MS27-2-1 High-pressure high-temperature crystallography of silicon #MS27-2-1

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Abstract

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 semiconductor Si-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 Sibased photovoltaics. The study of silicon allotropic transformation in Na-Si and K-Si systems at high pressure, high temperature conditions indicated new interesting results on the second-order character of Si-II-Si-XI transformation and will be discussed in the presentation. The impact of the second order character on the topology of the pressuretemperature phase diagram of silicon will be analyzed.

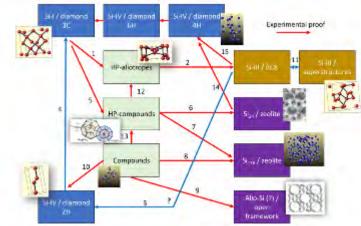
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Silicon allotropes by HPHT synthesis