Ab initio calculation of the ideal tensile and shear strength of cubic silicon nitride

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In this study, the ideal tensile and shear strength of the recently discovered cubic spinel silicon nitride polymorph was calculated using an *ab initio* density functional technique. The stress-strain curve of the cubic silicon nitride structure was calculated from simulations of applied ε_{11} and ε_{23} components of strain, and the ideal strengths were estimated at ~45 and ~49 GPa, respectively. In addition, the elastic constants of the cubic structure were determined and a value of ~311 and ~349 GPa was estimated for the bulk and shear modulus, respectively. The estimates of the elastic constants were found to be in reasonable agreement with existing data. Using a previously reported empirical relation, the hardness of the cubic phase was also estimated: ~47 GPa.

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I. INTRODUCTION

Silicon nitride (Si_3N_4) has been a material of great research interest over the years because of its unique mechanical and electronic properties. It is well known that silicon nitride exhibits excellent resistance to wear, corrosion, and thermal shock.[1] Furthermore, silicon nitride exhibits superior mechanical properties at high temperatures, and thus, it is considered to be an ideal material for use in various applications, such as engine components, extrusion dies, and cutting tools.[1]

The two well-known polymorphs of silicon nitride are the α- and β-Si_3N_4 phases. The α phase, with a density of approximately 3.183 g cm^{-3}, is generally synthesized at ambient pressure and below temperatures of 2000 K. The β phase, with a density of approximately 3.200 g cm^{-3}, is the more stable of the two and is obtained from a transformation of the α to β phase at high temperatures.[2] Both of the configurations have an underlying atomic structure, which is hexagonal and only differs along the *z* axis in the stacking sequence. In particular, the α phase has a space group of $P3_1c$, with 28 atoms in the unit cell, and the β phase has the space group $P6_3/m$ (with the subgroup $P6_3$), with 14 atoms in the unit cell.[3]

Over the last decade, particular interest in the high-pressure behavior of Si_3N_4 has grown. This was due to theoretical predictions that indicated that nitride materials, in particular, carbon nitrides, may be produced where the structure may exhibit a hardness comparable to, if not greater than, diamond.[4–8] In 1999, Zerr *et al.*[9] reported the synthesis of a cubic Si_3N_4 spinel structure (c-Si_3N_4, space group Fd-$3m$ or subgroup $Fd3$). The authors showed that the new polymorph of silicon nitride has a density of 3.93 $\pm$0.12 g cm^{-3} (~23% higher than the α or β phases). In addition, the spinel structure of cubic silicon nitride was found to have an atomic arrangement of silicon atoms coordinated fourfold and sixfold to the nitrogen atoms in a 1:2 ratio, whereas in the α and β phases the silicon atoms are only fourfold coordinated with the nitrogen atoms.

Various studies have been reported that have employed theoretical methods to understand better the properties of silicon nitride. Using various methods the atomic and electronic structure, bulk modulus, various mechanical properties, and the lattice parameters of crystalline α- and β-Si_3N_4 have been studied.[3,10–13] This is also the case with the new cubic c-Si_3N_4 polymorph. Various physical properties have been reported, including the electronic properties,[14,15] lattice parameters,[9,14,16–18] material properties,[14,16,17,19,20] and thermal properties.[21] However, the calculation of the ''ideal'' strength of cubic silicon nitride has not so far been reported.

In this paper, an *ab initio* numerical calculation of the stress-strain curves of c-Si_3N_4 is discussed. Initially, the method of calculation used to investigate the material behavior is outlined. Following this, the results obtained from the simulation procedure are presented, and finally, these results are discussed in detail.

II. CALCULATION METHOD & RESULTS

The equilibrium structure, elastic constants, and other properties of a single-crystal cubic silicon nitride were determined using the Vienna ab-initio simulation package (VASP). The core region and valence electrons of the atoms in the supercell are described by the Vanderbilt ultrasoft pseudopotential.[22] In addition, the electron-electron exchange interaction was described using the generalized gradient approximation (GGA) and the local density approximation (LDA).[23–25] The GGA employed a Perdew-91 (PW91) functional form,[26] and a Ceperley-Alder[27] form was employed in the LDA. In both cases, the numerical integration of the Brillouin zone was performed using a discrete $4\times4\times4$ Monkhorst-Pack[28] *k*-point sampling and the plane-wave cutoff was chosen as 31.96 Ry.

The underlying c-Si_3N_4 unit cell structure was obtained from the cubic Fd-$3m$ space group configuration. In the unit cell there are 56 atoms: using the Wyckoff notation, there is one group of Si atoms (octahedral bonds) in the $8a$ $[\frac{1}{8},\frac{1}{8},\frac{1}{8}]$ position, the second group of Si atoms (tetrahedral bonds) in the $16d$ $[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ position, and the N group of atoms in the $32e$ ($[x,x,x]$, where $x=0.25+\delta$) position. The lattice constant de-

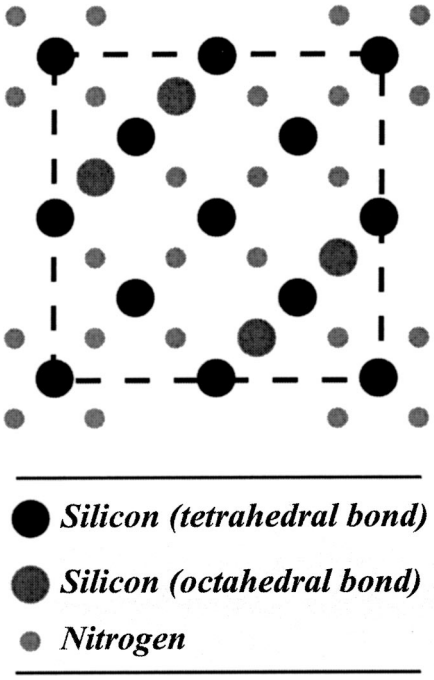

FIG. 1. Unit cell representation of the spinel cubic Si_3N_4 lattice structure, in the [100] direction: the cell origin is defined at the bottom left silicon atom.

termined experimentally and the optimized δ value were originally reported by Zerr *et al.* as $a=7.80\pm0.08$ Å and $\delta \cong 0.0074$, respectively.[9] However, in this study the values obtained by Jiang *et al.*[29] were employed for the initial dimensions of the supercell, $a\cong 7.733\,91$ Å and $\delta\cong 0.0084$.

As mentioned, the initial supercell was configured using the dimensions given by Jiang *et al.*[29] and subsequently a procedure was applied to relax the structure. The relaxation process was performed for a peak force at each atomic site of 0.01 eV $Å^{-1}$ and a peak stress in the supercell of 0.1 GPa. The tensile and shearing simulations were performed by applying a ε_{11} and ε_{23} strain, respectively. At each step the applied strain was increased by a uniform strain of 0.01, and the atomic structure of the supercell was relaxed using the conjugate gradient method, in all directions except in the direction of the applied strain. At each step the supercell configuration of the previous step was employed.[30] It is important to note that at each step the conjugate gradient method was performed only after a finite temperature of 1 K was applied to the supercell structure for 0.1 ps. In this case, the predefined temperature value was selected to provide a sufficient amount of energy to the supercell to displace the atomic configuration by a small amount.

In this study the stress-strain curves for an applied tensile and shear stress were modeled. It is clear that beyond the point of maximum strain deformation the relaxed structure may show increased bond lengths at certain bonds, suggestive of fracture. However, it is beyond the scope of the current paper to present such results and, thus, only the stress-strain data to the point of failure is presented. The relevant elastic constants for the cubic structure are C_{11}, C_{12}, and C_{44} because of the high symmetry. The unit cell configuration of the cubic phase is illustrated in Fig. 1. From the simulation procedure the tensile and shear stresses determined as a function of strain deformation are presented in Fig. 2. Additionally, certain material parameters were estimated. The elastic constants, bulk and shear moduli, and the optimized lattice constant were estimated and are given in Table I: where possible the results are compared to values found in the literature. It is important to note that the bulk modulus was defined as $[(C_{11}+2C_{12})/3]$ in this study. Furthermore, the shear modulus was defined as the average of the tetragonal and rhombohedral shear moduli, $(C_{11}-C_{12})/2$ and C_{44}, respectively. The results for the data obtained from both the GGA and LDA methods are presented in Table I.

III. DISCUSSION

In this study, two different exchange-correlation potential functions, the LDA and GGA, where employed to characterize the atomic behavior of the cubic phase of silicon nitride. In many cases, the two potential functions provide comparable results. In this study, as a matter of convenience only, the LDA results are presented in Fig. 2. Furthermore, in the case of the shear and bulk moduli, an average result of the two functions is presented in the following discussion. However, as mentioned, in Table I all the LDA and GGA results are presented for each parameter. Even though there is no conclusive argument to use an average value, it is suggested that a better estimate of the true value can be obtained since, generally, the LDA results tend to overestimate and the GGA results underestimate the modeled elastic constants. In the case of the lattice constants, the LDA results tend to underestimate and the GGA results overestimate.[16,31] Additionally, it is important to note that the results obtained in this study are for an applied temperature of 0 K, where all experimental results were, in general, measured at room temperature. Thus it is reasonable to expect a discrepancy between the data presented in Table I.

In Fig. 2 the tensile stress response as a function of applied strain is plotted for an applied ε_{11} strain component. From this data the ideal tensile strength of c-Si_3N_4 can be estimated: ~45 GPa. It is clear that the maximum tensile strength is taken as the maximum in the stress-strain curve. Beyond the point of maximum tensile stress, the curve monotonically decreases indicating the failure of the lattice. Similarly, the shear stress as a function of the applied ε_{23} strain component is given. From these data the ideal shear strength in this direction was estimated: ~49 GPa. Unlike the tensile stress data, in this case, the data do not exhibit a decrease in the stress for an increase in the applied strain above a value of 0.15. For a ε_{23} strain of 0.16 the simulation procedure could not be completed, due to the fact that a large change in the structure was induced, representative of structural failure. Thus the stress value at a strain of 0.16 could not be calculated and the maximum shear stress is defined at a strain of 0.15. It should be noted that since the shear strength strongly depends on the shear direction, determining the weakest shear direction, which may be the slip plane or direction, is important. This particular question is currently

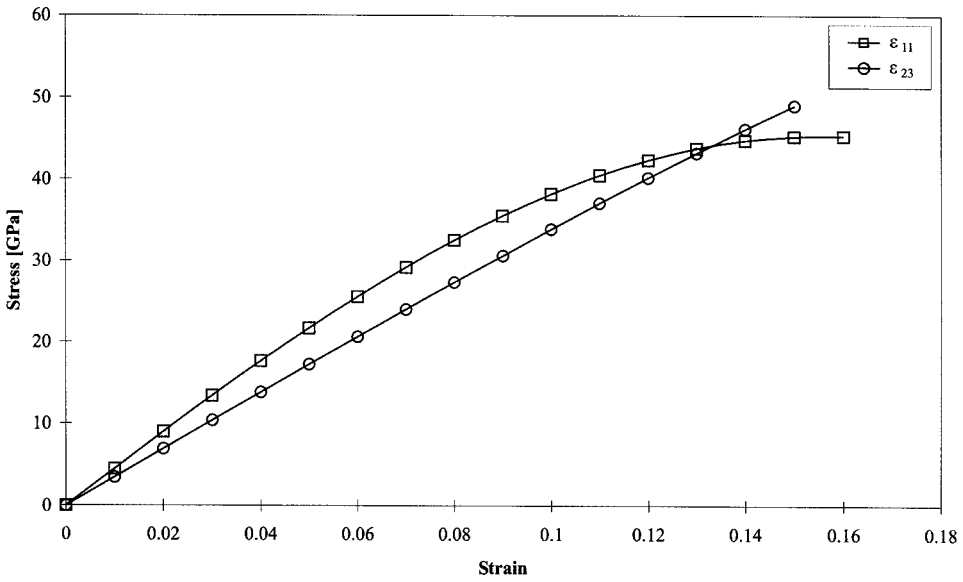

FIG. 2. Induced tensile and shear stress (at a temperature of 0 K) as a function of applied strain deformation, ε_{11} and ε_{23}, respectively.

under consideration and will be a part of future work. Furthermore, it is worthy of note that the strain definition used in this study is equivalent to the ''engineering strain'' definition used by Morris *et al.*[32]

As mentioned previously, the relevant elastic constants C_{11}, C_{12}, and C_{44} were calculated and these three independent elastic constants describe completely the elastic behavior of the cubic spinel structure. The LDA and GGA results of the elastic constants, presented in Table I, are compared with the theoretical and experimental data obtained from the literature. It is clear that all the results are in reasonable agreement. It is important to note that the difference in the shear modulus is due to the different methods used to estimate the value. For example, Soignard *et al.*[16] used an average of the Hashin-Shtrikman bounds to estimate the shear modulus.

TABLE I. Bulk (B_0) and shear (G_0) moduli, relevant elastic constants (in units of GPa), and lattice parameters (in units of Å), estimated from the current *ab initio* numerical procedure (at a temperature of 0 K) and compared to the range of experimental and theoretical data obtained from the literature. Where possible both LDA and GGA results from the simulation procedure are presented.

	This work		Past work	
	LDA	GGA	Experiment[a]	Theory[b]
		Material properties (GPa)		
B_0	310.9	272.5	300–308	280–411
G_0	264.6	252.0		258–340
		Elastic constants (GPa)		
C_{11}	550.6	499.6		532.6
C_{12}	191.0	159.0		191.2
C_{44}	349.4	333.6		341.0
		Lattice parameters		
a (Å)	7.6640	7.7585	7.80	7.72–7.76
δ	0.0072	0.0072		0.0074–0.008

[a]References 9, 15, and 17.
[b]References 9, 14, 16, and 19.

In 1998, Teter[6] reported that a good correlation exists between the shear modulus and the Vickers indentation hardness value of many of the known high-strength materials. Thus, using the result presented in Table I for the shear modulus and the correlation reported by Teter, it is estimated that cubic spinel silicon nitride has a Vickers indentation hardness of approximately 47 GPa. In this case an average of the LDA and GGA results of the shear modulus was used to estimate the hardness value. The current value is higher than the value reported by Soignard *et al.*,[16] ~30 GPa. However, considering the fact that different methods were used to estimate the shear modulus, the values are in reasonable agreement. Even if a large error margin is assumed for the estimate in this study of the hardness (greater than 10%, it is likely to be less than this limit), the spinel cubic silicon nitride structure, nevertheless, can be classified as a ''hard'' to ''superhard'' material based on the data presented. Experimental values reported in the literature[19] also give a lower value for the shear modulus and, thus, a lower hardness value, ~43 GPa in the latter case. Nevertheless, the experimental value is in reasonable agreement with the results given in this study and does suggest that c-Si_3N_4 is currently the second hardest material synthesized after diamond (considering the data of Teter).[6,9,19] It is important to note that in the Teter publication, there is no explicit definition of the shear modulus. However, in the author's opinion Teter defines the shear modulus as the average value of the C_{44} and $(C_{11}-C_{12})/2$ elastic constants, which is also indicated in a publication of Tanaka *et al.*[19] Thus, in this study, the shear modulus is the average of the tetragonal and rhombohedral shear moduli.

It is interesting to note that the spinel structure is not rare by any account. The structure has been reported for many binary and ternary metal oxides, silicates, and sulphides.[9,16] It has been argued that the higher shear modulus and, thus,

hardness values observed in c-Si_3N_4 can be attributed to the stronger bonds in silicon nitride since the nitride exhibits much greater covalent bonding. For example, in the oxide spinels the degree of Cauchy violation

$$\left| \frac{C_{44}}{C_{12}} \neq 1 \right|$$

is virtually nonexistent: $C_{44}/C_{12} \square 1$. However, in this study it is found that for c-Si_3N_4, $C_{44}/C_{12} \square 1.95$. Such a high value is indicative of covalent bonding and a similar result has been reported in the literature.[16]

It should be noted that fracture in ''real'' materials would be assumed to originate at points of weakness such as surface flaws, microcracks in the bulk of the structure, or bulk structural defects (including the effects of dislocations on the strength of the structure). In this study, the lattice contains no such points of weakness. Therefore, it is reasonable to expect that the present estimate of the ''ideal'' strength should be considerably greater than experimental measurements.

IV. SUMMARY

An *ab initio* density functional numerical technique used to determine the induced stresses in cubic Si_3N_4, as a function of applied strain deformation. The ''ideal'' tensile and a shear strength of the cubic silicon nitride polymorph under fully relaxed condition was determined to be $\sim$ 45 and $\sim$ 49 GPa, respectively. The elastic constants for the cubic structure were also determined and comparison with existing results demonstrated good agreement. Using a previously reported correlation between the shear modulus and hardness of several materials, an estimate of the hardness of cubic silicon nitride was determined: $\sim$47 GPa.

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