Contact induced crystallization of amorphous layers

Silicon and germanium are of considerable technological and scientific interest. When subjected to sufficiently high hydrostatic and non-hydrostatic pressures these materials undergo structural phase transitions. As regards the amorphous films of silicon and germanium, the amorphous to crystalline phases transition was reported recently with induced changes in physical properties [1-3].

Transmission electron microscopy (TEM) images of amorphous germanium or silicon films within the residual indentations allow the detection and imaging of the transition events (Figs. 1). When indenting with a sharp tip (Berkovich) with loads of up to 5 mN, no phase transformation or crystallization is observed for a 0.3 µm thick a-Ge film on GaAs substrate as revealed by the continuous ring on the diffraction pattern. When the indenter load is increased to 10 mN, a mixture of face centred cubic (f.c.c) germanium (i.e. Ge-I) and amorphous germanium is found. The dark-field image of this indentation (Fig. 1d) shows that close to the indenter tip brighter regions that correspond to the transformed crystalline face-centred-cubic phase of Ge. As the indenter load is increased to 50 mN, in addition to the amorphous and cubic phases, the primitive tetragonal phase Ge-III is also seen in the electron diffraction pattern (Fig. 1e). The dark-field TEM image of this indentation again shows that most of the crystalline phases are concentrated close to the indentation tip (Fig. 1f).

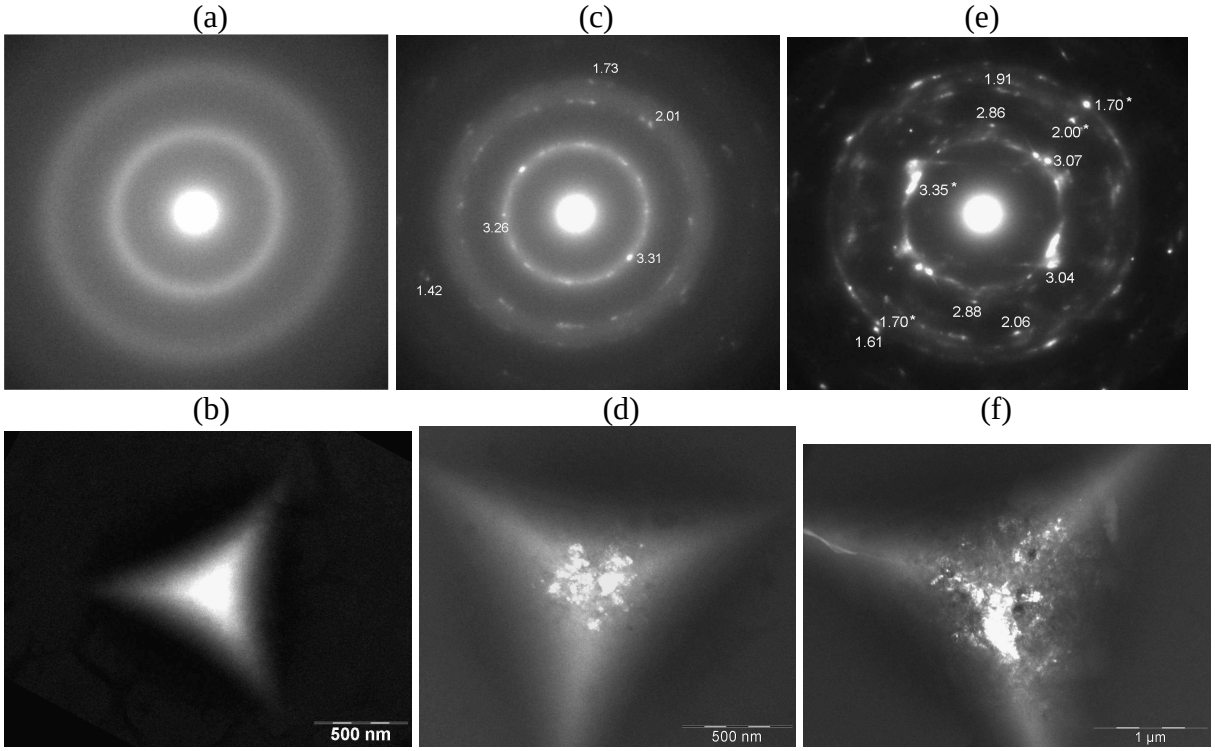

Figure 1 : Electron diffraction patterns (a,c,e), bright field (b) and dark field (d,f) images of indent sites realised in a 0.3µm thick amorphous Ge film deposited on GaAs. Indents under 5 mN show no evidence of phase transformation (a,b), the film remains perfectly amorphous. When the maximum load is increased to 10 mN (c,d) crystallites appear with the Ge-I cubic phase. For a 50 mN load, Ge-I and Ge-III (tetragonal or ST-12) phases are detected [2].

The related properties are modified as revealed by Raman spectra of the pristine 0.3 µm *a*-Ge film deposited on the GaAs substrate and that of the material from within a recovered 53 mN Vickers indentation in the film. Whereas the pristine *a*-Ge shows broad

bands centred at 165, 275 and 550 cm^{-1}, there are several sharp peaks for the material from within the residual indentation (Fig. 2). The most intense and sharpest peak is at 301 cm^{-1}, which is almost the same frequency as that of a pristine Ge (100) single crystal while the sharpest and the strongest Raman peak of a pristine single crystal of Ge (100) was found to be at 300.7 cm^{-1} (not shown). Other peaks from the indented *a*-Ge film are at 168.4, 219, 277.3 and 291.3 cm^{-1}. The peak at 291.3 cm^{-1} is likely to be that due to the GaAs substrate, whose main peak is at 292 cm^{-1} (not shown). However, the peak at 272.3 cm^{-1} could possibly be due to the tetragonal Ge (i.e. Ge-III), although, as suggested by Olijynk and Jephcoat [4], the Ge-III phase is unstable when irradiated with red laser light. The broad band centred at 168.4 cm^{-1}, which corresponds to the *a*-Ge phase, is still present. On the other hand, the broad band at 550 cm^{-1} is very much reduced in its intensity.

Within the plastically deformed zone around the indenter tip, the hydrostatic component of the stress is about 80% of the indentation hardness value. Thus, the hydrostatic component of the stress within the plastically deformed a-Ge will be just over 6 GPa when, Shimomura et al [5] using high-pressure cell experiments on a-Ge, showed that for pressures greater than 6 GPa a-Ge in the semiconductor state first transforms to the a-Ge metallic state, which then gradually transforms into the Ge-I crystalline phase. Shimomura et al [5] also showed that the transition to the Ge-II metallic phase occurs for pressures greater than 10 GPa. However, it is also known that in the presence of shear stresses and shear strains the component of the hydrostatic pressure required to cause a phase transition to the metallic Ge-II phase becomes lower. This phenomenon would cause indentation-induced crystallization and phase transition of a-Ge, requiring both a component of high hydrostatic pressure as well as high plastic strains. In fact, under 10 mN, although the indentation hardness is about 8 GPa (well below the 10 GPa threshold), the conditions seem suitable for causing the transition from the amorphous germanium to amorphous metal, which then transforms to the Ge-I phase with time. At indenter loads greater than 50 mN plastic strains further increase in the film, leading to a Ge-I to Ge-II (i.e. β-Sn structure) transition during indenter loading. On removal of the indenter, the Ge-II phase will then transform to the Ge-III phase.

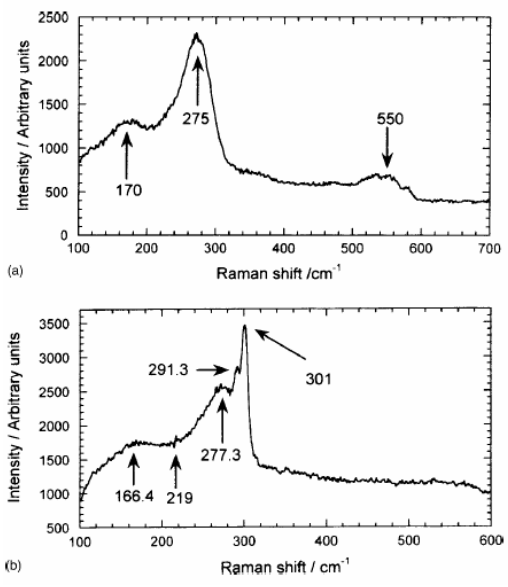

Figure 2 : Raman spectra of (a) the pristine 0.3 μm thick amorphous germanium film and (b) a 53 mN residual Vickers diamond indentation in the amorphous Ge film. Note that the indentation causes a dramatic change in the Raman spectrum. The sharp peak at 301 cm^{-1} is the same as that of a pristine Ge-I single crystal (not shown) [2].

Further Reading

[1] Khayyat et al. J. Phys. D : Appl. Phys. 36, 2003, 1300

[2] Patriarche et al. J. Appl. Phys. 96, 2004, 1464

[3] Haberl et al. Appl. Phys. Lett. 85, 2004, 5559

[4] Olijnyk et al. Phys. Stat. Sol. 211, 1999, 413

[5] Shimomura et al. Phil. Mag. 29, 1973, 547