PHYSICAL REVIEW B **73**, 132104 (2006)

Theoretical model of intrinsic hardness

Faming Gao*
Department of Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

(Received 1 July 2005; published 26 April 2006)

Intense theoretical and experimental interest has been focused on the possibility of new materials with hardness exceeding that of diamond. However, building the link between the information that first-principles calculations can produce and the hardness of materials remains one of the challenges of computational materials science. In this paper, a calculated method of hardness based on the Mulliken overlap population analysis in first principles has been presented. In particular, the effects of stress strain on intrinsic hardness were studied, and a formula of hardness under stress is established. It can be employed to explain the hardening phenomenon resulting from the stress of film and grain boundary and nanoeffects. The theoretical results revealed that nanodiamond films obtained by careful experiments can be harder than bulk single-crystal diamonds.

DOI: 10.1103/PhysRevB.73.132104 PACS number(s): 62.20.Qp, 71.15.Mb

The search for new materials in hardness comparable to that of diamond is of great interest in modern science and technology.[1–8] Over the past two decades, the quest for hard materials has had to be simplified to a search for materials with a large bulk modulus or shear modulus, which can be evaluated directly by first principles. In fact, there is no one-to-one correspondence between hardness and other properties. Hardness is different from the bulk modulus or shear modulus.[4] Superhard materials can be divided into the intrinsic superhard materials, in which hardness is mainly defined by the bonding and the extrinsic superhard materials, in which hardness is mainly determined by their microstructure.[9] It is accepted generally that the hardness of a perfect crystal is intrinsic and that of nanocrystalline and polycrystalline is extrisic. The recent works hunting new superhard materials indicate that the synthesis of materials with intrinsic hardness exceeding that of diamond is unsuccessful. But the materials with extrinsic hardness exceeding that of diamond were reported frequently.[8–10] Since the nonequilibrium systems such as thin films with high stress and nanocomposites could be a more fruitful route in the hunting for new superhard materials,[8–10] it is of ultraimportance to elucidate the correlation between the stress strain and hardness. Anyway, the first key step of designing intrinsic or extrinsic ultrahard materials is to understand deeply the origin of intrinsic hardness on the atomistic level and to calculate accurately the values of intrinsic hardness. Although Ref. 11 sheds more light on the origin of the hardness of covalent crystals, a calculated method based on first principles is desirable. According to Ref. 11, the hardness of a covalent material is determined by two factors: the number of bonds per unit area and the strength of bonding. Ultimately, the key issue is how to characterize the strength of bonds. Ding *et al.*,[12] Wu *et al.*,[13] and Y. Zhang *et al.*[14] tried to characterize the strength of bonds using surface energy, elastic modulus, and tensile strength, respectively. However, since atomic bonds are broken in the process of indentation, it certainly cannot be fully characterized with elastic parameters alone. And the tensile stress on the bonding is not the compressional stress, it far deviate from the indentation reality for the hardness measurement. It is also difficult to determine exactly the distribution of electron density in various bonds in crystals by using the empirical method. The current standard model is based on an *ab initio* approach requiring no experimental input. In this paper, our aim is establishing a method calculating hardness from the information of first-principles calculations and the correlation between stress strain and hardness.

A technique for the projection of plane-wave states onto a localized basis set is used to calculate atomic charges and bond populations by means of a Mulliken analysis.[15,16] The integration of the electron probability distribution function $\rho(r)$ leads to

$$\int \rho(r)d\tau=\sum_{\mu}^{N}\sum_{\nu}^{N}P_{\mu\nu}\int \Phi_{\mu}\Phi_{\nu}d\tau=\sum_{\mu}^{N}\sum_{\nu}^{N}S_{\mu\nu}P_{\mu\nu}=P, \tag{1}$$

TABLE I. The hardness and the Mulliken bond overlap population P of crystals with a zinc blende structure, where H_{vcalc} and H_{vexp} are the calculated hardness and the experimental Vickers hardness, respectively. The experimental Knoop hardness is displayed as a comparison.

	v_b (Å^3)	P	H_{vcalc}	H_{vexp} (GPa)
Diamond	2.836	0.75	97.7	100.6[a], 96±5[b], 60–150[c], 90[d]
Si	10.010	0.74	11.8	12[e], 14[d], 11.3[f]
Ge	11.318	0.54	7.0	7.2[a], 8.8[d], 11.3[f]
Sn	17.084	0.67	4.4	4.5[d]
SiC,	5.138	0.69	33.1	26–37[c], 28±3[b], 24.8[d]
BN	2.953	0.65	79.1	95–100[a], 46–80[c], 63±5[b]
BP	5.841	0.75	29.3	33[c], 33±3[b], 32[d]
BAs	6.813	0.73	22.1	19[f]
AlP	10.124	0.63	9.8	9.4[d]
AlAs	11.346	0.62	8.0	5.0[d]
AlSb	14.435	0.65	5.6	4.0[d]
GaP	10.120	0.63	9.8	9.5[d]
GaSb	14.154	0.55	4.9	4.4[d]
InP	12.633	0.57	6.2	5.4[d]
InAs	13.898	0.51	4.7	3.8[d]
InSb	16.997	0.57	3.7	2.2[d]

[a] Reference 19.
[b] Reference 2.
[c] Reference 4.
[d] Knoop hardness from Ref. 20.
[e] Reference 21.
[f] Knoop hardness from Ref. 22.

TABLE II. A hardness and a Mulliken bond overlap population P^{μ} of typical hard crystals, where H^{μ}_{vcalc} and H_{vexp} are the calculated hardness and the experimental Vickers hardness, respectively. The experimental shear modulus G and bulk modulus B have been displayed as a comparison.

	d^{μ} (Å)	v^{μ}_{b} (Å^3)	P^{μ}	H^{μ}_{v}	H_{vcalc}	H_{vexp}(GPa)	G(GPa)	B(GPa)
Diamond	1.544	2.836	0.75		97.7	100.6^{a}, 96 ± 5^{b}	535^{b}	443^{b}
Londsdaleite	1.546	2.843	0.43	66.4	66.4	$60–70^{c}$		382^{c}
(Hexagonal C)	1.546	2.843	0.85	131.2				
C_{60}(3D)^{d}	1.613	5.749	0.64	34.4	34.4	30^{d}		
Beta-C_3N_4^{c}	1.456	3.602	0.69	60.4	60.4		320^{b}	437^{b}
	1.448	3.543	0.69	62.1				
	1.447	3.537	0.82	74.0				
Cubic-C_3N_4^{e}	1.461	3.276	0.85	87.1	87.1		332^{b}	496^{b}
Beta-BC_2N^{f}	1.564	2.940	0.60	73.6	73.6	76 ± 4^{g}	445^{b}	408^{b}
	1.562	2.672	0.61	75.3				
	1.573	2.929	0.71	84.7				
	1.515	2.991	0.83	119.4				
Cubic BN	1.568	2.953	0.65		79.1	$46–80^{c}$	409^{c}	$368–401^{c}$
Wurtzite BN	1.575	3.008	0.35	49.6	49.6	$50–60^{c}$	330^{c}	390^{c}
	1.555	2.895	0.74	111.2				
BP	1.966	5.841	0.75		29.3	33^{c}, 33 ± 3^{b}	174^{c}	169^{c}
$B_{13}C_2$^{h}	1.798	2.913	0.47	58.6	58.6	$56–58^{a}$, 57^{c}	203^{c}	
B_4C^{i}	1.784	2.841	0.39	50.7	50.7	49.5^{a}, $42–49^{c}$	201^{c}	200^{c}
B_6O^{j}	1.834	3.056	0.38	43.7	43.7	45^{k}, $35\pm5^{a,b}$	204^{c}	200^{c}
β-Boron^{l}	1.811	2.237	0.15	29.0	$30–34^{c}$		170^{c}	
$B_{12}N_2Be$^{m}	1.780	2.716	0.44	61.6	61.6			
	1.800	2.809	0.54	71.5				
	1.768	2.662	0.56	81.1				
	1.724	2.468	1.08	177.5				
	1.723	2.463	0.64	105.5				
	1.547	1.783	0.57	160.9				
	1.518	1.685	0.79	245.2				
WC	2.197	3.457	0.38	35.6	35.6	32^{c},30 ± 3^{b}	269^{c}	421^{c}
Alpha-SiC	1.900	5.281	0.43	26.2	26.2	$21–29^{c}$	200^{c}	221^{c}
	1.885	5.155	0.77	48.7				
Beta-SiC	1.887	5.138	0.69		33.1	$26–37^{b}$, 28 ± 3^{c}	173^{c}	210^{c}
Gamma-Si_3N_4^{n}	1.889	3.856	0.48	37.5	37.5	$30–43^{o}$		
	1.823	3.468	0.73	68.0				
Beta-Si_3N_4	1.752	6.270	0.58	20.2	20.2	21 ± 3^{c},^{b}	123^{c}	249^{c}
	1.705	5.780	0.60	23.9				
	1.739	6.132	0.71	25.5				
Al_2O_3	1.969	3.847	0.28	22.0	22.0	22 ± 2^{b}, $20–27^{c}$	160^{c}	246^{c}
	1.856	3.226	0.35	36.8				
SiO_2(Stishovite)	1.809	4.043	0.35	25.3	25.3	33 ± 2^{c},^{b}	187^{c}	305^{c}
	1.757	3.706	0.42	34.7				
Alpha-SiO_2	1.615	9.528	0.51	8.8	8.8	11.3^{a},8.2(K)^{p}		
	1.60	9.267	0.55	10.0				
RuO_2	1.989	4.780	0.36	19.7		20(K)^{q}	150^{q}	400^{q}
BeO	1.675	3.560	0.17	15.2	15.2	$10–15^{c}$	159^{c}	250^{c}
	1.64	3.341	0.51	50.2				
alpha-AlN	1.886	5.125	0.24	11.7	11.7	12 ± 1^{b}	128^{b}	203^{b}
	1.870	4.997	0.59	29.8				
alpha-GaN	1.961	5.709	0.29	11.8	11.8	12 ± 2^{b}	120^{b}	210^{b}
	1.921	5.366	0.62	27.9				
TiO_2	1.980	5.325	0.26	11.9	11.9	12^{r}		
	1.948	5.073	0.39	19.1				
SnO_2	2.056	5.961	0.32	12.1	12.1	11.1^{a}		
	2.052	5.957	0.38	14.2				
m-ZrO_2	2.285	5.917	0.25	9.6	13^{rp}, 11.6(K)			
Y_2O_3	2.344	6.705	0.23	7.1	7.1	7.5(K)^{s}		

TABLE II. (*Continued.*)

	d^{μ} (Å)	v_b^{μ} (Å^3)	P^{μ}	H_v^{μ}	H_{vcalc}	H_{vexp}(GPa)	G(GPa)	B(GPa)
c-Zr_3N_4[t]	2.488	3.789	0.11	8.8	8.8			
	2.192	2.591	0.42	63.6				
c-Hf_3N_4[t]	2.474	3.725	0.12	9.9	9.9			
	2.179	2.544	0.58	90.6				

[a] Reference 19.
[b] Reference 2.
[c] Reference 4.
[d] One of the three-dimensional-polymerized fullerites from Ref. 24.
[e] Reference 25.
[f] Reference 11.
[g] Reference 26.
[h] Reference 27.
[i] Reference 28.
[j] Reference 29.
[k] Reference 30.
[l] Reference 31.
[m] Reference 32.
[n] Reference 6.
[o] Reference 33.
[p] Knoophardness from Ref. 20.
[q] Knoop hardness from Ref. 3.
[r] Reference 21.
[s] Reference 34.
[t] Knoop hardness from Ref. 35.

where $P_{\mu\nu}$ is elements of the density matrix, Φ_{μ} is basis functions, and $S_{\mu\nu}$ is the overlap matrix. The sum of nondiagonal components of Eq. (1) is referred to as overlap population P. The Mulliken population analysis can help us allocate the electrons in some fractional manner among the various parts of bonds. Segall *et al.*[16] found correlations of the overlap population with covalency of bonding and bond strength. Reference 17 indicated that the overlap population is a convenient way to quantify the strength of bonding in first principles.

In our opinion, the strength of the bond can be characterized by using average overlap populations per the unit volume of bond. Based on this idea, the hardness of crystals is express as follow:

$$H_v = AN_a\left[\int \rho(r)d\tau \Big/ \int d\tau\right] \tag{2}$$

or simplified as

$$H_v = AN_a(P/v_b), \tag{3}$$

where N_a is the covalent bond number per unit area, A is a proportional coefficient, P is the Mulliken overlap population, and v_b is the bond volume. For the crystals with diamond structure, there are 16 bonds in a cell with the cell volume V, the bond volume can then be expressed as $v_b = V/16$. N_a can be expressed as $(16/V)^{2/3}$ or $v_b^{-2/3}$. Thus, their hardness should have the following form:

$$H_v(\mathrm{GPa}) = APv_b^{-5/3} \tag{4}$$

In order to calculate Mulliken population, we have carried out electronic structure calculations using the CASTEP code in the framework of density functional theory with the Material Studio.[18] The interactions between the ions and the electrons are described by using ultrasoft Vanderbilt pseudopotentials and the electron-electron interaction is treated within the local density approximation by the Ceperley-Alder exchange correlation potential. For the zinc blende structure, the calculations were performed using an energy cutoff of 330 eV for the plane-wave basis set and converged with respect to the k-point integration. The Brillouin zone is sampled on a [888] Monkhorst-Pack k-point mesh. The technique for the projection of plane-wave states onto a linear combination of an atomic orbitals basis set was used to perform Mulliken population calculations. The calculated Mulliken's bond overlap populations of crystals with zinc blende structure were listed in Table I. According to diamond, the value of the proportional coefficient A in Eq. (4) is suggested as 740. The hardnesses of other crystals were also calculated using Eq. (3) and listed in Table I. For complex multibond compounds, the hardness of the μ-type bond can be calculated as follows:

$$H_v^{\mu}(\mathrm{GPa}) = AP^{\mu}(v_b^{\mu})^{-5/3}, \quad v_b^{\mu} = (d^{\mu})^3 \Big/ \sum_{\nu} [(d^{\nu})^3 N_b^{\nu}], \tag{5}$$

where P^{μ} is the Mulliken overlap population of the μ-type bond, v_b^{μ} is the volume of a bond of type μ,[23] d^{μ} is the bondlength of type μ, and N_b^{ν} is the bond number of type ν per unit volume. The calculated hardness H_v^{μ} of a μ-type bond of some crystals were listed in Table II, and since there are many bonds for compounds such as m-ZrO_2 in Table II, their H_v^{μ} have been displayed in Fig. 1. From Table II and Fig. 1, it can be seen that the calculated value of hardness of the weakest bond is more close to the measurement value. We agree to the supposition that breaking the bonds will start from softer ones when there are differences in the strength among different types of bonds. In other words, the weakest bond plays a determinative role in the hardness of materials. Because the Mulliken population analysis in the first-principles technique can describe exactly the distribution of electron density in various bonds and a high overlap can also

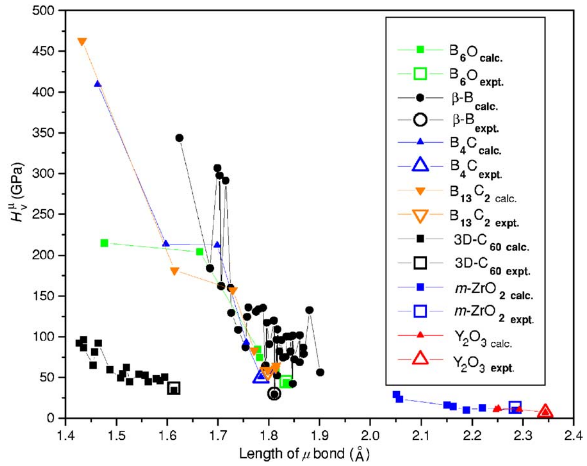

FIG. 1. (Color online) Correlation between calculated hardness H_v^{μ} and a bondlength of a μ-type bond of some crystals.

indicate a low degree of ionicity in the bond, the present method provides more excellent results for the compounds listed in the table, especially α-SiO$_2$ and compounds with Wurtzite structure (such as hexagonal C, BN, SiC, AlN, and GaN), than that of calculating by the empirical method of Ref. 11. Although the atomic coordination of compounds with Wurtzite structure such as hexagonal C, BN, SiC, AlN, and GaN are the same as that of cubic diamond, but their four coordinations are not equivalence and a bond with a smallest Mulliken population is remarkably weaker than the other three bonds, which cannot be addressed by the empirical method presented in Ref. 11. From Table II, it can be seen that their lower hardness rather than the cubic diamond structure results just from the weakest bond with the smallest overlap population. In particular, although the longest bond 1.456 Å/in β-C$_3$N$_4$ is shorter than the C-C bond in cubic diamond, its Mulliken population is obviously smaller than that of diamond. Thus the predicted hardness of β-C$_3$N$_4$ is even less than that of c-BN.

Now, we study the effect of hydrostatic stress on intrinsic hardness. According Ref. 36, the volume after strain withapplied pressure σ can be calculated using the following: $V(\sigma)=V(0)[1+(B'/B)\sigma]^{1/B'}$, where $V(0)$ is equilibrium volume and B is the bulk moduli and B' is the first pressure derivatives. Thus the hardness under hydrostatic pressure can be expressed as

$$H_v(\sigma) = 740PV(\sigma)^{-5/3} = 740PV(0)^{-5/3}[1 + (B'/B)\sigma]^{-5/3B'}. \tag{6}$$

The residual stress of films is a widespread phenomenon due to the ion bombardment during the growth. The compressive stress [even up to 30 GPa (Ref. 37)] can increase the hardness of film. According to Eq. (6), the hardness of single-crystal films of diamonds can increases up to 14% as the stress increases to 30 GPa. For polycrystalline materials, the presence of grain boundaries (GBs) can produce short-range stress fields around them. The GBs-induced stress affects the intrinsic hardness of the crystalline inside the grains. Thus according to Eq. (6), it can be readily understood why the polycrystalline diamond is usually harder than the single crystal diamond. When the size of grains decrease to nanorange, the grain boundaries would considerably increase, and result in a larger GBs-induced stress field. Therefore, the presence of nanoeffects can remarkably enhance the hardness of materials. Of course, a number of dangling bonds in the surface of nanograins might also result in the redistributing of the electron population, further resulting in the change of hardness. For nanodiamond films, due to the common existence of residual compressive stress and GBs-induced stress and nanoeffects, it is not a surprise that nanodiamond films possess the hardness remarkable higher than that of a single-crystal diamond.[10]

In summary, based on the idea that the strength of the bond can be characterized by using bond overlap population per unit volume, the first-principles method of hardness was proposed. It can bring obvious advantages to superhard materials research because no empirical input is needed. The effect of pressure on the hardness of materials can be predicted by an established formula. The correlation between the stress strain and hardness can provide an understanding for the mechanical behavior. The approach presented here would be a step towards a nonempirical basis for predicting the materials with superhardness exceeding that of diamond.

The author acknowledges the financial support from the National Natural Science Foundation of China (Grant No. 50472050) and the Program for New Century Excellent Talents in University and the FANEDD (Grant No. 200434).

---

*Email address: fmgao@ysu.edu.cn

[1] R. B. Kaner *et al.*, Science **308**, 1268 (2005).
[2] D. M. Teter, MRS Bull. **23**, 22 (1998).
[3] J. Haines *et al.*, Annu. Rev. Mater. Res. **31**, 1 (2001).
[4] V. V. Brazhkin *et al.*, Philos. Mag. A **82**, 231 (2002).
[5] E. Kim *et al.*, Phys. Rev. Lett. **86**, 652 (2001).
[6] S. D. Mo *et al.*, Phys. Rev. Lett. **83**, 5046 (1999).
[7] M. P. Grumbach *et al.*, Phys. Rev. B **52**, 15807 (1995).
[8] T. Irifune *et al.*, Nature (London) **421**, 599 (2003).
[9] S. Veprek, J. Vac. Sci. Technol. A **17**, 2401 (1999).
[10] C. S. Yan *et al.*, Phys. Status Solidi A **201**, 25 (2004).
[11] F. M. Gao *et al.*, Phys. Rev. Lett. **91**, 015502 (2003).
[12] Zenong Ding *et al.*, Phys. Rev. B **70**, 184117 (2004).
[13] B. R. Wu *et al.*, Chin. J. Phys. (Taipei) **40**, 187 (2002).
[14] Y. Zhang *et al.*, Phys. Rev. Lett. **93**, 195504 (2004).
[15] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).
[16] M. D. Segall *et al.*, Phys. Rev. B **54**, 16317 (1996).
[17] W. Y. Ching and Y. N. Xu, Phys. Rev. B **59**, 12815 (1999).
[18] *Materials Studio* (Accelrys Inc., San Diego, CA, 2002), Version 2.1.5.
[19] A. Szymanski and J. M. Szymanski, *Hardness Estimation of Minerals Rocks and Ceramic Materials* (Elsevier, Amsterdam, 1989).
[20] C. M. Sung and M. Song, Mater. Chem. Phys. **43**, 1 (1996).
[21] J. H. Westbrook and H. Conrad, *The Science of Hardness Testing and Its Research Applications* (ASM, Ohio, 1973).
[22] R. C. Weast *et al.*, *Handbook of Chemical Physics*, 69th ed. (CRC Press, Florida, 1989).
[23] B. F. Levine, J. Chem. Phys. **59**, 1463 (1973).
[24] C. A. Perottoni and J. A. H. da Jornada, Phys. Rev. B **65**, 224208 (2002).
[25] D. M. Teter and R. J. Hemley, Science **271**, 53 (1996).
[26] V. L. Solozhenko *et al.*, Appl. Phys. Lett. **78**, 1385 (2001).
[27] V. I. Matkovich, J. Less-Common Met. **47**, 39 (1976).
[28] B. Morosin *et al.*, J. Alloys Compd. **226**, 121 (1995).
[29] M. Olofsson and T. Lundstrom, J. Alloys Compd. **257**, 91 (1997).
[30] D. He *et al.*, Appl. Phys. Lett. **81**, 643 (2002).
[31] J. L. Hoard *et al.*, J. Solid State Chem. **1**, 268 (1970).
[32] Faming Gao *et al.*, J. Phys. Chem. B **108**, 13069 (2004).
[33] J. Dong *et al.*, Phys. Rev. B **67**, 094104 (2003).
[34] M. J. Weber, *CRC Handbook of Laser Science and Technology* (CRC Press, Florida, 1987), Vol. 5, Part 3, p. 328.
[35] A. Zerr *et al.*, Nat. Mater. **2**, 185 (2003).
[36] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 5390 (1944).
[37] T. Sharda, T. Soga, T. Jimbo, and M. Umeno, Diamond Relat. Mater. **10**, 352 (2001).