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Effect of normal stress on the ideal shear strength in covalent crystals

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Critical shear stress under the superimposed hydrostatic and uniaxial normal stress conditions of C, Si, Ge, and SiC is evaluated by *ab initio* density functional theory calculations to investigate the response of ideal shear strength (ISS) to superimposed normal stresses in covalent crystals. We find a substantial difference in the responses of ISS to normal stress among the covalent crystals examined; e.g., hydrostatic compression increases the ISS of C but decreases that of Si, Ge, and SiC. The ISS is mostly a highly nonlinear and anisotropic function of normal stress. The results thus indicate that normal stresses can significantly affect the critical shear stress, which is crucial to interpreting experimental observations of crystal deformation, e.g., dislocation nucleation in nanoindentation.

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The ideal strength is defined as the maximum (critical) stress in a perfect crystal under a uniform deformation mode.[1–3] Since the ideal strength is an important parameter for understanding the deformation mechanisms of materials, it has so far been investigated using rigorous theoretical approaches such as *ab initio* methods for various crystals.[4–11] In particular, the ideal shear strength (ISS) has been intensively studied because it is closely related to the resolved shear stress of dislocation nucleation in a pristine crystal and it gives fundamental insights into the microscopic mechanisms of plasticity. For example, calculations based on density functional theory (DFT) have been carried out for C, Si, and Ge by Roundy and Cohen[7] and for C, Si, and SiC($3C$) by Ogata *et al.*[12]

In cases of deformation in real materials, however, lattices are locally subject to stress conditions involving not only shear but also normal stresses. In fact, Krenn *et al.*[13] pointed out that the effect of compression on shear stress played a significant role in evaluating the critical shear stress at the onset of plastic deformation observed in nanoindentation, which emphasizes the importance of studying critical shear stress under normal stress conditions. Although theoretical approaches have been dedicated to metallic systems to elucidate what effect compression has on ISS,[9,10] this has not sufficiently been investigated for covalent systems. As has recently been reported, *ab initio* analysis[11] has revealed that hexagonal polytypes of SiC exhibit an opposite tendency to metals, i.e., a decrease in ISS under compression. This finding indicates that different materials may demonstrate significantly different behaviors and increases the necessity for individual evaluations of various crystals.

We therefore examined what effect normal stresses had on the ISS in covalent crystals in this study, i.e., C, Si, Ge, and SiC, by means of *ab initio* DFT calculations. We simulated a homogeneous shear deformation in the $[11\bar{2}]$ direction on the (111) plane for crystals with a diamond structure and in the $[01\bar{1}0]$ direction on the (0001) plane for SiC($4H$), which are related to major slip systems.

We employed *ab initio* calculations using the Vienna *ab initio* simulation package (VASP),[14,15] which enables efficient calculations using plane wave basis sets based on the projector augmented waves method. We selected the exchange-correlation functional such that the equilibrium lattice parameter would agree well with the experimental value, i.e., the generalized gradient approximation functional by Perdew and Wang[16] for Si, C, and SiC and the local density approximation (LDA) by Ceperley and Alder[17] for Ge. A $10\times10\times10$ Monkhorst-Pack k-point mesh[18] in the Brillouin zone was used for the diamond structure and $8\times8\times2$ was used for SiC($4H$).

We analyzed shear deformation as follows. First, the equilibrium lattice constant was obtained by energy minimization under a predetermined normal stress for each model. We studied the hydrostatic ($\sigma_h=\sigma_{xx}=\sigma_{yy}=\sigma_{zz}$) and the uniaxial (only one of the normal stresses, σ_{xx}, σ_{yy}, or σ_{zz}, is nonzero) stress conditions. Then, a shear strain γ_{zx} was applied to the cell and the atomic configuration was relaxed until the forces on the atoms became within 0.005 eV Å^{-1}; normal strains were adjusted so that the normal stresses deviated from predetermined values by less than 0.1 GPa. The coordinate system was chosen so that the x, y, and z axes were parallel to their corresponding $[11\bar{2}]$, $[\bar{1}10]$, and $[111]$ crystallographic directions.

The computed values for the equilibrium lattice parameter, bulk modulus, and the shear modulus corresponding to the previously mentioned slip systems are listed in Table I along with the experimental data. There was excellent agreement between the DFT calculations and the experiments, which supported the validity of the method we employed in this study.

Table II lists the values of ISS and critical strain assessed in this study together with data available from the literature. We found good agreement with the values cited in the preceding DFT studies.[7,27] The slight deviations could be attributed to the differences in computational parameters, i.e., the types of pseudopotentials and k-point meshes.

It should be noted that Dubois *et al.* reported an extremely high ideal strength for silicon in $\{111\}\langle112\rangle$ shears, which was even higher than the $\{111\}\langle110\rangle$ in their recent publication,[28] which contradicts the widely accepted results obtained by Roundy and Cohen[7] and by Ogata *et al.*[12] Since Dubois *et al.* were unable to explain this significant discrep-

TABLE I. Equilibrium lattice constant a_0, bulk modulus B, and shear modulus, G ({111}⟨112⟩ for cubic crystals and C_{44} for SiC[4H] together with experimental data.

	a_0 (Å)		B (GPa)		G (GPa)	
	Computation	Expt.	Computation	Expt.	Computation	Expt.
C	3.58	3.56[a]	426	443[b]	528	504[b]
Si	5.47	5.43[a]	97	102[d]	58.6	58.5[c,d]
Ge	5.65	5.66[a]	83	77[d]	46.2	47.0[c,d]
SiC(3C)	4.38	4.35[e]	212	211[f]	145	130[f]
SiC(4H)	3.09	3.08[g]	215	221[h]	167	159[h]
	(c/a=3.273)	(3.27)[g]				

[a] Reference 19.
[b] Reference 20.
[c] Reference 21.
[d] Reference 22.
[e] Reference 23.
[f] Reference 24.
[g] Reference 25.
[h] Reference 26.

ancy, we have omitted their evaluations from the discussion in this paper.

The response of ISS to hydrostatic stress is plotted in Fig. 1, where the ordinate and the abscissa have been normalized by the ISS under σ_h=0 GPa (τ^0_{is}). Interestingly, the ISS has been decreased by compression (increased by tension) in Si, Ge, and SiC(3C), while the opposite tendency can be seen in C. The response in SiC(4H) is highly nonlinear and both tension and compression lower the ISS. The critical shear strain in crystals under hydrostatic stress is plotted in Fig. 2. We can see a similar tendency to that in the graphs for ISS.

Figure 3 displays ISS and critical strain under superimposed uniaxial normal stresses. Obviously, the ISS is a highly anisotropic function of normal stresses; e.g., ISS in Ge is increased by compression in the y direction but is decreased by that in the x or z direction. It should be noted that Si, Ge, and SiC(3C) exhibit different responses to uniaxial normal stress while they behave similarly in the case of hydrostatic stress. Some curves indicate nonlinear behavior. The curves for carbon have a particularly sharp bend at σ=0 [Figs. 3(a) and 3(c)] and uniaxial tension in the x or z direction significantly reduces ISS.

The variety of responses ISS has to normal stress in covalent systems is interesting. How critical shear stress (or strain) changes under compression or tension must originate in the nature of interatomic bonding. With the exception of carbon, the response of ISS to hydrostatic stress in cubic covalent crystals [Si, Ge, and SiC(3C)] is in contrast to what Ogata *et al.* reported on metals (Au and Cu).[9] The present finding is also in contrast with the behavior of metals reported so far for the response of ISS to uniaxial stress. While Černý and Pokluda[10] found that normal compressive stress on the slip plane increases {111}⟨112⟩ shear strength for various metal crystals, our results revealed that covalent crystals exhibit different responses of ISS to normal stress. The mechanism of shear-strength hardening by compression in metals can be explained with the intuitive hard-sphere model; atoms are squeezed by compression resulting in larger resistance against shear. In contrast, the change in shear stability of covalent bonding in response to compression (or tension) differs depending on the crystal (atom species). It should be noted that carbon demonstrates a similar trend to metals, while Si and Ge do not, although the covalency in diamond crystal is even higher than that in Si and Ge.[29]

The anomaly of carbon described in the present work may be due to a different mechanism governing the critical strain. As was reported by Roundy and Cohen,[7] the properties of

TABLE II. ISS τ^0_{is} and the critical shear strain γ^0_{cs} under vanishing normal stress along with data available from literature.

	This work		Literature	
	τ^0_{is} (GPa)	γ^0_{cs}	τ^0_{is}	γ^0_{cs}
C	96.6	0.31	93 (LDA)[a]	0.3
Si	8.6	0.31	6.8 (LDA)[a]	0.3
Ge	5.4	0.27	4.3 (LDA)[a]	0.25
SiC(3C)	30.3	0.42	29.5 (LDA)[b]	
SiC(4H)	30.6	0.27		

[a] Reference 7.
[b] Reference 27.

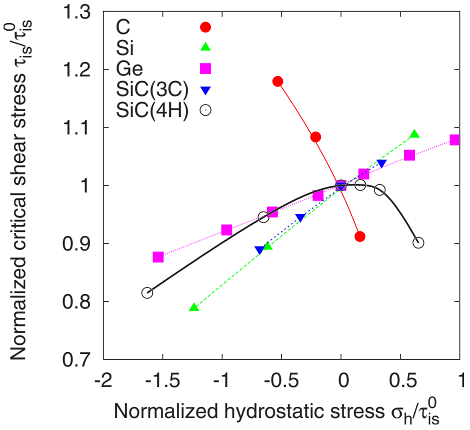

FIG. 1. (Color online) ISS τ_{is} as a function of hydrostatic stress σ_h. Both abscissa and ordinate are normalized by τ^0_{is} (ISS at σ_h=0).

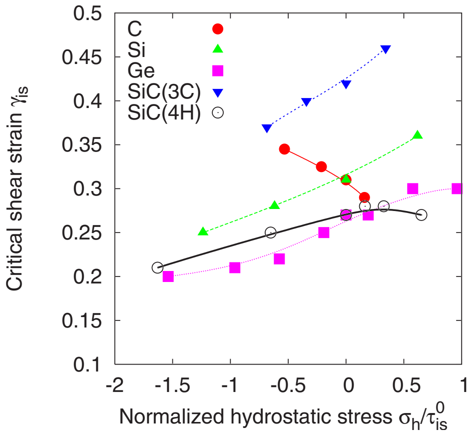

FIG. 2. (Color online) Critical shear strain γ_{cs} as a function of hydrostatic stress σ_h.

diamond under strain are dominated by the stability of its graphitic structure; the structure of carbon (diamond) was found to relax into a graphitic structure shortly after shear instability because carbon is able to form strong π bonds, while Si and Ge cannot form π bonds owing to the presence of p electrons in the core, which makes their instability much less dramatic. This indicates that the structural transformation into graphite under the critical shear strain is suppressed by hydrostatic compression, resulting in a higher critical stress and strain.

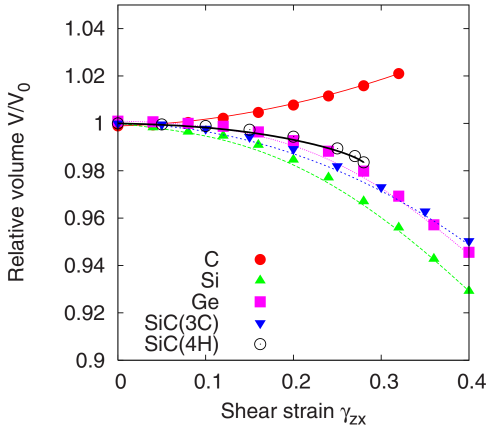

FIG. 4. (Color online) Evolution of the relative volume during shear. The displayed data correspond to a pure shear stress ($\sigma_{xx}=\sigma_{yy}=\sigma_{zz}=0$).

Carbon exhibits another anomaly in a volume change under pure shear stress (all the stress components except τ_{zx} are zero), as shown in Fig. 4. Similarly to metals, the volume of carbon is increased by shear with normal stress being zero, which is in a good agreement with previous calculations.[7] This seems to be related to the difference in the response of ISS to hydrostatic stress, i.e., in the crystals with a decreasing volume under shear, compression works as a driving force of shear deformation and thus lowers ISS. The effect of uniaxial normal stress on ISS, however, cannot be explained by the dimension change (change in crystal cell size in each direction corresponding to the normal stress). For example, although both Si and SiC(3C) crystals shrink in the x direc-

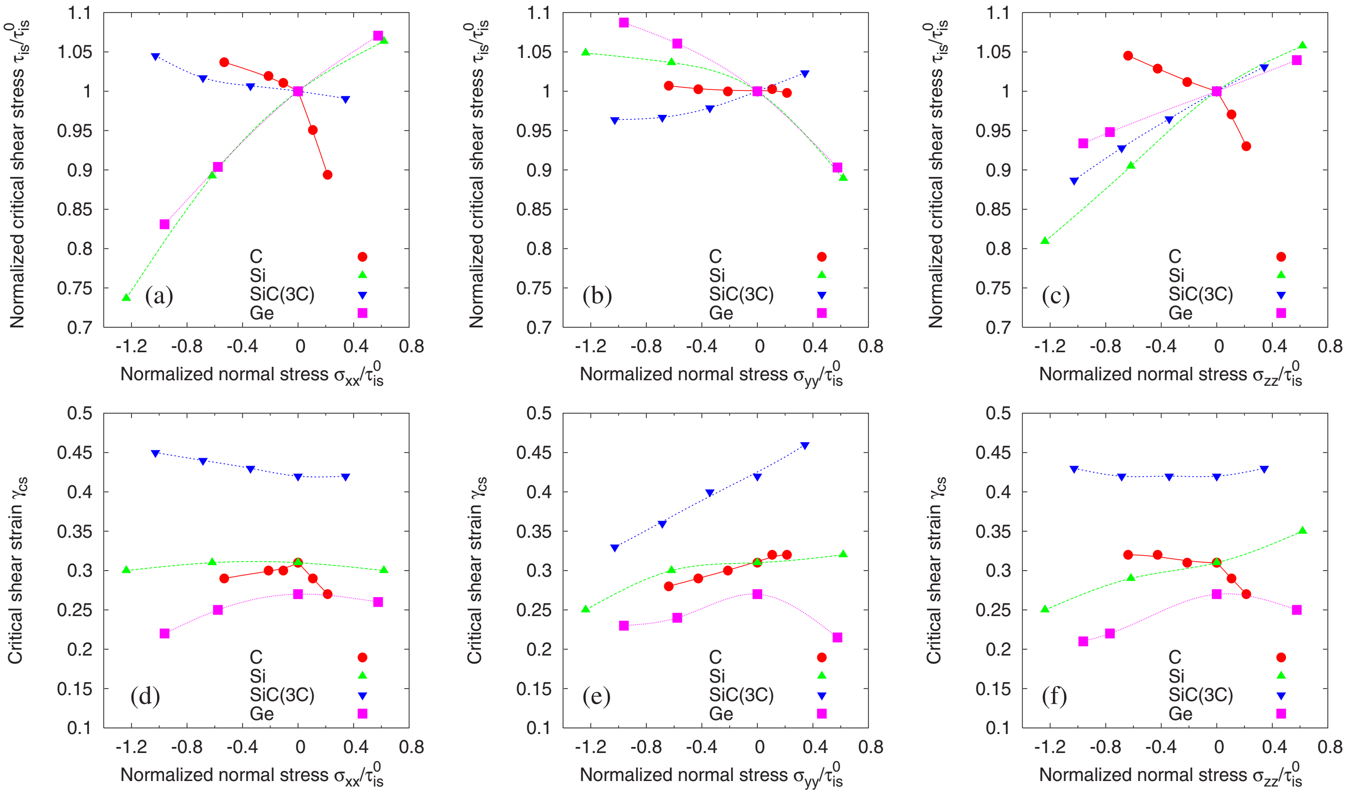

FIG. 3. (Color online) [(a)–(c)] ISS and [(d)–(f)] critical shear strain as functions of superimposed uniaxial stresses. All stresses were normalized by corresponding τ_{is}^0 values (as in Fig. 1). Just one of the σ_{xx}, σ_{yy}, and σ_{zz} stresses was variable, while the other two were relaxed.

tion under pure shear, they exhibit different responses of ISS to σ_{xx} [see Fig. 3(a)].

The complicated response of ISS to normal stress presented in this study suggests the importance of taking the effect of normal stress into account when interpreting experimental observations such as nanoindentation, where lattices are locally (particularly near the defect nucleation site) subjected to the superimposition of normal and shear stresses. Our results also suggest caution in multiscale approaches to the deformation problem based on empirical interatomic potential functions. As potential functions have usually been constructed to represent various properties around equilibrium states, their transferability to highly strained conditions may occasionally have been unclear. When they are used for deformation simulations to investigate criteria for defect nucleation (which is often accompanied by extremely high strain), special attention should be paid to the choice of a sufficiently transferable potential function; otherwise, the computational approach could lead to unreliable results.

To summarize, our study on ISS under superimposed normal stress by means of *ab initio* DFT calculations revealed that the response of ISS substantially differs among covalent systems. Highly nonlinear and anisotropic responses were observed. The results we obtained are important for understanding the criteria for defect nucleation in experiments.

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