Compressive Strength of Diamond From First-Principles Calculation

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Compressive Strength of Diamond from First-Principles Calculation

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Compressive strength, like tensile and shear strength, is one of the intrinsic mechanical properties of solid materials. We investigated the ideal compressive strength and corresponding compressive deformation of diamond using pseudopotential density functional theory. The calculated uniaxial compressive strength of diamond is −223.1, −469.0, and −470.4 GPa along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions, respectively. The elastic deformation of diamond in compressive strain below the proportional limit of 17% has been determined from the perfect linear response between strain and stress along the ⟨100⟩ direction. The present work should be helpful to the understanding of the compressive property of diamond and to the explanation of the limit strength of diamond anvil cell.

I. Introduction

Diamond is the hardest known natural material, showing ultimate strength, ultra incompressibility, and high bulk and shear moduli, which give it a wide range of applications in science and technology. Various theoretical and experimental studies have been carried out on the mechanical properties of diamond.[1−5] Usually, diamond is used under nonhydrostatic conditions, such as a diamond indenter in the nanoindentation test and as diamond tips of the diamond anvil cell (DAC) in ultrahigh-pressure research. Therefore, theoretical investigations into the mechanical properties of diamond under nonhydrostatic conditions should be important.

Under nonhydrostatic conditions, the mechanical properties of materials are always explored through the strength of materials. The strength is often considered in terms of tensile strength, compressive strength, and shear strength with corresponding applied loads and deformations. Recent advances in first-principles methods have made it possible to investigate these basic deformations of crystals at the atomistic level. The stress−strain relation and atomistic deformation mechanism of tensile and shear deformation have been thoroughly examined for diamond.[6−10] Recently, some complex deformations of diamond have also been reported. Pan et al.[11] calculated indenter-angle-sensitive fracture modes of diamond with the combination of compressive and shear stress, which should be more suitable for the situation of a diamond indenter in the nanoindentation test. Oleynik et al.[12] investigated the shear stress of uniaxially compressed diamond with constraints of the fixed lateral dimensions of crystal cell, corresponding to strong shock wave compressed diamond. Wen et al.[13] investigated the stability limit of diamond under nonhydrostatic compression and reported that the diamond phase would transform to a lonsdaleite phase with a stress of 26 GPa. However, despite early theoretical investigations of diamond under anisotropic high pressure,[14−18] the basic compressive strength and the corresponding compressive deformation of diamond still are not well understood. In experimental work, the compressive strength of diamond can be roughly obtained from the strength of DAC. However, the pressure limits of DAC reported by different groups are not in accordance.[19−23] Therefore, it is necessary to obtain the pressure limit of diamond through uniaxial compression of diamond using first-principles methods.

In this article, we present first-principles calculation of uniaxial compressive strength and compressive deformation of diamond, comparing this with the corresponding tensile strength and tensile deformation. The compressive and tensile deformations of diamond along various nonequivalent crystallographic directions are calculated, revealing that the uniaxial compressive deformation of diamond is different from the corresponding tensile deformation. The atomistic compressive strength and deformation mechanism of diamond should be helpful to the understanding of the mechanical properties of diamond and to the explanation of the limit strength of DAC.

II. Calculation Methods

The first-principles calculations were performed with CASTEP code based on density functional theory.[24] The exchange-correlation function was treated by local density approximation (LDA-CAPZ), and the norm-conserving pseudopotential with cutoff energy of 770 eV was used. Observed from different crystal directions, the structure of diamond can be regarded as shown in Figure 1 for ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions. Different C−C bond types can be seen in the stressed diamond structure. For the ⟨100⟩ direction, only one type of C−C bond exists in the stressed crystal structure (denoted as type I). For the ⟨110⟩ and ⟨111⟩ directions, there are two different types of C−C bonds under deformation. One type is similar to that in the ⟨100⟩ direction, and the other type is perpendicular to the direction of stress (denoted as type II). The $1 \times 1 \times 2$ unit cell was selected for compressive calculation of the ⟨100⟩ and ⟨110⟩ directions. The $1 \times 1 \times 1$ unit cell was used for compressive deformation of the ⟨111⟩ direction and tensile deformation of ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions. According to the Monkhorst−Pack scheme, the k points of 0.04 1/Å were used. The calculation

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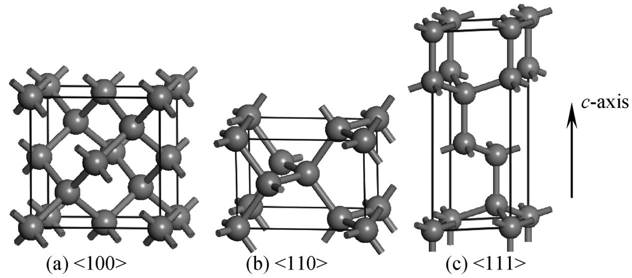

Figure 1. 1 × 1 × 1 diamond structure for the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions.

TABLE 1: Tensile and Compressive Strength of Diamond and the Corresponding Strain along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ Directions

		⟨100⟩		⟨110⟩		⟨111⟩	
		strain	stress (GPa)	strain	stress (GPa)	strain	stress (GPa)
tensile	R. H. Telling[a]	–	225	–	130	–	90
	Y. Zhang[b]	0.39	223.3	0.24	126.3	0.13	92.8
	this work	0.38	222.5	0.24	125.5	0.13	90.6
compressive	this work	−0.28	−223.1	−0.23	−469.0	−0.23	−470.4

[a] Reference 7. [b] Reference 10.

methods of tensile strength and compressive strength are similar to those of previous studies.[25,26] At each step, the fixed tensile strain was applied in the selected direction, and then the structural parameters were relaxed until the stress tensors orthogonal to the applied stress were less than 0.02 GPa. In this way, a series of tensile stresses corresponding to the incrementally applied tensile strains could be obtained.

III. Results and Discussion

We have calculated the stress−strain relation of diamond in three principal crystallographic directions, the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions. Our calculated tensile strength and corresponding strain are shown in Table 1, which are in excellent agreement with previous calculations.[7,10] Whitlock and Ruoff[14] have calculated the [100], [110], and [111] compressive and tensile strength of diamond using finite elasticity method based on strain energy with strain terms. Their calculated compressive strength of diamond along the [100], [110], and [111] directions is −219, −284, and −558 GPa, respectively. The difference in compressive strength along the [110] and [111] directions in comparison with our first-principles work may result from the high-order strain terms being missed.

The stress−strain relations of diamond along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions are shown in Figure 2a, Figure 3a, and Figure 4a, respectively. The calculated stress−strain relation of diamond in tension is in good agreement with results from previous studies.[10] Our calculation results show that the stress−strain relation of diamond shows little difference at small strains (−0.01−0.01) along any of the three primary directions. However, the anisotropy of the stress−strain relation of diamond can be seen at larger strains, both in tension and in compression. The larger anisotropy of the stress−strain relation of diamond in compression can be examined by the slope of stress−strain curve. Here, we select the data point in the stress−strain curves corresponding to the first minimum bond length in compression as a characteristic point. Therefore, the ratio of compressive stress to compressive strain can be illustrated as the red lines shown in Figure 2a, Figure 3a, and Figure 4a. For the compressive deformation along the ⟨100⟩ direction, almost linear

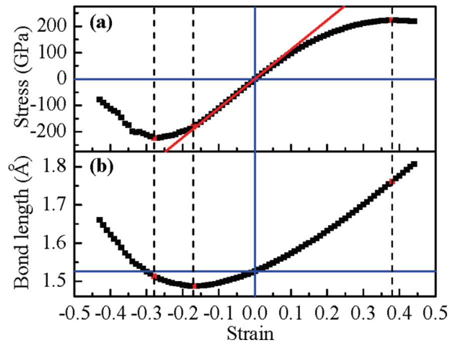

Figure 2. Calculated stress−strain curve and bond length versus strain of diamond along the ⟨100⟩ direction. For an explanation for the different subpanels, dashed lines, and slopes, please refer to the text.

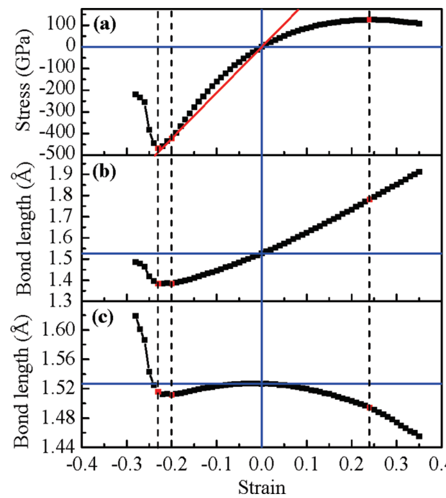

Figure 3. Calculated stress−strain curve and bond length versus strain of diamond along the ⟨110⟩ direction. For an explanation for the different subpanels, dashed lines, and slopes, please refer to the text.

proportionality up to about 17% compressive strain can be found. The fixed slope of the stress−strain curve indicates that the present deformation is an elastic deformation. The calculated compressive elastic modulus in this region is 1066.5 GPa, which is almost equal to the calculated Young's modulus of diamond (1063.0 GPa). For the compressive deformation of diamond along the ⟨110⟩ and ⟨111⟩ directions, the slope of the red line is 2112.0 and 1858.8 GPa, respectively. According to the close compressive strength of −469.0 and −470.4 GPa along ⟨110⟩ and ⟨111⟩, respectively, the rough isotropic stress−strain relation to a reasonable approximation of diamond in compression along the ⟨110⟩ and ⟨111⟩ directions can be inferred from the present results.

Next, the atomistic deformation mechanism of diamond in compressive deformation is presented. The different stress−strain relation of diamond in tension and in compression should be first examined regarding the crystal structure of diamond. As shown in Figure 2b, the C−C bond length under tension rises with increasing strain until the diamond structure is broken, which is in good agreement with a previous study.[10] However, under compressive deformation, the decrease in the C−C bond length shows one minimal value of 1.488 Å with a corresponding strain of −0.17 and stress of −181.3 GPa. As strain continues to increase, the C−C bond length increases, as shown in Figure 2b. At a bond length of 1.513 Å, with corresponding strain of −0.28, the maximum compressive stress of −223.1 GPa is produced. For the C−C bond of type I, the bond length in response to strain along ⟨110⟩ is similar to that along ⟨100⟩

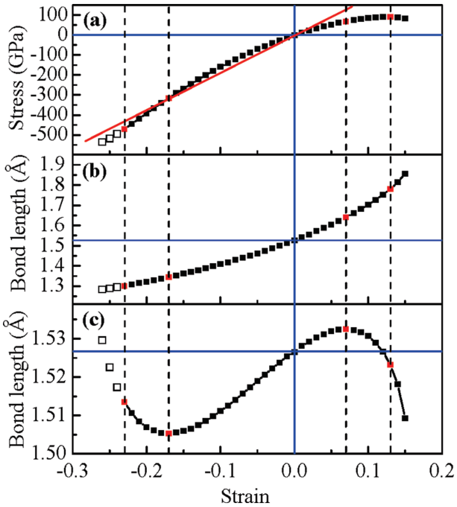

Figure 4. Calculated stress−strain curve and bond length versus strain of diamond along the ⟨111⟩ direction. The maximum compressive strain is −0.23 within the convergence tolerance of stress of 0.02 GPa in the strain−stress relation calculation. If the convergence tolerance of stress of 0.1 GPa is used in calculation, three more compressive strains (−0.24, −0.25, and −0.26) can be achieved, as shown by the hollow boxes. The phonon calculation results show that the structures corresponding to these three strains are not dynamically stable.

and two particular bond lengths of 1.385 and 1.781 Å can be seen in Figure 3b, while a monotonic curve of bond length in response to strain along the ⟨111⟩ direction can be seen in Figure 4b. For the C−C bond of type II along the ⟨110⟩ direction, as shown in Figure 3c, the C−C bond length decreases under both tensile and compressive deformation. A local minimum of 1.512 Å, with the corresponding stress of −422.4 GPa and strain of −0.20, can be seen in compressive deformation. For the second type of C−C bond of the ⟨111⟩ direction, as shown in Figure 4c, the local maximum and minimum of C−C bond length can be seen in tension and compression, respectively. However, the local minimum of bond length does not correspond to the limit strength of diamond. The local maximum tensile bond length of 1.532 Å corresponds to the stress of 67.8 GPa and strain of 0.07, while the local minimum compressive bond length of 1.505 Å is for a response to the stress of −316.0 GPa and strain of −0.17, as shown by the red point in Figure 4c. Because of the convergence tolerance of the maximum stress of 0.02 GPa in the stress−strain calculation, the maximum converged compressive strain of diamond along the ⟨111⟩ direction is −0.23 with a limit compressive strength of −470.4 GPa. It should be noted that the new C−C bond between the next nearest neighbors of carbon atoms along the ⟨100⟩ and ⟨110⟩ directions can be formed at extreme compressive conditions after the maximum compressive strength is reached.

The compressive strength of diamond is one of its most important parameters, especially in designing and using DAC. The working conditions of DAC can be roughly considered as representing uniaxial compressive deformation, since mainly axial loads are applied to diamond tips. Therefore, the stress−strain relation of uniaxially compressed diamond can give meaningful information. Because of the perfect linear response between compressive stress and strain along the ⟨100⟩ direction before the strain of −0.17, as shown in Figure 2a, the ⟨100⟩ direction is one perfect working direction of DAC, with the maximum compressive strength of −181.3 GPa in the elastic deformation region. Our calculation results are consistent with the experimental results that show plastic deformation of DAC beginning at the pressures of 170 and 200 GPa.[20,22] From the maximum compressive strength of diamond, it can be inferred that the limit strength of DAC should be −223.1, −469.0, and −470.4 GPa with the corresponding strain of −0.28, −0.23, and −0.23 along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions, respectively. According to the deformation mechanism of diamond, the safety limit strength of DAC should be −181.3, −422.4, and −316.0 GPa with the corresponding strain of −0.17, −0.20, and −0.17 along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions, respectively. In other words, the ⟨110⟩ and ⟨111⟩ directions are good choices for producing pressures above 200 GPa.

IV. Conclusions

In summary, the uniaxial compressive deformation of diamond along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions has been calculated using first-principles methods. The calculated compressive strength along these three directions is −223.1, −469.0, and −470.4 GPa, respectively. The stress−strain relation and atomistic deformation mechanism of diamond in compression are identical to those in tension. The elastic deformation region within the compressive strain less than 17% along the ⟨100⟩ direction has been determined. From the mechanism under compressive deformation of diamond, we can estimate that the limit strength of DAC should be about 470 GPa.

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