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Comment

New hopes for allotropes

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Recent theoretical and experimental discoveries suggest improved photovoltaic performance might be realized via novel crystalline modifications of elemental silicon

The particular arrangement adopted by the atoms in a crystalline solid has a profound impact on the material's mechanical, electronic, optical, and thermal properties. This well known fact applies not only to crystalline compounds, but also to some elements that can exist as different crystalline allotropes. Carbon is a familiar example: the distinctive atomic arrangements and corresponding chemical bonding in graphite and in diamond result in very different macroscopic appearance (opaque vs. transparent) and mechanical properties (easily cleaved vs. superhard) for these two materials. Although graphite is the most thermodynamically stable allotrope of carbon at room temperature and atmospheric pressure, once formed the activation barrier for the transformation of diamond into graphite is sufficiently large that the metastable diamond phase can persist under ambient conditions, for all practical purposes, indefinitely.

Carbon readily adopts sp^2 or sp^3 bonding arrangements in the graphite and diamond crystal structures, respectively. In contrast, silicon, carbon's downstairs neighbor in the periodic table, usually prefers the tetrahedral bonding arrangement that it adopts in the diamond structured ground state commonly known as α-Si (Pearson symbol *cF*8; structure **a** in Fig. 1). Nevertheless, hundreds of distinct crystalline polymorphs that accommodate each silicon atom in a four-bonded geometry are conceivable, with varying levels of deviation in bond lengths, bond angles, and atomic density in comparison to α-Si [1–6]. Since each of these distinct forms of silicon should have correspondingly distinct properties, the possibility of manipulating the properties of silicon by changing its crystalline structure is enticing. This is particularly true given silicon's central importance in semiconductor and photovoltaic technologies, its mature industrial processing methods, and the high cost of device fabrication imposed by α-silicon's indirect electronic band gap.

Alternative polymorphs of silicon (other than α-Si and amorphous Si) were first discovered in high-pressure experiments more than fifty years ago [2]. A recent resurgence of interest in silicon allotropes in the past two decades has been driven in large part by the availability of first principles approaches for calculation of electronic structure. In particular, density functional theory (DFT) studies revealed intriguing possibilities for modifying the electronic and optical properties of silicon by changing the crystal structure [3,4]. However, given the exceedingly large phase space of possible structures and lack of a priori knowledge of energetic stability, how does one efficiently predict low-energy modifications that not only have promising electronic properties, but also have the best chances of being synthesized in the lab? Picking out the low-energy metastable polymorphs from the large number of possible phases without calculating the ground state energy of every possible structure is seemingly nontrivial. Indeed, not only can such an exhaustive evaluation of all conceivable structures be impractical, it also does not guarantee that a promising low-energy structure will not be overlooked.

Fortunately, new computational approaches for crystal structure prediction are making headway in these challenges. These methods are now being applied to identify low-energy crystalline allotropes of group 14 elements that may motivate the efforts of experimentalists to try to synthesize these materials in the lab. Examples include particle swarm optimization [5] and minima hopping [1] methods, which combine DFT and/or molecular dynamics calculations with intelligent algorithms to efficiently predict low-energy crystal structures. Once potential structures are identified, their corresponding electronic structure can be more carefully examined. Such approaches have recently led to the prediction of a number of hypothetical low-energy allotropes of silicon that may possess promising features in their electronic

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structure for light absorption, including a wide range of direct or quasi-direct band gaps from 0.4 to 1.5 eV with dipole allowed optical transitions (examples include *mP*8, structure **b** in Fig. 1, and *hp*12, structure **c** in Fig. 1) [1,5]. Several of these polymorphs are predicted to have lower formation energies than other experimentally known phases, suggesting these new allotropes too might be obtained as metastable phases.

Of course, even when a promising low-energy allotrope is predicted by theory, identifying an effective synthetic route to prepare the material in the lab is no easy task. On the one hand, just as diamond is a high-pressure (and high-temperature) phase of carbon, silicon undergoes a series of structural phase transitions as the external pressure is increased, and some high-pressure polymorphs can be recovered to ambient conditions as metastable phases upon decompression [2]. In recent years, the experimentalist's synthetic toolkit has significantly expanded with the advent of a variety of non-equilibrium approaches that allow access to metastable allotropes. Thermal decomposition of Na_4Si_4 to Na_xSi_{136} followed by thermal evaporation of Na under high vacuum and subsequent density separation was used to isolate the cage-like clathrate allotrope Si_{136} for the first time (*cF*136, structure **e** in Fig. 1) [6]. In contrast, chemical oxidation of $Na_{12}Ge_{17}$ was used to prepare the Ge analogue, Ge_{136} [7]. Very recently, a new open-framework modification Si_{24} (*oC*24, structure **d** in Fig. 1) was obtained by thermal evaporation of Na from the recently discovered high-pressure binary phase, Na_4Si_{24} [8]. The Si_{24} modification is a particularly exciting result: not only was this material reported to be thermally stable to above 450 °C, it was also reported to have a direct band gap of ~1.3 eV. The first solution-phase preparation of a silicon allotrope (high-pressure "BC8" modification, *cI*16) by colloidal synthesis [9] constitutes another synthetic advance in this area, as the proof of principle that colloidal synthesis can be used to prepare a metastable allotrope of silicon opens a door to new opportunities to prepare related materials of technological interest via solution chemistry.

Given the accelerated pace of progress in the past three years, more important theoretical and experimental results on silicon allotropes can be expected in the near future. Alkali metal-silicon precursor-based methods have been particularly fruitful in the synthesis of these materials, deserving further exploration and development. Of course, the true promise of direct band gap silicon allotropes lies in thin film devices, a processing challenge that has yet to be addressed for these emerging materials. Indeed, all preparation routes employed to synthesize crystalline silicon allotropes at ambient pressure so far result in microcrystalline or nanocrystalline products. While only time will tell if these materials can actually revolutionize photovoltaic technology, there are plenty opportunities in this area for interesting science to be done in the meantime.

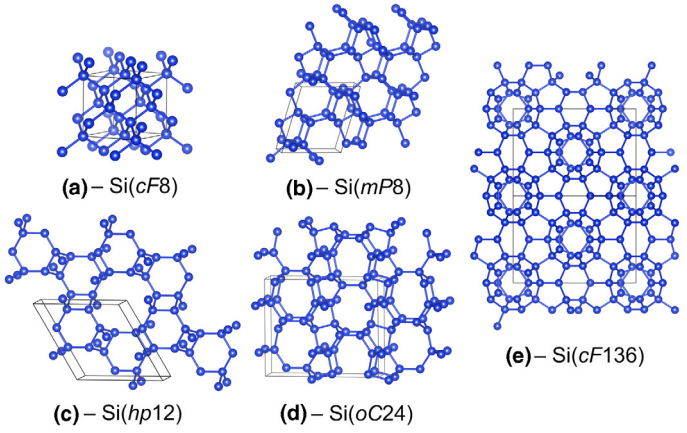

FIG. 1
Crystal structures [10] of several known (**a**, **d**, and **e**) and hypothetical (**b** and **c**) allotropes of the element silicon.

Further reading

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