

Pressure-induced phase transformations in diamond

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The stability of diamond under pressure and the structure of hypothetical high-pressure phases have been a controversial issue for a long time. “Will diamond transform under megabar pressures?” asked Yin and Cohen in the title of their paper [Phys. Rev. Lett. **50**, 2006 (1983)] which attempted to predict an answer to this question 15 years ago. Before and after that, many other scientists tried to find the answer doing both modeling and experiments. However, the cubic structure of diamond seems to be experimentally stable up to the highest static pressures that the modern high-pressure technology can achieve. We addressed the problem by decreasing the contact area of pressurization instead of increasing the total load. Experimentally this can be easily done in indentation tests using a sharp diamond indenter. In addition to hydrostatic stresses, such a test creates shear stresses as well. Here deformations may be realized, which are either impossible or would require much higher pressures when utilizing only hydrostatic stresses. By coupling the indentation loading with micro-Raman spectroscopy, we were able to drive and monitor phase transformations in diamond. A very similar phenomenon can be observed by scratching a diamond with another diamond. Thus, phase transformations in diamond may in fact be a very common feature of wear. © 1998 American Institute of Physics. [S0021-8979(98)08015-3]

I. INTRODUCTION

Diamond is extremely hard, and although the discovery of carbon nitrides and ultrahard fullerites¹ seems to challenge the position of diamond as the hardest material known to science, it is still the only available structural material that can be used under extreme pressures, particularly for cutting tools, indenters, pressure cells, etc. Therefore, scientists are concerned with the limit for the pressure stability of diamond. The importance of this issue has motivated many theoretical²⁻⁴ and experimental⁵ attempts to determine the ultimate pressure limit for diamond.

Similar to other semiconductors, carbon is expected to undergo a phase transformation to a metallic phase at very high pressures. Closure of the valence-conduction band gap due to overlapping of wave functions and delocalization of the valence electrons is now known as Herzfeld–Mott transition⁶ and has been experimentally verified for a variety of semiconductors. Theoretically predicted values for the Herzfeld–Mott transition and a number of other transformations in diamond under hydrostatic and uniaxial compression vary from 170⁷ to thousands of GPa. The band gap of diamond is calculated to go to zero under hydrostatic compression at 760 GPa based on a dielectric model⁸ and below 900 GPa based on extrapolation of measurements to 405 GPa.⁹ However, predictions of a band gap closure of diamond based on hydrostatic compression have been recently challenged. Numerical calculations based on band gap theory have shown that hydrostatic compression should not lead to a

gap closure, but to cause the energy gap in diamond to increase; only compression including shear (e.g., by uniaxial compression) should cause it to decrease.¹⁰⁻¹² Uniaxial compression along [001] should lead to metallic carbon at about 285 GPa.¹¹ Nielsen¹³ predicted the formation of metallic carbon by uniaxial compression of diamond along the [110] and [111] crystal axes at pressures of about 400 GPa. Experimental evidence for the dependence of phase transitions on crystallographic orientation in uniaxial compression in other materials has been given by Ruoff.⁸

Thus, there are many discrepancies in the published predictions of the transition pressure. However, there is no experimental evidence of the Herzfeld–Mott transition for diamond. In contrast, diamond anvils can support hydrostatic pressures of up to 400–500 GPa. No transformation has been reported and the cubic diamond structure was retained at least up to 378 GPa.¹⁴ The latest theoretical analysis performed by Gilman¹⁵ suggests that diamond does not metalize in the range of pressures that might be achieved because it has too few valence electrons. Ultimately, complete structural collapse must occur under extreme pressures.

Nonetheless, an evidence for structural changes of diamond under pressure can be found in literature. For example, deformation twinning on (111) planes was observed after plastic deformation of diamond at room temperature.¹⁶ The color of diamond anvils was reported to change from transparent to yellow, brown, and eventually red during pressurization to about 300 GPa.⁵ The red shift of the absorption edge is consistent with a gradual closing of the band gap. Pressure of about 560 GPa (Ref. 8) closed the optical win-

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dow of diamond. However, no evidence of irreversible phase transformations has been supplied.

It was demonstrated that combination of shear and hydrostatic stress leading to significant deformations is an efficient way to drive phase transformations in materials.^{6,12} It is known that indentation of materials with diamond indenters creates high shear plus hydrostatic stresses under the indenter. In indentation experiments, the shear stress is higher than in the case of uniaxial compression, and a much higher displacement of atoms can be reached using a sharp indenter. High shear stresses in indentation experiments and the possibility to vary the loading conditions can drive phase transformation, that cannot occur under hydrostatic stresses in high-pressure cells, or would occur at much higher pressures. Hardness tests using various indenters have been conducted on diamond.^{2,17-20} The values of up to 286 GPa have been reported at small loads on the (001) plane.¹⁹ Thus, very high stresses can be achieved by using the indentation technique. The latest study conducted using ultrahard fullerite tips² reports the values of 137 ± 6 GPa and 167 ± 5 GPa for (001) and (111) diamond faces, respectively. This demonstrates that a (111) diamond face is about 20% harder than (001) face and the stress under the indenter tip can approach the values predicted for the metallization of diamond. However, we are not aware of any previous observations of phase transformations in diamond caused by indentation. The possibility of phase transformation was considered as a possible failure mode for a spherical diamond indenter pressed against a diamond flat,²¹ but no evidence of transformation was found. Thus, a direct observation of phase changes of the material under or after loading was missing.

The analysis of the transformation zone in the case of indentation is complicated by its small size (several microns or less). Micro-Raman spectroscopy is probably the best method of investigation of this question as it allows the non-destructive phase analysis of materials to be conducted within seconds with a spatial resolution in the order of $1 \mu\text{m}$ on a nonprepared surface of the material or under the surface.^{22,23} Raman analysis can be conducted *in situ* as well, i.e., in transparent materials such as diamond, Raman studies can be done while conducting the indentation experiment.

Recently, we conducted Raman spectroscopy studies of indentations on several ceramics and semiconductors and demonstrated that the combination of indentation tests with micro-Raman spectroscopy provides a powerful and fast tool for monitoring pressure induced phase transformations, including metallization. For Si (Ref. 22) and Ge,²⁴ metastable phases in the hardness impressions were found. Since the observed phases can only form via metallic Si and Ge, these experiments produce direct evidence of the metallization of semiconductors under contact loading. *The objective of this work* was to verify experimentally whether irreversible phase transformations can occur in diamond under pressure. Here we report on our findings in the attempt to apply the combined indentation/micro-Raman method to diamond.

II. EXPERIMENT

The experiments were conducted using a LabRam II micro-Raman spectrometer (Dilor, France) equipped with

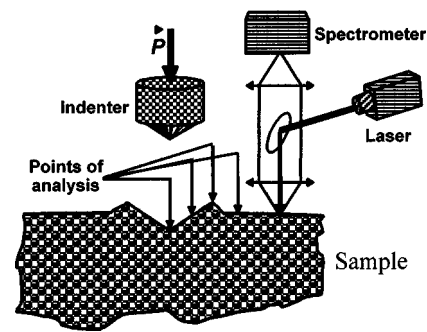


FIG. 1. Schematic of indentation/Raman experiments.

Ar⁺ (514.5 nm) and He-Ne (632.8 nm) lasers at the University of Tübingen and using a Raman microprobe Ramascope 2000 (Renishaw, UK) with a diode laser (780 nm) at the University of Illinois at Chicago. Additionally, a Fourier transform (FT)-Raman spectrometer (Nicolet, USA) at 1064 nm was used to investigate the dependence of band positions on the excitation wavelength and distinguish between the fluorescence and Raman bands. Raman analysis was conducted after indentation (Fig. 1) or scratching, and *in situ* during the indentation as described in Ref. 23. Fourier-transform infrared (FTIR) microspectroscopy (BioRad UMA 500 microscope) was used to supplement the Raman data. The minimum spot size for FTIR analysis was $10 \mu\text{m}$. Scanning electron microscopy and light microscopy were used for analysis of the indenters and impressions on the diamond surface. *In situ* monitoring of the penetration of a diamond indenter into diamond was conducted using light microscopy and long-focus objective lenses with the total magnification of $100\times$ to $500\times$.

III. MATERIALS

We used standard Vickers pyramidal indenters and diamond cones sharpened to a point (90 deg angle, Lunzer, USA) to produce indentations and scratches on the (111) surface of a large synthetic diamond single crystal (a yellow high-pressure diamond from Russia). Several other synthetic (0.1-karat crystals, General Electric, USA) and colorless natural diamonds of gem quality were studied to ensure that the obtained results can be generalized for all kinds of diamond. FTIR spectra of typical diamonds used in this research are shown in Fig. 2. Natural diamonds, including the indenters, were of *Ia* type. GE diamond crystals were of *Ib* type. The Russian octahedral crystal was of *II* type. This crystal was nitrogen free and had no metallic impurities. More than 20 diamond indenters of three different kinds were broken during indentation experiments with the purpose to obtain reproducible results, and their fractured tips have also been studied. Hundreds of Raman and FTIR spectra have been recorded to obtain statistically reliable data.

IV. RESULTS

In situ light microscopy observation of the indentation process demonstrated (Fig. 3) that diamond becomes non-transparent to visible light (white areas show the reflection of light) in the loaded area. This is in agreement with closing

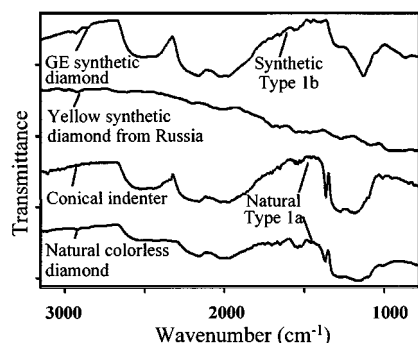


FIG. 2. FTIR absorption spectra of a conical indenter, colorless natural diamond, GE synthetic diamond and Russian synthetic diamond.

the optical window in a diamond anvil that was observed at much higher pressures under hydrostatic loading.⁸ Although microfracture and a double refraction of light can also be responsible for this optical effect, a visible deformation of the tip [Fig. 3(c)] is a good argument in favor of a high ductility of diamond under contact loading. The size of this reflecting area increases with pressure, and it noticeably deforms before the indenter collapses and pressure decreases at the same load. Only in certain spots, the reflecting phase remains after unloading, probably due to strong residual stresses and sluggish reverse transformation. It is important to note that only sufficiently sharp indenters produced the picture shown in Fig. 3. Otherwise, brittle fracture of the indenter was observed.

Optically, the indented or scratched surfaces of diamond were bright and yellowish under the microscope, compared to dark-yellow translucent synthetic single crystals or colorless and translucent diamond of the indenters. This distinct optical effect changes after several hours, probably due to the reverse phase transformation and stress relaxation, and dark and opaque spots appear on the surface of diamond.

Scanning electron microscopy demonstrated unusual features of the indentation site and indenter after tests (Fig. 4). Analysis of impressions [Figs. 4(a) and 4(b)] shows a significant amount of brittle fracture. In particular, cracks propagate along the edges of the pyramid [Fig. 4(b)]. However, the formation of ductile extrusions and small elevations in the same area along the edge of the Vickers impression is clearly visible. Thus, a significant morphological change of the surface occurred only in the area of the indentation, where the highest stress was applied [Fig. 4(a)]. The maxi-

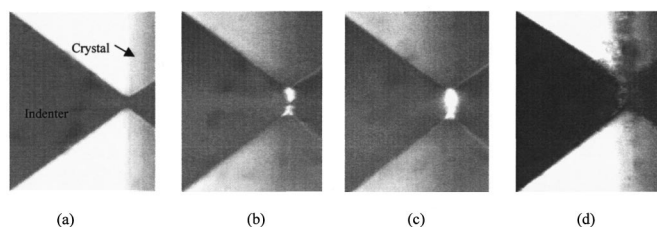


FIG. 3. Optical micrographs of the diamond cone in contact with the (111) surface of a synthetic diamond single crystal: (a) prior to loading, (b,c) increasing load from the minimum to maximum, (d) collapsed diamond tip.

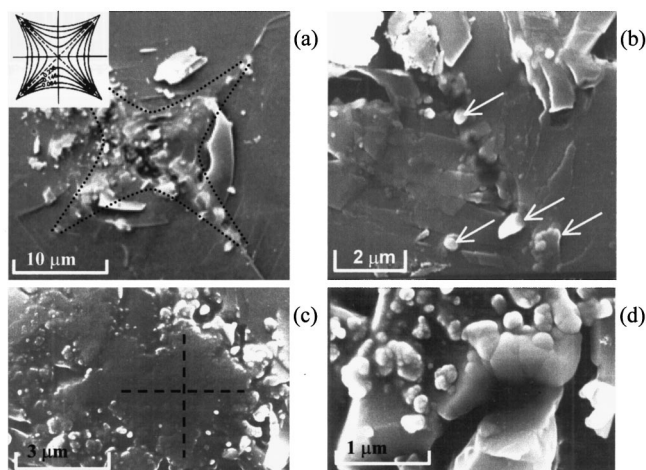


FIG. 4. Calculated stress isobars in a Vickers indentation (a), SEM micrographs of an impression in diamond flat (a,b), and a Vickers indenter (c,d) after a test under the load of ~ 30 N.

imum contact stresses occur in the center of the indentation and decrease according to the stress isobars.²⁵ Such stress reduction depends on the interfacial friction and on the amount of plastic deformation or phase transformation. A volume increase during decompression must be the reason for the observed surface changes. We assume that a new phase of carbon, which has a larger volume compared to diamond, was formed during decompression along the edge where the highest stress existed during indentation (Fig. 4). The tip of the indenter was flattened and rounded with no visible brittle fracture in the contact area [Fig. 4(c)]. A ring crack was sometimes observed above the contact area on the indenter. However, the flat top of the indenter [Fig. 4(c)] was surrounded by rounded particles [Fig. 4(a)] similar to that observed on the diamond flat [Fig. 4(b)]. Thus, similar transformations occurred in both the indenter and the crystal.

Spectroscopic investigations demonstrated dramatic broadening and weakening of the Raman band of diamond at 1332 cm^{-1} after indentation, as well as increasing background and appearance of several additional new bands in the Raman spectrum (Fig. 5). A band of amorphous diamond appeared at about $1100\text{--}1130\text{ cm}^{-1}$ [Fig. 5(a)].

This band has been observed in nanocrystalline diamond samples obtained by shock synthesis and chemical vapor deposition (CVD).²⁶ It is not to be confused with another strong and a broad band the position of which changes with the excitation wavelength from $\sim 1045\text{ cm}^{-1}$ at 1064 nm to $\sim 1110\text{ cm}^{-1}$ at 514.5 nm . The dependence on the excitation wavelength suggests that the latter band may be similar to the *D* band of graphite and can be considered as a similar disorder-induced band of diamond. Additionally to the band of cubic diamond, a band of hexagonal diamond (lonsdaleite) appears at $\sim 1315\text{ cm}^{-1}$ [Fig. 5(b)]. It is about an order of magnitude stronger than that registered on cut surfaces.²⁷ Since the Raman response of hexagonal diamond is many times smaller than that of cubic diamond, the presence of the strong peak of lonsdaleite suggests its significant content in the indentation region. Hexagonal diamond can be formed by deformation-induced twinning of the cubic diamond struc-

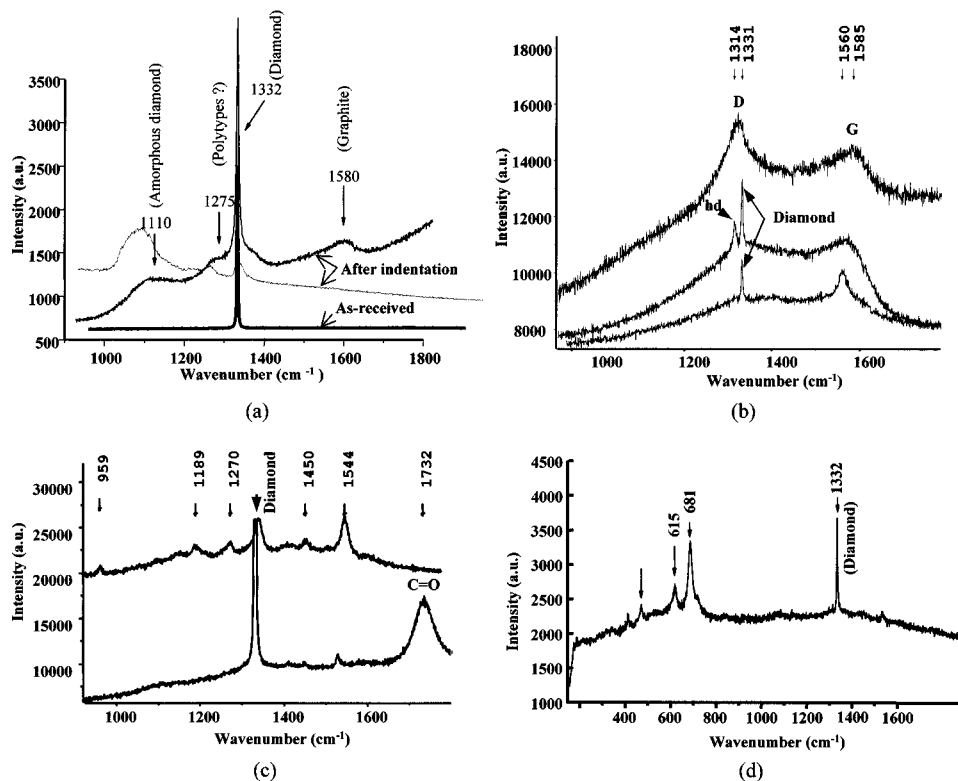


FIG. 5. (a) Typical Raman spectra from the (111) surface of a synthetic diamond single crystal, (b) from the tip of an indenter immediately after indentation tests on diamond, and (c) from aged indenter tips. Excitation wavelength is 632.8 nm.

ture. Twinning is the most elementary crystallographic change. Formation of hexagonal silicon from diamond-structure silicon by twinning mechanism has also been observed.²²

In spectra from the Vickers indentations, two strong and broad bands appear at ~ 1580 and ~ 1350 cm^{-1} (the positions for the 514.5 nm excitation wavelength) [Figs. 5(a) and 5(b)]. The former is referred to as *G* mode and assigned to C=C stretching vibrations E_{2g} of graphite.²⁷ The latter is referred to as *D* mode of graphite, and known to become active in small graphite crystallites. These bands confirm the formation of threefold-coordinated carbon during indentation of diamond. Both, well-crystallized graphite [a narrow *G* band in the lowest spectrum in Fig. 5(b)] and amorphous sp^2 carbon [upper spectra in Fig. 5(b)] were observed. In the extreme case, the signal from sp^2 carbon became strong enough to cover completely the diamond band [the upper spectrum in Fig. 5(b)]. Quantitative evaluation of the amount of the graphitic carbon is complicated due to the fact that the Raman cross section of graphite is approximately 50 times higher than that of crystalline diamond and hence sp^2 -bonded regions dominate the Raman spectra even at small contents of sp^2 carbon. However, comparison with amorphous carbon coatings on diamond single crystals shows that the film must be about 100-nm thick to become nontransparent for the laser light with these wavelengths. Probably amorphous or graphitic carbon which have a lower density compared to diamond, formed the protrusions along the impression edge (Fig. 4). Very high residual stresses that were found in graphitic carbon after unloading supply evidence that the transformation occurred within the volume of

the material, which is in agreement with the optical observations (Fig. 3), and not just on the surface of diamond. These stresses sometimes led to about 50–60 cm^{-1} upshifts of *D* and *G* bands. It is important to note that the highest shear stress can be achieved under surface and thus result in a phase transformation in the subsurface region.

Two sharp Raman bands at ~ 1450 and 1530 cm^{-1} were found in the region between the diamond and graphite bands [Fig. 5(c)]. These bands do not disappear after a week in vacuum. Therefore, we suggest that these bands occur due to a certain carbon structure. Bands with similar positions have been observed in Raman spectra of CVD diamond.²⁸ The additional feature observed on the Raman spectra at about 1265–1275 cm^{-1} [Fig. 5(a)] can be ascribed to hexagonal (6H) and rhombohedral (21R) diamond polytypes that exhibit several Raman bands in that range.²⁹ We observed a number of other weak bands that can be assigned to the 21R polytype and to cubic diamond with twins and stacking faults. A distinctive Raman spectrum with the strongest band at 680 cm^{-1} has been registered from several samples [Fig. 5(d)], although only the strongest band at 680 cm^{-1} was observed in most of the measurements. It cannot be ascribed to any of the known carbon phases. We cannot rule out the possibility of the formation of *bc8* or *r8* phases (Raman spectra unknown) similar to such phases of Si,²² or new phases built of both sp^3 - and sp^2 -bonded carbon atoms, as well as linear (sp^1) carbon chains. However, we never observed a Raman band of carbene that is expected at about 2100 cm^{-1} . Thus, the assignment for these bands is only preliminary. In any case, the presence of new Raman bands

is the most striking evidence of the phase transformation in diamond.

The additional important feature of Raman spectra of diamond after indentation is the presence of peaks due to mechanochemical reactions between the diamond surface and environment (ambient air). The most prominent feature was observed at 1730 cm^{-1} and can be ascribed to C=O stretching (carbonyl group on the surface of carbon). It appears during indentation and can be observed *in situ*, as well as after the indentation. The high intensity of this band may be due to surface enhanced Raman effect. A band with a similar position ($\sim 1750\text{ cm}^{-1}$) was also found on FTIR spectra from the indenter tip. Some other bands that can be ascribed to various CH vibrations have been registered on both Raman and FTIR spectra, but further discussion of the mechanochemical reactions is outside the scope of this paper.

V. DISCUSSION

The observed changes in the Raman spectra demonstrate the amorphization and graphitization of diamond and the presence of other diamond polytypes in the impressions. Transformations were observed for the first time on the surface of both the indented diamond and the indenter. However, these observations are in agreement with the previous research. Thorough analysis and reevaluation of the published data show that there may exist indirect evidence of the phase transformation in diamond under high shear stress and/or contact loading.

For example, plastic deformation of diamond was observed at about 150 GPa (Refs. 5 and 16) under hydrostatic pressure, and it was demonstrated in a number of indentation studies at room temperature.^{1,18} In some of the studies, a plateau on the temperature dependence of hardness of diamond was observed,²⁰ which contradicts to the hypothesis of plasticity due to thermally activated motion of dislocations.¹² Silicon and germanium, which experience the transition to the metallic β -Sn structure, have a very similar temperature dependence of hardness.²⁰ In this plateau region, the hardness level depends on the stress needed to initiate the transformation, which is hardly dependent on temperature.²⁰ Thus, the shape of the temperature dependence of diamond hardness supplies additional evidence for the phase transition.

Another important observation is that a diamond anvil fractured at above 300 GPa (Ref. 30) did not shatter into small pieces, as would be expected for a brittle material, but retained its original shape. This can also be explained by the formation of a ductile phase in cracks due to high shear stresses. Additionally, fracture of this diamond anvil resulted³⁰ in the formation of nanocrystalline graphite and an unknown phase producing a Raman band at 1491 cm^{-1} (we can assume a disordered network of sp^2 and sp^3 arranged carbon atoms). The formation of 2H hexagonal diamond (lonsdaleite) has been reported on the cut surfaces (shear again) of diamond crystals.²⁷ Finally, a significant increase in electrical resistivity under contact loading has been reported for diamond by several researchers.¹⁸ Although a disbelief

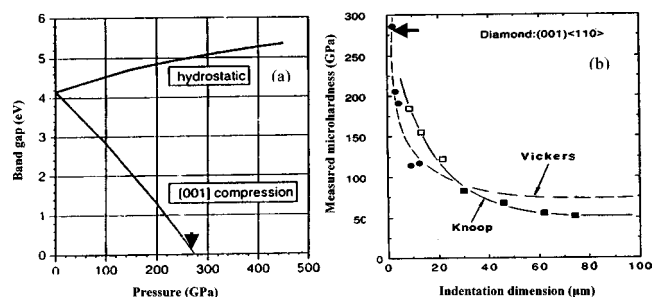


FIG. 6. (a) Calculated band gaps for diamond as a function of applied pressure for the case of hydrostatic compression and for compression along the fourfold axis of diamond (combined shear and hydrostatic) (see Ref. 10). (b) The experimental Knoop and Vickers microhardness of diamond on the (001) (see Ref. 17). Metallization pressures are marked by arrows.

has been expressed regarding the conductivity measurements on diamond, similar data obtained by the same research group on Si (Ref. 20) is widely used for illustration of its metallization. The observed composition of the indented region is in good agreement with that of silicon and germanium,^{20,22} and with the theoretical predictions for diamond.¹³

The above facts are in agreement with the hypothesis that diamond experiences a phase transition upon contact loading. The question is remaining, whether the appearance of the new phases after decompression supplies evidence for transition to metallic carbon or another high-pressure phase. Graphite and amorphous graphitic carbon were probably formed upon unloading. Their formation upon loading would contradict to the Le Chatelier principle, because of a larger specific volume of graphite compared to diamond. Although the analogy to Si and Ge would suggest that the pass through the metallic phase is the most probable one, conventional pressurization experiments have hitherto shown no sign of it. Some work has been done to predict metastable phases that may be formed during decompression of metallic carbon. A body-centered cubic $bc8$ structure that is stable in the case of Si (Ref. 20) was predicted to be unstable with respect to either diamond or $r8$ at any given pressure.⁹ Other calculations show that metallic high-coordinated forms of carbon should be mechanically unstable against spontaneous transformation to the cubic diamond structure, and should decay to threefold-coordinated graphitic structures and to the hexagonal form of diamond. These predictions are in agreement with our experiments.

Comparison of the calculated pressures, that are necessary to close the band gap in diamond under the simultaneous effect of shear and hydrostatic stress with the plot of the diamond hardness vs indent dimension (Fig. 6), shows that at small loads on the initial stage of indentation the stress can be sufficient to close the band gap. Thus, if the theoretical prediction claiming that the metallization of diamond can occur only under combined influence of shear and compression is true, the indentation experiments may lead to metallization. The observed shift of graphite bands corresponds to residual compressive stresses of about 10–15 GPa (upshift of about $5\text{ cm}^{-1}/\text{GPa}$ has been reported).³¹ A graphite layer on the surface cannot support stresses of this mag-

nitude, thus excluding the possible explanation of the presence of threefold coordinated carbon by surface graphitization. Calculations based on the maximum shift of the diamond band (upshift of 13 cm^{-1}) predict the residual compressive stress of 8 GPa. ($1.693 \text{ cm}^{-1}/\text{GPa}^{14}$). We measured stress values of up to 3 GPa in Si indentations, and consequently higher stresses have been measured in indentations on diamond. A microfractured diamond layer in the impression cannot support such stresses, if we assume that the formation of nanocrystalline diamond occurs due to brittle fracture of the indentation region. Thus, the explanation for the observed effects can be given by assuming the transformation of diamond into a high-pressure phase and a subsequent reverse phase transformations under decompression. A possible mechanism for this behavior has been suggested by Gilman.¹² Shear stress causes one axis of the diamond lattice to increase, and the other to decrease. Therefore, band gap midpoints shift in opposite directions. When the strain becomes large enough to close the gap, the bonding electrons can delocalize into the antibonding states. In other words, the activation energy for the transformation becomes zero, and it can proceed athermally.

Plastic flow of diamond, plastic character of scratches (no microcracking or brittle fracture), the preservation of the shape of diamond crystals fractured under high pressures, the parallels in the indentation behavior of all Group IV semiconductors with plateaus on the temperature dependence of hardness, an increased electrical conductivity and optical reflectivity of stressed zones, as well as presence of plastic extrusions in the impressions point to the phase transformation under combined shear and hydrostatic compression stresses and confirm the likelihood of a metallic phase as a precursor for the postindentation phases.

Understanding of the contact-induced transformation in diamond may help to develop more efficient methods of cutting and polishing of diamond.³² The formation of graphite, that was observed after tribological tests on diamond,^{33–35} is in agreement with our observations of graphitic carbon after indentation. Transformation of diamond into softer phases under contact loading can be used to accelerate machining of this extremely hard material.

VI. CONCLUSIONS

We have demonstrated that a phase transformation in diamond occurs under indentation. Upon unloading, the material transforms to nanocrystalline or amorphous diamond, noncubic diamond polytypes including lonsdaleite, graphitic carbon, and possibly new phases of carbon. The absence of this transformation under hydrostatic load suggests that the phase transformation of diamond can be, as predicted by Gilman,¹² a deformation induced, not just “pressure” induced phenomenon. Scratching of the diamond surface with diamond resulted in similar transformations as observed under an indenter. Thus, common wear processes may be seen in a new light: it is potentially possible to cut and polish diamond by diamond, because of its transformation to a ductile phase as an intermediate. Diamond is not as stable as it has been assumed, and everyone can easily drive it to the

limit. No super-pressure cells are required—just a combination of compression with shear. Anyone can perform this test at home, for example, by scratching one diamond ring with a sharp edge of another diamond.

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- ¹V. D. Blank, S. G. Buga, N. R. Serebryannaya, G. A. Dubitsky, R. H. Bagramov, M. Yu. Popov, V. M. Prokhorov, and S. A. Sulzanov, *Appl. Phys. A: Mater. Sci. Process.* **64**, 247 (1997).
- ²M. T. Yin and M. L. Cohen, *Phys. Rev. Lett.* **50**, 2006 (1983).
- ³R. Biswas, R. M. Martin, R. J. Needs, and O. H. Nielsen, *Phys. Rev. B* **30**, 3210 (1984).
- ⁴C. Mailhot and A. K. McMahan, *Phys. Rev. B* **44**, 11578 (1991).
- ⁵H. K. Mao and R. J. Hemley, *Nature (London)* **351**, 721 (1991).
- ⁶J. J. Gilman, *J. Mater. Res.* **7**, 535 (1992).
- ⁷J. A. Van Vechten, *Phys. Rev. B* **7**, 1479 (1973).
- ⁸A. L. Ruoff, H. Luo, and Y. K. Vohra, *J. Appl. Phys.* **69**, 6413 (1991).
- ⁹S. J. Clark, G. J. Ackland, and J. Crain, *Phys. Rev. B* **52**, 15035 (1995).
- ¹⁰M. P. Surh, S. G. Louie, and M. L. Cohen, *Phys. Rev. B* **45**, 8239 (1992).
- ¹¹P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, *Solid State Commun.* **84**, 731 (1992).
- ¹²J. J. Gilman, *Czech. J. Phys.* **45**, 913 (1995).
- ¹³O. H. Nielsen, *Phys. Rev. B* **34**, 5808 (1986).
- ¹⁴Y. K. Vohra, T. S. McCauley, and S. S. Vagarali, in *Advances in New Diamond Science and Technology*, edited by S. Saito *et al.* (MYU, Tokyo, 1994), pp. 391–394.
- ¹⁵J. J. Gilman, Pacific Coast Meeting of the American Ceramic Society, San Francisco, October 1997.
- ¹⁶H. K. Mao, P. M. Bell, K. J. Duna, R. M. Chrenko, and R. C. DeVries, *Rev. Sci. Instrum.* **50**, 1002 (1979).
- ¹⁷H. Li and R. C. Bradt, *Diamond Relat. Mater.* **1**, 1161 (1992).
- ¹⁸V. A. Borisenko, A. K. Butylenko, O. N. Grigor'ev, Yu. V. Milman, and V. I. Trefilov, in *Synthetic Diamonds—a Key to Technical Progress*, (Naukova Dumka, 1977), Vol. 1, pp. 53–59.
- ¹⁹N. V. Novikov and S. N. Dub, *J. Hard Mater.* **2**, 1 (1991).
- ²⁰I. V. Gridneva, Y. V. Milman, and V. I. Trefilov, *Phys. Status Solidi A* **9**, 177 (1972).
- ²¹A. L. Ruoff and J. Wanagel, *Science* **198**, 1037 (1977).
- ²²A. Kailer, Y. G. Gogotsi, and K. G. Nickel, *J. Appl. Phys.* **81**, 3057 (1997).
- ²³Y. G. Gogotsi, A. Kailer, and K. G. Nickel, *Materials Research Innovations* **1**, 3 (1997).
- ²⁴A. Kailer, Y. G. Gogotsi, and K. G. Nickel, in *Proceedings of the Fifth International Conference on Advanced Materials Processes and Applications, Maastricht, The Netherlands, April 1997* (The Netherlands Society, Maastricht, 1997), Vol. 4, pp. 171–174.
- ²⁵B. A. Galanov, *Sov. Appl. Mech.* **18**, 711 (1983).
- ²⁶R. J. Nemanich, J. T. Glass, G. Lukovsky, and R. E. Shroder, *J. Vac. Sci. Technol. A* **6**, 1783 (1988).
- ²⁷D. S. Knight and W. B. White, *J. Mater. Res.* **4**, 385 (1989).
- ²⁸B. Zhang and S. Chen, *J. Appl. Phys.* **79**, 7241 (1996).
- ²⁹K. E. Spear, A. W. Phelps, and W. B. White, *J. Mater. Res.* **5**, 2277 (1990).
- ³⁰Y. K. Vohra and T. S. McCauley, *Diamond Relat. Mater.* **3**, 1087 (1993).
- ³¹O. Van der Biest, T. Laoui, J. Vleugels, K. Sumanasiri, H. Mohrbacher, B. Blanbain, and J. P. Celis, in *Corrosion of Advanced Ceramics*, edited by K. G. Nickel (Kluwer, Dordrecht, 1994), p. 385–397.
- ³²F. M. van Bouwelen, L. M. Brown, and J. E. Field, *Ind. Diam. Review* **57**, 21 (1997).
- ³³A. Erdemir, M. Halter, G. R. Fenske, C. Zuiker, R. Csenisits, A. R. Krauss, and D. M. Gruen, *Tribol. Trans.* **40**, 667 (1997).
- ³⁴A. Erdemir, C. Bindal, G. R. Fenske, C. Zuiker, R. Csenisits, A. R. Krauss, and D. M. Gruen, *Diamond Films Technol.* **6**, 31 (1996).
- ³⁵Y. Liu and E. I. Meletis, *J. Mater. Sci.* **32**, 3491 (1997).