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Anomalous Dynamical Charge Change Behavior of Nanocrystalline 3C-SiC upon Compression

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Using diamond anvil cell (DAC) technique, in situ high-pressure Raman scattering and energy-dispersive X-ray diffraction (EDXRD) experiments were used at room temperature to study 3C-SiC with an average grain size of 30 nm. In contrast to its bulk counterpart, a decrease of the Born's transverse effective charge of these nanocrystals was observed with increasing pressure from measurements of the longitudinal and transverse optical phonon modes (longitudinal optical–transverse optical) splitting. This is therefore indicative of a diminishing ionicity of nanocrystalline 3C-SiC on compression.

I. Introduction

SILICON CARBIDE has been an industrial product such as polishing material for over a century because of its excellent chemical stability, high stiffness, and extreme hardness. In the Past few decades, its behavior under high pressure was systemically studied,[1–11] but the effect of grain size was largely neglected in these studies. Recently, X-ray diffraction data from 3C-SiC with nanometer grain size were reported,[12–15] in which the differences between the nanocrystalline and bulk 3C-SiC, together with the grain-size-dependence behavior on compression, were studied. However, the effect of pressure on the phonons of 3C-SiC with nanometer gain size has not been investigated. This was the motivation behind the work reported here, in which the dependence of the Born's transverse effective charge, i.e., the dynamical charge, of nanocrystalline 3C-SiC was determined from its longitudinal optical–transverse optical (LO–TO) phonons splitting as a function of pressure using high-pressure energy-dispersive X-ray diffraction (EDXRD) and Raman techniques.

II. Experimental Procedure

The nanocrystalline 3C-SiC studied here was synthesized by laser-induced vapor-phase reactions, and its average particle diameter was determined to be about 30 nm.[16] The EDXRD experiments were performed at room temperature using silicone oil as a pressure-transmitting medium to obtain quasi-hydrostatic conditions, and without any pressure transmitting medium to obtain non-hydrostatic compression. Ruby chips and a small amount of Au powder were added for pressure calibration.[17,18] The EDXRD data were obtained using an incident synchrotron radiation beam focused down to a size of about 20 μm × 20 μm, and a Ge solid-state detector at a fixed angle of $2\theta = 12°$. With the same experimental arrangement, high-pressure Raman spectra were collected at room temperature using a Jobin-Yvon LabRAM micro Raman system with excitation line of 632.8 nm (He–Ne laser).

III. Results and Discussion

Selected EDXRD spectra as a function of pressure are shown in Fig. 1. It is clear that all the diffraction lines shift to higher energy with increasing pressure, hence, that the *d*-spacings decrease and that no new diffraction peaks appear. In addition to the peak broadening due to grain size, the SiC diffraction peaks broaden further with pressure due to the differential strain introduced in the individual crystal grains.

Recently, Palosz et al. studied nanometer SiC with various grain sizes under pressure,[12] and a model of a three-stages relation

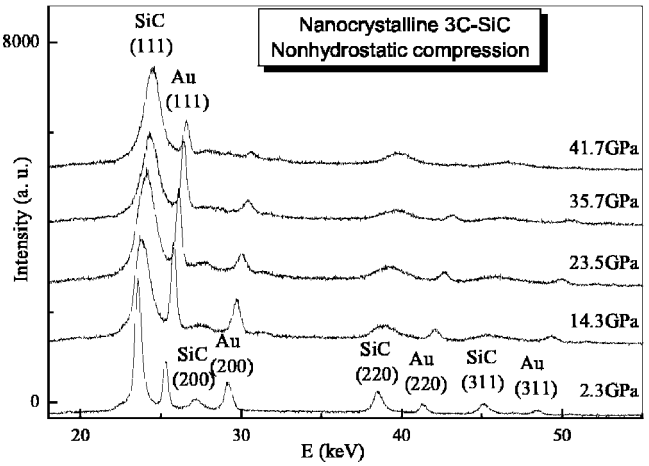

Fig. 1. Typical EDXRD patterns of nanocrystalline 3C-SiC under various pressures during compressing process without pressure medium.

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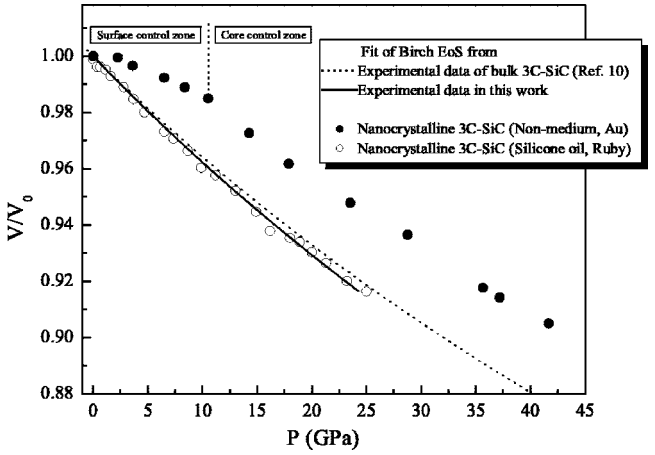

Fig. 2. Relative volume as a function of pressure for nanocrystalline 3C-SiC, in which open circles and solid circles represent experimental data obtained in quasi-hydrostatic and non-hydrostatic compressions for nanocrystalline 3C-SiC in this study, respectively. The error bars are omitted since they are smaller than the symbol size. The solid line illustrates the fitting result (B_0 = 245 GPa, B_0' = 2.9) for the experimental data according to Birch EoS, while dotted curve illustrates the experimental result (B_0 = 260 GPa, B_0' = 2.9) for bulk crystalline 3C-SiC cited from Ref. 10.

between the compressibility and the microstructure of the SiC was proposed to explain the dramatic change of lattice parameter on compression. In this paper, the lattice parameters of nanocrystalline 3C-SiC are obtained by whole-pattern LeBail refinement, and then the compressibility of nanometer SiC is studied, especially under non-hydrostatic compression to highlight the influence from the interfaces of the nanoscale powder. Figure 2 shows the relative volume of nanocrystalline 3C-SiC versus pressure. It is noticed that non-hydrostatic compression could be treated as a two-stage process based on a simple model related to the three-stage model in Ref. 12, in which the contribution to the compressibility is mainly attributed to the surface of the grains below 10 GPa and to the core of the grains beyond 10 GPa. However, the "hard-to-compress" behavior observed in the no pressure medium case is to some extent similar to the results obtained in lattice strains research on gold and rhenium, in which the lattice strain was analyzed using DAC radial-diffraction techniques.[19,20]

The zero-pressure bulk modulus B_0 and its pressure derivative B_0' of the nanocrystalline 3C-SiC are derived by fitting the relative volume data from quasi-hydrostatic compression to the Birch equation of state (EoS).[21] Previous EoS results obtained experimentally for coarse-grain SiC are also given in Table I,[10,22,23] while only the result from Ref. 10 is plotted in Fig. 2 for comparison. In the present work, although silicone oil was used as the pressure medium which produced relatively poor hydrostatic conditions, the nanocrystalline 3C-SiC has a bulk modulus comparable to the previous data for bulk 3C-SiC. The value of B_0 for nanocrystalline 3C-SiC is estimated as 245 ± 2 GPa, while B_0' remains as 2.9. This B_0 will be used in the effective charge calculation below.

In the zinc-blende structure SiC, the Born's transverse effective charge Z^* (i.e., the dynamical charge) results from the coupling

Table I. Experimental Data of Bulk Modulus and Its Pressure Derivative for 3C-SiC

Sample type	B_0 (GPa)	B_0'	Pressure range (GPa)	Reference and year
Nanocrystal (30 nm)	245 ± 2	2.9 (fixed)	25	This work
Bulk	248 ± 9	4.0 ± 0.3	25	22, in 1987
	227 ± 3	4.1 ± 0.1	42.5	23, in 1989
	260 ± 9	2.9 ± 0.3	95	10, in 1993

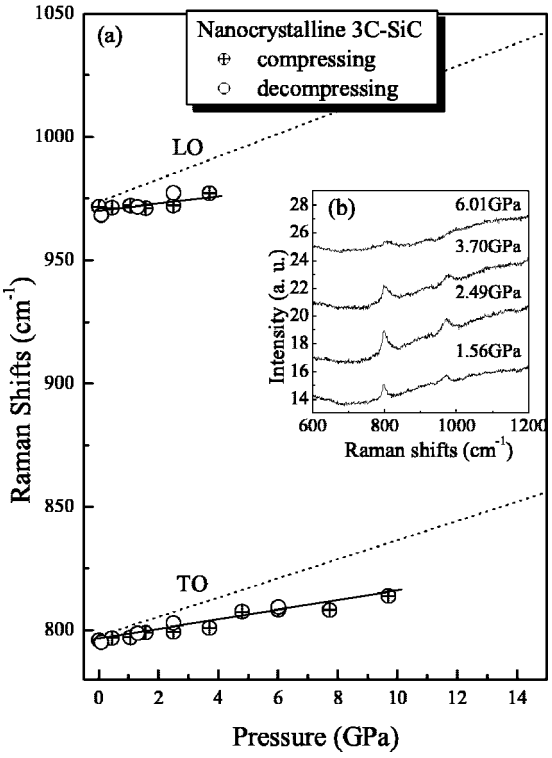

Fig. 3. Pressure dependence of ω_{LO} and ω_{TO} of nanocrystalline 3C-SiC, in which the experimental results from Ref. 7 of bulk 3C-SiC (dotted line) are illustrated for reference. The error bars are omitted since they are smaller than the symbol size. The insert shows the typical Raman spectra of nanocrystalline 3C-SiC under pressure.

between transverse lattice vibration and light, and it is defined as the macroscopic dipole moment per unit displacement of the sublattice of Si or C when the macroscopic electronic field in the crystal is kept at zero. Because Z^* is related to the macroscopic electric field associated with the LO phonon displacement, it has a relation with the LO–TO splitting as follows:[1,7,24]

$$\omega_{LO}^2 - \omega_{TO}^2 = \frac{4\pi N_d Z^*}{\varepsilon_\infty M_\mu \Omega}$$

in which M_μ is the reduced mass of Si and C, Ω the unit cell volume, ε_∞ the high-frequency (optical) dielectric constant, and N_d the number of anion–cation dipole pairs in the unit cell. In previous studies,[1,7] the increase of the LO–TO splitting with compression and therefore the increase of dynamical charge were observed for bulk 3C-SiC. This behavior can be related to an increase of the ionicity of SiC under pressure and was explained by a charge transfer from Si to C due to the strong 2p potential of C atom resulting from the lack of p electrons in the C core.[2] A pressure dependence of the LO–TO splitting with a tendency toward saturation was expected, and the turnover behavior of the

Table II. Phonon Frequencies of Nanoscale Crystal (NC) vs Bulk 3C-SiC, Their Pressure Coefficients, and Corresponding Mode Grüneisen Parameters γ_G (ω, cm^{-1}; P, GPa, Evaluated at Zero Pressure)

	ω_0		$\partial\omega/\partial P$		γ_G	
	NC	Bulk†	NC	Bulk†	NC	Bulk†
TO	796.0	797.7	1.85 (1.99)‡	3.88	0.62	1.105
LO	971.8	973.6	1.31 (1.41)‡	4.59	0.36	1.072
LO–TO	175.8	175.9			−0.82	1.051

†Ref. 7. ‡Linear fitting using the data within 5 GPa in compressing process.

Table III. Dynamical Charge Z^* and Their Pressure Dependence for Nanocrystalline and Bulk 3C-SiC (ω, cm^{-1}; P, GPa, Evaluated at Zero Pressure)

	NC	Bulk[†]
Z^*	2.678	2.681
$-\partial Z^*/\partial P$	−0.0057[‡]	0.0033
$-\partial \ln Z^*/\partial \ln V$	−0.521	0.280

[†]Ref. 7. [‡]Calculated by using experimental LO–TO splitting data in this study and theoretical calculation value of $\partial\varepsilon_\infty/\partial P$ cited from Ref. 7.

LO–TO splitting was observed experimentally in 6H-SiC above 60 GPa.[3]

The LO Raman mode of nanocrystalline 3C-SiC is measurable only below 5GPa, and this mode becomes less recognizable at higher pressure. After increasing pressure beyond 10 GPa, the Raman spectra become featureless. Figure 3 illustrates the pressure dependence of ω_{LO} and ω_{TO} for nanocrystalline 3C-SiC, and the experimental results for bulk 3C-SiC (dotted lines, cited from Ref. 7) are also illustrated for reference. The insert shows the typical Raman spectra from nanocrystalline 3C-SiC under pressure. It is obvious that the pressure dependence of the phonon modes in nanocrystalline sample is relatively weak. Table II lists the phonon frequencies of nanoscale crystalline (NC) versus bulk 3C-SiC, their pressure coefficients, and corresponding mode Grüneisen parameters γ_G. All the data points collected during compression and decompression were used for the linear fitting of their pressure coefficients, and the corresponding fit parameters from the data obtained below 5 GPa in compression are also given in the brackets. The negative Grüneisen parameter for LO–TO splitting, resulting from the decrease of the LO–TO splitting with increasing pressure, implies an anomalous dynamical charge change in nanocrystalline 3C-SiC compared with its bulk counterpart. Using the ε_∞ value of 6.52 and its pressure dependence $\partial\varepsilon_\infty/\partial P$ of $-0.0104\ GPa^{-1}$, the latter being the only theoretical calculation datum available,[7] and assuming that these values are close to those for nanocrystalline 3C-SiC, the dynamical charge Z^* and its pressure dependence evaluated at zero pressure were derived. Table III lists the corresponding dynamical charges and their pressure dependence for nanocrystalline and bulk 3C-SiC. The bulk data cited from Ref. 7, in which a bulk modulus of 227 GPa was used.

Despite the fact that LO–TO splitting data are only available below 5 GPa, a pressure range within the surface controlling zone in the non-hydrostatic compression case, the negative pressure dependence of the dynamical charge implies a more covalent feature of the nanocrystalline 3C-SiC on compression, in contrast to the behavior of bulk SiC which shows an increase of ionicity with pressure. The nanocrystals are usually treated as a two-phase structure material in the simple core-shell model.[12,15] The apparent anomalous dynamical charge behavior, reported here for the first time in this rapidly developing field of nanostructured materials, is the average effect from the core and shell components of the nanocrystalline sample, and the contribution from the surface should play the main role. A more physical explanation of this anomalous behavior is expected from first-principles simulations, by comparing the charge transfer between Si and C under pressure using the nanometer SiC configuration with surface effect, and bulk SiC with periodic boundary conditions. The quantitative comparison with the experimental data reported here is important since computations on nanometer 3C-SiC are the subjects of first-principle molecular dynamics simulations.

IV. Conclusion

In conclusion, nanocrystalline 3C-SiC with 30 nm grain size was studied under high pressure using EDXRD and Raman scattering. The zero-pressure bulk modulus for nanocrystalline 3C-SiC is estimated as 245 GPa when using silicone oil as the pressure transmitting medium. The dynamical charge change was determined from the pressure dependence of the splitting between longitudinal optical (LO) and transverse optical (TO) phonon modes. In contrast to the behavior of bulk SiC, the nanocrystalline 3C-SiC becomes more covalent on compression within the range controlled by surface effects.

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