Crystallography of silicon element: stable and metastable crystalline forms

Alexandre Courac (Kurakevych)

IMPMC - Sorbonne University, Paris, France;

alexandre.courac@sorbonne-universite.fr

HP research on Si started more than 50 years ago and since then several allotropes, displaying a wide variety of physical properties, have been reported. The narrow-bandgap semiconductorSi-III with BC8 structure (originally believed to be semimetal) can be obtained from the high-pressure tetragonal metallic phase, Si-II, formed during compression of common silicon according to Si-I→Si-II. Such a transformation during decompression can be either direct, Si-II→Si-III, or with an intermediate step Si-II→Si-XII→SiIII. Our in situ studies of pure Si in oxygen-free environment indicated that in the absence of pressure medium, Si-I remains metastable at least up to ~14 GPa, while the pressure medium allows reducing the onset pressure of transformation to ~10 GPa. Upon heating Si-III at ambient pressure a hexagonal structure, named Si-IV, was observed. This allotrope was believed to be a structural analogue of the hexagonal diamond found in meteorites (called also lonsdaleite) with the 2H polytypestructure. Calculations have predicted several hexagonal polytypes of Si and of other Group-IV elements to be metastable, such as 2H (AB), 4H (ABCB) and 6H (ABCACB). Exhaustive structural analysis, combining fine-powder X-ray and electron diffraction, afforded resolution of the crystal structure. We demonstrate that hexagonal Si obtained by high-pressure synthesis correspond to Si-4H polytype (ABCB stacking), in contrast with Si-2H (AB stacking) proposed previously. The sequence of transformations Si-III→Si-IV(4H)→Si-IV(6H) has been observed in situ by powder X-ray diffraction. This result agrees with prior calculations that predicted a higher stability of the 4H form over 2H form. Further physical characterization, combining experimental data and ab-initio calculations, have shown a good agreement with the established structure. Strong photoluminescence emission was observed in the visible region, for which we foresee optimistic perspectives for the use of this material in Si-based photovoltaics. The study of silicon allotropic transformation in Na-Si and K-Si systems at high pressure led to new open-framework allotrope of Si, Si24 with zeolite structure and promising optoelectronic properties.

Keywords: silicon, direct bandgap material, high pressure, metastability, open framework structure