Transformation-induced plasticity and cascading structural changes in hexagonal boron nitride under high pressure and shear

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In situ x-ray diffraction study and modeling of the degree of disorder, *s*, and phase transformation (PT) in hexagonal hBN were performed. It was proven that changes in *s* are strain-induced and that *s* can be used to quantify plastic strain. During the strain-induced hBN→wurtzitic wBN PT, the transformation-induced plasticity (TRIP) was exposed and quantified. TRIP exceeds conventional plasticity by a factor of 20. Cascading structural changes were revealed. Strain-induced disorder explains why PT under hydrostatic and nonhydrostatic conditions started at the same pressure ~10 GPa. For the same disorder, plastic shear reduces PT pressure by a factor of 3–4. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1866226]

Plastic strain-induced phase transformations (PTs) under high pressure are widespread in nature, physical experiments,[1–4] and modern technologies (e.g., material synthesis by ball milling or explosion). For example, one of the mechanisms of deep earthquakes is related to the instability caused by shear induced PT.[5] It is well known that the superposition of large plastic shear on high pressure in rotational diamond anvil cell (RDAC) drastically (by a factor of 3–5) reduces the PT pressure for various materials.[2–4] The basic difference between the pressure-induced PT (which occurs predominantly at pre-existing defects) and *strain-induced PTs* under high pressure (which occur by nucleation at new defects generated during plastic flow) was recently discussed in Refs. 6 and 7. However, despite the strong fundamental and applied interest, *quantitative characterization and understanding of the basic physics of strain-induced PTs are lacking.*

Here, a paradoxical result was obtained: PT of hBN to superhard wBN phase under pressure and shear started at the same pressure, $p \sim 10$ (p is in GPa), as under hydrostatic conditions. Graphite-like hBN→wBN PT represents a unique case of martensitic PT with extremely large volumetric transformation strain, $\epsilon_0 = 0.53$. Superhard phases of BN also have broad technical applications. A change in bonding during this PT was recently studied in Ref. 8. The previously unexplored topic of strain-induced hBN→wBN PT and disorder, their nontrivial interaction, transformation-induced plasticity (TRIP) phenomenon, and cascading structural changes was the focus of this study. The reason for the aforementioned paradox was found to be related to the fact that the *PT pressure in hexagonal systems essentially increases with increase in the degree of disorder characterized by the* turbostratic stacking fault concentration (TSF), *s*. These faults are formed by relative rotation or displacement of two parts of crystal lattice in (001) planes to arbitrary positions.[9,10] To understand the underlying physics, simultaneous *in situ* x-ray diffraction study and modeling of disorder and PT in hBN was performed. There is not any evidence of another *study of BN in RDAC, or in situ synchrotron x-ray diffraction research of any material in RDAC. In situ* evolu-

tion of disorder has not been studied under high pressure. Two hBN samples were subjected to a complex compression and shear loading program in a RDAC. Two other samples were studied under hydrostatic conditions. *In situ* synchrotron x-ray diffraction was conducted at Brookhaven National Laboratory at beam lines X17C and X17B using the energy dispersive method (Fig. 1). The volume fraction of wBN and hBN was, respectively, estimated using relationships $c_1 = 45.009x^3 + 18.737x^2 + 34.872x$, and $c_2 = 57.269y^3 - 162.26y^2 + 205.72y$ (plotted in Ref. 10), where $x = I_{110}^w/(I_{110}^w + I_{110}^h)$, $y = I_{100}^h/(I_{100}^w + I_{100}^h)$, and I_{ijk} is the integral intensity of *ijk* diffraction lines of wBN (superscript w) and hBN (superscript h). Both equations produce similar results. The average wBN volume fraction, *c*, was determined as $c = c_1/(c_1 + c_2)$. The concentration of TSF was determined by a method developed by Kurdyumov[9,10] through measurement of broadening of diffraction lines (112) and (110). Pressure distribution was measured by the ruby fluorescence technique. The conditions were theoretically predicted and experimentally confirmed
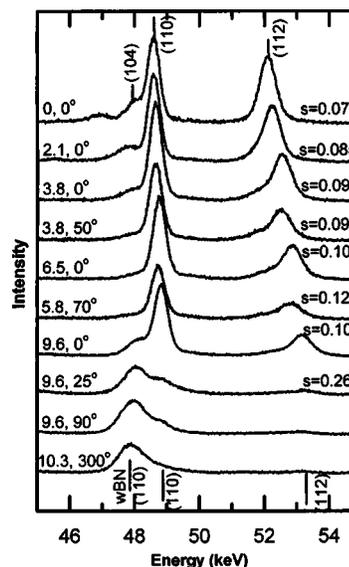

FIG. 1. X-ray diffraction patterns of boron nitride during compression and shear stages. Pressure (in GPa) and rotation angle increment, as well as degree of disorder are shown near curves.

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for quasihomogeneous pressure distribution in a sample during compression, rotation, and PT.[11] This allowed the quantitative characterization of strain-induced PT, in contrast to all previous studies in RDAC.

Under hydrostatic loading up to 9.4 GPa (before PT), the degree of disorder was $s = 0.04$ and did not change. The PT pressure for the initiation of hBN→wBN PT was 10.4 GPa. Further loading up to 13.4 GPa, during quite intensive PT, changed s ($c \cong 0.2-0.4$) from 0.04 to 0.06, which is within the discrepancy of the experiment. The experimental results obtained here and in Refs. 9–13 regarding PT pressure can be approximated by

$$p = 3.333 + 17.54(c - 0.05) + 175.44s \quad \text{for } 0 < s < 0.1,$$
$$p = 20.26 + 17.54(c - 0.05) + 6.14s \quad \text{for } s > 0.1, \tag{1}$$

where $c = 0.05$ is accepted as the smallest concentration that can be detected experimentally. Pressure-induced PTs predominantly occur at pre-existing defects (one needs to increase pressure to activate less potent defects). The suppressing effect of TSF is related to an increase in resistance to the nucleus growth, just as is the case with other obstacles (point defects, dislocations, various boundaries, etc.). Time is not included in Eq. (1) because thermally activated nucleation of critical nuclei at defects and their growth until arrested by a strong obstacle is considered. Under plastic straining (i.e., without a hydrostatic medium), disorder changes during both compression and rotation of the anvil. During rotation and PT,

$$s = s_0 + m(\phi - \phi_0) + n(c - c_0), \tag{2}$$

where the rotation angle, ϕ, is in radians. Five experiments, enumerated in the following, either before or after PT (first sample, change in s from 0.082 to 0.094 due to rotation by 50° at 4 GPa; change in s from 0.098 to 0.103 due to rotation by 20° and from 0.103 to 0.127 due to additional rotation by 70° at 6 GPa; change in s from 0.266 to 0.278 due to rotation by 70° at 10 GPa, when $c = 0.7$ did not change; second sample, change in s from 0.124 to 0.218 due to rotation by 360° in the pressure range 6–7.5) are well described by $m = 0.017$. Thus, m is independent of p, c, and s. The parameter $n = 0.235$ was determined from the changes in c and s during rotation at 10 GPa. Complete irreversible PT was observed after rotation by 300° during which pressure homogeneously increased from 9.6 to 10.3 (despite the volume decrease by 53%). Thus, the homogeneous pressure self-multiplication effect was revealed in contrast to strongly heterogeneous results for other materials.[2–4] The paradoxical equality of PT initiation pressure for pressure- and strain-induced PT is explained by the values $s = 0.04$ for hydrostatic loading and $s = 0.11$ under plastic shear.

From the experiments without PT, it follows that disorder is plastic strain-induced. However, during the PT the major part of disorder in Eq. (2) is due to change in c. The question arises: why does a growth in c induce disorder? The only reasonable explanation for transformation-induced disorder is based on TRIP phenomenon that is well studied for uniaxial loading of steels under normal pressure,[14,15] but not in any known high-pressure experiment in diamond anvil cell. Volumetric transformation strain, ε_0, during any PT, creates large internal stresses which in combination with external nonhydrostatic stresses lead to TRIP.[14,15] For shear under pressure, transformation-induced plastic shear, γ, is deter-

mined by[16,17] $\gamma = \varepsilon_0 c \tau / \tau_Y / \sqrt{1 - (\tau / \tau_Y)^2}$, where τ is the shear stress and τ_Y is the yield stress in shear. When $\tau \to \tau_Y$, $\gamma \to \infty$. For hBN→wBN PT, TRIP has to be much stronger than that for steels, because for steels $\varepsilon_0 = 0.02-0.05$, is significantly lower. Usually, TRIP is experimentally determined under $\tau < \tau_Y$ (stress-induced PT); thus traditional plasticity is absent and TRIP can be measured. In strain-induced experiments, plastic flow takes place even without PT, thus it was impossible to directly measure TRIP to prove its existence. However, the fact that a large part of s is proportional to c is the evidence that part of plastic shear is also proportional to c, i.e., *existence of TRIP*.

Note that rotation angle of an anvil, ϕ, is a convenient measurable geometric characteristic of plastic deformation, but not physically meaningful because it does not reflect the state of the material. In metal plasticity, dislocation density or grain size is usually used to reflect the state of the material. Since disorder is strain-induced, the increment Δs is proportional to the total plastic strain increment independent of whether it is caused by external stress or by TRIP. Thus, for hexagonal systems change in s can be considered as a natural physical measure of plastic strain, evolution of which can be determined *in situ*. It can characterize the plastic strain under any arbitrary complex loading, in particular, during the compression stage. Then Eq. (2) allows us to separate the conventional plasticity, $\Delta s_p = m\Delta\phi$, and TRIP, $\Delta s_t = n\Delta c$. In the experiment, the rotation by $\Delta\phi = 0.436$ at 9.6 GPa leads to $\Delta s = 0.160$ and $\Delta c = 0.65$. Thus $\Delta s_p = 0.007$ and $\Delta s_t = 0.153$, i.e., TRIP exceeds the conventional plasticity by a factor of 20. Thus, the proof is independent of any possible experimental error and is also consistent with the prediction of the equation for γ for shear stress approaching the yield stress. This also solves the paradox of why we were unable to find a difference in c along the radius of the sample, despite the fact that shear strain for torsion is proportional to the radius: TRIP is proportional to shear stress rather than shear strain which is practically independent of radius for plastic torsion.

TRIP is the same as conventional plasticity, but caused by internal plus external stresses rather than by external stresses alone. That is why TRIP, in the same way as conventional plasticity, generates TSF (the dominating part) and new nucleating defects. Thus, the cascading mechanism of structural changes was revealed (Fig. 2).

A simple thermodynamic model was developed for strain-induced nucleation at stress concentrators (defects) generated during plastic flow,[6,7] resulting in strain controlled kinetic equation for $dc/d\phi$. In this study, the terms were added related to s [Eqs. (1) and (2)] and to defects generation by TRIP. It was obtained that: (a) TRIP generates new defects which nearly replicate the pre-existing defects already utilized for wBN nucleation [i.e., almost eliminates the term $17.54c$ in Eq. (1)]; (b) for the same initial disorder, plastic shear indeed reduces PT pressure significantly (for $s_0 = 0.11$, by a factor of 3 for initiation and 4 for completing the PT) in comparison with hydrostatic loading; (c) for relatively small constant p, strain-induced PT is arrested at some value c_{max} due to increase in s; (d) rotation ϕ to obtain maximum value c_{max} does not exceed 5.5 for any s_0; thus traditional wisdom "the larger the shear the more product phase appears" is not valid; (e) for $s_0 = 0.11$, pressures for initiation and completing the PT are 6.25 and 9.25, respectively.
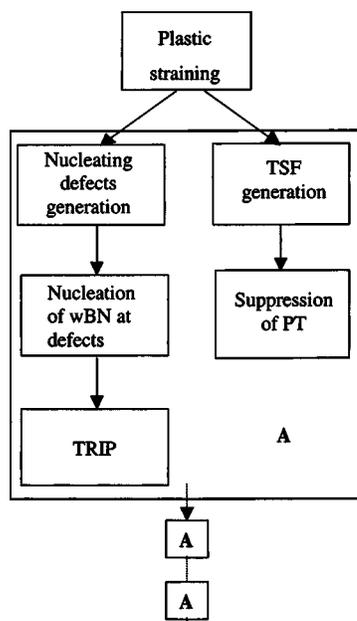
FIG. 2. The cascading mechanism of structural changes during continuous rotation of an anvil. Plastic straining generates both TSFs, which suppress the PT, and nucleating defects (e.g., dislocation pile-ups and various tilt boundaries) which promote the PT. PT under shear stresses produces strong TRIP; TRIP, in the same way as conventional plasticity, generates the TSF (the dominating part) and new nucleating defects; the new nucleating defects again promote the PT, which produces TRIP, and so on. When rotation stops, each of these processes stop as well.

Thus, it was shown that for the study of strain-induced PTs in hexagonal systems that are sensitive to disorder, an additional dimension related to TSF must be considered. Since it was proven that a change in concentration of TSFs is strain-induced, change in s is a natural physical measure of plastic strain, evolution of which was studied *in situ*. Strong dependence of Δs on Δc proves the existence of TRIP and allows the quantitative separation of conventional plasticity and TRIP. The cascading mechanism of structural changes is revealed during continuous rotation of an anvil (Fig. 2). Since TRIP exceeds the conventional plasticity by a factor of 20, actual plasticity involved in the PT process is much larger than that prescribed by ϕ, which was neglected in literature. TRIP and cascade mechanism allow the completion PT at a much lower pressure. They also make all hBN–wBN interfaces semicoherent, which arrests the reverse PT

after complete unloading and allows a complete irreversible PT.

We believe that similar results are valid for PT in all disorder-sensitive hexagonal and rhombohedral crystals with appreciable ε_0, e.g., for PT in graphite and rhombohedral BN. Strong TRIP is expected to be found for strain-induced PT in any material with large ε_0 (according to theory),[16,17] however to prove its existence and to quantify it, some strain measures (similar for s in hexagonal and rhombohedral crystals) must be found. Additionally, strong TRIP and cascading mechanism are expected to be found in shear bands, which must be considered, e.g., for analyses of the earthquakes[5] and chemical reactions.[17] Since disorder suppresses PT to wBN, it can be used as a controlling parameter to search for alternative PT, in particular PT to amorphous state.

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