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John Patten, Ronnie Fesperman, Satya Kumar, et al.

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High-pressure phase transformation of silicon nitride

John Patten,^{a)} Ronnie Fesperman, and Satya Kumar University of North Carolina at Charlotte, Charlotte, North Carolina 28223

Sam McSpadden, Jun Qu, and Michael Lance Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6062

Robert Nemanich and Jennifer Huening

North Carolina State University, Raleigh, North Carolina 27695

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We provide evidence for a high-pressure phase transformation (HPPT) in the ceramic material silicon nitride. This HPPT is inferred by a high-pressure diamond anvil cell, Raman spectroscopy, scanning/transmission electron microscopy, and optical and acoustic microscope inspection. In the case of silicon nitride, the HPPT involves a ductile or metallike behavior that is observed in severe deformation processes, such as nanoindentation and micromachining. This pressure-induced plasticity is believed to be similar to that found in silicon and germanium with its origin in the high-pressure metallic β -Sn phase formation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1632031]

There is considerable interest in the production and manufacture of engineered systems using advanced ceramic materials such as silicon nitride (Si₃N₄) and silicon carbide (SiC).¹ Insulators, such as Si₃N₄ and SiC, are currently widely used in microelectronic and mechanical components. The high cost of fabricating these hard and brittle materials has thwarted efforts to significantly integrate them into advanced industrial applications, such as engines, including seals, bearings, pistons, and turbine blades. A fundamental understanding of the deformation mechanisms of ceramics will certainly lead to advances in the fabrication science and technology of semiconductor and mechanical devices for high-temperature applications. Recently, a technology for ductile-regime processing of nominally brittle semiconductors and ceramics has demonstrated the potential for generating surfaces and components with minimal surface and subsurface damage.² The high-pressure metallic nature of these materials may also be employed as active or passive components for nano- and microintegrated circuits, replacing the need to add metals for conductors and circuits. The local high pressure (HP) that may occur during heteroepitaxial growth, may be responsible for a phase transformation into a quasi-liquid phase, as evidenced by recent theoretical calculations.3

The plastic deformation of these materials at room temperature is believed to be caused by its transformation to HP phases during mechanical contact.⁴ These HP (metallic) phases may also exhibit superconducting characteristics.⁵ The extent or generation of the HP phase is limited due to the propensity of the material to fracture as a brittle solid. The scale or size of the HP phase transformation (HPPT) is thus limited by the fracture behavior of the material for nonhydrostatic stress states. Therefore, the extent of the ductile or plastic behavior of these materials occurs between the nanometer and micrometer length scales. A thorough description of the ductile behavior of ceramics, and evidence of HP phases of these nominally brittle materials, is presently not available. In particular, the *in situ* detection of the HPPT of silicon nitride has not been previously reported.

We report on evidence of these HPPTs. Our work employs postprocess characterization techniques to identify the HPPT of silicon nitride. In all cases reported herein, the starting material is polycrystalline Si₃N₄. However, the resulting material, produced after release of the pressure, is amorphous. This order-to-disorder transition, from crystalline to amorphous, is strong evidence of a HPPT.⁶ In the case of a highly studied material, such as silicon, the amorphous phase that results after depressurization occurs from a back transformation from the HP phase. The exact nature of the HP phase of Si₃N₄ is currently not known, but it is expected to be similar to that of semiconductors, such as silicon and germanium, i.e., a β -Sn metallic phase.⁷ In these materials, if the magnitude of the pressure or stress to initiate the phase transformation is equivalent to the hardness of the material (GPa), then, it is likely that the resultant plastic deformation is due to a HP phase. $^{8-10}$

The original evidence of a HPPT of Si₃N₄ was due to the observed ductility during mechanical deformation, such as indentation and grinding.^{11,12} Plastic deformation at room temperature is severely restricted in semiconductors and ceramics. Mesoscale (>micrometer size) deformation is not expected to occur in these materials at low temperatures, i.e., up to their transition temperatures (~one half of the melting temperature (T_m), for example, about 600 °C for silicon).⁶

One of the authors (J.P.) conducted preliminary diamond anvil cell (DAC) experiments on Si_3N_4 to investigate the presence of HP phases. At pressures between 20 and 35 GPa, some low-energy x-ray diffraction peaks occurred (corresponding to 17.38 to 24.21 eV), which are a signature of a HP phase of silicon nitride.¹² This finding is significant in the present context because (1) it shows that a HPPT did occur, and that this one was not the same as the atmospheric Si_3N_4 ,

^{a)}Present address: Western Michigan University, Kalamazoo, MI 49008-5336; electronic mail: john.patten@wmich.edu



FIG. 1. (a) UV Raman of machined (500 nm depth of cut) and nonmachined Si_3N_4 surface. The broadening in the UV Raman spectra indicates that the machined material near the surface is amorphous; within 0.5 μ m of the surface (UV light does not penetrate the material as deep as visible light and, therefore, allows for analysis of the material's surface of the material). (b) UV Raman of machined Si_3N_4 debris or chips generated by removing 5 μ m of material from the surface of silicon nitride.

and (2) The HPPT pressure occurred at or near the hardness of the material.^{13,14} As the goal of the DAC experiment was to identify a HPPT, we made no attempt to identify the crystal structure of the resultant material. However, we noted that the HPP was denser than the starting phase (at atmospheric pressure) as inferred by the location of the diffraction peaks of the phase being shifted to lower-energy peaks compared to the atmospheric phase.

UV (wavelength 244 nm) and visible (wavelength 514.5 nm) Raman spectroscopy were used to analyze the structure of micro- and nanomachined Si_3N_4 . The following spectra, presented in Figs. 1(a) and 1(b), represent data collection taken from the surface of machined Si_3N_4 [Fig. 1(a)] and the chips or debris, i.e., removed material that is created during the machining process [Fig. 1(b)]. The Raman spectra, Fig. 1(a) nonmachined surface, exhibits peaks that are a signature for crystalline bulk material; therefore, a phase transformation has occurred at the surface due to the machining process, with the resulting phase being amorphous. The chips also appear to have a higher amorphous phase content as evidenced by the peak broadening, probably a consequence of the extent of the higher compressive stresses generated within the chip.¹⁵

We also used acoustic microscopy to image the surface and subsurface structure of Si_3N_4 .¹⁶ These images (not shown here) show evidence of a significantly deformed ma-





FIG. 2. Micro-Raman results indicating approximately 5 μ m of subsurface damage for a 5 μ m depth of cut on silicon nitride.

terial, which was produced by the ductile or plastic deformation process. The depth of this plastically deformed material layer is 0.5 μ m or less below the surface, for a 250 nm depth of cut. This surface material is believed to consist of the amorphous remnant identified by Raman Spectroscopy. The depth of the damage layer below the surface is proportional to the amount of material removed from the original surface; i.e., a 5 μ m depth of cut resulted in approximately 5 μ m of subsurface damage in the form of an amorphous or plastically deformed layer, as shown in Fig. 2 for a cross section μ -Raman.

Comparable images of the chips or debris generated during processing, shown in Fig. 3, provide clear evidence, that the material deformed in a ductile or plastic manner. The material removed is severely deformed, and the image indicates that the material was able to bend back over upon itself, *without fracture*. The chips are typically quite thin, of the order of a micrometer thick.¹⁷

Temperatures during these mechanical deformation processes need not be high. These processes have been demonstrated (experimentally and via simulation) to occur at room temperature, without any appreciable heating taking place.² We conclude, therefore, that thermal process mechanisms are not the driving force for the observed order-to-disorder phase transformation.^{18,19}

By employing various analytical techniques, we consistently detected indications of a HPPT in Si_3N_4 . We have provided a quantitative evaluation of the magnitude of the transformation pressure and the extent or range of the phase transformation based upon mechanical contact and deformation, and the resultant amorphous remnant. All indications



FIG. 3. Scanning electron microscope image of chip/debris from machined Si_3N_4 , area 400 μ m×400 μ m.

from these and other related experiments suggest the occurrence of a HPPT of silicon nitride during mechanical deformation at room temperature. The length scale of the phase transformation is approximately the same as the penetration depth for mechanical contact. The HPPT, which happens at small scales and in the absence of brittle fracture, appears to be the origin of the ductile or plastic behavior of this material at room temperature. Larger penetration depths, from mechanical contact, result in brittle fracture, typical of ceramic materials at low temperature. The final phase, after depressurization, in all cases appears to be amorphous. A direct crystalline-to-amorphous phase transformation is not expected in this material, and thus an intermediate HP phase is believed to be responsible for the behavior of the material when subjected to high compressive and shear stresses.²⁰ This process mechanism should be of fundamental importance in ceramics research in general and silicon nitride in particular. A review of HP phases of semiconductors, excluding silicon nitride, has recently been published.²¹

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