

Nanoindentation and Raman spectroscopy studies of boron carbide single crystals

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The measurements of hardness and elastic modulus have been conducted on the (0001) and (10 $\bar{1}$ 1) faces of B_{4.3}C single crystals using nanoindentation. The results are in good agreement with the corresponding values obtained using a conventional microhardness technique on polycrystalline ceramics. Raman microspectroscopy analysis of the nanoindentations shows the appearance of several bands which suggest dramatic structural changes in the indented material. Localized contact loading may lead to damage in boron carbide resulting in disorder or a pressure-induced solid state phase transformation in the region under the indenter, although the exact mechanism responsible for the observed Raman spectra could not be identified at this time. This may explain why little variation in mechanical properties was observed with respect to the crystallographic orientation. © 2002 American Institute of Physics. [DOI: 10.1063/1.1521580]

Boron carbide is one of the hardest materials known and it is widely used as an abrasive and in lightweight armor applications.¹ Given the high hardness of boron carbide, it is of fundamental interest to explore its mechanical properties under conditions of extreme contact pressures. A technique to approach this task is through indentation testing combined with Raman microspectroscopy.² The method has been successfully used to identify pressure-induced phase transitions during nanoindentation of Si and Ge,^{3,4} and to observe the indentation-induced transformation of diamond to graphite.⁵ Because mechanical properties vary with crystallographic orientation, and polycrystalline boron carbides are known to contain grains of different stoichiometries and free carbon, it is advantageous to make the measurements on oriented single crystal samples. However, no nanoindentation or other mechanical property studies have ever been reported for single crystals. In this letter, we report the results of the nanoindentation and Raman microspectroscopy studies on the (0001) and (10 $\bar{1}$ 1) faces of boron carbide single crystals.

The samples were grown, cut, and polished at the Advanced Materials Laboratory of the National Institute for Materials Research in Tsukuba, Japan by the following procedures. Boron carbide powder (3N, Koujundo-kagaku Co., Japan) was pressed into a rod 8 mm in diameter and 100 mm long and then sintered in a graphite crucible at 2000 °C in vacuum for several hours. Floating zone crystal growth was carried out in a xenon image furnace under flowing argon with a growth rate of 10 mm/h. The crystal composition was determined to be B_{4.3}C by analyzing the carbon content using a carbon determinator (WR-12, Leco Co., USA). The sample was oriented to within 0.5° using Laue backreflection and cut by spark erosion. The surface was polished using

diamond abrasives of 9 μm followed by 3 μm grit size with a final polish using 0.1 μm Al₂O₃.

Nanoindentation experiments were performed using a Nano Indenter XP® tester (MTS) equipped with a Berkovich diamond indenter. The tests were performed as follows: loading to the maximum load and unloading by 90%; reloading to the maximum load and unloading by 95%; holding for 20 s at 5% of the maximum load for thermal drift correction; and complete unloading. The maximum loads ranged from 10 to 300 mN. The loading and unloading rates were equal to the maximum load divided by 100 s. Ten indentations were produced at each load, totaling at 170 indentations per specimen of a particular orientation.

Nanoindentation load-displacement curves of B_{4.3}C are featureless and show neither steps nor slope changes, unlike those of Al₂O₃ or SiC crystals in which slip occurs during loading, or Si and Ge crystals in which a reversible phase transformation can be seen in the unloading curves.⁶ The hardness and elastic modulus were determined from the slope of the second unloading curve using the Oliver and Pharr method.⁷ Figure 1 shows the experimental results plotted as a function of the applied load. Within the error bars, there is little variation of the measured quantities with respect to the applied load. As seen in Fig. 1, the (10 $\bar{1}$ 1) surface appears to have slightly higher hardness and elastic modulus than the (0001) surface. An increased scattering of the experimental data at low loads may be due to the surface roughness of the specimens (~100 nm) and/or to the deviation of the indenter tip shape (~100 nm radius) from that of a perfect triangular pyramid, which renders the Oliver and Pharr method inapplicable. Thus, we found that a load of 100 mN or higher is required for reliable measurement of the properties of boron carbide. In general, the hardness and elastic modulus of B_{4.3}C single crystals reported here are in

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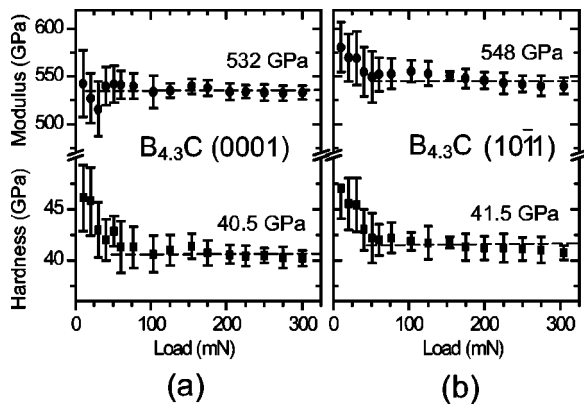


FIG. 1. Hardness and elastic modulus as a function of indentation load for (a) (0001) and (b) (10 $\bar{1}1$) surfaces of B_{4.3}C. Each data point corresponds to ten measurements. Vertical bars show standard deviations.

good agreement with the literature data obtained on polycrystalline samples using conventional techniques.^{1,8} This is probably the result of the weak anisotropy of the mechanical properties of boron carbide observed in our experiments. This finding is of technological importance for development of boron carbide ceramics with improved properties.

Postindentation characterization of the samples was performed using a Ramascope 1000 Raman spectrometer (Renishaw, UK) equipped with a charge coupled device detector and a microscope for focusing the incident laser beam to a 1 μm spot size. The 514.5 nm (Ar ion laser), 633 nm (He-Ne laser), and 785 nm (diode laser) excitation lines were used. Additional spectra were recorded using an AlmegaTM Dispersive Raman spectrometer (Nicolet) at the 532 nm excitation line of a diode laser. In all cases, the beam intensity was kept low to avoid artifacts due to laser heating.

Figure 2 shows typical Raman spectra of the (0001) surface of B_{4.3}C before and after nanoindentation at three different laser wavelengths. The spectra obtained before indentation show a series of Raman bands extending from 200 to 1200 cm^{-1} and are generally in good agreement with the spectra recorded previously for boron carbide.^{9–11} In the literature, there are conflicting assignments^{11–14} of the Raman peaks to vibrations of the principal structural elements in

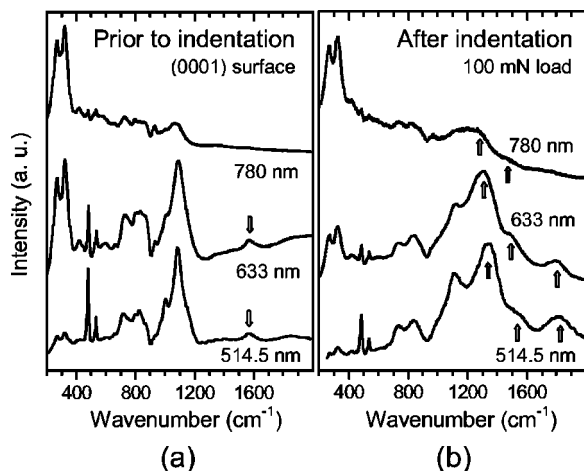


FIG. 2. Raman spectra from (a) the polished (0001) surface and (b) a 100 mN indentation in B_{4.3}C recorded using three different excitation wavelengths. Arrows indicate (a) the 1570 cm^{-1} peak of the pristine surface and (b) the peaks appearing after indentation.

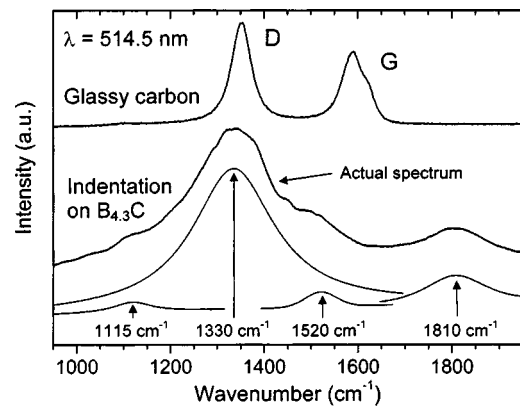


FIG. 3. Raman spectrum of a 100 mN indentation in B_{4.3}C in comparison with a spectrum of glassy carbon. The deconvoluted peaks are marked with arrows.

boron carbide, the icosahedra, and the three-atom linear chains. However, the detailed interpretation of the pristine boron carbide spectra is outside the scope of the present letter and will be discussed elsewhere.

The results shown in Fig. 2 make it quite clear that the indented regions have profoundly different Raman spectra. We note here that the spectra of the sample after nanoindentations made on the (10 $\bar{1}1$) surface of B_{4.3}C were similar to the spectra shown in Fig. 2(b). The most dramatic changes are the appearance of high frequency bands, the most intense of which is at $\sim 1330 \text{ cm}^{-1}$. Weaker but still prominent are the bands at 1520 and 1810 cm^{-1} , with the latter frequency well above any band observed in boron carbide or any related compound. The fact that these high-frequency Raman bands are present for all three laser wavelengths indicates that they are not due to a fluorescence feature or similar artifact. Note that because the spot size of the focused laser is larger than the indented area, the Raman spectra of nanoindentations are a superposition of spectra from pristine and indented regions. This is confirmed by the fact that the spectra obtained from larger Vickers indents (10 μm in size) in the same specimen showed much weaker features associated with the pristine surface.

The fact that indentation leads to relatively high frequency Raman peaks might suggest that a chemical reaction such as oxidation or decomposition to carbon and boron has taken place. Oxidation can be ruled out, as electron beam microanalysis shows no oxygen in the indented region. Disproportionation would not be expected to alter the boron to carbon ratio and none is seen. The positions of the Raman peaks are too high in frequency to be due to elemental boron. However, Raman spectra of different forms of carbon can show enough variations¹⁵ to encompass the spectral features observed here. Graphitic carbon generally has two Raman lines at ~ 1355 and 1582 cm^{-1} (see Fig. 3). The 1582 cm^{-1} peak is the only peak observed for single crystal graphite and it is frequently labeled the G (for graphite) band.¹⁵ In disordered and amorphous carbon, another peak is also observed, referred to as the D (for disorder) band. The occurrence of the D band in carbon materials is due to a double resonance Raman process, and its frequency shifts with excitation energy at a rate of $40\text{--}50 \text{ cm}^{-1}/\text{eV}$.^{16,17}

As seen in Fig. 4, there is some correlation between the

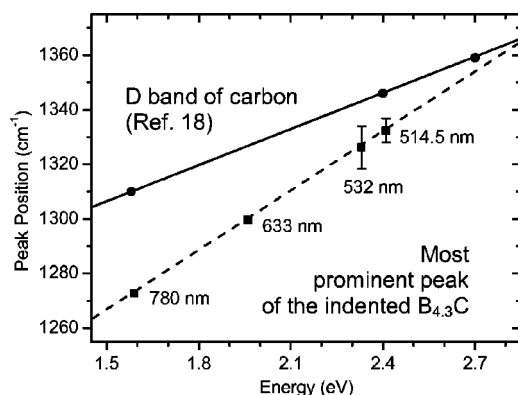


FIG. 4. Dependence of the most prominent peak in the spectra of indented $B_{4.3}C$ (squares) on the laser excitation energy in comparison with a similar dependence of the D band of disordered carbon (circles, data from Ref. 18). Indentation load varied from 30 mN to 2 N.

position of the most prominent band in the indented boron carbide at $\sim 1330\text{ cm}^{-1}$ as a function of excitation wavelength and a similar dependence of the D band position in disordered carbon. This may imply disorder or amorphization of boron carbide during indentation leading to the destruction of $B_{4.3}C$ structure and formation of carbon rings, possibly incorporating some boron, from the broken $C-B$ bonds. However, this explanation seems to be in conflict with the following observations: (i) The intensity of the D band of disordered carbon increases with the increasing excitation wavelength,¹⁸ while the peak at $\sim 1330\text{ cm}^{-1}$ does not show such dependence [Fig. 2(b)]; (ii) The G band is a prominent band in all carbon structures involving sp^2 bonding¹⁵ and the intensity ratio I_D/I_G in disordered/amorphous carbon never exceeds 2.5,¹⁹ whereas the peak at $\sim 1520\text{ cm}^{-1}$ is of extremely low intensity (Fig. 3); and (iii) The position of the peak at $\sim 1520\text{ cm}^{-1}$ (Fig. 3) is strongly downshifted compared to the G band of graphite.¹⁵ Note also that the Raman band at $\sim 1520\text{ cm}^{-1}$ is not related to the 1570 cm^{-1} band of the pristine $B_{4.3}C$ surface [shown with arrows in Fig. 2(a)], which has been attributed either to the presence of graphite-free carbon in boron carbides or to the vibrations of the $C-B-B$ chains (see Ref. 10, and references therein).

Rather broad features at ~ 1330 and $\sim 1520\text{ cm}^{-1}$ in the Raman spectra of the indented surfaces may also result from the superposition of several narrower bands. Thus, we do not rule out the possibility of an indentation-induced solid state phase transformation in boron carbide. The only published Raman study of boron carbide at high pressures did not show a phase transition up to 21 GPa,²⁰ but the spectral window was limited by 1200 cm^{-1} and the peaks that we report would not be noticed. That same group recently announced a transition into an orthorhombic structure of boron carbide at

the hydrostatic pressure of about 20 GPa.²¹ This is a significantly lower pressure than the contact pressures of ~ 40 GPa that we achieve during nanoindentation.⁶ Unfortunately, the Raman spectra of the orthorhombic boron carbide have not been published. Therefore, the exact mechanism responsible for the observed large change in the Raman spectra of boron carbide after indentation could not be identified at this time. Additional characterization of the material in the vicinity of indentations by diffraction techniques will be required to establish definitely whether a new phase has been produced in indentation of boron carbide.

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