Revisiting transitions in silicon under high pressure: a new look at the stability of the Imma, Cmce, and other compressed phases

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On account of its abundance and recognized technological importance, silicon (Si) is a material that has been (and still is) extensively studied. In particular, the sequence of pressure-driven transitions undergone by Si in a hydrostatic or quasi-hydrostatic environment is experimentally well established up to about 250 GPa. From the ambient pressure Si-I phase (cubic diamond) into the metallic Si-II phase with the ß-Sn─type structure at around 12 GPa, and then into a sequence of metallic phases with ever increasing coordinations: the intermediate Si-XI phase (Imma, a distortion of ß-Sn which is only observed in a rather small pressure range); Si-V (simple hexagonal, sh) at *ca*. 15 GPa; Si-VI (Cmce, an intermediate phase itself, whose structure remained for many years elusive [1]) at *ca*. 38 GPa; Si-VII (hexagonal close-packed, hcp) at *ca*. 42 GPa; and, finally (in what regards to experiments) Si-X (face-centred cubic, fcc), above *ca*. 80 GPa and persisting up to the highest pressures reached in laboratory, of 250 GPa. Other phases persisting metastably at low pressures have been observed upon decompression from the high-pressure phases, or have been obtained by nanoindentation, or produced in the laboratory using high-pressure synthesis methods. Yet other phases have been theoretically proposed on the basis of first-principles calculations.

A number of the high-pressure phases in the established phase diagram of Si are structurally related, which invites their simultaneous theoretical study in terms of group/subgroup relations and the evolution of their structural parameters within some common description, together with the analysis of their local as well as relative stability on an enlarged energy landscape. On the other hand, given the advances in instrumentation witnessed in the field of high-pressures, and those envisaged for the next decades, there will probably be soon an urge to extend the experimental studies of silicon to even larger pressures, of the TPa order, for which a more thorough understanding of the mechanisms of the transitions in the sub-TPa regime would be desirable and could moreover provide guidance.

In this contribution we revisit the theoretical study of Si in the sub-TPa regime mainly focusing on the role of the intermediate phases like Imma and Cmce. Cmce, in particular, has not been as thoroughly studied as other phases of the phase diagram of Si, and there have even been contrasting theoretical claims regarding its stability. We address this issue in our survey. We have worked within the first-principles framework of the density functional theory (DFT) using the Quantum-ESPRESSO computational package [2] as well as the Vienna *ab initio* simulation package (VASP) [3] to explore the relevant energy landscape pertinent to the studied phases, and in particular the two main groups of high-pressure transition sequences ß-Sn─Imma─sh and sh─Cmce─hcp─fcc. We focus on the local dynamical and mechanical stability (or lack thereof) of the different equilibrium states under changing pressure conditions as well as their mutual relationship. We further provide a picture of the changes in the bonding through the changes of the electronic localization as the compression proceeds.

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