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Citation: Applied Physics Letters **76**, 3706 (2000); doi: 10.1063/1.126756
View online: http://dx.doi.org/10.1063/1.126756
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/76/25?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS VOLUME 76, NUMBER 25 19 JUNE 2000

Shock-induced transformation of β-Si_3N_4 to a high-pressure cubic-spinel phase

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(Received 24 January 2000; accepted for publication 24 April 2000)

β-Si_3N_4 powders were shock compressed and quenched from 12 to 115 GPa. β-Si_3N_4 transforms to the spinel-type Si_3N_4 (c-Si_3N_4) by a fast reconstructive process at pressures above about 20 GPa. The yield of c-Si_3N_4 recovered from 50 GPa and about 2400 K reaches about 80% and the grain sizes are about 10–50 nm. It is proposed that the fast transformation to c-Si_3N_4 occurs by rearrangement of nitrogen stacking layers, which initiates partial breakup of the SiN_4 tetrahedra and formation of SiN_6 octahedra at high density. Because of the advantages of massive production and the nanometer characteristics of shock-synthesized c-Si_3N_4, it is possible to investigate the mechanical properties experimentally and to develop new industrial applications. © *2000 American Institute of Physics.* [S0003-6951(00)02025-8]

Silicon nitride is an advanced ceramic and has the potential to be used in various applications due to good performance in mechanical, chemical, electronic, and thermal properties. This is due to highly covalent chemical bonding (70% covalence).[1] In addition to the two known polymorphs of α-Si_3N_4 and β-Si_3N_4, a third cubic form (c-Si_3N_4) with a spinel structure[2] has been found recently at pressures above 15 GPa and at temperatures over 2000 K, in several tens of nanograms, in a laser-heated diamond anvil cell for reaction times of about 1–10 min. This phase, c-Si_3N_4, is expected to be a hard material because of its greater bulk modulus and shear modulus than those of α-Si_3N_4 and β-Si_3N_4 (Ref. 2) and should also be a semiconductor due to its possible smaller band gap induced by the characteristic structure of octahedral silicon.[3] Because of the highly covalent nature of Si–N bonding, the high-pressure behavior of α- and β-Si_3N_4 is of great interest over a wide range of pressure and temperature. Although the high-pressure behaviors of Si_3N_4 have been studied at static high pressures[4,5] and dynamic high pressures,[6,7] only the spinel-type high-pressure phase has been observed experimentally as the high-pressure and high-temperature phase.[2] In this structure 2/3 of the silicon atoms are octahedrally coordinated and 1/3 of the silicon atoms remain tetrahedrally coordinated. It would be expected that all silicons have octahedral coordinations with increasing pressure, analogous to stishovite SiO_2.

For synthesis of the high-pressure and high-temperature form of Si_3N_4, we investigated the shock-induced transformation of β-Si_3N_4 powders using a propellant gun, because shock compression generates high-pressure and high-temperature simultaneously. We used two starting β-Si_3N_4 powders. The first one contained about 5 wt % α-Si_3N_4 and less than 1.9 wt % oxygen impurity and the second was pure β-Si_3N_4 with 0.5 wt % oxygen and did not show the presence of α-Si_3N_4 in x-ray analysis [Fig. 1(c)]. The grain sizes of both β-Si_3N_4 powders were in the submicron range. In the experiments, either pressed β-Si_3N_4 powder with 50%–60% of the crystal density or pressed mixtures of β-Si_3N_4 and copper powders with 50%–80% of the theoretical density were encapsulated in containers of platinum or copper. Detailed descriptions of the shock recovery experiments have been published elsewhere.[8]

Metal flyer plates such as steel and platinum impacted samples in containers. The pressure generated in the sample was calculated by the impedance match method[9] using the measured flyer velocity.[8] The flyer velocities ranged between 1.5 and 2.1 km/s. The shock pressure varied from 12 to 115 GPa, depending on the Hugoniot of the flyer material[10] and impact velocity, and the compression lasted about a microsecond. The bulk temperature for each sample was computed by the thermodynamic method.[11] We used the Birch–Murnaghan equation[12] and thermodynamic parameters[13] for β-Si_3N_4 and Hugoniot for copper powders[10] to estimate the Hugoniot for mixtures. In our calculation the fusion energy of copper is taken into account but the transformation energy of β-Si_3N_4 to c-Si_3N_4 is not included due to lack of data.

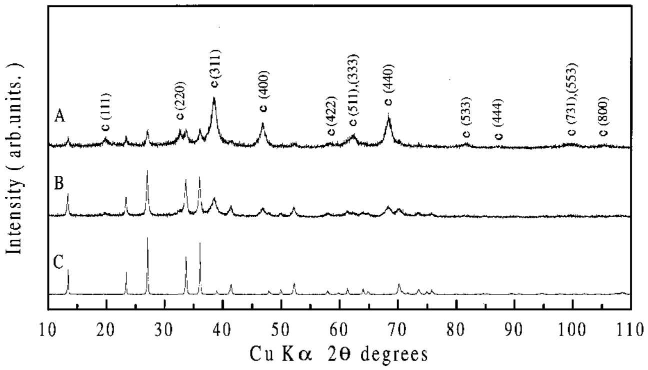

FIG. 1. XRD patterns of two recovered samples (a) from 49 GPa and 2400 K and (b) from 33 GPa and 1770 K and the starting material, pure β-Si_3N_4 (c). The peaks marked by c correspond to the cubic spinel-type Si_3N_4. The peak broadening is due to the fine grains.

After successful recovery, the container was cut open to take out the sample. To remove the copper matrix nitric acid was used at room temperature. The residue was collected after washing repeatedly with water. The color of the re-

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0003-6951/2000/76(25)/3706/3/$17.00

TABLE I. XRD data of cubic spinel-type c-Si_3N_4. $a = 0.774\,40 \pm 0.001\,06$ nm, $d = 4.012$ g/cm^3.

hkl	$2\theta_{obs}$ (deg)	d_{obs} (nm)	I/I_0	d_{cal} (nm)	I_{cal}
111	19.80	0.448 02	11	0.447 17	10
220	32.74	0.273 63	27	0.273 84	27
311	38.49	0.233 70	100	0.233 53	100
400	46.82	0.193 88	35	0.193 63	35
422	58.26	0.158 24	10	0.158 10	10
511, 333	62.33	0.148 85	33	0.149 06	34
440	68.39	0.137 06	56	0.136 92	57
620	77.88	0.122 56	4	0.122 46	4
533	81.56	0.117 93	11	0.118 12	11
444	87.01	0.111 89	5	0.111 79	5
642	97.42	0.102 52	5	0.103 50	5
731, 553	99.71	0.100 77	21	0.100 84	19
800	105.38	0.096 85	11	0.096 816	10
751, 555	119.20	0.089 31	16	0.089 435	15
840	125.74	0.086 55	12	0.086 595	12

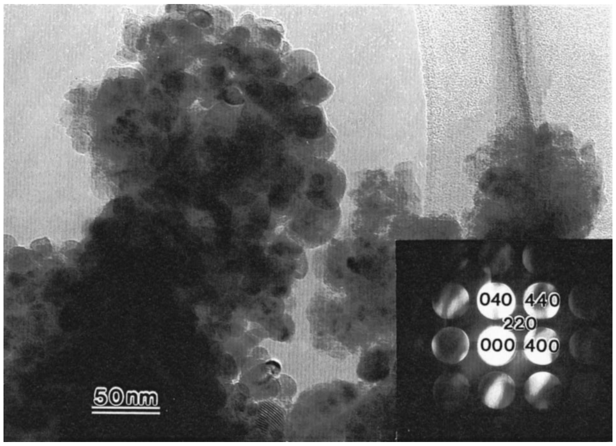

FIG. 3. Microphotographs of TEM and electron nanodiffraction of shock-synthesized, nanometer grains of spinel-type Si_3N_4. The observed d values are 0.273, 0.193, and 0.138 nm for diffractions (220), (400), and (440), respectively.

sidual powder was gray, compared with the milky white of β-Si_3N_4. We used x-ray diffraction (XRD) (Rigaku RINT 2200 V/pc) and analytical electron microscopy (TEM) (JEM 3000F) equipped with energy dispersive x-ray spectroscopy (EDX) to investigate the structure and chemistry of the shock-recovered sample.

Figure 1 illustrates a comparison of typical XRD patterns of the starting β-Si_3N_4 and two recovered samples from mixtures with copper powders shock compressed at 33 GPa and 1770 K [Fig. 1(b)] and 49 GPa and 2400 K [Fig. 1(a)], respectively. In the recovered samples the peaks of β-Si_3N_4 become weaker with increasing shock pressure and the newly appearing peaks correspond to the cubic spinel structure. The yield of c-Si_3N_4 reaches about 80%. Table I lists XRD data of c-Si_3N_4 produced from pure β-Si_3N_4, together with the calculation results of the Rietveld method. The lattice parameter of c-Si_3N_4 is $0.774\,40 \pm 0.001\,06$ nm and the calculated density is 4.012 g/cm^3, which is 26% denser than that of β-Si_3N_4. The XRD measured lattice parameter of c-Si_3N_4 is slightly (0.7%) smaller than the value $(0.780 \pm 0.003$ nm$)^2$ measured by electron diffraction and the result (0.783 67 nm)[3] calculated by first principles. As shown in Fig. 2, EDX analyses of c-Si_3N_4 showed the presence of Si and N, with the same ratio as the starting β-Si_3N_4, and detected a small amount of oxygen as a very weak shoulder on the N peak.[14] Therefore, the slight difference in the lattice parameter is due to the low precision of the measurement by electron diffraction.[2] The grain sizes of c-Si_3N_4 are 10–50 nm, which is about one tenth of the initial β-Si_3N_4, as shown in Fig. 3 together with an electron nanodiffraction pattern indicating the presence of a cubic, nanometer-size single crystal.

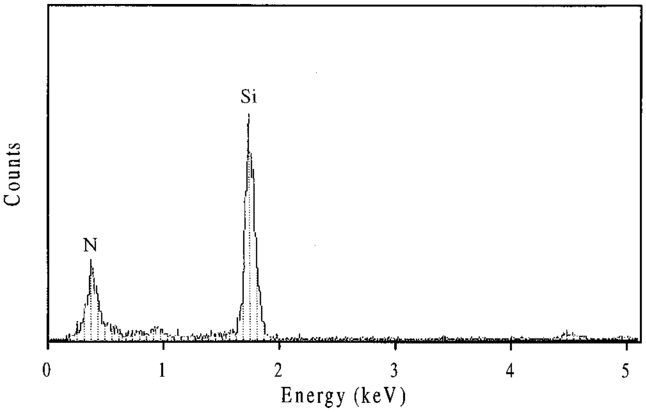

FIG. 2. EDX spectrum of shock-synthesized cubic spinel-type Si_3N_4. Only N and Si are observed and a very weak shoulder can be seen due to oxygen (0.5 keV) near the N peak. High backgrounds near 1 and 4.5 keV correspond to Cu and Ti impurities, respectively.

The minimum shock pressure required for the formation of c-Si_3N_4 from β-Si_3N_4 is less than 20 GPa, but the yield from the run at 19 GPa and about 3000 K was the smallest that we could detect in the course of electron microscopy observation. The change to c-Si_3N_4 was not detected in samples subjected to shock temperatures of 1270 K at a pressure of 21 GPa, indicating the presence of a threshold minimum temperature. Too high a temperature causes decomposition and/or melting of Si_3N_4. In the case of samples of β-Si_3N_4 powders, the platinum container was broken and all the samples were exploded out above 80 GPa. This indicates that Si_3N_4 decomposed to Si and N_2 during shock compression, or during the adiabatic release process after shock compression, because of the higher temperatures. Even in the presence of copper in the mixture, the containers of highly porous samples were blown out when the calculated shock temperature was higher than 3000 K at 50 GPa. The α-Si_3N_4 phase, coexisting in one of our starting β-Si_3N_4 powders, survived under shock conditions where most of the β-Si_3N_4 transformed to c-Si_3N_4, suggesting that α-Si_3N_4 has a higher activation barrier for phase transformation. The higher activation energy for the transformation of α-Si_3N_4 to c-Si_3N_4 has also been demonstrated by the survival of α-Si_3N_4 after being subjected to pressures of 37 GPa and temperatures of 3700 K in the diamond anvil cell.[5]

Compared with the duration of static high pressure work,[2] the present shock wave study has verified that the transformation to c-Si_3N_4 phase occurs within a microsecond. This suggests that a fast and probably diffusionless mechanism has played an important role. A fast phase transformation of β-Si_3N_4 to c-Si_3N_4, through a solid–solid reaction, can be explained in terms of the anisotropic compression of SiN_4 tetrahedra in β-Si_3N_4. In β-Si_3N_4,[1] the structure units consist of slightly distorted tetrahedral SiN_4 (sp^3 hybridization of Si) and planar NSi_3 (sp^3 hybridization of N). Tetrahedra SiN_4 are linked by sharing nitrogen corners so that each nitrogen is common to three tetrahedrons. The puckered rings of alternating Si and N atoms have a stacking sequence of ABAB...and form channels (diameter about 0.15 nm) along the *c* direction. The lattice parameters are $a = 0.2911$ nm and $c = 0.7595$ nm and the density is 3.19 g/cm^3. On the other hand, in the spinel structure tetrahedral SiN_4 and octahedral SiN_6 are the basic units. The N atoms are cubic close packed in a stacking sequence ABCABC... . The SiN_4 tetrahedron is linked to the SiN_6 octahedra by sharing nitrogen corners, and each of the SiN_6 octahedra is joined by sharing edges so that each nitrogen is common to one tetrahedron and two octahedrons.

The basic SiN_4 tetrahedron unit in β-Si_3N_4 is slightly distorted, and only the longest bond in the SiN_4 tetrahedron may shorten significantly by compression. This distortion of the tetrahedral unit has been confirmed by neutron diffraction study at high pressure of $Si_2N_2O(=Si_3N_4 \cdot SiO_2)$[16] with a similar structure to β-Si_3N_4. The large open channel along the *c* axis is destroyed to make new bonds and the coordination number of 2/3 of the Si atoms increases from 4 to 6. As a result, this transformation involves a change of stacking sequence of N layers from ABAB...to ABCABC... .

The shock compression technique has verified a fast transformation of β-Si_3N_4 to c-Si_3N_4, a spinel-type high-pressure phase. This implies that the shock compression technique could be useful for synthesizing a high-pressure c-C_3N_4 phase and other related materials such as a spinel solid solution between Si_3N_4 and C_3N_4. As demonstrated by shock synthesis of diamond in industry, it has been thought that shock compression has several advantages over static compression for material synthesis. For example, higher pressures can be achieved more easily, simultaneously with high temperatures, and a large amount of samples are treated in each synthesis. Therefore, shock-synthesized c-Si_3N_4 could become an important industrial material. The shock synthesis of high-pressure Si_3N_4 has important implications for making hypothetical, hard materials of β-C_3N_4 with the β-Si_3N_4 structure[17] and cubic C_3N_4 with the structure of high-pressure Zn_2SiO_4 (willemite II).[18] The presence of stable C_3N_4 forms has not been confirmed experimentally yet, although the phases as a possible hard material have been predicted theoretically.[17,18] In this sense the transformation to the high-pressure cubic spinel form of Si_3N_4 can be used as a guide for making C_3N_4.

This research was carried out in the COE project in NIRIM while H. L. He, M. Zhang, and F. F. Xu were supported as STA fellows. The Rietveld analysis was carried out by Dr. F. Izumi and Dr. T. Ikeda. The β-Si_3N_4 starting materials were kindly provided by Dr. M. Mitomo and Dr. G. D. Zhan. The authors wish to thank Dr. James Hester for improving the manuscript.

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[14] When a significant amount of oxygen is dissolved as SiO_2 in c-Si_3N_4, the lattice parameter becomes smaller because the radius of N is larger than that of O. A similar observation can be seen in the Alon (Al_2O_3–AlN) spinel solid solution.[15] Our sample contains only a little oxygen, which does not affect the lattice parameter significantly. The lattice parameter of c-Si_3N_4 produced from β-Si_3N_4 with 1.9 wt % oxygen is measured to be $0.775\,05 \pm 0.000\,69$ nm.

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