DOI: 10.1017/S1431927605501715
Microsc Microanal 11(Suppl 2), 2005

Nanoindentation-Induced Phase Transformations in Ge Studied by Electron Microscopy and Raman Spectroscopy

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The sequences of hydrostatic pressure-induced phase transformations in Si and Ge have been established in diamond anvil studies [1]. At sufficient pressure the normal diamond-cubic structure Si-I/Ge-I transforms to the metallic β-tin structure; upon unloading, several metastable phases can form depending on the maximum load and/or unloading rate. In the case of Ge, the metastable phases are Ge-III(ST12) or Ge-IV(BC8). Since microstructural investigations of Si indents have revealed metastable crystalline phases, it was expected that Ge indents could demonstrate similar phenomena. However, there is no prior evidence of phase transformations from indentation load-displacement (P-h) curves or electron microscopy. In this study, nanoindentations were made on undoped (100) Ge at room temperature with triangular pyramidal indenters with centerline-to-face angles of 35° (cube-corner) and 65° (Berkovich) at loads of 10, 50 and 80 mN and a loading/unloading rate of 5mN/s. The indents were examined by SEM, micro-Raman analyses and TEM of cross-sections prepared by dual-beam FIB milling.

SEM and TEM images of indents made at 10mN maximum load revealed that the residual impression is deeper for the sharp 35° indent (Figure 1). For both indents, the bend contour patterns indicate a high degree of residual stress with significant lattice rotation next to the transformed zone. The 35° indent exhibits material plastically extruded out of the indent in a fashion similar to that reported for Si [2,3]. Raman spectra were obtained from the 50-mN 35° indents with the use of a Dilor XY800 Microprobe at periods of 1, 20 and 44 h after the indentation test (Figure 2a). Besides broad bands around 150 and 270 cm^{-1} attributed to amorphous Ge (a-Ge), narrow peaks at 205, 230, 250 and 264 cm^{-1} were observed soon after the indentation but decay with elapsed time, as seen in the 20 and 44-h spectra. The peaks were tentatively assigned to Ge-IV (BC8) based on their similarity to those for Si-III (BC8) and to ones observed during diamond anvil experiments on Ge. A micro-Raman map of this 50mN indent created with the 205 cm^{-1} Ge-IV peak (Figure 2b) shows significant signal only within the indent, especially at the indenter edge locations. Mapping with the a-Ge peak (Figure 2c) indicates the extruded material has a high concentration of a-Ge. Frequency-shift micro-Raman maps were also made for the primary Ge-I peak at ~300 cm^{-1} to characterize residual stress (Figure 3). The maps indicate compressive residual stress around the 65° indent and, surprisingly, tensile stress around the 35° indent. The extruded material is expected to be stress-free, so the apparent tensile stress may in fact indicate the presence of nanocrystalline Ge-I possibly formed by laser heating in a similar fashion to nanocrystals that are induced by the electron beam to form in cross-sectional TEM samples of Si indents [3]. Additional cross-sectional TEM characterization and in-situ Raman observations are planned to further understand the deformation mechanisms for indented Ge [4].

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[4] This research was sponsored by the NSF under grant number DMR-0203552 (SW, JJ, GMP), and at the ORNL SHaRE User Facility (MJL, JB, GMP) by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC. The authors also thank Dr. T. Tsui at Texas Instruments, Dallas for helping with FIB sample preparation.

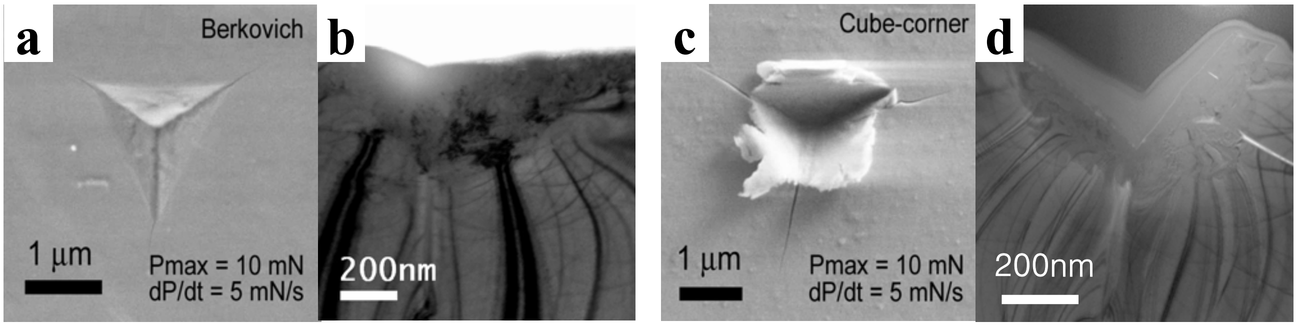

FIG. 1. (a,c) SEM and (b,d) TEM cross-sections of indents from (a,b) 65° Berkovich indenter and (c,d) 35° cube-corner indenter. (P_{max} = 10 mN, Rate = 5 mN/s)

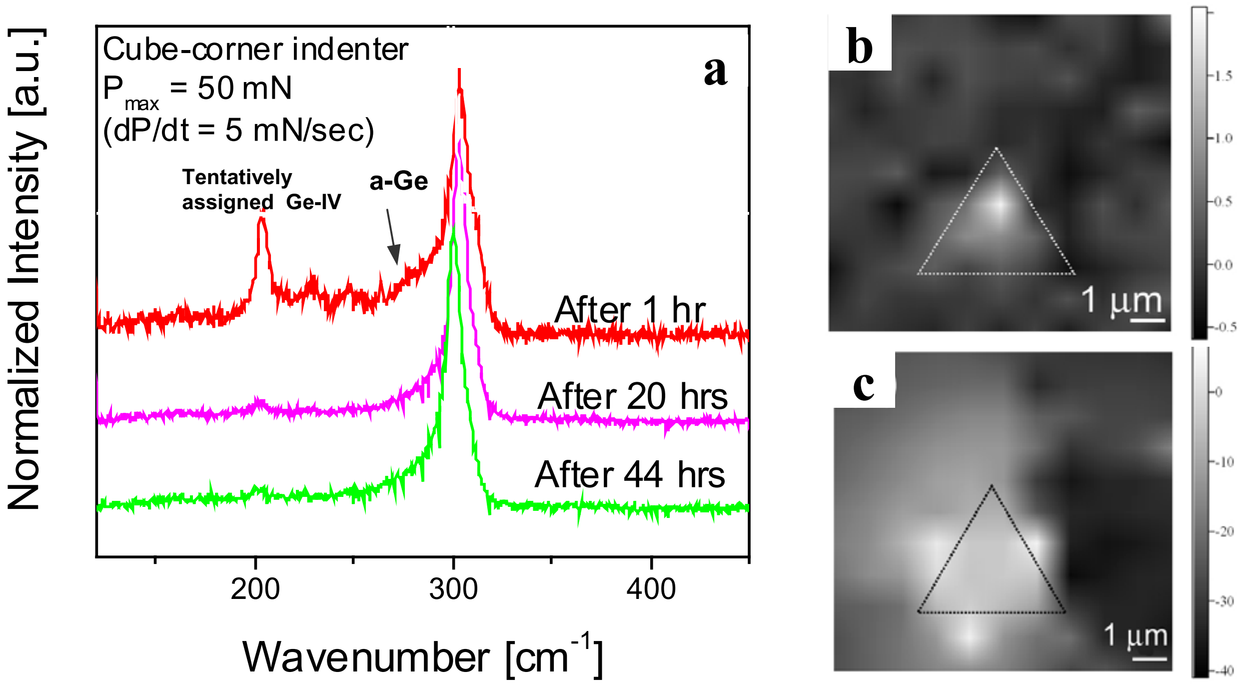

FIG. 2. Raman characterization of Ge cube-corner indent made at 5 mN/s to P_{max}=50 mN (a) Raman spectra recorded 1, 20 and 44 h after indentation (b) Raman map at 205 cm^{-1} tentatively assigned to Ge-IV (c) Raman map indicating amorphous Ge.

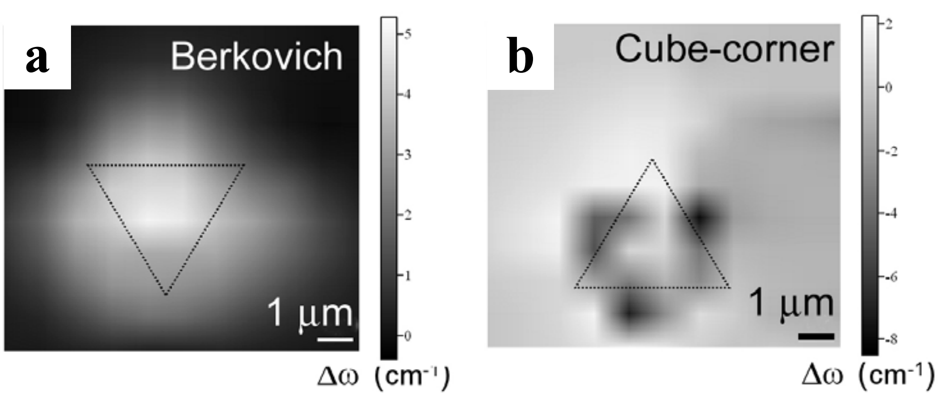

FIG. 3. Raman peak-shift maps of (a) 65° Berkovich and (b) 35° cube-corner indentations. (P_{max} = 50 mN, Rate = 5 mN/s)