Enhancement of the Superconducting Transition Temperature of MgB_2 by a Strain-Induced Bond-Stretching Mode Softening

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We report a systematic increase of the superconducting transition temperature T_c with a biaxial tensile strain in MgB_2 films to well beyond the bulk value. The tensile strain increases with the MgB_2 film thickness, caused primarily by the coalescence of initially nucleated discrete islands (the Volmer-Weber growth mode.) The T_c increase was observed in epitaxial films on SiC and sapphire substrates, although the T_c values were different for the two substrates due to different lattice parameters and thermal expansion coefficients. 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.

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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 substrates 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.

MgB_2 is a clear and rather extreme example of a "two gap" superconductor [10–12], arising due to two qualitatively different Fermi surfaces (called σ and π) and their different pairing strengths (extremely strong and weak, respectively). The σ 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]. Therefore, it suffices to consider only the σ contribution to T_c. According to the McMillan-Allen-Dynes analysis,

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

where ω is the phonon frequency, $f(\lambda, \hat{\mu}) = (1 + \lambda)/(\lambda - \hat{\mu})$, and $\hat{\mu}$ is similar to the Coulomb repulsion μ^*. The electron-phonon coupling due to the σ band and the bond-stretching mode becomes [14]

$$\lambda_{E_{2g}}^{\sigma\sigma} \propto \frac{m^*|\mathcal{D}|^2}{M\omega^2}, \tag{2}$$

where the σ band effective mass m^* is proportional to the density of states of holes in the σ band at the Fermi level, $\mathcal{D}$ is the σ-band deformation potential, and M is the B mass. A change in T_c can arise from any combination of changes in ω, $\mathcal{D}$, m^*, or $\hat{\mu}$.

The epitaxial MgB_2 films in this work were deposited by hybrid physical-chemical vapor deposition (HPCVD) [15]. 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. 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 [16]. 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 [15].

We have reported previously that the properties of MgB_2 films on (0001) SiC depend on film thickness [9].

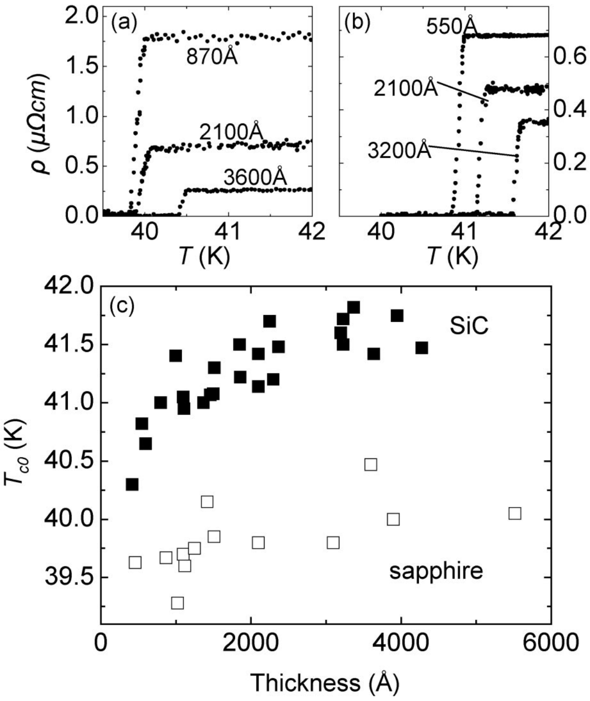

FIG. 1. Superconducting transition in MgB_2 films of different thicknesses on (a) (0001) sapphire and (b) (0001) SiC substrates. (c) Zero-resistance T_{c0} as a function of film thickness on both sapphire and SiC substrates.

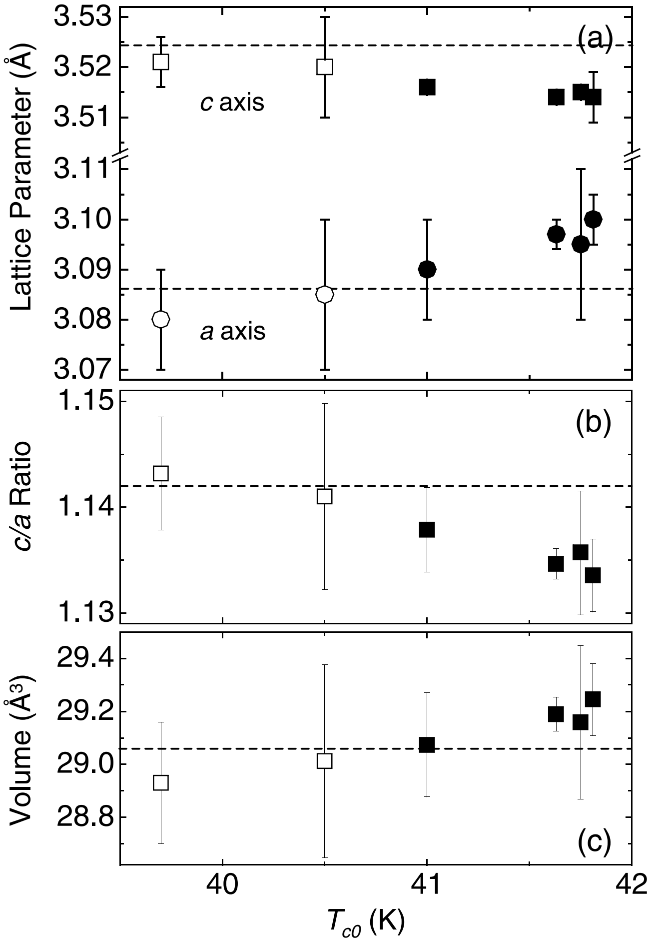

FIG. 2. (a) T_{c0} versus a-axis and c-axis lattice constants. (b) T_{c0} versus the c/a ratio. (c) T_{c0} versus the MgB_2 unit cell volume. The open symbols are for sapphire, and the solid symbols are for the SiC substrate. The error bars indicate the accuracy of the measurement. The dashed lines are the bulk values.

We found a similar trend of thickness dependence on (0001) sapphire substrates. Figure 1 shows resistivity versus temperature curves for MgB_2 films with different thicknesses grown on sapphire [Fig. 1(a)] and SiC [Fig. 1(b)] 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 K higher in films on SiC than on sapphire. The highest T_{c0} observed (41.8 K) is 2 K higher than the bulk value.

X-ray diffraction analysis, from both $\theta - 2\theta$ and ϕ scans, shows a direct correlation between the film strain and T_{c0}. 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. Clearly, a higher T_{c0} corresponds to a larger a-axis and smaller c-axis lattice constants. 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 the same curves in Fig. 2. 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 [17,18]. 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 [19]. 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 [20]. Therefore, the tensile strain continues to increase with film thickness toward the upper bound value predicted by the Nix-Clemens model [19].

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 Figs. 3(a) (thickness 75 Å) and 3(b) (thickness 900 Å). 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 the 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 6.5 MPa [21]). The grain growth as the film becomes thicker may also contribute to the tensile strain [22]. This is supported by the cross-section transmission electron microscopy (TEM) images of a 2100 Å thick MgB_2 film on (0001) SiC in Fig. 3(c) (low magnification) and Fig. 3(d) (high resolution), which show that the defect density is high near the film/substrate interface and decreases as the film thickness increases.

The lattice mismatch could result in 11% compressive strain (with a 30° in-plane rotation) in MgB_2 films on sapphire ($a = 3.07$ Å) and 0.1% compressive strain on SiC ($a = 4.765$ Å). The coefficient of thermal expansion in the (0001) plane at room temperature is $5.5 \times 10^{-6}\ \mathrm{K}^{-1}$ for MgB_2 [23], $3.0 \times 10^{-6}\ \mathrm{K}^{-1}$ for SiC [24], and $6.7 \times 10^{-6}\ \mathrm{K}^{-1}$ for sapphire [25]. Therefore, the thermal expansion mismatch will lead to a tensile strain in films on SiC, and a compressive strain on sapphire. The combined effect of all the sources of strain results in larger tensile strain in MgB_2 films on SiC than on sapphire. It is difficult to accurately predict the maximum tensile strain attainable in MgB_2 films. A rough estimate from Eq. (1) in Ref. [19] [taking the following parameters: grain boundary energy $=$ 0 J/cm^2, solid/vapor surface energy $= 1$ J/m^2, biaxial modulus of $MgB_2 = 421$ GPa [26], and grain size at coalescence $= 1300$ Å from Fig. 3(a)] indicates an upper bound value of ~0.8%, which is larger than the maximum tensile strain reported here (~ 0.55%). However, this stress estimation may be oversimplified and the films may partially relax as the thickness increases.

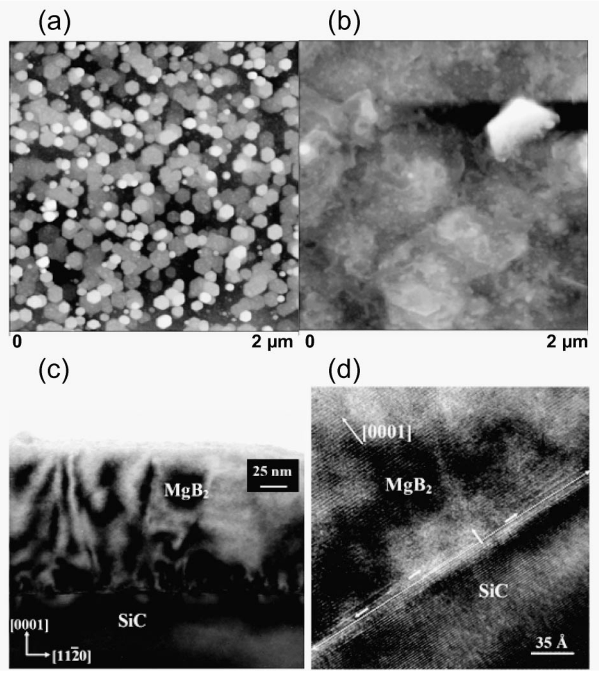

FIG. 3. AFM images of (a) a 75 Å and (b) a 900 Å thick MgB_2 films grown on (0001) SiC substrates at 720 °C. (c) Low-magnification and (d) high-resolution cross-section TEM images of a 2100 Å thick MgB_2 film on (0001) SiC taken along the $[1\bar{1}00]$ direction. The dotted line in (d) indicates the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

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 by first-principles calculations. For the highest T_c sample in Fig. 2, $\Delta a/a = +0.55\%$ and $\Delta c/c = -0.25\%$, which 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 [27]. From these values and using Eq. (2), we obtain

$$\frac{\Delta\lambda^{\sigma\sigma}_{E_{2g}}}{\lambda^{\sigma\sigma}_{E_{2g}}} = \frac{\Delta m^*}{m^*} + 2\frac{\Delta|\mathcal{D}|}{|\mathcal{D}|} - 2\frac{\Delta\omega}{\omega} \approx +7\%. \qquad (3)$$

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

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

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 decrease in the E_{2g} phonon frequency. It leads to the large (7%) increase in the σ band coupling strength, which, being leveraged in $f(\lambda, \hat{\mu})$, more than compensates the 5% lowering of the temperature/energy scale governed by ω. The result is consistent with that of Yildirim and Gülseren on the pressure effects in MgB_2 [28], although this previous work did not address biaxial strain.

The E_{2g} phonon frequencies of MgB_2 films of different thicknesses were measured by Raman scattering using a SPEX Triplemate spectrometer in backscattering geometry with the 514.5 nm Ar^+ laser excitation. 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 [27]. 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%.

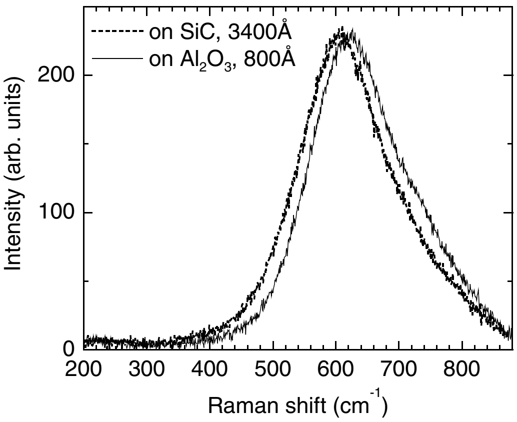

FIG. 4. Raman spectra of two MgB_2 films: 3400 Å thick on SiC and 800 Å thick on sapphire. The former shows a lower E_{2g} phonon frequency.

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 [27,29]. Our result is the first example that lowering the E_{2g} phonon frequency can increase T_c to above the bulk value. In this work, the T_c enhancement seems to saturate at large film thicknesses. If one could reduce the E_{2g} phonon frequency further using other techniques, the T_c of MgB_2 should be even higher than what we have shown here.

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