Amorphization and Conductivity of Silicon and Germanium Induced by Indentation

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We report the observation, by transmission electron microscopy, that single-crystal silicon and germanium are converted to an amorphous state at room temperature directly under both Vickers and Knoop indentations. The effect is seen for crystal orientations of [001], [011], and [111], and with applied loads between 0.1 and 0.5 N. We also observe that the materials become electrically conducting under load and that the process is reversible on subsequent unloading and reloading. Furthermore, the transformed phase is found to make Ohmic contact to the surrounding, untransformed, semiconductor.

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It has long been recognized that extremely high (hydrostatic and deviatoric) stresses are generated when a sharp indenter is loaded onto a flat surface of a solid. The exact details of the stress fields depend on the shape of the indenter and on the constitutive equations describing flow in the particular material, a subject that has now become the province of the theories of the hardness of materials and its measurement by indentation methods.[1] The existence of high hydrostatic stress has led investigators to suggest that the indentation experiment could be used to study high-pressure phase transformations, although it is recognized that the large deviatoric stresses make calculations difficult. Indeed Eremenko and Nikitenko,[2] and more recently Pirouz, Chaim, and Samuels,[3] report the formation of the hexagonal polymorph (Si IV) when silicon is indented at temperatures of 450–700 °C. Similarly, there is the suggestion by Gerk and Tabor[4] that silicon, germanium, and diamond may undergo a semiconductor-to-metal transition, as the pressures under an indenter are similar to those predicted for such a transition. We report here our findings of a rather different phase transformation in both silicon and germanium, the transition, through an electrically conducting state under load, to a metastable amorphous form after unloading, directly under an indentation. Such a crystalline-to-amorphous transition has not been observed in conventional high-pressure experiments.

As part of our studies of cracks in brittle solids we have prepared samples containing arrays of small indentations together with their attendant cracks for transmission electron microscopy. Single crystals, mechanically ground and polished to a thickness of ≃100 μm, were patterned with arrays of regularly spaced indentations with typically 100 indentations in a 3-mm-diam disk. The indentation impressions, produced by pyramidal diamond indenters having either the Vickers (148° included edge angle) or Knoop (asymmetric pyramid with included edge angles of 130° and 172.5°) configuration, were formed with loads in the range 0.1 and 0.5 N. In all cases the constant loading and unloading rates were 16.67 N s^{-1}. With the top, indented, surface protected by a glass cover slip, the samples were then ion thinned from the back until suitably thin for viewing in the transmission electron microscope.

Figure 1 is a transmission electron micrograph of a 0.5-N Vickers indentation impression in a [011] silicon surface and its immediate vicinity imaged in a multibeam diffraction condition. The indentation is conspicu-

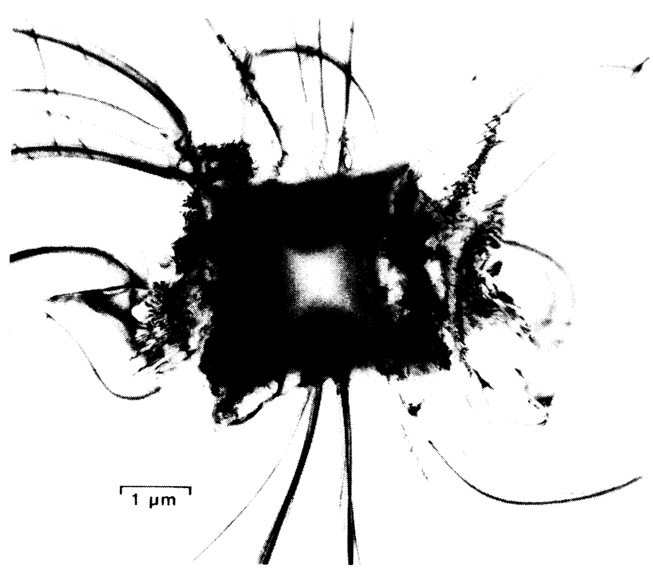

FIG. 1. Bright-field transmission electron micrograph of an indented region in a single crystal of Si. Note the lack of penetration of the bend contours into the grey, central region of the indentation.

ous for three reasons in addition to its shape: (1) The center is grey and devoid of crystallographic contrast, (2) the periphery is marked by contrast indicative of extreme (plastic) deformation, and (3) the "bend" contours characteristic of the surrounding single crystal abruptly end at the boundary of the indentation and do not continue into the center region. On tilting of the sample with respect to the electron beam (to change the operating diffraction conditions), the "bend" contours shift and the deformation contrast alters as to be expected, but the noncrystallographic contrast in the central region remains unaltered. Confirmation of the noncrystalline nature of the central region comes from the selected-area diffraction pattern (Fig. 2) showing the characteristic pattern of an amorphous material. No evidence for elements other than silicon in the indented region was found by either x-ray microanalysis or electron energy-loss spectroscopy. Neither was any indication found for the existence within the indented region of remnants of any high-pressure, crystalline forms of silicon.

Similar observations have been made for loads of 0.1, 0.25, and 0.5 N with both the Vickers and Knoop indenters for [001]-, [011]-, and [111]-oriented silicon and germanium. On subsequent annealing of the indented samples, the amorphous regions could be crystallized at temperatures above about 550 °C to form fine-grained, diamond cubic structure material. When the same indentation experiment was performed on other crystalline solids, sapphire, magnesium oxide, and gallium arsenide, no such amorphization was observed. As with other plastically deforming materials, the indented region was heavily dislocated.

As the high-pressure polymorphs of silicon and germanium are known to be either semimetals or metallic, a series of indentation experiments, similar to that introduced by Gridneva, Milman, and Trefilov,[5] were carried out to test whether the material became electrically conducting while under load. The test samples consisted of a linear array of rectangular, 10-μm-wide metal pads, separated by a series of spacings ranging from 0.5 through 5 μm, deposited onto polished and chemically cleaned wafers. The metal pads were produced by a standard photolithographic method with vacuum evaporation of first a $\simeq$10-nm layer of chromium (for enhanced adhesion) followed by a $\simeq$150-nm layer of gold. Both n- and p-type silicon wafers of $\sim$10 Ω cm resistivity were used.

The experiment was simply to monitor the current, I, as a function of voltage applied to the pads, V, as the

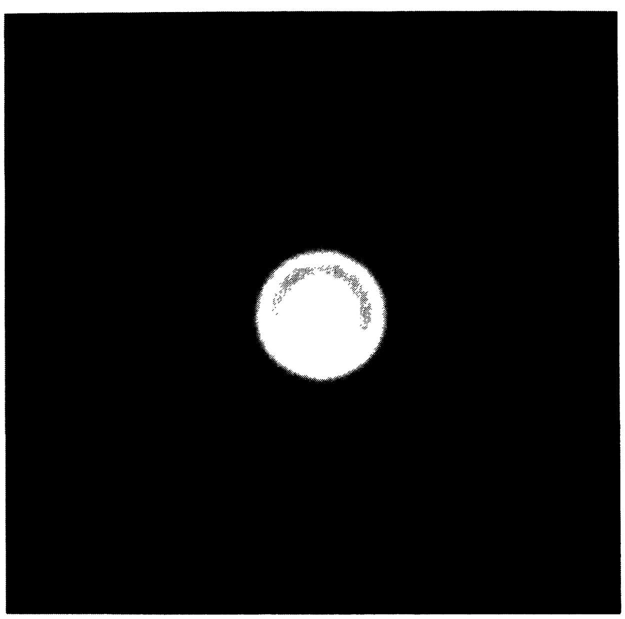

FIG. 2. Selected-area electron diffraction pattern taken from the central region of the indentation in Fig. 1. The concentric rings are characteristic of an amorphous structure.

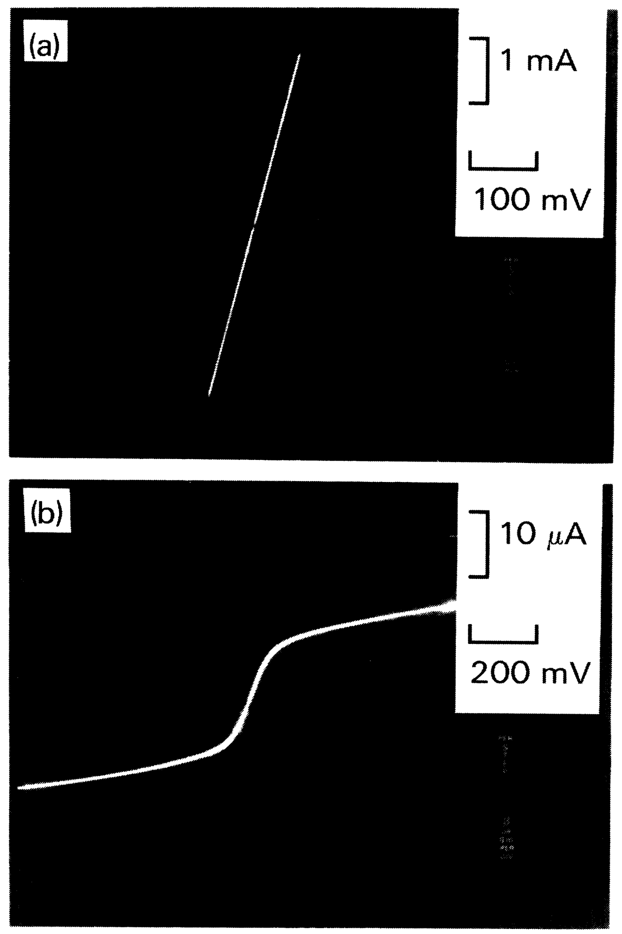

FIG. 3. Electrical conductivity behavior for Si between the electrodes described in the text (a) during indentation contact (under load) and (b) before (and after) indentation contact. The change in scale indicates an increase in conduction of 2 orders of magnitude between (b) and (a).

diamond indenter was loaded into the surface of the silicon in the gaps between adjacent pads. The result of one such experiment, when the indentation size was approximately equal to the width of the gap, is reproduced in Fig. 3. Before loading the electrical characteristic is of two back-to-back Schottky diodes corresponding to the Schottky barriers formed by the two silicon/metal-pad contacts. During the indentation loading, the behavior changed abruptly to that of a conductor making Ohmic contact to both electrodes, when the indented region spanned the two pads. On removal of the load, and even though there was a permanent deformation in the silicon surface, the electrical behavior reverted to that of the high-resistance, back-to-back Schottky diode characteristic. When the diamond was reloaded into the same location, the high conductivity reappeared, a behavior that was reversible on subsequent loadings and unloadings, and over a load range of 0.1–10 N. The transition to an electrically conducting state is a direct confirmation of Gridneva, Milman, and Trefilov's interpretation of their observation of a change in resistance in silicon on indentation.[5] No effect on the $I(V)$ characteristic was observed when the diamond indenter was loaded into the bare silicon adjacent to one or the other of the pads but not in the gap. When the indentation was made directly through one or the other of the pads, the electrical character of the contact of that electrode to the underlying silicon changed from rectifying to Ohmic, producing the $I(V)$ characteristic of a single Schottky diode. As in the indented gap, the Ohmic character of the indented electrode disappeared on removal of the load and was reestablished on reloading. The Ohmic behavior was independent of whether the doping was of n or p type, and the same findings were also established for n-type and p-type germanium. Similarly, when crystalline silicon was replaced by amorphous silicon (prepared by homogeneous chemical-vapor deposition technique) it too became reversibly, electrically conducting under load. This is consistent with the results on pressure-induced semiconductor-to-metal transitions in amorphous silicon and germanium reported by Shimomura *et al.*[6] However, in addition to the results of Ref. 6, we find that the conducting material makes Ohmic contact with the electrodes. No corresponding change in conductivity was observed when the experiment was repeated on gallium arsenide and magnesium oxide single crystals.

Measurement of the interfacial resistance between the transformed material and the bulk semiconductor was difficult to establish. As the size of the indentations was on the order of 1 μm, the measured resistance was dominated by the spreading resistance in the semiconductor, and in the case of silicon, the total measured resistance of several thousand ohms corresponds closely to that calculated for the spreading resistance. Our ignoring the resistance of the unindented (forward-biased) electrode leads us to a generous upper bound of $10^4\ \Omega\ \mathrm{cm}^{-2}$ for the interfacial resistance. The metallization to germanium resulted in more leakage conduction, leading to a less dramatic change in resistance on indentation. There was also enhanced reverse leakage current following indentation. However, the upper limit of the interfacial resistance is of the same order as that of the silicon.

By simultaneous monitoring of both the conductivity of the samples and the load during indentation loading and unloading, it was observed that the transformation to the electrically conducting form of silicon occurs instantaneously as the load is applied. As the load is increased the current increases, indicating that the volume of transformed material increases with load. However, there are indications that the supported area (and hence transformed volume) does not scale with the load in this small-load regime as it usually does at much higher loads. At large loads (>10 N) the measured hardness of silicon is $\simeq 8.5$ GPa, but it increases to $\simeq 16$ GPa at the small loads considered here. This compares with the reported transformation pressure to the β-Sn polymorph (Si II) of 11.3–12.5 GPa,[7] suggesting that the pressures generated in the initial stages of indentation contact may easily be enough to drive the transformation. The continued transformation of material at increased loads, but lower pressures, is attributed to the large deviatoric stresses around the indentation and the consequent generation of dislocations which we believe nucleate the transformation. This is consistent with remarks in the literature that the transformation pressure is dependent on the degree of deviatoric loading and that the transition can occur at pressures as low as 8 GPa [7,8] when uniaxial pressure is applied along the [111] direction.[8]

Two possible explanations are suggested for the formation of the amorphous form of silicon (and germanium) observed after indentation, one a structural frustration kinetic argument and the other direct pressure-induced equilibrium amorphization. At the relatively rapid unloading rates employed (the unloading occurs in $\simeq 30$ ms) and the nonhydrostatic constraint imposed on the transformed region, it is proposed that the high-pressure, crystalline form cannot transform back fast enough, and without complications, that the amorphous phase forms metastably. In support of this notion is the fact that the reverse β-Sn (sixfold coordination) to diamond cubic (fourfold) transformation (Si II to Si I) is known from hydrostatic experiments to be a sluggish one.[7-9] Similarly, there are reports[9] that a bcc polymorph of silicon (Si III) is formed as a metastable phase on unloading of hydrostatic experiments. Likewise, the tetragonal polymorph of germanium (Ge III) is reported[10] to form as a metastable phase on unloading. The second possible explanation is that during indentation loading the local pressure exceeds the metastable extension of the liquidus curve on the T-P phase diagram and that the amorphous phase is formed directly on loading and persists on unloading because of insufficient thermal energy to allow rearrangement back to the diamond cubic form. This is plausible since the liquid form of silicon (and germanium) is denser than that of the diamond cubic crystalline form, so that in the Clapeyron equation the derivative $dT_m(P)/dP$ is negative. This slope[11] has a value at low pressures of about -58 K/GPa, which, extrapolated linearly to room temperature, suggests that a pressure of approximately 24 GPa would be required for such a direct conversion. Although this is considerably higher than the previously accepted hardness of silicon ($\simeq 8.5$ GPa), it is only about 30% higher than the recently observed hardnesses reported[12] for silicon measured with microhardness techniques ($\simeq 17$ GPa at dimensions of 50–500 nm), and that extrapolated from hardness at low indentation loads (18.5 GPa at 1.7 μm). If, as is more likely, the liquidus extrapolation actually should be concave downwards, the discrepancy between the room-temperature extrapolation and the more recent hardness values is even less. Thus, direct pressure-induced amorphization under the indentation cannot be ruled out on the basis of our presently available experimental data. This is also the case for the germanium amorphization. It is interesting to note that no evidence was found for either amorphization or transition to an electrically conducting state in GaAs although a phase transition has been reported[13] to occur at a pressure of $\simeq 17$ GPa. However, the accepted hardness of GaAs is considerably lower than that of silicon.

The picture that emerges from these experiments is that as the indenter is loaded into the surface, the stress builds up until the local pressure exceeds that to transform the silicon to one or the other of its electrically conducting high-pressure phases. On unloading, the applied pressure is released (but because of the elastic constraint of the surrounding, untransformed material, not to zero effective pressure) and the high-pressure phase converts to a metastable, noncrystalline semiconductor. On subsequent reloading, the amorphous region is pressurized back to a denser form that is electrically conducting, and the process is structurally and electrically reversible.

Finally, it is interesting to speculate on the possible role such indentation-induced amorphization and conductivity may have played in the operation of the original point-contact diodes and transistors.

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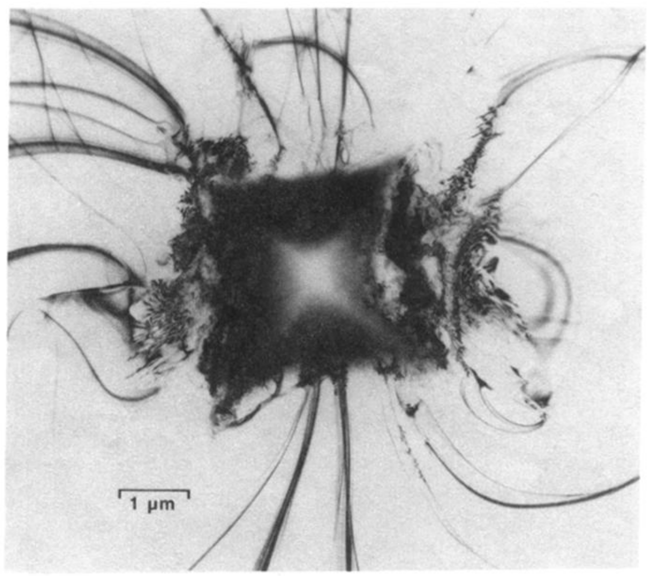

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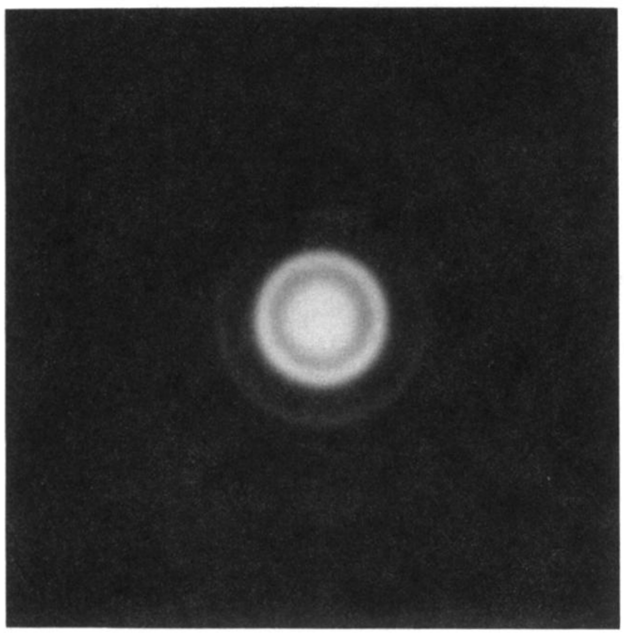

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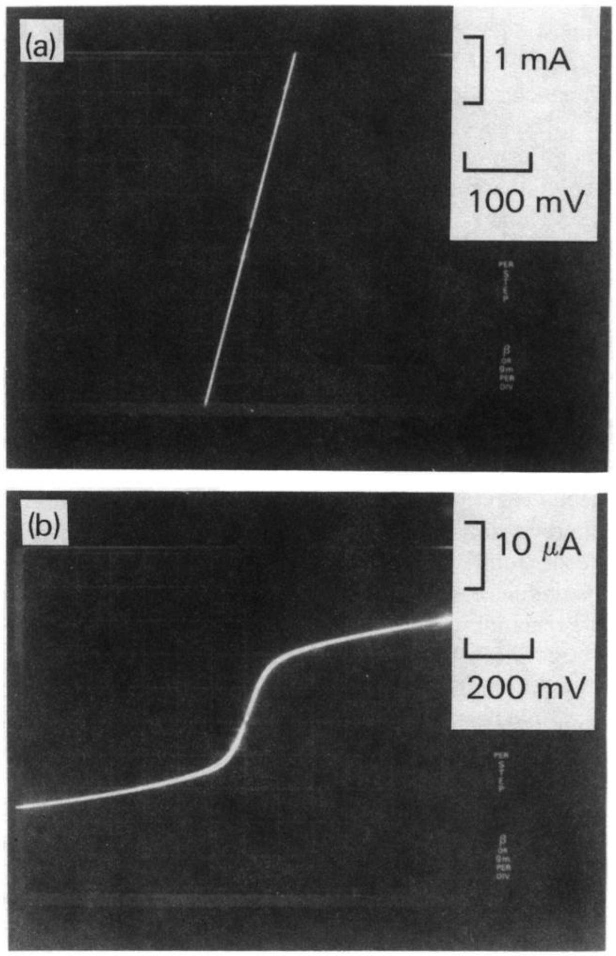

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