An *ab initio* Study of Si$_3$N$_4$ Single Crystal Polymorphs

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ABSTRACT

The single crystal structures of α-, β- and c- Si$_3$N$_4$ were modeled using an *ab initio* density functional technique. The stress – strain behavior of the silicon nitride structures were characterized from the modeling of pre-defined strain deformation in various directions. In particular, the ideal strength calculated for an applied tensile γ_{11} strain, in the [100] plane, was estimated to be ~ 51, 57 and 45 GPa, for α-, β- and c- Si$_3$N$_4$, respectively. Using a reported empirical method, an estimate was also made of the Vickers indentation hardness of the three polymorphs, ~ 23.0, 20.4 and 47.0 GPa, respectively. Comparison of structural parameters, and estimated elastic constants, indicates good agreement with existing data reported in the literature.

Key Words: Mechanical Properties, Stress-Strain Curves, Silicon Nitride.

1. INTRODUCTION

Over the last decade an intense amount of research effort has been invested in an attempt to understand better the underlying structure of super hard materials. Silicon nitride (Si$_3$N$_4$) is one such material that exhibits such hardness and other desirable mechanical properties.[1] The work of many researchers has provided a greater understanding of the mechanical properties of this material. However, certain properties of the silicon nitride polymorphs are still poorly understood.

In general, the mechanical properties of silicon nitride are characterized through the material morphology and structure. The two well-known polymorphs of silicon nitride are the, α - and β - phases. The structures of these two polymorphs have been outlined by many workers,[2] and various properties have been investigated in detail: the atomic and electronic structure, bulk modulus, various mechanical properties and the lattice parameters.[3,4,5,6,7] Both of the phases have an underlying atomic structure that is hexagonal and only differs along the z-axis in the stacking sequence. The α- phase, (density of ~ 3.183 g cm^{-3}) is generally synthesized at ambient pressure (below ~2000 K) and the β- phase, the more stable of the two, (density of ~ 3.200 g cm^{-3}) is obtained from a transformation of the α- to β- phase at high temperatures.[8] Moreover, it is generally believed that both polymorphs can be synthesized concurrently over a wide temperature range. In particular, Zerr *et al.*[9] reported, in 1999, the synthesis of a cubic spinel structure, c- Si$_3$N$_4$ (density of ~ 3.93 ± 0.12 g cm^{-3}, ~ 23% higher than the α - or β - phases).

It is important to note that, the characteristic mechanical response of the single crystal structure of the three silicon nitride phases has not previously been investigated. In this paper, an *ab initio* numerical calculation of the stress – strain response of α-, β- and c- Si$_3$N$_4$ are presented, for various directions in the single crystal structures. Initially, the method of calculation is outlined, followed by the results obtained from the simulation procedure. Finally, these results are discussed in some detail.

2. SIMULATION METHOD AND RESULTS

In this work the 'ideal' single crystal structure (with no structural defects included) was used to estimate the 'ideal' stress - strain response of the crystal structure of the three phases. In the following section, unless otherwise specified, the descriptions and pre-defined parameters apply to all three phases of silicon nitride investigated.

The equilibrium structure, elastic constants and other properties of the single crystal structures were determined using the Vienna Ab-initio Simulation Package (VASP).[10,11,12] Using VASP the interaction between the core region and valence electrons of the atoms was described by the Vanderbilt ultrasoft pseudopotential.[13] The electron – electron exchange-correlation function was described using the local density approximation (LDA), where a Ceperley-Alder[14] form was employed. The numerical integration of the Brillouin zone was performed using a discrete 4 x 4 x 4 and 4 x 4 x 8 Monkhorst-Pack[15] k-point sampling for the α- and c-, and β- phases, respectively. The plane wave cutoff was chosen as 31.96 Ryd.

Table I. The maximum induced stress (GPa) and strain at failure, for the three single crystal phases of Si₃N₄, with respect to the various applied strain components, γ_{ij}, where i = 1,2,3 and j = 1,2,3.

Strain	Maximum Induced Stress {GPa}			Strain at Failure		
	α-	β-	c-	α-	β-	c-
γ_{11}	51	57	45	0.17	0.19	0.16
γ_{12}	40	40		0.33	0.46	
γ_{13}	24	20		0.26	0.27	
γ_{22}	55	63		0.17	0.21	
γ_{21}	29	26		0.29	0.26	
γ_{23}	27	19	49	0.27	0.23	0.15
γ_{31}	32	26		0.30	0.28	
γ_{32}	39	22		0.35	0.25	
γ_{33}	60	55		0.24	0.20	

To perform accurate simulations of applied tensile and shear strains, a small strain was applied sequentially to the supercell. Initially, the supercell was relaxed such that the force at each atomic site, and the stress components of the supercell, were less than 0.01 eV A^{-1} and 0.1GPa, respectively. A 1% level of strain was predefined as the small strain increment for each simulation step.[16] At each step the previous step supercell was used, after the supercell was relaxed until the force at each atomic site, and the stress components of the supercell, other than the corresponding component of applied strain, reached a level less than 0.01eV A^{-1} and 0.1 GPa, respectively. Furthermore, it is important to note that at each step a finite temperature of 1K was applied to the supercell structure for 0.1 ps. However, all stress results were obtained for a supercell temperature of 0K.

For each phase the supercell was constructed of 1 or 2 unit cells for each polymorph. For α- Si₃N₄ the hexagonal $P3_1c$ configuration, with an orthorhombic structure containing 28 atoms: 16 nitrogen and 12 silicon atoms, was used. For β- Si₃N₄ a hexagonal $P6_3$ configuration, with an orthorhombic structure containing 14 atoms: 8 nitrogen and 6 silicon atoms was used. It is generally accepted that the $P6_3/m$ and $P6_3$ configurations result in similar data of the structural properties of the single crystal.[17] For c- Si₃N₄ a cubic Fd-$3m$ configuration with 56 atoms was employed, where one group of Si atoms (octahedral bonds) in the $8a$ position, the second group of Si atoms (tetrahedral bonds) in the $16d$ position and the N group of atoms in the $32e$ position (using Wyckoff notation). Various other parameters, such as the lattice constants, are given in the literature.[2,5,6,18]

It is clear from published work that some stress-strain data for silicon nitride has been reported. Previously published experimental and numerical data reports, for β- Si₃N₄, a maximum tensile strength dependent on various factors, in the range of 400 MPa to 2 GPa.[5,19,20,21,22,25,26] However, to the best of the author's knowledge, results for the tensile and shear strength of the α- and c- phase have not been published. In Table I,

for each of the three phases of silicon nitride, the maximum induced stress and strain at failure are presented for the applied strain components γ_{11}, γ_{12}, γ_{13}, γ_{21}, γ_{22}, γ_{23}, γ_{31}, γ_{32}, and γ_{33}. In each case the complete stress - strain curve is not given as a matter of brevity. Nevertheless, in figures 1 and 2 the stress - strain curve for the applied strain components γ_{11} and γ_{23}, respectively, are presented.

Finally, the relevant elastic constants for the investigated structures[25] are C_{11}, C_{33}, C_{44}, C_{12}, and C_{13}. In Table II, the estimated elastic constants from this work are presented and are compared to values obtained from the literature.[25,26,27]

Table II. The elastic constants calculated for the three single crystal phases of Si₃N₄, and values obtained from the literature (labeled 'Past Work')[24,25,26] are also presented.

	α-Si₃N₄ {GPa}		β-Si₃N₄ {GPa}		c-Si₃N₄ {GPa}	
	This Study	Past Work	This Study	Past Work	This Study	Past Work
C_{11}	412	437	423	448	551	533
C_{33}	450	509	538	580		
C_{12}	138	175	196	215	191	191
C_{13}	122	176	115	165		
C_{44}	130	132	104	115	349	341

3. DISCUSSION

The data presented in figures 1 and 2, beyond the point of maximum stress, the curves, in general, monotonically decrease indicating a significant change in the crystal structure. However, it is important to note that the change in the structure in each case is characterized by a different change in the stress – strain curve response. This is particularly the case for c - Si₃N₄ given in figure 2, where the data indicates a continued increase. As mentioned, a monotonic decrease in the induced stress is expected for a corresponding increase in the applied strain after structural failure. However, in particular cases a sudden decrease or an indeterminate value, for the induced stress is observed. This is the case, since the lattice structure has changed significantly over a single increment of the applied strain.

Furthermore, it is clear that the stress data, presented in figures 1 and 2, exhibits a non-regular dependence between the Young's (elastic) modulus, calculated in the linear region at low strains, and the maximum induced stress (also observed for the response obtained in the other applied strain directions). Other workers have reported that the maximum stress can be estimated using only the stress – strain behavior at low strains, assuming that beyond the low strain region the data can be extrapolated using a sine curve function. However, extrapolation does not provide accurate results in all cases.[23] For example, in this work, in the case of the γ_{11} strain component in figure 1 the β- Si₃N₄ result exhibits the higher maximum induced stress, even though the observed gradient is approximately equal to
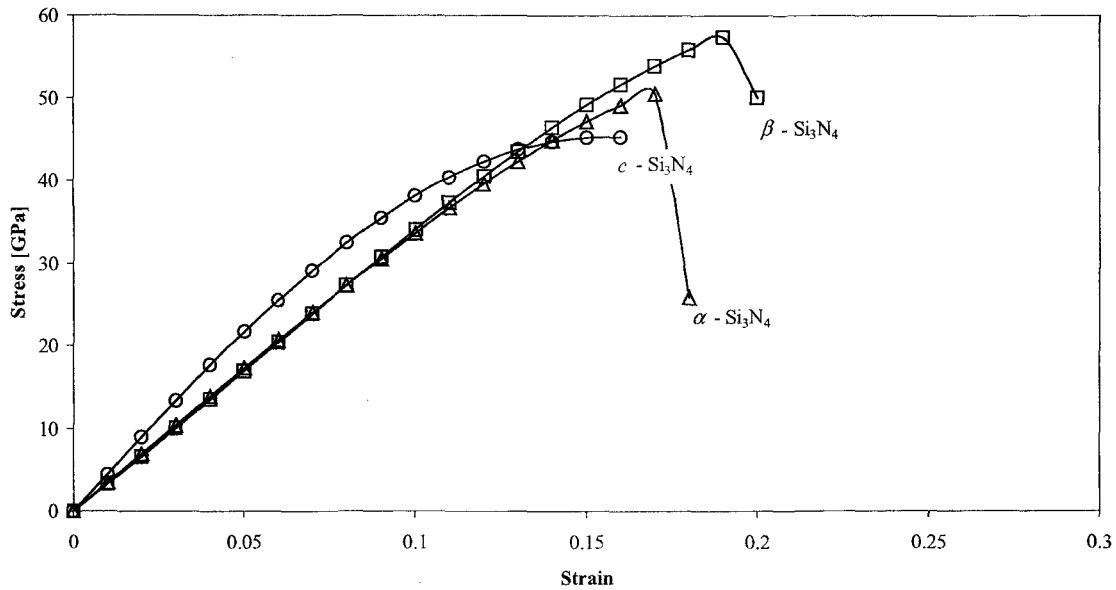
Fig.1, A plot of the induced stress as a function of applied strain $[\gamma_{11}]$, for the three single crystal phases of silicon nitride, as labled on the plot.

the α- Si_3N_4 result. Thus, in order to ensure an accurate estimate of the maximum induced stress, the complete behavior of the induced stress over a wide range of strain levels was essential.

From the results presented in Table I, it is concluded that the maximum strength observed in the various directions for the α- and β- phases are reasonably comparable. In particular, the case of the out of basal plane shear (the γ_{13}, γ_{31}, γ_{23} and γ_{32} components) the α- phase exhibits a higher strength compared to the β- phase. Particularly, the typical strain deformation in the basal plane, (in the γ_{11} and γ_{22} directions) the β- phase exhibits a higher strength compared to the α- phase. Moreover, strain deformation in the γ_{33} direction results in a higher strength in the α- phase. Therefore,

for deformations in the basal plane the β- phase is stronger and the α- phase is stronger with respect to out of basal plane deformations. It is interesting to note that in the α- phase the stacking sequence of the structure is coupled by a c-glide plane, which means that in the α- phase the spacing along the c-axis is twice that of the β- phase.[24] This difference in the structure could explain the differences that are observed in the data presented in this study.

Furthermore, from the results obtained some insight into the symmetry of the lattice structures can be gained. For small strains σ_{ij} (γ_{ij}) is equal to σ_{ji} (γ_{ji}) because of the crystal symmetry of the hexagonal system. However, at finite strain this condition is not satisfied, since σ_{ij} (γ_{ij}) is not equal to σ_{ji} (γ_{ji}). The strain at failure
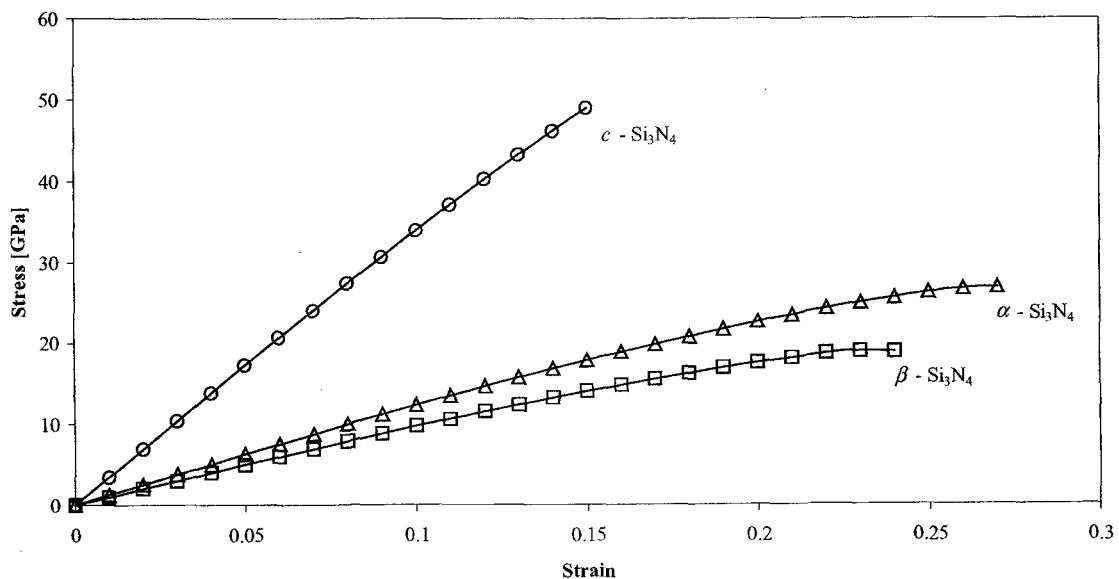
Fig.2, A plot of the induced stress as a function of applied strain $[\gamma_{23}]$, for the three single crystal phases of silicon nitride, as labled on the plot.

of γ_{12}, in the β - phase is significantly greater than the other shear cases. This is the case, since in the β- crystal lattice there are large atomic rings elongated in the shear direction. In general, fracture of brittle solids originates at points of weakness such as surface flaws or from bulk structural defects. Thus, it is reasonable to expect that the present estimate of the ideal tensile and shear strength should be considerably greater than experimental measurements.

Due to the limited data obtained for the c-phase it is difficult to drawn specific conclusions about the spinel structure. However, it is clear from the data that the spinel structure exhibits significantly different behavior compared to the other phases. At present it is the focus of ongoing research to characterize completely the mechanical response of the spinel structure.

As mentioned previously, the elastic constants, C_{11}, C_{33}, C_{12}, C_{13} and C_{44} were estimated for the silicon nitride phases. The current results of the elastic constants, presented in Table II, are compared with data obtained from the literature.[25,26,27] It is clear that the results are in reasonable agreement. In 1998, Teter[28] reported that a good correlation exists between the shear modulus and the Vickers indentation hardness value of many of the known high strength materials, assuming a perfect underlying lattice structure. It is important to note, however, that in the Teter publication, there is no explicit definition of the shear modulus. However, it is suggested that Teter defines the shear modulus as the

average value of the C_{44} and $\dfrac{(C_{11} - C_{12})}{2}$ elastic

constants, which is also indicated in a publication of Tanaka *et al.*.[29] As a matter of interest, the shear modulus of the three phases were taken as the average of the tetragonal and rhombohedral shear moduli, and thus, an estimate of the Vickers hardness was obtained using the correlation reported by Teter. For the single crystal α-, β- and c- phases the estimated Vickers hardness is approximately 23.0, 20.4 and 47.0 GPa, respectively. Interestingly, an average value of the Vickers hardness reported for polycrystalline silicon nitride is ~21.0 GPa.[28]

4. SUMMARY

In this study an *ab initio* density functional numerical technique was used to determine the induced stresses in α-, β- and c- Si₃N₄, as a function of applied strain deformation. The 'ideal' tensile and shear strength of the single crystal silicon nitride phases was determined for various applied strains. The elastic constants for the various phases were also determined and a comparison with results obtained from the literature demonstrated good agreement.

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