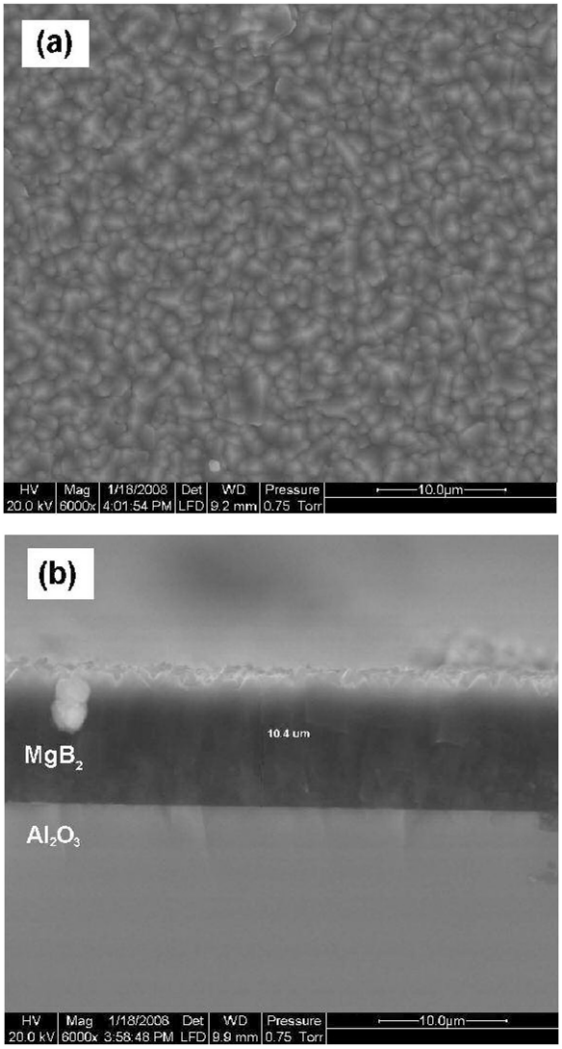

Figure 4. SEM images of (a) the surface and (b) the cross section for a 10 μm thick MgB_2 film on *c*-sapphire.

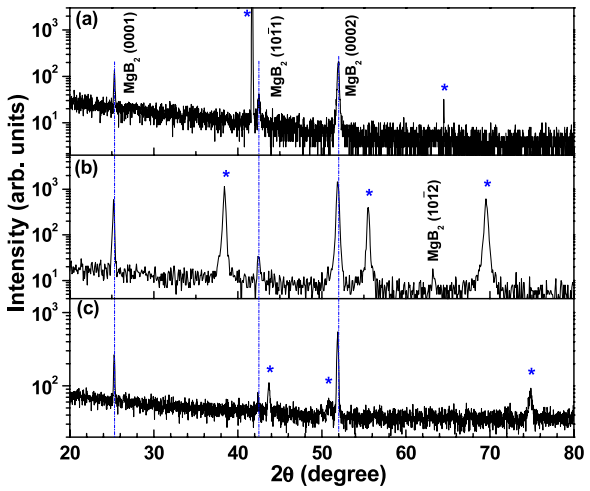

Figure 5. DXRD θ–2θ scans for 10 μm thick MgB_2 films on (a) (0001) sapphire, (b) Nb, and (c) unpolished stainless steel substrates. Substrate peaks are marked with asterisks.

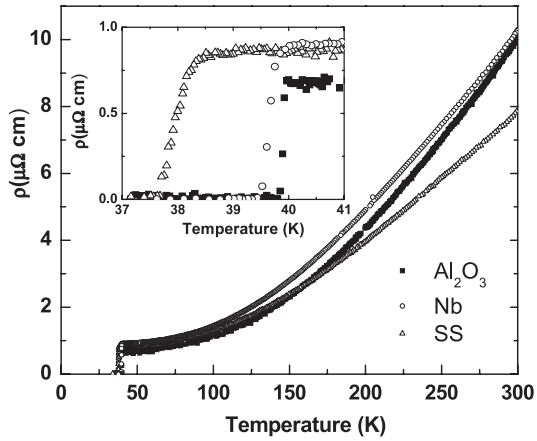

Figure 6. Resistivity versus temperature plots for the 10 μm thick MgB_2 films on *c*-sapphire, Nb and unpolished stainless steel substrates. Inset shows details near the superconducting transition.

(0001) single crystal sapphire substrate. The film surface is dense, smooth and no crack is observed. The cross sectional SEM image shown in figure 4(b) reveals a clean interface between the film and substrate and indicates a thickness of about 10.4 μm. The thickness distribution across the film is uniform: for a 15×15 mm^2 film, the measured thickness across the sample varies within 200 nm.

Thick MgB_2 films have also been grown on Nb and stainless steel. Figure 5 shows XRD θ–2θ scans of 10 μm thick MgB_2 films on single crystal sapphire and nontextured metals Nb and stainless steel (SS). The films on all the three types of substrates are strongly *c*-axis textured. Using a texturing coefficient $A = (P - P_0)/(1 - P_0)$ with $P = \sum I_{(000l)} / \sum I_{(hkil)}$ for films and P_0 for the random oriented powders (I is the peak intensity of a Bragg reflection) [22], we find that $A \sim 0.9$ for all the samples, revealing a very high degree of *c*-axis texture in these thick films. The *c*-axis texture of MgB_2 thick films on nontextured metallic substrates may be due to the growth mode of the films.

Figure 6 presents the resistivity versus temperature plots for 10 μm thick films on *c*-cut sapphire, Nb and unpolished stainless steel substrates. Film on sapphire shows a sharp superconducting transition at about 40 K and a low residual resistivity of 0.75 $\mu\Omega$ cm, which are comparable to values reported in clean HPCVD MgB_2 thin films [12]. The RRR for this thick film is about 15, suggesting a good connectivity and cleanness. The values of T_c and RRR are 39.6 K and 12 for film on Nb, and 38 K and 9.4 for film on stainless steel. The resistivity for films on the metallic substrates is difficult to estimate because of the contribution to transport by the substrates. The results in figure 6, calculated with only the thicknesses of the films, show similar values to that in the film on sapphire, indicating that there may exist an insulating layer between the MgB_2 film and the metal substrates.

Figure 7 is a typical J_c versus magnetic field result at 5 and 20 K for a 10 μm thick MgB_2 film on *c*-cut sapphire. At self-field, the measured value of J_c is 2.5×10^6 A cm^{-2} at 5 K and it can reach 1.6×10^6 A cm^{-2} even at 20 K. Like most clean HPCVD thin films, the J_c of the thick film drops rapidly with magnetic field due to the lack of pinning in the film.

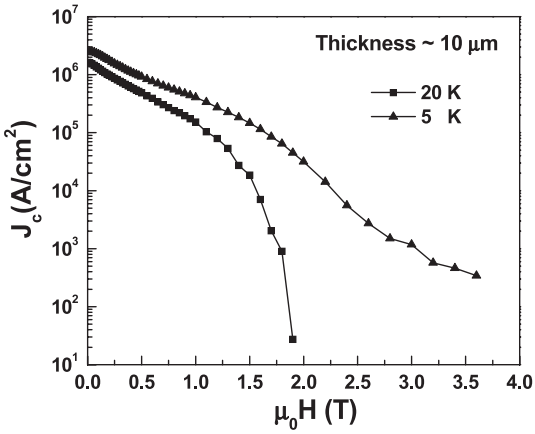

Figure 7. Critical current density versus applied magnetic field for a 10 μm thick MgB_2 film on *c*-sapphire substrate at 5 and 20 K.

4. Conclusion

In summary, we have succeeded in fabricating high quality large-area epitaxial MgB_2 thin films and *c*-axis textured MgB_2 thick films using the HPCVD technique with a pocket heater. The 2 inch thin film shows uniform superconducting and normal-state transport properties with T_c of ~40 K, RRR of ~10 and J_c of $\sim 10^7$ A cm^{-2} (0 T and 5 K). The 10 μm thick MgB_2 film is dense, smooth and uniform in thickness, with the self-field J_c reaching 1.6×10^6 A cm^{-2} even at 20 K. The results indicate that the technique or its modified variations are effective tools for various applications such as coated conductors, RF cavities, and Josephson devices and circuits.

Acknowledgments

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