# Enhancement of superconducting transition temperature in $MgB_2$ by strain-induced bond-stretching mode softening

A. V. Pogrebnyakov,[1,2,3] J. M. Redwing,[2,3] S. Raghavan,[2,3] V. Vaithyanathan,[2,3] D. G. Schlom,[2,3] S. Y. Xu,[1,3] Qi Li,[1,3] D. A. Tenne,[1,3] A. Soukiassian,[2,3] X. X. Xi,[1,2,3] M. D. Johannes,[4] D. Kasinathan,[4] W. E. Pickett,[4] J. S. Wu,[5] and J. C. H. Spence[5]

[1] *Department of Physics, The Pennsylvania State University, University Park, PA 16802*
[2] *Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802*
[3] *Materials Research Institute, The Pennsylvania State University, University Park, PA 16802*
[4] *Department of Physics, University of California, Davis, CA 95616*
[5] *Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287*

We report a systematic increase of superconducting transition temperature, $T_c$, with biaxial tensile strain to well beyond the bulk value in $MgB_2$ films grown by hybrid physical-chemical vapor deposition. The increase was observed in epitaxial films on SiC and sapphire substrates. The tensile strain in the films arises primarily from the coalescence of initially nucleated discrete islands (the Volmer-Weber growth mode) and increases with $MgB_2$ film thickness. We identified, by first-principles calculations, the underlying mechanism for the $T_c$ increase to be the softening of the bond-stretching $E_{2g}$ phonon mode, and we confirmed this conclusion by Raman scattering measurements. The result suggests that the $E_{2g}$ phonon softening is a possible avenue to achieve even higher $T_c$ in $MgB_2$-related material systems.

Since the discovery of superconductivity in $MgB_2$ by Nagamatsu *et al.* [1], many techniques, including substitution, disorder and pressure, have been used in an attempt to further increase the transition temperature $T_c$. However, the highest $T_c$ in $MgB_2$ has remained at about 40 K. Doping and chemical substitution in $MgB_2$ are difficult [2]. The successful cases such as substitution of Mg by Al [3] and B with C [4] have so far always suppressed $T_c$. Although atomic disorder induced by proton irradiation enhances the pinning of vortices, it reduces $T_c$ [5]. Subjecting $MgB_2$ to pressure also causes $T_c$ to decrease [6]. The only higher $T_c$ values reported are from the $^{10}$B isotope effect ($T_c = 40.2$ K) [7] and by Hur *et al.* when they exposed B crystals to Mg vapor (zero-resistance $T_{c0} = 39.8$ K) [8]. Recently, we have shown that $T_c$ of $MgB_2$ films on (0001) SiC increases with film thickness [9]. There have been speculations that a tensile strain may be the cause of enhanced $T_c$ in the films [8, 9]. In this Letter, we show unambiguously a systematic increase of $T_c$ with epitaxial tensile strain in $MgB_2$ films on both SiC and sapphire substrate to well beyond the bulk value (the highest $T_{c0} = 41.8$ K). Moreover, we identify the underlying mechanism, among several materials characteristics that determine $T_c$, to be the softening of the $E_{2g}$ phonon.

There are two new and remarkable features of $MgB_2$: its high value of $T_c$, almost twice as high as any other intermetallic material, and that it is a clear and rather extreme example of a "two gap" superconductor which has interested theorists for decades [10–12]. This two gap character arises due to two qualitatively different Fermi surfaces (called $\sigma$ and $\pi$) and their different pairing strengths (extremely strong and weak, respectively). The $\sigma$ contribution is dominant, however, and specifically the contribution from the B-B stretch modes (of $E_{2g}$ symmetry) in the $B_2$ graphene layer [13, 14]. Since any significant change in $T_c$ should arise from this dominant contribution, it suffices to consider only this contribution. According to the McMillan-Allen-Dynes analysis,

$$T_c \propto \omega e^{-f(\lambda,\hat{\mu})}, \quad (1)$$

where $\omega$ is the phonon frequency, $f(\lambda,\hat{\mu}) = (1+\lambda)/(\lambda-\hat{\mu})$, and $\hat{\mu}$ is similar to the Coulomb repulsion $\mu^*$. The electron-phonon coupling in a multiband superconductor is a matrix, but here we only consider the maximum element $\lambda^{\sigma\sigma}_{E_{2g}}$, which due to dominance of the bond-stretching mode becomes [14]

$$\lambda^{\sigma\sigma}_{E_{2g}} \propto \frac{m^*|\mathcal{D}|^2}{M\omega^2}, \quad (2)$$

where the $\sigma$ band effective mass $m^*$ is proportional to the density of states of holes in the $\sigma$ band at the Fermi level, $\mathcal{D}$ is the $\sigma$-band deformation potential, and $M$ is the B mass. A change in $T_c$ can arise from any combination of changes in $\omega$, $\mathcal{D}$, $m^*$, or $\hat{\mu}$. For example, the experimentally observed suppression of $T_c$ by Al doping can be attributed to a decrease in the $\sigma$-band hole density of states [3], and the pressure effect attributed to an increase in the $E_{2g}$ phonon frequency [15].

The epitaxial $MgB_2$ films in this work were deposited by a hybrid physical-chemical vapor deposition (HPCVD) technique [16]. Pure magnesium chips were heated simultaneously with the substrate to 720°C to generate a high Mg pressure, and 1000 ppm diborane ($B_2H_6$) in $H_2$ was used as the B precursor. The carrier gas was a $H_2$ flow of 450 sccm at a pressure of 100 Torr. The films were deposited on both (0001) 4H-SiC and

(0001) sapphire substrates. We have shown previously that films on (0001) SiC are $c$-axis oriented and epitaxial with an in-plane alignment of the $a$-axis of $MgB_2$ with that of SiC [17]. Films on (0001) sapphire are also $c$-axis oriented and epitaxial, but the $a$-axis of $MgB_2$ is rotated by 30° in-plane from the $a$-axis of sapphire [16]. Because of the highly reducing $H_2$ ambient during the deposition and the high purity source of B from $B_2H_6$, the HPCVD technique produces very clean $MgB_2$ thin films with a residual resistivity at $T_c$ as low as 0.26 $\mu\Omega$cm [9].

We have reported previously that the properties of $MgB_2$ films on (0001) SiC depend on film thickness [9]. In order to elucidate the role of biaxial strain we deposited $MgB_2$ of different thicknesses on (0001) sapphire substrates, and we found that a similar trend of thickness dependence to that on SiC. Figure 1(a) shows resistivity versus temperature curves for $MgB_2$ films with different thicknesses grown on sapphire substrates, and Fig. 1(b) shows the curves for films on SiC substrates. Both figures clearly show that $T_c$ becomes higher as the film thickness increases. The thickness dependence of the zero-resistance $T_{c0}$ for both substrates is plotted in Fig. 1(c). A clear trend of increasing $T_{c0}$ with film thickness is seen for both substrates with $T_{c0}$ consistently 1 - 1.5 degree higher in films on SiC than on sapphire. The highest $T_{c0}$ was observed in a 3400 Å thick $MgB_2$ film on a SiC substrate with $T_{c0} = 41.8$ K, two degrees higher than the bulk value.

X-ray diffraction analysis shows a direct correlation between the lattice constants of the films, thus the film strain, and $T_{c0}$. From $\theta - 2\theta$ scans we measured the $c$-axis lattice constants, and in conjunction with $\phi$ scans of asymmetric reflections we determined the $a$-axis lattice constants. Figure 2(a) shows the $a$-axis and $c$-axis lattice constants of several $MgB_2$ films, of different thicknesses and on sapphire (open symbols) and SiC (solid symbols) substrates, versus their $T_{c0}$ values. We clearly see that a higher $T_{c0}$ corresponds to a larger $a$-axis lattice constant and a smaller $c$-axis lattice constant. Consequently, as $T_{c0}$ increases, the $c/a$ ratio decreases (see Fig. 2(b)) and the unit cell volume increases (see Fig. 2(c)). Most strikingly, although the results on SiC and sapphire follow two different $T_{c0}$ versus thickness curves in Fig. 1(c), they fall on same curves in Fig. 2, indicating that a common factor determines $T_{c0}$ in this series of $MgB_2$ films, and it is the biaxial strain. Compared to the bulk values indicated by the dashed lines in Fig. 2 ($a = 3.086$ Å $c = 3.524$ Å [1], $c/a = 1.142$, and cell volume of 29.06 Å$^3$), it is evident that the tensile strain in the films causes $T_{c0}$ to increase beyond the bulk value, and the thicker the films the larger the tensile strain.

An increase of tensile strain with film thickness has been observed in films grown in the Volmer-Weber mode: film growth by initial nucleation of discrete islands which later coalesce [18, 19]. When the islands coalesce, they "zip up" because the surface energy of the islands is larger than the free energy of the grain boundaries, thus creating a tensile strain which increases with film thickness [20]. In the so-called "low-mobility" films, the height of the zipped boundary is less than the film thickness when the islands coalesce, and the "zipping-up" continues at the surface terrace level long afterwards [21]. Therefore, the tensile strain continues to increase with film thickness toward the upper bound value predicted by the Nix model [20]. The coalescence tensile strain has been suggested for GaN, a wide-band-gap compound semiconductor with a similar crystal structure to $MgB_2$ [22].

Atomic force microscopy (AFM) images confirm that $MgB_2$ films grow in the Volmer-Weber mode. AFM images of two $MgB_2$ films on SiC are shown in Fig. 3(a) (thickness 75 Å) and 3(b) (thickness 900 Å). Both were grown at 720°C with a $B_2H_6$ gas mixture flow rate of 50 sccm. Hexagonal-shaped $MgB_2$ crystallites are seen in the thinner film, which coalesce into a continuous film at larger film thickness. The continued increase of tensile strain beyond coalescence and the surface terraces that are readily observable in thicker films indicate that $MgB_2$ behaves like a low-mobility system at 720°C. This is consistent with the high melting temperature of B (2075°C) or $MgB_2$ (it melts congruently at 2430 °C with pressure higher than 49000 Torr [23]). The grain growth as the film becomes thicker may also contribute to the tensile strain as the reduction of the defect density can generate a tensile strain in the film on the top [24]. This is supported by the cross-section transmission electron microscopy (TEM) images of a 2100 Å-thick $MgB_2$ film on (0001) SiC shown in Fig. 3(c) (low-magnification) and Fig. 3(d) (high-resolution). The images were taken along the $[1\bar{1}00]$ direction. The dotted line in (d) indicates the $MgB_2$/SiC interface and the small arrows show the lattice deformation due to dislocations, most of which have Burgers vectors **b**=[0001]. Both Fig. 3(c) and Fig. 3(d) show that the defect density is high near the film/substrate interface and decreases as the film thickness increases.

The magnitudes of the tensile strain are different on SiC and sapphire substrates, reflecting the differences in the lattice mismatch and thermal expansion mismatch. The in-plane lattice constant is $a = 3.07$ Å for 4H-SiC and $a = 4.765$ Å for sapphire, and thus the lattice mismatch could result in a much larger compressive strain for sapphire (11% compressive with the 30° in-plane rotation) than for SiC (0.1% compressive). The coefficient of thermal expansion in the (0001) plane at room temperature is 5.5 $\times 10^{-6}$ K$^{-1}$ for $MgB_2$ [25], 3.0 $\times 10^{-6}$ K$^{-1}$ for SiC [26], and 6.7 $\times 10^{-6}$ K$^{-1}$ for sapphire [27]. Therefore, the thermal expansion mismatch will lead to a tensile strain in films on SiC, and a compressive strain in films on sapphire when the film is cooled from the deposition temperature. These factors are combined with the coalescence tensile strain to determine that there is a larger tensile strain in the $MgB_2$ films grown on SiC

substrates.

The systematic increase of $T_c$ with tensile strain shown in Fig. 2 has led us to search for the mechanism responsible for the rise in $T_c$ of $MgB_2$. For this purpose we have carried out first-principles calculations for a variety of strains including that for the highest $T_c$ sample in Fig. 2, which are $\Delta a/a = +0.55\%$ and $\Delta c/c = -0.25\%$. We found that this strain leads to changes $\Delta m^*/m^* = -1.2\%$ and $2\Delta|\mathcal{D}|/|\mathcal{D}| = -2.6\%$. The calculated change in the $E_{2g}$ phonon frequency, $\Delta\omega/\omega$= -5.5%, is in agreement with the experimentally extrapolated value [15]. From these values and using Eq. (2), we obtain

$$\frac{\Delta\lambda^{\sigma\sigma}_{E_{2g}}}{\lambda^{\sigma\sigma}_{E_{2g}}} = \frac{\Delta m^*}{m^*} + 2\frac{\Delta|\mathcal{D}|}{|\mathcal{D}|} - 2\frac{\Delta\omega}{\omega} = -1.2\% - 2.6\% + 11\% \approx +7\%. \tag{3}$$

From Eq. (1) and using representative numbers, $\lambda = \lambda_\sigma + \lambda_\pi = 0.9 + 0.2 = 1.1$, and $\hat{\mu} = 0.2$:

$$\frac{\Delta T_c}{T_c} = \frac{\Delta\omega}{\omega} - \Delta f = -5.5\% + 10.4\% \approx +5\%. \tag{4}$$

This value is quite close to the experimental enhancement of $T_c$. This analysis identifies the underlying mechanism of the tensile-strain-induced increase in $T_c$ as the softening of the $E_{2g}$ bond-stretching mode. The decrease in the $E_{2g}$ phonon frequency leads to the large relative increase in the $\sigma$ band coupling strength (7%), which more than compensates the lowering of the temperature/energy scale governed by $\omega$ (and as mentioned, decreases by 5%). The result is consistent with a previous first-principles calculation by Yildirim and Gülseren on the pressure effects in $MgB_2$ [28], although this previous work did not address biaxial strain.

As a check on the validity of the theoretical calculations, we have measured the $E_{2g}$ phonon frequencies of $MgB_2$ films of different thicknesses by Raman scattering. Raman spectra were taken using a SPEX Triplemate spectrometer in backscattering geometry with the 514.5 nm $Ar^+$ laser line as the excitation source. Figure 4 shows the spectra of two films: a 3400 Å-thick film on SiC and a 800 Å-thick film on sapphire. The thicker film on SiC has larger tensile strain than the thinner film on sapphire, and consequently has a higher $T_{c0}$ as compared to the film on sapphire. The broad peak around 600 $cm^{-1}$ has been assigned to the $E_{2g}$ mode [15]. A clear difference between the peak energies for the two films is seen. The higher $T_c$ film on SiC has a softer $E_{2g}$ mode than the lower $T_c$ film on sapphire by about 20 $cm^{-1}$, i.e 3.3%.

In conclusion, we have shown unambiguously that $T_{c0}$ in $MgB_2$ films deposited by HPCVD increases with biaxial tensile strain. The highest $T_{c0}$ obtained in the $MgB_2$ films, 41.8 K, is well above the bulk value. First-principles calculations show that the $T_c$ increase is due to the softening of the bond-stretching $E_{2g}$ phonon mode, which is confirmed by Raman scattering measurements. There have been reports that a reduced $T_c$ in $MgB_2$ corresponds to a higher $E_{2g}$ phonon frequency [15, 29]. Our result is the first example that lowering the $E_{2g}$ phonon frequency can increase $T_c$ to above the bulk value. In our work, this was accomplished by the tensile strain built into the films during the HPCVD growth process, and the $E_{2g}$ phonon softening is about 5.5%. An inspection of Eqns. (3) and (4) shows that if one can reduce the $E_{2g}$ phonon frequency further, the $T_c$ of $MgB_2$ could be increased more than what we have shown here.

We gratefully acknowledge Bill Nix for an extremely useful discussion concerning the coalescence tensile strain, and E. Wertz for his help with the temperature measurement. The work at Penn State is supported in part by ONR under grant Nos. N00014-00-1-0294 (Xi) and N0014-01-1-0006 (Redwing), by NSF under grant Nos. DMR-0306746 (Xi and Redwing), DMR-9876266 and DMR-9972973 (Li), and by DOE under grant Nos. DE-FG02-03ER46063 (Schlom) and DE-FG02-01ER45907 (Xi). The work at UC Davis is supported by NSF under grant No. DMR-0114818. The work at ASU is supported by NSF under grant No. DMR-0245702.

REFERENCES


[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] R. J. Cava, H. W. Zandbergen, and K. Inumaru, Physica C **385**, 8 (2003).
[3] J. S. Slusky, N. Rogado, K. A. Regan, M. A. Hayward, P. Khalifah, T. He, K. Inumaru, S. M. Loureiro, M. K. Haas, H. W. Zandbergen, et al., Nature (London) **410**, 343 (2001).
[4] S. Lee, T. Masui, A. Yamamoto, H. Uchiyama, and S. Tajima, Physica C **397**, 7 (2003).
[5] Y. Bugoslavsky, G. K. Perkins, X. Qi, L. F. Cohen, and A. D. Caplin, Nature (London) **410**, 563 (2001).
[6] M. Monteverde, M. Núñez-Regueiro, N. Rogado, K. A. Regan, M. A. Hayward, T. He, S. M. Loureiro, and R. J. Cava, Science **292**, 75 (2001).
[7] D. G. Hinks, H. Claus, and J. D. Jorgensen, Nature (London) **411**, 457 (2001).
[8] 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).
[9] A. V. Pogrebnyakov, J. M. Redwing, J. E. Jones, X. X. Xi, S. Y. Xu, Q. Li, V. Vaithyanathan, and D. G. Schlom, Appl. Phys. Lett. **82**, 4319 (2003).
[10] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, Nature (London) **418**, 758 (2002).
[11] W. Pickett, Nature (London) **418**, 733 (2002).
[12] S. Souma, Y. Machida, T. Sato, T. Takahashi, H. Matsui, S.-C. Wang, H. Ding, A. Kaminski, J. C. Campuzano, S. Sasaki, et al., Nature (London) **423**, 65 (2003).
[13] A. Y. Liu, I. I. Mazin, and J. Kortus, Phys. Rev. Lett. **87**, 087005 (2001).
[14] J. M. An and W. E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001).
[15] A. F. Goncharov and V. V. Struzhkin, Physica C **385**, 117 (2003).
[16] 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, et al., Nature Materials **1**, 35 (2002).
[17] X. H. Zeng, A. V. Pogrebnyakov, M. H. Zhu, J. E. Jones, X. X. Xi, S. Y. Xu, E. Wertz, Q. Li, J. M. Redwing, J. Lettieri, et al., Appl. Phys. Lett. **82**, 2097 (2003).
[18] J. A. Floro, E. Chason, R. C. Cammarata, and D. J. Srolovitz, MRS Bulletin **27(1)**, 19 (2002).
[19] R. Koch, J. Phys.: Condens. Matter **6**, 9519 (1994).
[20] W. D. Nix and B. M. Clemens, J. Mater. Res. **14**, 3467 (1999).
[21] B. W. Sheldon, K. H. A. Lau, and A. Rajamani, J. Appl. Phys. **90**, 5097 (2001).
[22] E. V. Etzkorn and D. R. Clarke, J. Appl. Phys. **89**, 1025 (2001).
[23] Z. K. Liu, D. G. Schlom, Q. Li, and X. X. Xi, Appl. Phys. Lett. **78**, 3678 (2001).
[24] P. Chaudhari, J. Vac. Sci. Technol. **9**, 520 (1972).
[25] C. Buzea and T. Yamashita, Supercond. Sci. Tech. **14**, R115 (2001).
[26] Z. Li and R. Brandt, J. Amer. Chem. Soc. **69**, 863 (1986).
[27] Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and T. Y. R. Lee, *Thermophysical Properties of Matter* (Plenum, New York, 1977), vol. 13.
[28] T. Yildirim and O. Gülseren, J. Phys. Chem. Sol. **63**, 2201 (2002).
[29] T. Masui, S. Lee, and S. Tajima, cond-mat/0312458 (2003).

## FIGURE CAPTIONS

FIG. 1: Superconducting transition in $MgB_2$ films of different thicknesses on (a) (0001) sapphire and (b) (0001) SiC substrates. (c) Zero-resistance $T_{c0}$ as a function of film thickness on both sapphire and SiC substrates.

FIG. 2: (a) $T_{c0}$ versus $a$-axis and $c$-axis lattice constants. (b) $T_{c0}$ versus the $c/a$ ratio. (c) $T_{c0}$ versus the $MgB_2$ unit cell volume. The error bars indicate the accuracy of the measurement. The dashed lines are the bulk values.

FIG. 3: AFM images of (a) a 75 Åand (b) a 900 Å-thick $MgB_2$ films grown on (0001) SiC substrates at 720°C. (c) Low-magnification and (d) high-resolution cross-section TEM images of a 2100 Å-thick $MgB_2$ film on (0001) SiC taken along the $[1\bar{1}00]$ direction. The dotted line in (d) indicates the $MgB_2$/SiC interface and the small arrows show the lattice deformation due to dislocations.

FIG. 4: Raman spectra of two $MgB_2$ films: 3400 Å-thick on SiC and 800 Å-thick on sapphire. The thicker film on SiC has larger tensile strain and a higher $T_{c0}$ than the thinner film on sapphire. The Raman result shows that the $E_{2g}$ phonon in it has a lower frequency.