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In situ high-pressure spectroscopic studies using moissanite (4H-SiC) anvils

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We examined the Raman scattering and IR absorption spectroscopy of 4H-SiC and its performance as an anvil material for high-pressure UV-visible absorption spectroscopic measurements. The first- and second-order Raman peaks of 4H-SiC and diamond do not coincide. 4H-SiC does not have obvious signals from 2330-5000 cm^{-1}, suggesting that 4H-SiC anvils are beneficial for high-pressure studies of samples whose Raman signals locate in the region of diamond. Above 1800 cm^{-1}, the transmitted signal of 4H-SiC in the IR absorption spectra, measured through 4.6 mm thickness is much higher than that of type IIa diamond. An *in situ* high-pressure UV-visible absorption spectroscopy study on CdI_2 was carried out up to 28.0 GPa using 4H-SiC anvil cells (4H-SAC) with a 400 μm culet and the acquired band gap narrowed with increasing pressure. These results show that 4H-SiC has an excellent performance in high-pressure spectroscopic studies.
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I. INTRODUCTION

Owing to the synergic development of various pressure devices and probing technology, high-pressure research has been progressing rapidly during recent decades.[1] The diamond anvil cell (DAC) is a unique pressure device due to the excellent properties of diamond.[2] The static pressure that can be obtained in the lab has been greatly improved by use of the DAC, especially the Mao-Bell cell,[3] which has achieved pressures that exceed 400 GPa.[4] The use of diamonds, however, also imposes limitations. The IR and Raman characteristics of diamond interfere with measurements of sample peaks in similar spectral regions.[2] For example, the diamond first- and second-order Raman scattering at 1333 cm^{-1} and from 2300 to 2700 cm^{-1}, respectively, may overlap with the sample signal, while the IR diamond absorption of diamond from 1500 cm^{-1} to 2665 cm^{-1} obscures the sample signal. Moreover, the strong absorption of diamond at 420nm makes it impossible to measure a wide band gap (larger than 2.95eV) in the UV visible absorption spectrum. The most significant constraint is that perfect diamonds are limited and very expensive.

SiC is second in hardness to diamond and has been studied to replace or complement diamond in high-pressure experiments. A 6H-SiC anvil cell achieved pressure over 55 GPa.[2,5,6] Xu et al. conducted powder neutron diffraction of wüstite (FeO) to 12 GPa by using large 6H-SiC as anvils.[7] SiC is also suitable for electric conductivity measurements due to its wide-gap[8,9] and has no detectable magnetic signal to interfere with high-pressure magnetic measurements.[2] A 6H-SiC anvil cell was also used to perform *in situ* synchrotron X-ray diffraction and double-sided laser heating experiments, achieving high temperatures of 3700 K.[10]

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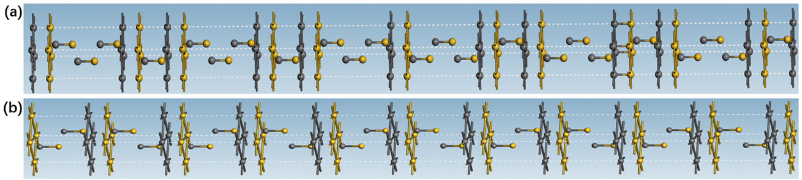

FIG. 1. Crystal structure of 4H-SiC (a) and 6H- SiC (b).

From a crystallographic perspective, SiC is polymorphic with different stacking sequences; 4H- and 6H-SiC are the most common. Figure 1 shows that 4H- and 6H-SiC have stacking sequences of ABACA and ABCACBA, respectively. Besides 6H-SiC, 4H–SiC is the only moissanite that can be grown in large crystals. Compared to 6H–SiC, 4H–SiC has a wider bandgap and higher carrier mobility, suggesting better performance as an optical window and in high-temperature power electronics.[9,11] However, the feasibility of 4H-SiC as high-pressure anvils has never been investigated. In this paper, we performed Raman, IR absorption, and *in situ* high-pressure UV-visible absorption studies on 4H-SiC to compare 4H-SAC and DAC performance. Our results show that 4H-SiC is a preferable substitution for diamond in high-pressure spectroscopic study.

II. EXPERIMENT

Single crystal 4H-SiC was commercially purchased and then cut into 2.3 mm high hexadecagon anvils with 400 µm culets. The top and side views of the faint yellow 4H-SiC anvil are shown in Fig. 2(a) and Fig. 2(b). The assembly of the 4H-SiC anvil in a Mao-type cell is shown in Fig. 2(c). A micro-Raman system (Renishaw, UK) with a 532 nm laser excitation with 2400 g/mm grating was used. IR spectra were collected on a Bruker VERTEX 70v FTIR spectrometer and a custom-built IR microscope with type IIa diamonds. A CdI_2 sample was used to compare the 4H-SAC and DAC *in situ* high-pressure UV-visible absorption spectra.

III. RESULTS

Raman spectroscopy is an important method to investigate the lattice vibration of materials. Raman scattering is a very weak phenomenon with a typical intensity of only 10^{-8} of conventional Rayleigh scattering, however, some studies have successfully applied Raman spectroscopy to characterize SiC crystal polymorphism.[12–16] Figure 3 compares the Raman spectra of 4H-SiC and type Ia diamond in the 50–5000 cm^{-1} region under the same experimental conditions. The position and corresponding symmetry assignment for each first-order band are also shown. The band positions of 4H-SiC are consistent with those reported by Burton *et al*[12] and Nakashima *et al*,[16] which confirms that the moissanite is polymorphic 4H-SiC. As shown in Fig. 3(a), before 1940 cm^{-1}, 4H-SiC has strong Raman scattering except 1333 cm^{-1}. Moreover, there is no 4H-SiC peak after 2330 cm^{-1}. Two peaks at 4348 cm^{-1} and 4378 cm^{-1} belong to ruby. In contrast, from 2300 cm^{-1} to 2700 cm^{-1} there is a

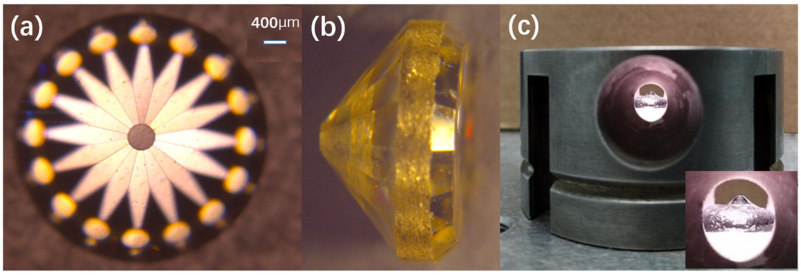

FIG. 2. The photographs of 4H-SiC (a) top view (b) side view and (c) 4H-SAC.

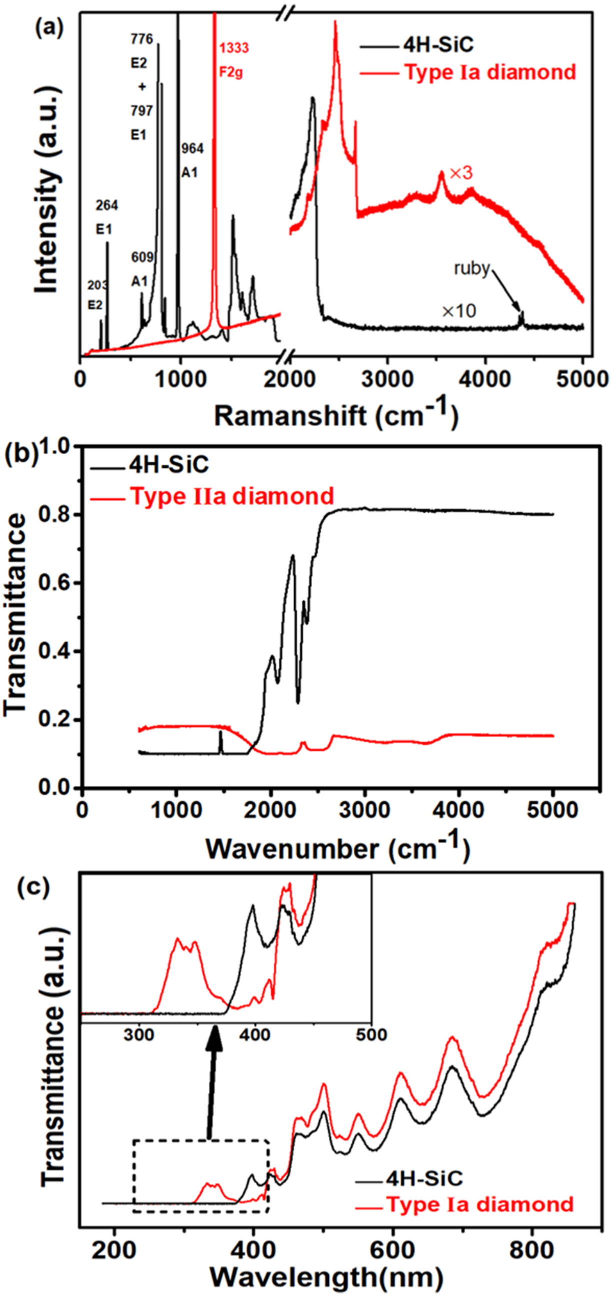

FIG. 3. (a) A comparison of 4H-SiC and type Ia diamond Raman spectra from 50–5000 cm^{-1} under the same experimental conditions. The extended mode was employed with an exposure time of 30 seconds and accumulation of 2; (b) A comparison of 4H-SiC and type IIa diamond IR spectra from 500–5000 cm^{-1} under the same experimental conditions; (c) UV-visible absorption spectra of bare 4H-SiC and bare type Ia diamond.

multi-phonon second-order diamond Raman band. Thus, 4H-SAC is advantageous for high-pressure Raman experiments for samples with signals in these ranges.

IR spectroscopy is another important method to investigate the lattice vibration of materials. Type IIa diamond has fewer impurities than type Ia diamond, and is usually used in high-pressure IR studies. We also characterized the 4H-SiC anvil with IR spectroscopy. Figure 3(b) compares the IR spectra of 4H-SiC and type IIa diamond (with similar thicknesses), collected under the same experimental conditions. Before 1800 cm^{-1}, diamond has obviously less absorption than 4H-SiC, which absorbs

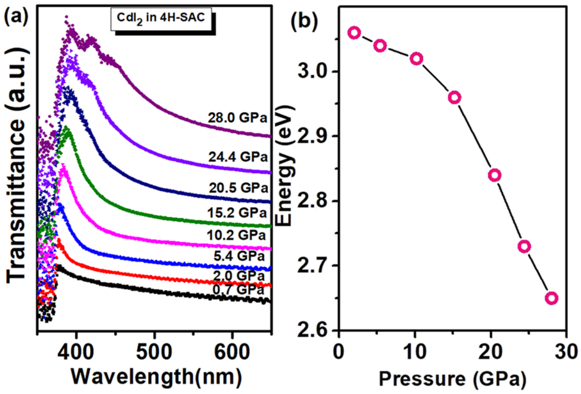

FIG. 4. (a) In-situ high-pressure UV-visible absorption spectroscopy study on CdI_2 in 4H-SAC; (b) The bandgap change with pressure.

all IR radiation before 1750cm^{-1}. After 1800 cm^{-1}, 4H-SiC transmittance is much better than type IIa diamond, though there are two strong absorption peaks at 2070 cm^{-1} and 2290 cm^{-1}. This agrees with Xu's results, which reported the transmitted signal measured with 4 mm thick 6H-SiC anvils was up to an order of magnitude higher than type-II diamond anvils.[2] For type IIa diamond, from 1600 cm^{-1} to 2670 cm^{-1} there is a strong absorption band that is troublesome in IR spectra when a DAC is used in high-pressure experiments. Furthermore, type IIa diamond has transmittance lower than 20% in all ranges. As shown in Fig. 3(b), the shortage of type IIa diamond can be complemented by using a 4H-SiC in IR spectra.

We also investigated the absorption of the 4H-SiC anvil in the UV-visible range. Figure 3(c) shows the comparison of the absorption spectra of bare 4H-SiC and type Ia diamond with similar thicknesses. It is clear that they have similar transmittance in the region from 420-850 nm. 4H-SiC has a cut-off at 370nm. The diamond cut-off starts at around 420 nm but it absorbs almost all light from 370 to 420 nm, making the measurable region smaller than 4H-SiC.

UV-visible absorption spectroscopy is usually used to obtain the band gap of a semiconductor from the absorption edge.[17–19] Figure 4(a) shows our *in situ* high-pressure UV-visible absorption spectroscopy study on CdI_2 in 4H-SAC at selected pressures at room temperature. With the increase in pressure, the absorption edge shifts to a longer wavelength. However, before 370 cm^{-1} (3.35 eV), the stage is incomplete due to the absorption of 4H-SiC, as confirmed by the UV-visible absorption spectrum of bare 4H-SiC in Fig. 3(c), which clearly shows that transmittance of 4H-SiC starts from 370 cm^{-1}. Owing to the absorption boundary at 370 cm^{-1}, the stages are partially visible at 0.7 GPa. We estimated the band gap of CdI_2 by extrapolating the linear portion of the $(\alpha h\nu)^{1/2}$ versus the $h\nu$ curve in the indirect band-gap Tauc plots under different pressure except 0.7 GPa. The band gap change with pressure is shown in Fig. 4(b).

IV. CONCLUSION

We investigated the vibrational spectra of single-crystal 4H-SiC by Raman and IR. The effect of pressure on the UV-visible absorption of CdI_2 in 4H-SAC was presented up to 28.0 GPa. For comparison, type Ia and type IIa diamonds were also examined. The first-and second-order Raman peaks of 4H-SiC do not coincide with those of diamond. Furthermore, it shows a flat feature in the range of 2330-5000 cm^{-1}, suggesting that 4H-SiC is beneficial for high-pressure studies of samples with Raman signals in the range that overlaps with diamond. In the region above 1800 cm^{-1}, the transmitted signal in the IR absorption spectroscopy measured through 4.6 mm of 4H-SiC was much higher than that of type IIa diamond. A high pressure of 28.0 GPa was achieved using a 400 μm 4H-SiC culet. The absorption boundary was extended from 420 nm (type Ia diamond) to 370 nm (4H-SiC) in *in situ* high-pressure UV- visible absorption spectroscopy.

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[1] H. K. Mao, X. J. Chen, Y. Ding, B. Li, and L. Wang, Review of Modern Physics **90**(1) (2018).
[2] J. A. Xu and H. K. Mao, Science **290**(5492), 783 (2000).
[3] H. K. Mao and P. M. Bell, Science **200**(4346), 1145 (1978).
[4] A. Jayaraman, Reviews of Modern Physics **55**(1), 65 (1983).
[5] Z. Liu, J. Xu, H. P. Scott, Q. Williams, H.-K. Mao, and R. J. Hemley, Review of Scientific Instruments **75**(11), 5026 (2004).
[6] J. Xu, H. Mao, J. H. Russell, and E. Hines, Journal of Physics-Condensed Matter **14**(44), 11543 (2002).
[7] J. Xu, Y. Ding, S. D. Jacobsen, H. K. Mao, R. J. Hemley, J. Zhang, J. Qian, C. Pantea, S. C. Vogel, and D. J. Williams, High Pressure Research **24**(2), 247 (2004).
[8] H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, Journal of Applied Physics **76**(3), 1363 (1994).
[9] C. E. Weitzel, J. W. Palmour, C. H. Carter, and K. Moore, IEEE Transactions on Electron Devices **43**(10), 1732 (1996).
[10] J. Hu, J. Xu, M. Somayazulu, Q. Guo, R. Hemley, and H. K. Mao, Journal of Physics Condensed Matter **14**(44), 10479 (2002).
[11] W. J. Schaffer, G. H. Negley, K. G. Irvine, and J. W. Palmour, MRS Proceedings **339** (1994).
[12] J. C. Burton, L. Sun, F. H. Long, Z. C. Feng, and I. T. Ferguson, Physical Review B **59**(11), 7282 (1999).
[13] Y. Ward, R. J. Young, and R. A. Shatwell, Journal of Materials Science **39**(22), 6781 (2004).
[14] M. Bechelany, A. Brioude, D. Cornu, G. Ferro, and P. Miele, Advanced Functional Materials **17**(6), 939 (2007).
[15] M. Wieligor, Y. Wang, and T. W. Zerda, Journal of Physics: Condensed Matter **17**(15), 2387 (2005).
[16] S. I. Nakashima, M. Higashihira, K. Maeda, and H. Tanaka, Journal of the American Ceramic Society **86**(5), 823 (2010).
[17] M. Szafrański and A. Katrusiak, Journal of Physical Chemistry Letters **7**(17), 3458 (2016).
[18] Q. Li, Y. Wang, W. Pan, W. Yang, B. Zou, J. Tang, and Z. Quan, Angewandte Chemie (2017).
[19] L. Kong, G. Liu, J. Gong, Q. Hu, R. D. Schaller, P. Dera, D. Zhang, Z. Liu, W. Yang, and K. Zhu, Proc Natl Acad Sci U S A **113**(32), 8910 (2016).