Hardness of Covalent Crystals

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(Received 17 January 2003; published 2 July 2003)

Based on the idea that the hardness of covalent crystal is intrinsic and equivalent to the sum of the resistance to the indenter of each bond per unit area, a semiempirical method for the evaluation of hardness of multicomponent crystals is presented. Applied to β-BC_2N crystal, the predicted value of hardness is in good agreement with the experimental value. It is found that bond density or electronic density, bond length, and degree of covalent bonding are three determinative factors for the hardness of a polar covalent crystal. Our method offers the advantage of applicability to a broad class of materials and initializes a link between macroscopic property and electronic structure from first principles calculation.

DOI: 10.1103/PhysRevLett.91.015502 PACS numbers: 62.20.Qp, 71.15.Mb, 81.05.Zx

Superhard materials are of primary importance in modern science and technology. Intense theoretical and experimental efforts have been focused on the possibility of finding new low compressibility materials with hardness comparable to diamond. In order to design the new superhard materials, clarifying the meaning of hardness is of utmost importance [1–3]. Over the last two decades, material scientists have aimed at finding materials with high values of bulk modulus E and shear modulus G [4–7]. In fact, bulk modulus measures resistance to volume change, which has little direct connection with hardness, as is well known from dislocation theory [8]. A better correlation has been observed between hardness and G, although, in this case too, the dependence is not unequivocal and monotonic. For example, the bulk and shear moduli of tungsten carbide which are as high as 439 and 282 GPa, respectively, are among the highest as known, but its hardness is only 30 GPa [1]. This implies that it is difficult to describe hardness quantitatively only by macroscopic physical properties of E and G.

In simple metals and ionic substances, the bonding is delocalized, and hardness is determined by extrinsic factors such as impurities, precipitates, grain boundaries, and the like. However, in covalent substances, the bonding is localized in electron spin pairs, thus hardness is intrinsic. Gilman's theory indicates that chemical hardness and mechanical hardness have the same reaction barrier, which is the difference between energy of the lowest unoccupied electronic orbital and the highest occupied orbital [7]. Recently, Jhi *et al.* have investigated the correlation between valence electron concentration and hardness [9]. Their work has given a clue that hardness could be understood in terms of their electronic band structure. In our opinion, the hardness of covalent crystals is intrinsic and equivalent to the sum of resistance of each bond per unit area to indenter. This resistant force of bond can be characterized by energy gap, and the number of bond per unit area is determined by valence electron density. Based on this assumption, we represent a semiempirical method for the evaluation of hardness in covalent crystals.

Hardness was defined as the resistance offered by a given material to external mechanical action. Vickers and Knoop scales are frequently used. In static indentation tests, pyramid is forced into a surface and the load per unit area of impression is taken as the measure of hardness. Therefore, it is not surprising that the resistant force per unit area could play a key role in determining hardness of materials.

Generally speaking, hardness depends strongly on plastic deformation, which is related to the creation and motion of dislocations [1]. In a covalent crystal, bonding is highly stereospecific and dislocation energy depends strongly on its position. Regardless of details, a basic fact remains that, in order to plastically shear such a crystal, electron-pair bonds must first be broken and then remade, resulting in two unpaired electrons when an atomic shear process is half completed. Energetically breaking an electron-pair bond inside a crystal means that two electrons become excited from the valence band to the conduction band so the activation energy required for plastic glide is twice the band gap, E_g [10]. Thus, the resistant force of bond can be evaluated by energy gap E_g and the hardness of overly covalent crystals should have a following form:

$$H(\mathrm{GPa}) = AN_aE_g, \tag{1}$$

where N_a is the covalent bond number per unit area and A is a proportional coefficient. For a crystal with cell volume V, N_a can be expressed as

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$$N_a = \left(\sum_i n_i Z_i / 2V\right)^{2/3} = (N_e/2)^{2/3}, \quad (2)$$

where n_i is the number of i atom in the cell, Z_i is the valence electron number of i atom. N_e is the electron density expressed in number of valence electrons per cubic angstroms.

Equation (1) is suitable only for pure covalent crystals. For polar covalent crystals, besides the covalent component, a partial ionic component has to be considered. The average energy gap E_g for a binary polar covalent AB_m type crystal can be separated into both of covalent or homopolar gap E_h and ionic or heteropolar gap C by Phillips [11]

$$E_g^2 = E_h^2 + C^2, \quad (3)$$

where C represents the ionic or charge-transfer contribution, E_h represents the pure covalent contribution, and is equal to E_g in the case of a purely covalent Group IV crystal such as diamond or Si. Ionic bonding results from long-range electrostatic force which is not directly related to hardness [8]. Recent work also indicates that the activation energies of dislocation glide in polar covalent crystals are proportional to Phillips's homopolar band gap E_h [12], which characterizes the strength of the covalent bond. Therefore, we can deduct the ionic contribution C from the factor E_g, leave only a homopolar component E_h for the hardness of polar covalent crystals, which is given as follows [11] :

$$E_h = 39.74/d^{2.5}, \quad (4)$$

where d is the bond length in angstroms, E_h is in electronvolts. However, the partly ionic bonding results in the loss of covalent bond charge [13]. In other words, an electron-pair localized on a chosen bond is screened due to partly

TABLE I. Hardness and parameters related to the hardness calculations of typical covalent and polar covalent crystals, where $H_{v\,\mathrm{calc}}$ and $H_{v\,\mathrm{exp}}$ are calculated and experimental Vickers hardness, respectively. Since there are no H_v measurements for compounds from HfO_2 and below, experimental Knoop hardness H_k has been displayed as a comparison.

Crystals	N_a	d (Å)	E_h (eV)	E_g (eV)	f_i	$H_{v\,\mathrm{calc}}$ (GPa)	$H_{v\,\mathrm{exp}}$ (GPa)	$H_{\mathrm{k\,exp}}$ (GPa)
Diamond	0.499	1.554	13.2	13.2	0[a]	93.6	96 ± 5[e]	90[l]
Si	0.215	2.351	4.7	4.7	0[a]	13.6	12[f]	14[i]
Ge	0.198	2.449	···	···	0[a]	11.7	···	···
BP	0.308	1.966	7.3	7.4	0.006[a]	31.2	33 ± 2[e]	32[i]
c-BN	0.486	1.568	12.9	15.0	0.256[a]	64.5	66[f], 63 ± 5[e]	48[i]
β-Si_3N_4	0.363	1.734	10.0	13.0	0.4[b]	30.3	30 ± 2[e]	21[i]
AlN	0.332	1.901	8.0	10.7	0.449[a]	21.7	18[g]	···
GaN	0.315	1.946	7.5	10.6	0.500[a]	18.1	15.1[h]	···
InN	0.256	2.160	5.8	8.9	0.578[a]	10.4	···	···
β-SiC	0.334	1.887	8.1	9.0	0.177[a]	30.3	34[f], 26 ± 2[e]	···
WC	0.386	2.197	5.5	6.0	0.140[c]	26.4	···	30[j], 24[f]
Stishovite	0.490	1.770	9.5	14.5	0.57[b]	30.4	33 ± 2[e]	···
Al_2O_3	0.461	1.900	8.0	17.7	0.796[b]	20.6	20 ± 2[e]	21[i]
RuO_2	0.495	1.990	7.1	12.7	0.687[c]	20.6	···	20[j]
SnO_2	0.399	2.010	6.9	14.8	0.78[b]	13.8	···	···
BeO	0.163	1.648	10.8	17.1	0.602[a]	12.7	13[f]	12.5[i]
ZrO_2	0.396	2.200	5.5	15.4	0.870[c]	10.8	13[f]	11.6[i]
α-SiO_2	0.356	1.609	12.1	18.5	0.570[b]	30.6	11[f]	8.2[i]
HfO_2	0.385	2.215	5.4	14.1	0.850[c]	9.8	···	9.9[k]
Y_2O_3	0.296	2.284	5.0	12.7	0.843[d]	7.7	···	7.5[l]
AlP	0.214	2.365	4.6	5.5	0.307[a]	9.6	···	9.4[i]
AlAs	0.198	2.442	4.3	5.0	0.274[a]	8.5	···	5.0[i]
AlSb	0.169	2.646	3.5	3.8	0.426[a]	4.9	···	4.0[i]
GaP	0.214	2.359	4.6	5.9	0.374[a]	8.9	···	9.5[i]
GaAs	0.198	2.456	4.2	5.1	0.31[a]	8.0	···	7.5[i]
GaSb	0.171	2.650	3.5	4.0	0.261[a]	6.0	···	4.4[i]
InP	0.184	2.542	3.9	5.1	0.421[a]	6.0	···	5.4[i]
InAs	0.173	2.619	3.6	4.5	0.357[a]	5.7	···	3.8[i]
InSb	0.151	2.806	3.0	3.7	0.321[a]	4.3	···	2.2[i]

[a]Reference [11]. [b]Reference [14]. [c]Calculated by authors using the method [14,15]. [d]Reference [16]. [e]Reference [17]. [f]Reference [8]. [g]Reference [18]. [h]Reference [19]. [i]Reference [2]. [j]Reference [1]. [k]Reference [20]. [l]Reference [21].

ionic bonding and results in a smaller effective covalent bond number per unit area in comparison with that of N_a for pure covalent crystals. Here we introduce a correction factor $\exp(-\alpha f_i)$ to describe this screening effect of many bonds, i.e., use $N_a \exp(-\alpha f_i)$ for polar covalent crystals instead of N_a for pure covalent crystals in Eq. (1), where α is a constant, f_i is ionicity of chemical bond in crystal scaled by Phillips [11]:

$$f_i = 1 - E_h^2/E_g^2. \tag{5}$$

In order to determine the correlation between the hardness H_v and ionicity f_i, we plot $H_v/E_h N_a$ against f_i for some typical crystals from Table I as shown in Fig. 1. The exponential regression equation is obtained as follows:

$$H_v(\mathrm{GPa}) = A(N_a e^{-\alpha f_i})E_h = 14(N_a e^{-1.191 f_i})E_h. \tag{6}$$

For practical calculation of hardness, Eq. (6) can be expressed as

$$H_v(\mathrm{GPa}) = 556\frac{N_a e^{-1.191 f_i}}{d^{2.5}} = 350\frac{N_e^{2/3} e^{-1.191 f_i}}{d^{2.5}}. \tag{7}$$

In order to confirm the practicability of Eq. (7), we calculated the Vickers hardness of typical covalent and polar covalent crystals and listed the results in Table I. The good agreements between the experimental and calculated values for the crystals with Vickers hardness above 10 GPa demonstrate the predictive power of Eq. (7). From the data in Table I, it can be deduced that the unexpected smaller hardness of tungsten carbide results from its larger bond length and smaller bond density.

Martin has revealed that the elastic properties of the sphalerite structure crystals, especially the shear modulus G, follow approximately linear trends as functions of the ionicity f_i [22]. However, if we take into account polar covalent crystals with different structures, the shear modulus G does not show a systematic variation trends

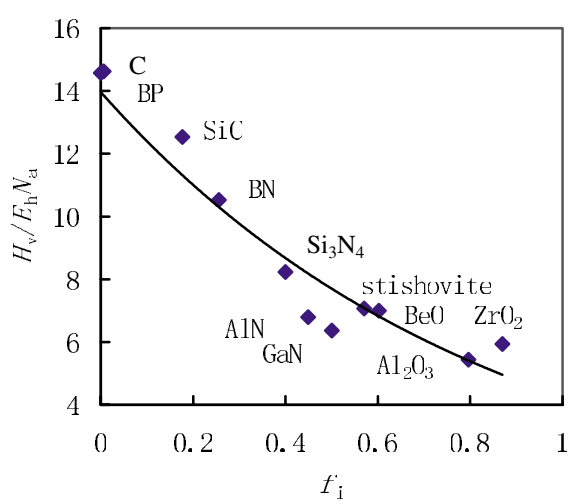

FIG. 1 (color online). $H_v/E_h N_a$ as a function of ionicity f_i. The solid line is from Eq. (7).

with f_i, and no direct relation between hardness and shear modulus G can be established. Whereas as shown in Fig. 1, the hardness can be approximately described by an exponential function of ionicity.

It should be noticed that some secondary factors [7] affecting hardness have not been considered in our present model. As shown in Table I, α-SiO_2 is such an example. Its experimental hardness is only 11 GPa, remarkably lower than its calculated value of 30.6 GPa. This is due to its open crystal structure, which is built up of SiO_4 tetrahedra. These tetrahedra are linked only by their corners and can easily tilt. Under pressure of the indenter, the mechanism for plastic deformation and volume change in α-SiO_2 is the rotation and bending of the framework tetrahedra about their shared oxygen atoms rather than the broken of the bonds of the frameworks [1,23].

Equation (7) will also be useful in predicting the trends of hardness for new materials. Since multicomponent compound systems are dominant in new materials, it is necessary to extend Eq. (7) to these systems. Based on Phillips scheme [11,14], a theory describing the chemical bond of complex crystals has been developed by Zhang *et al.* [15,16,24,25]. In the theory, "crystal formula" is a combination of subformula of chemical bond. The subformula of any type of chemical bond A-B in the multibond crystal $A_aB_b\ldots$ can be expressed by the following formula:

$$[N(\mathrm{B\text{-}A})a/N_{\mathrm{CA}}]\mathrm{A}[N(\mathrm{A\text{-}B})b/N_{\mathrm{CB}}]\mathrm{B}, \tag{8}$$

where A, B, ... represent different elements or different sites of the same element in the crystal formula, and $a, b, \ldots$ represent numbers of the corresponding element, N(B-A) represents the number of B ions in the coordination group of A ion, and N_{CA} represents the nearest coordination number of A ion.

Similarly, the hardness of muticomponent compound systems can be expressed as an average of hardness of all binary systems in the solid [26,27]. When there are differences in the strength among different types of bonds, the trend of breaking the bonds will start from a softer one. Therefore, the hardness H_v of complex crystals should be calculated by a geometric average of all bonds as follow:

$$H_v = \left[\prod^{\mu}(H_v^{\mu})^{n^{\mu}}\right]^{1/\Sigma n^{\mu}}, \tag{9}$$

where $H_v^{\mu} = 350(N_e^{\mu})^{2/3}e^{-1.191 f_i^{\mu}}/(d^{\mu})^{2.5}$ is the hardness of binary compound composed by μ-type bond, n^{μ} is the number of bond of type μ composing the actual complex crystal, f_i^{μ} is the ionicity of binary compound composed by μ-type bond, which can be calculated according to the literature [15,16,24,25], N_e^{μ} is the number of valence electrons of type μ per cubic angstroms and is expressed as follows [15,16,24,25]:

$$N_e^{\mu} = (n_e^{\mu})^*/v_b^{\mu}, \tag{10}$$

TABLE II. Chemical bond parameters and hardness of predicted β-BC_2N crystal.

Phase	Cell (Å)	Bond type	d^μ (Å)	N_e^μ	E_h (eV)	E_g (eV)	f_i^μ	H_ν^μ	$H_{\nu\,\mathrm{calc}}$ (GPa)	$H_{\nu\,\mathrm{expt}}$ (GPa)
β-BC_2N	$a = 3.576$	BN	1.562	0.680	13.2	15.0	0.227	66.9	78	76 ± 4[a]
	$b = 3.576$	BC(2)	1.573	0.498	12.9	12.9	0.000	70.7		
	$c = 3.608$	C(1)C(2)	1.515	0.930	14.2	14.2	0.000	118.1		
	$Z = 2$	C(1)N	1.564	0.679	13.1	14.9	0.228	66.5		

[a]Reference [28].

$$(n_e^\mu)^* = [(Z_A^\mu)^*/N_{CA} + (Z_B^\mu)^*/N_{CB}], \tag{11}$$

$$v_b^\mu = (d^\mu)^3/\sum_\nu[(d^\nu)^3 N_b^\nu], \tag{12}$$

where $(n_e^\mu)^*$ is the number of valence electrons per μ bond, $(Z_A^\mu)^*$ or $(Z_B^\mu)^*$ is the valence electron number of the A or B atom constructing μ bond, respectively, v_b^μ is the bond volume, and N_b^ν is the bond number of type ν per unit volume.

Ternary B-C-N compounds have also been considered as potential superhard materials. Cubic BC_2N has been synthesized [28], whereas there have been no corresponding data of atom positions for cubic BC_2N in the literature. In order to calculate the hardness H_v, we have carried out first principles calculation using the GGA approach of density functional theory with the Material studio [29]. In the calculations, geometry optimization for BC_2N was performed with the same procedure as in the literature [5], a β-BC_2N type structure is derived from the optimization. According to the calculated crystal structure of β-BC_2N, and the chemical bond theory [15,16,24,25], we can write its bond-valence equation as follows:

$$\beta\text{-}BC_2N = BC(1)C(2)N = 1/2BN + 1/2BC(2) + 1/2C(1)C(2) + 1/2C(1)N.$$

The parameters of each type of chemical bond are calculated and listed in Table II. Based on this information and Eq. (9), the Vickers hardness of β-BC_2N crystal is calculated and listed also in Table II. It can be seen that the calculated Vickers hardness value for β-BC_2N crystal is very close to the experimental value of the synthesized cubic BC_2N crystal [28].

In conclusion, three conditions should be met for a superhard material: higher bond density or electronic density, shorter bond length, and greater degree of covalent bonding. Our method presented here has satisfactorily predicted the trend of hardness for polar covalent solids. It has also built up a link between hardness and first principles calculation, and thus could play an important role in the design of new superhard materials.

This work was supported by the National Science Foundation of China (Grant No. 50225207) and the State Key Project for Foundamental Research of the Ministry of Science and Technology of China (Grant No. 2002ccc02300).

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