Metastable amorphous-crystalline transition in Group IVa elements

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The phase diagrams of the elemental semiconductors silicon and germanium exhibit intriguing irreversibility upon room temperature (de-)compression. This irreversibility allows for exotic metastable structures that can be recovered to ambient conditions. Many of these structures are kinetically stable at ambient conditions and exhibit altered band gap characteristics over the standard diamond-cubic phase of Si and Ge. This makes them highly interesting for future applications in semiconductor devices or for solar power conversion [1]. The major challenge for any exploitation has however, been the pressures required for their synthesis: typically diamond-cubic Si and Ge are converted to metallic structures upon compression, which then on decompression form the desired exotic phases. This requires pressures of ~12 GPa or higher, which is technologically not useful. Here we use amorphous Si (a-Si) and Ge (a-Ge) as precursor material since their inherent disorder, structural flexibility and spread in bond-angles allow for better access to local minima in the energy landscape of their pressure-temperature phase diagram. Past high pressure studies on a-Si and a-Ge using diamond anvil cells (DAC) have largely reported amorphous-amorphous [2,3] transitions or retardation in metatllization [4], clearly not behaviours conducive to lower pressure synthesis of metastable crystalline phases. In contrast, however, past point loading works on entirely pure, c-Si and a-Ge have found transitions to the desirable exotic structures [5,6]. Therefore, we conducted high pressure DAC studies using a-Si and a-Ge material as pure as possible, e.g. made through pressure-quenching in the case of a-Si and through molecular-beam-epitaxy in the case of a-Ge. Upon compression to ~8 GPa, both amorphous materials commence to crystallize, including crystallization into the desirable metastable r8 structure as observed by synchrotron X-ray diffraction (see Fig. 1). Further studies using Raman spectroscopy and synthesis in large-volume neutron DACs will be presented, which further the understanding of the complex phase diagrams of Si and Ge with their strong metastability.

References:

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Figure 1. In situ synchrotron X-ray diffraction data of a-Si and a-Ge compressed in a DAC to ~9 GPa. Diffraction clearly reveals pressure-induced crystallization into the metastable r8 structure in addition to a smaller component of the metallic β-Sn phase.