Raman scattering in pure and carbon-doped MgB_2 films

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We have studied Raman scattering in MgB_2 thin films grown by hybrid physical-chemical vapor deposition on SiC and Al_2O_3 substrates. The Cooper-pair-breaking peak corresponding to the larger gap was observed and its position correlates with the value of T_c, which varies with film strain. The temperature dependence of the E_{2g} phonon frequency and linewidth was studied. Carbon doping of MgB_2 films suppresses T_c, and leads to a hardening of the E_{2g} phonon mode, an increased luminescence background in the spectra, and a stronger contribution of disorder-activated phonons to Raman spectra.

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The 39 K superconductor MgB_2 (Ref. 1) has attracted great interest stimulated by its remarkable superconducting properties and potential for applications. MgB_2 has been demonstrated to be a unique example of a two gap superconductor.[2,3] It is a phonon-mediated superconductor with strong electron-phonon coupling[4–9] and phonon anharmonicity.[2,5,8,10,11] Recently, epitaxial MgB_2 thin films have been produced by a hybrid physical-chemical vapor deposition (HPCVD) technique.[12] The HPCVD films are very clean [residual resistivity as low as 0.26 $\mu\Omega$ cm (Ref. 13)] due to the high purity source of B and the highly-reducing H_2 atmosphere during the deposition. The T_c of the film varies with film thickness, and a tensile strain in the film can raise T_c well above the bulk value to 41.8 K.[14] Dirty films can also be made using HPCVD by carbon doping, which suppresses T_c but dramatically enhances the upper critical field H_{c2} and vortex pinning.[15]

Raman studies on single crystal[16–20] and polycrystalline MgB_2 (Refs. 21–26) revealed features corresponding to the energy gaps and a phonon modes of E_{2g} symmetry. The latter is the B-B bond stretching mode playing a major role in the mechanism of superconductivity in MgB_2.[5,6] However, the correlation between the E_{2g} phonon frequency and T_c is not clear so far. Yates *et al.*[27] studied room-temperature Raman spectra of polycrystalline MgB_2 films with different T_c's and found that the E_{2g} mode frequency decreases with decreasing the T_c. Yates *et al.* associated the reduction of T_c in their samples with magnesium offstoichiometry and oxygen alloying. They explained the observed reduction of T_c by the drastic decrease of the electron-phonon coupling constant. The Raman studies of carbon-substituted single MgB_2 crystals[28] and polycrystalline powder samples[29] showed that the E_{2g} mode hardens with decreasing T_c caused by carbon substitution. The observed hardening of the E_{2g} mode was associated with the suppression of electron-phonon coupling by carbon substitution.[28] Recently, Pogrebnyakov *et al.* demonstrated theoretically and experimentally that the T_c in epitaxial MgB_2 films deposited by HPCVD increases with biaxial tensile strain, and that this increase is due to the softening of the E_{2g} phonon mode.[14] First-principles calculations showed that the E_{2g} phonon frequency decrease leads to the large increase in the σ band electron-phonon coupling strength, which more than compensates the lowering of the temperature or energy scale governed by the phonon frequency itself. In the present paper we report a Raman study of pure and carbon-doped MgB_2 films grown by HPCVD. It shows that the position of the pair-breaking peak correlates with the value of T_c, and the carbon doping leads to the hardening of the E_{2g} phonon mode. Together with the results of Masui *et al.*[28] and our recent result on the tensile strain-induced T_c increasing by the E_{2g} phonon mode softening,[14] the present result further confirms a correlation between the E_{2g} phonon frequency and T_c.

The MgB_2 films were grown on (0001) 4H-SiC and (0001) sapphire substrates. Details of the HPCVD growth have been described elsewhere.[12] 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.[30] 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.[12] Carbon doping was achieved by adding carbon-containing precursor metalorganic bis-(methylcyclopentadienyl)magnesium to the H_2 carrier gas during the film growth.[15] The carbon-doped films are *c* axis textured with columnar nanograins and highly resistive amorphous areas at the grain boundaries. Pure MgB_2 films studied have T_c between 39.7 and 41.8 K, depending on the substrate (SiC or sapphire) and film thickness. The carbon concentration in the doped films is between 8 and 29 atomic percent, causing a decrease of the zero-resistance T_c, which varies from 38.5 to 28.4 K in these samples. The structural and superconducting properties of carbon-doped films studied here were reported elsewhere.[15]

Raman spectra were recorded using a SPEX Triplemate spectrometer equipped with a liquid-nitrogen-cooled multichannel coupled-charge-device detector. The 514.5 nm line of an Ar^+ laser was used for excitation, and the laser power density was kept at a low level ($\lesssim$30 W/cm^2) to avoid heating of the sample. Raman spectra from the films were measured in backscattering geometry both in parallel $z(x,x)\bar{z}$ and perpendicular $z(x,y)\bar{z}$ polarization configurations (z direction is normal to the film plane).

MgB_2 has a hexagonal structure with point group $P6/mmm(D_{6h})$. Symmetry analysis[22] yields four zone-center

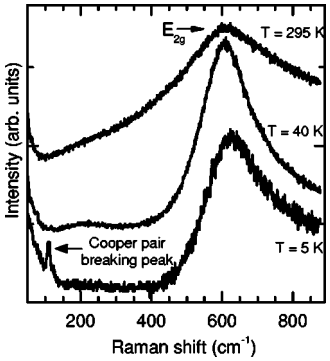

FIG. 1. Raman spectra of a 340-nm-thick MgB_2 film on SiC substrate.

optical phonon modes. Two of them, A_{2u} and B_{1g} involve atomic displacements along the c axis, and two doubly degenerate modes E_{1u} and E_{2g} have vibrations only in the ab plane. Only the E_{2g} modes are Raman active. According to the results of many studies,[4–9] the E_{2g} phonons, involving the in-plane vibrations of boron atoms, are strongly coupled to electrons and responsible for superconductivity. Experimentally, a broad, strongly damped phonon mode of E_{2g} symmetry at 600–630 cm^{-1} has been observed. The low-frequency Raman spectra below T_c contain the features of electronic Raman scattering, corresponding to superconducting gaps.[16–19,21] The larger gap appears as a sharp peak at about 110 cm^{-1} (13.6 meV) at 10 K, which is due to the breaking of Cooper pairs by the incident light. Its position corresponds to the double energy of the larger gap Δ_L. The smaller gap was observed as a threshold in the low-frequency Raman intensity[18,19] at the energy $2\Delta_s$ (about 30 cm^{-1} at 15 K), caused by the fact that in the superconducting state there are no electronic excitations below the gap.

Figure 1 shows typical Raman spectra of MgB_2 films. In the low-frequency range the spectra below T_c contain a sharp peak (at 110 cm^{-1} at 5 K), which is attributed to the Cooper-pair-breaking peak at the energy $2\Delta_L$ corresponding to the larger gap ($\Delta_L(5\ \mathrm{K})=6.8$ eV). Low-frequency region of the spectra taken at several temperatures is presented in Fig. 2. (The spectra in Fig. 2 are shown after Raleigh background subtraction.) A similar feature was reported for single crystal[16–19] and polycrystalline samples[21] at about 105 cm^{-1}. The higher frequency of the pair-breaking peak in our sample compared to that in the bulk samples is due to the higher T_c caused by the tensile strain in the film.[13,14] The spectra shown in Figs. 1 and 2 were measured on a 340-nm-thick film on SiC substrate, having the highest $T_c=41.8$ K. For comparison, the 5 K spectrum of a 80-nm-thick film on sapphire, having $T_c=39.7$ K is also shown in Fig. 2 (dotted line). As one can see, in the latter film the Cooper-pair-breaking peak appears at lower frequency compared to the film on SiC. We have shown that thicker films have higher T_c for both SiC and sapphire substrates, and T_c is higher on SiC than on sapphire for the same thickness.[13,14] The thinner film on sapphire with lower T_c shows a smaller gap than thicker film on SiC. The temperature dependence of the gap for all the samples measured is in very good agreement with the prediction of BCS theory. This is illustrated in the inset to

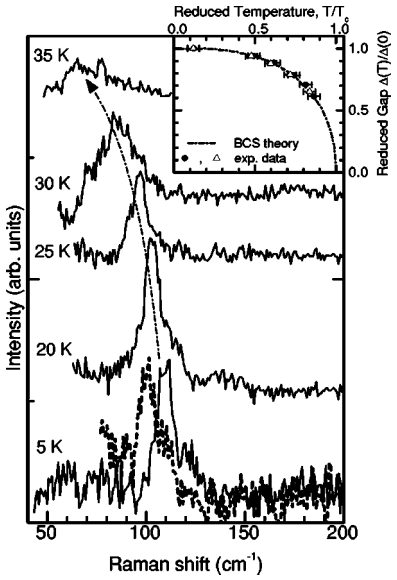

FIG. 2. The Cooper pair breaking peak at different temperatures for a 340-nm-thick MgB_2 film on SiC substrate (solid lines). The peak for 80-nm-thick film on sapphire at 5 K is shown for comparison (dotted line). Inset: temperature dependence of reduced gap for these films on SiC and sapphire substrates (circles and triangles, respectively). Dashed-dotted line shows the prediction of BCS theory.

Fig. 2, showing the reduced gap $\Delta_L(T)/\Delta_L(T_0)$ as a function of the reduced temperature T/T_c, where $\Delta_L(t_0)$ is the gap value at $T=0$ for two samples. The second, smaller gap should appear as a threshold in Raman intensity at about 30 cm^{-1}. We were not able to observe this feature because of the strong background of elastically scattered light.

The higher frequency part of the Raman spectra shown in Fig. 1 is dominated by the broad feature of the E_{2g} phonon, centered at about 615 cm^{-1}. The temperature dependence of the E_{2g} phonon peak position and linewidth for the 340 nm-thick MgB_2 film on SiC substrate is presented in Fig. 3. As can be seen from the figure, the phonon frequency shows almost no dependence on temperature over the entire temperature range 5–300 K, (the observed frequency shift between 5 and 300 K is about 10 cm^{-1}, which is within the experimental uncertainties) and does not undergo any notice-

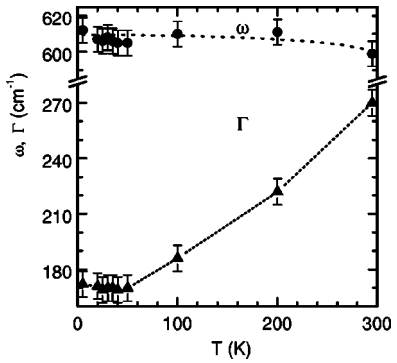

FIG. 3. Temperature dependence of the E_{2g} phonon frequency (circles) and linewidth (triangles) for MgB_2 film on SiC substrate.

able changes upon transition from normal to superconducting state predicted by density-functional calculations.[5] The E_{2g} mode is characterized by extremely large linewidth ($\sim$170 cm^{-1} at 5 K), similar to the observations of other authors on single crystal and polycrystalline MgB_2.[16,23–26] The linewidth remains nearly constant in the temperature range 5–50 K, and shows no change at T_c. Further temperature increase leads to gradual increase of the linewidth up to $\sim$270 cm^{-1} at room temperature. Similar temperature behavior of the E_{2g} phonon frequency and linewidth was observed for other samples studied here, and was also reported for bulk MgB_2.[25,26]

The phonon line broadening with increasing temperature may arise from the anharmonic decay of the E_{2g} mode into two other phonons, as strong anharmonicity of this mode has been predicted.[5,8] However, the phonon anharmonicity cannot explain the linewidth of 170 cm^{-1} at 5 K. The large E_{2g} phonon linewidth may be due to the strong electron-phonon interaction, causing the phonon decay into electron-hole pairs. A recent study by inelastic x-ray scattering[10] and calculations using density functional theory[10,11] showed that the contribution of phonon anharmonicity to the E_{2g} mode broadening is small and the dominant contribution to the linewidth is the electron-phonon coupling. The latter can also give rise to the increase of the linewidth with temperature,[25] similar to the experimentally observed behavior shown in Fig. 3.

Figure 4 shows a Raman spectrum of a carbon-doped MgB_2 film on SiC substrate (carbon concentration is 26 atomic percent, and zero-resistance T_c is 32.5 K) in comparison with a pure film (the latter is the same as shown in Fig. 1). Carbon doping strongly affects the Raman spectrum of the film, which is characterized by significantly higher background likely due to the luminescence from impurity phases.[25] The spectrum of the undoped film has a very low background because of the high purity of the film.[13] The E_{2g} peak of the pure film has a slightly asymmetric lineshape with a shoulder at the high frequency side due to the maximum in the phonon density of states at about 780 cm^{-1} (Refs. 8, 9, and 31). The phonon density-of-states peak becomes significantly stronger in carbon-doped films. (See the inset to Fig. 4, showing the fitting of the spectra after the linear background subtraction. As the luminescence peak is much broader than the whole range of the Raman spectra,[25] the linear approximation for the luminescence background, shown by thin dashed-dotted line on Fig. 4, is appropriate here.) This is due to increased disorder induced by carbon doping. Similar increase in the phonon density-of-states peaks was also observed in MgB_2 films after Ar ion bombardment.[32] Figure 4 clearly shows that the E_{2g} phonon line shifts substantially to a higher frequency upon carbon doping, from 605 to about 680 cm^{-1}. There have been previous reports that a reduced T_c in MgB_2 corresponds to a higher E_{2g} phonon frequency.[24,28] Our result confirms this correlation.

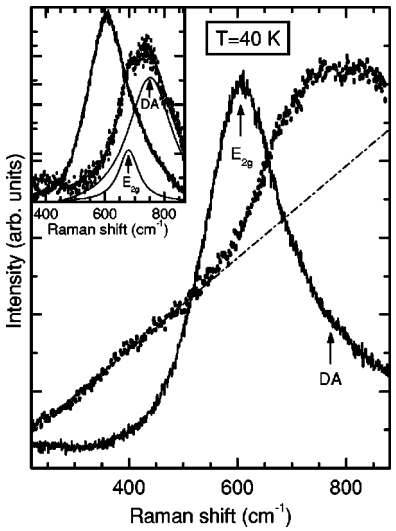

FIG. 4. Raman spectra of pure (black solid line) and carbon doped (grey dotted line) MgB_2 films on SiC substrate, measured at $T=40$ K. Inset shows the spectra after the linear background subtraction. Thin black lines show the result of fitting.

In summary, Raman spectroscopy was applied to study both pure and carbon-doped MgB_2 thin films grown by HPCVD. The pair-breaking peak corresponding to the larger superconducting gap was found to correlate with the value of T_c for different films, which is substrate- and thickness-dependent due to different strain state of the films. The frequency of the E_{2g} phonon mode in films increases with carbon substitution, which corresponds to the reduced T_c. This is in agreement with the recent results of Masui *et al.*[28] In our recent study we have demonstrated by first-principles calculations confirmed by experimental results, that a tensile strain-induced E_{2g} mode softening causes T_c to increase above the bulk value.[15] In combination with the results presented here that the carbon doping causes the E_{2g} mode hardening and reduces T_c, we believe that a correlation between the E_{2g} phonon frequency and T_c of MgB_2 can be established.

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