Superconducting MgB$_2$ thin films on silicon carbide substrates by hybrid physical–chemical vapor deposition

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We have used two polytypes of silicon carbide single crystals, 4H-SiC and 6H-SiC, as the substrates for MgB$_2$ thin films grown by hybrid physical-chemical vapor deposition (HPCVD). The c-cut surface of both polytypes has a hexagonal lattice that matches closely with that of MgB$_2$. Thermodynamic calculations indicate that SiC is chemically stable under the *in situ* deposition conditions for MgB$_2$ using HPCVD. The MgB$_2$ films on both polytypes show high-quality epitaxy with a Rutherford backscattering channeling yield of 12%. They have T_c above 40 K, low resistivities, high residual resistivity ratios, and high critical current densities. The results demonstrate that SiC is an ideal substrate for MgB$_2$ thin films. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1563840]

The superconductivity in MgB$_2$ has generated great interest in its applications in superconducting electronics.[1] It is hoped that reproducible and uniform Josephson junctions may be easier to fabricate using MgB$_2$ than high temperature superconductors. The transition temperature of 39 K allows operation of MgB$_2$-based circuits at above 20 K, very attractive for superconducting integrated circuits. The first step towards MgB$_2$ Josephson junctions and circuits is the high-quality thin film by an *in situ* deposition process. Recently, we have succeeded in depositing *in situ* epitaxial MgB$_2$ thin films by the hybrid physical-chemical vapor deposition (HPCVD) technique.[2] The choice of substrates has a direct impact on the quality of MgB$_2$ thin films.[3] The chemical stability of a substrate may also be influenced by the conditions in different deposition techniques such as *ex situ* annealing of B films in Mg vapor,[4,5] *in situ* annealing of Mg–B or Mg–MgB$_2$ mixtures,[6–8] low temperature *in situ* molecular-beam epitaxy growth,[9,10] or HPCVD. In our previous paper,[2] we have mentioned 4H-SiC as a substrate for MgB$_2$. In this letter, we present a systematic study of c-cut SiC, of both 4H and 6H polytypes, and show by thermodynamic calculation and excellent structural and electrical properties that silicon carbide is an excellent substrate for MgB$_2$ deposition by HPCVD.

SiC is a wide-band-gap semiconductor with an energy gap around 3 eV.[11] Its elementary structural unit is a C–Si

tetrahedron. SiC has over 170 polytypes, determined by the stacking sequence of the C–Si bilayer with a hexagonal structure.[12] If the first bilayer is called the "*A*" position, the next bilayer can be placed in either "*B*" or "*C*" position. The stacking sequences for the polytypes used in this work are $ABCB$ for 4H-SiC and $ABCACB$ for 6H-SiC. Both have a hexagonal structure with $a=3.073$ Å for 4H-SiC and $a=3.081$ Å for 6H-SiC. The c lattice constants are 10.053 Å for 4H-SiC and 15.12 Å for 6H-SiC.[12] In this work, substrates of both polytypes are (0001) oriented (c-cut), which provides a hexagonal lattice with a close lattice match to MgB$_2$ ($a=3.086$ Å[13]).

Details of the *in situ* deposition of epitaxial MgB$_2$ thin films by HPCVD have been described previously.[2] Briefly, in a hydrogen carrier gas of 100 Torr, bulk Mg chips and the substrate are heated inductively to 720–760 °C, which results in a high Mg vapor pressure locally around the substrate. Boron precursor gas, 1000-ppm diborane (B$_2$H$_6$) in H$_2$, is then introduced into the reactor to initiate the MgB$_2$ film growth. The flow rates are 400 sccm for the H$_2$ carrier gas and 50 sccm for the B$_2$H$_6$/H$_2$ mixture. The keys to the success of the HPCVD technique are the capability to generate a high Mg vapor pressure and the reducing hydrogen atmosphere used in the process which inhibits MgO formation.

He *et al.* have reported reactions between MgB$_2$ and SiC when SiC is mixed with elemental Mg and B in a pressed pellet and annealed at 800 °C in a sealed Ta tube.[3] In the HPCVD process, the SiC substrate is subject to Mg vapor at 720–760 °C before B$_2$H$_6$ is introduced. We have carried out a thermodynamic calculation taking into account all possible reactions between SiC, Mg, and B, and the resultant SiC–Mg

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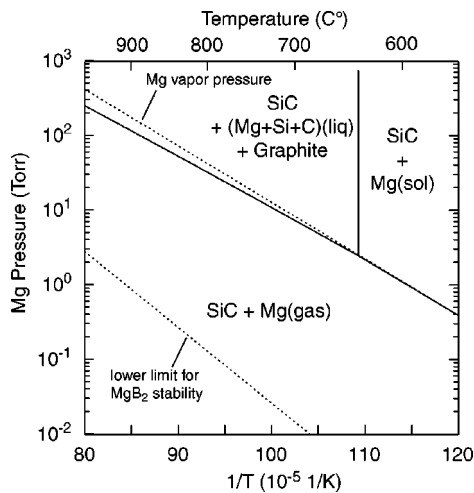[d)]Electronic mail: xxx4@psu.edu

FIG. 1. A thermodynamic phase diagram of the SiC–Mg system for 4H-SiC. The lower dotted line is the lower limit for MgB_2 phase stability and the upper dotted line indicates the Mg vapor pressure.

FIG. 2. X-ray diffraction spectra of a MgB_2 thin film on a (0001) 4H-SiC substrate. (a) $\theta - 2\theta$ scan and (b) ϕ scan of the $10\bar{1}2$ MgB_2 reflection. The substrate peaks are marked by $*$, while the unidentifiable substrate peaks (classified as substrate peaks based on their narrow width) are marked as $\triangle$.

phase diagram for 4H-SiC is shown in Fig. 1. A similar phase diagram is obtained for 6H-SiC. The lower dotted line is the lower limit for MgB_2 phase stability[14] and the upper dotted line indicates the Mg vapor pressure. It shows that no chemical reactions occur when the Mg partial pressure is about or below 95% of its vapor pressure at corresponding temperatures. Above this partial pressure, a reaction occurs to form a liquid solution of Mg, Si and C plus graphite. In the experiment of He *et al.*, the Mg pressure in the sealed Ta tube may very well be above 95% of its vapor pressure, causing a chemical reaction. In our experimental setting, although the Mg partial pressure is high enough to form the MgB_2 compound and keep it stable, continuous pumping during the deposition keeps the Mg partial pressure below 95% of its vapor pressure and therefore substrate reactions are avoided.

The epitaxial relationship and crystalline quality of the MgB_2 films on 4H-SiC and 6H-SiC substrates were measured by four-circle x-ray diffraction. Figure 2(a) shows the $\theta - 2\theta$ scan of a MgB_2 film grown on a (0001) 4H-SiC substrate. The substrate peaks are marked by "$*$." $000l$ MgB_2 peaks are the only nonsubstrate peaks observed, indicating that the film is phase-pure with its c-axis oriented normal to the film surface. The full width at half maximum (FWHM) of the 0002 MgB_2 peak in 2θ and ω (rocking curve) is 0.29° and 0.56°, respectively. The c-axis lattice constant measured was 3.52 ± 0.01 Å, the same as in bulk MgB_2.[13] Figure 2(b) shows the azimuthal scan (ϕ scan) of the MgB_2 $10\bar{1}2$ reflection, where $\phi = 0°$ is aligned parallel to $[11\bar{2}0]$ direction of the SiC substrate. The periodically spaced peaks separated by 60° in the scan reveal the sixfold hexagonal symmetry of the MgB_2 film and the presence of epitaxy. The FWHM of the in-plane peaks in ϕ is 0.9°. The in-plane lattice constant is 3.09 ± 0.03 Å, the same as in bulk MgB_2.[13] The small lattice mismatch between the MgB_2 film and SiC substrate (0.42%) enables the hexagonal MgB_2 to grow directly on top of hexagonal SiC, resulting in an epitaxial orientation of $(0001) [11\bar{2}0] MgB_2 \| (0001)[11\bar{2}0]$ SiC. Analogous epitaxy has been observed in MgB_2 films on (0001) 6H-SiC substrates.

The MgB_2 films on SiC substrates were investigated using Rutherford backscattering spectrometry (RBS) and chan-
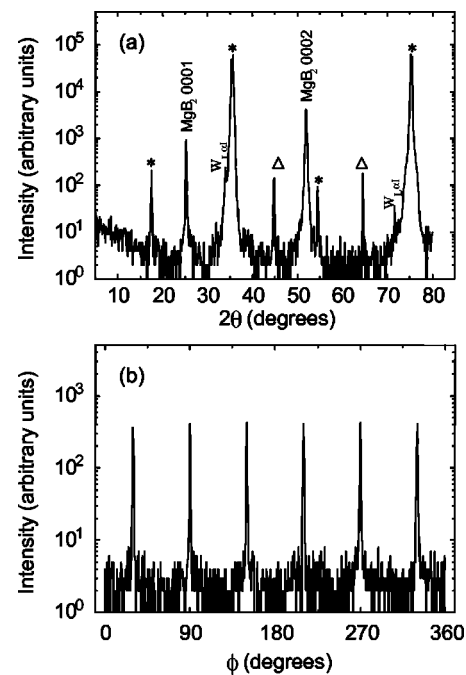
neling to measure the depth profile of composition and the crystalline quality. The experiments are performed with 1.4-MeV He^+ ions using an incident beam perpendicular to the substrate surface. The RBS and channeling results for a MgB_2 film on 4H-SiC are shown in Fig. 3. We find homogeneous depth profiles of both Mg and B on top of the SiC substrate signal within the resolution of the measurement. Oxygen is also found in the spectrum and the simulation shows that it is at the film surface with a thickness of around 6–8 nm, assuming that the surface layer is MgO. The minimum channeling yield as compared to the random spectrum is 12%, determined at the Mg signal at the surface, which verifies the good crystalline quality of the samples.

The superconducting and transport properties of MgB_2 films were characterized by resistivity measurements using the standard four-point method. Figure 4 shows resistivity versus temperature curves for two films on (a) 4H-SiC and (b) 6H-SiC substrates. The insets show the details near the superconducting transition. The films on both substrates have zero-resistance T_c above 40 K, higher than that in the bulk materials. The origin of the higher T_c is under investigation. It has been reported previously that T_c of MgB_2 decreases when a hydrostatic pressure is applied on it[15,16] or the lattice strain[17] increases. Hur *et al.* have reported a higher T_c in MgB_2 films on boron crystals and have suggested that it is possibly due to a tensile strain.[18] A tensile strain in the films on SiC, resulting from the mismatch in the thermal expansion coefficients, may be the cause of the higher T_c. The resistivities of our films are low, being about 1.0–1.3 $\mu\Omega$ cm for both substrates before the superconducting transition. The residual resistance ratio $RRR = R(300K)/R(43K)$ is about 12–13 in both films. These values are approaching those in the high quality bulk samples,[19] indicating clean films with good crystallinity.
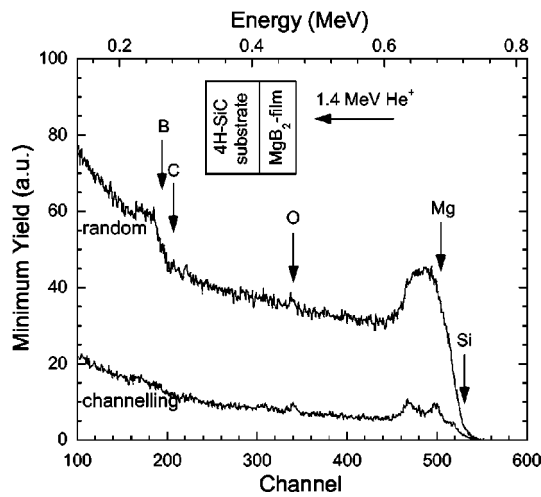
FIG. 3. RBS/channeling spectra of a MgB$_2$ film grown on 4H-SiC. A sketch of the measurement geometry is shown as an inset. The position of the different elements are indicated by arrows. A minimum channelling yield of 12% is obtained, indicating the good crystalline quality of the film.

FIG. 5. The transport critical current density J_c for a MgB$_2$ film on a 6H-SiC substrate as a function of temperature measured under different applied magnetic fields.

The transport critical current density J_c for a MgB$_2$ film on 6H-SiC substrate is shown in Fig. 5 as a function of temperature and applied magnetic field. It was measured on a 20-μm-wide bridge using a Quantum Design PPMS system with a 9-T superconducting magnet. In zero field, J_c is 3.5 $\times 10^7$ A/cm^2 at 4.2 K and above 10^7 A/cm^2 at 25 K. These are values comparable to the best J_c reported value in the literature.[20] The relatively quick suppression of J_c by applied magnetic fields is likely due to the lack of MgO contamination in the film. Comparable J_c have also been measured in MgB$_2$ films on (0001) 4H-SiC substrates.

In conclusion, 4H-SiC and 6H-SiC substrates were used for MgB$_2$ thin films growth by HPCVD. Thermodynamic calculations indicate that SiC is stable against reactions with Mg, B, and Mg–B compounds under HPCVD deposition conditions. The close lattice match between the c-cut surface
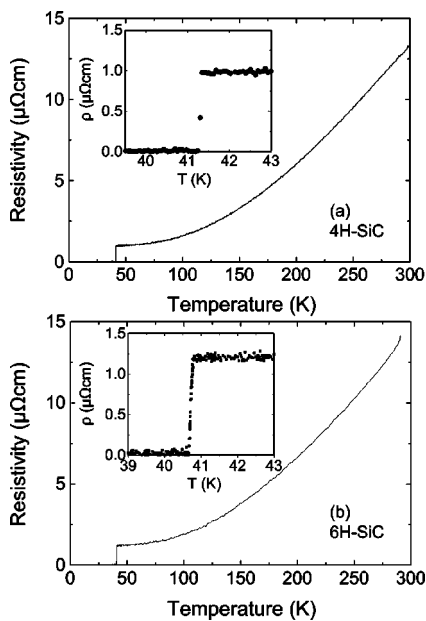
and that of MgB$_2$ results in high-quality epitaxy with a Rutherford backscattering channelling yield of 12%. They have excellent superconducting and transport properties. The results demonstrate that both 4H-SiC and 6H-SiC are ideal substrates for MgB$_2$ thin films.

FIG. 4. Resistivity vs temperature for two MgB$_2$ films on (a) 4H-SiC and (b) 6H-SiC substrates. The insets show the details near the superconducting transition.
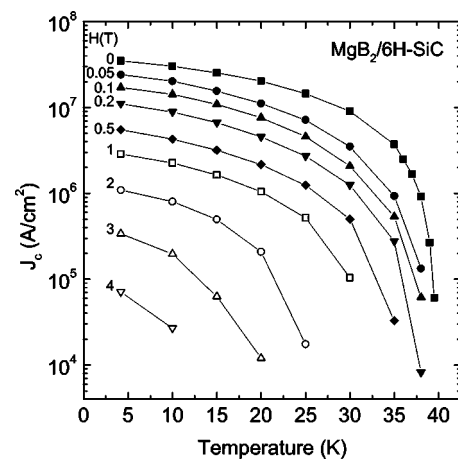
[1] J. Rowell, Nature Materials **1**, 5 (2002).
[2] X. H. Zeng, A. V. Pogrebnyakov, A. Kotcharov, J. E. Jones, X. X. Xi, E. M. Lysczek, J. M. Redwing, S. Y. Xu, Q. Li, J. Lettieri, D. G. Schlom, W. Tian, X. Q. Pan. and Z. K. Liu, Nature Materials **1**, 35 (2002).
[3] T. He, R. J. Cava, and J. M. Rowell, Appl. Phys. Lett. **80**, 291 (2002).
[4] W. N. Kang, H.-J. Kim, E.-M. Choi, C. U. Jung, and S.-I. Lee, Science **292**, 1521 (2001).
[5] S. D. Bu, D. M. Kim, J. H. Choi, J. Giencke, S. Patnaik, L. Cooley, E. E. Hellstrom, D. C. Larbalestier, C. B. Eom, J. Lettieri, D. G. Schlom, W. Tian, and X. G. Pan, Appl. Phys. Lett. **81**, 1851 (2002).
[6] D. H. A. Blank, H. Hilgenkamp, A. Brinkman, D. Mijatovic, G. Rijnders, and H. Rogalla, Appl. Phys. Lett. **79**, 394 (2001).
[7] H. Christen, H. Zhai, C. Cantoni, M. Paranthaman, B. Sales, C. Rouleau, D. Norton, D. Christen, and D. Lowndes, Physica C **353**, 157 (2001).
[8] S. R. Shinde, S. B. Ogale, R. L. Greene, T. Venkatesan, P. C. Canfield, S. Bud'ko, G. Lapertot, and C. Petrovic, Appl. Phys. Lett. **79**, 227 (2001).
[9] K. Ueda and M. Naito, Appl. Phys. Lett. **79**, 2046 (2001).
[10] W. Jo, J.-U. Huh, T. Ohnishi, A. F. Marshall, M. R. Beasley, and R. H. Hammond, Appl. Phys. Lett. **80**, 3563 (2002).
[11] R. Devaty, in *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series*, edited by U. Rössler (Springer, Berlin, 2002), Vol. III/41A1β, p. 20.
[12] A. R. Powell and L. B. Rowland, Proc. IEEE **90**, 942 (2002).
[13] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[14] Z. K. Liu, D. G. Schlom, Q. Li, and X. X. Xi, Appl. Phys. Lett. **78**, 3678 (2001).
[15] B. Lorenz, R. L. Meng, and C. W. Chu, Phys. Rev. B **64**, 012507 (2001).
[16] T. Tomita, J. J. Hamlin, J. S. Schilling, D. G. Hinks, and J. D. Jorgenson, Phys. Rev. B **64**, 092505 (2001).
[17] A. Serquis, Y. T. Zhu, E. J. Peterson, J. Y. Coulter, D. E. Peterson, and F. M. Mueller, Appl. Phys. Lett. **79**, 4399 (2001).
[18] N. Hur, P. A. Sharma, S. Guha, M. Z. Cieplak, D. J. Werder, Y. Horibe, C. H. Chen, and S.-W. Cheong, Appl. Phys. Lett. **79**, 4180 (2001).
[19] P. C. Canfield, D. K. Finnemore, S. L. Bud'ko, J. E. Ostenson, G. Lapertot, C. E. Cunningham, and C. Petrovic, Phys. Rev. Lett. **86**, 2423 (2001).
[20] H.-J. Kim, W. N. Kang, E.-M. Choi, M.-S. Kim, K. H. P. Kim, and S.-I. Lee, Phys. Rev. Lett. **87**, 087002 (2001).