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Silicon allotropy and chemistry at extreme conditions

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Abstract

Silicon is essential for today's electronics because of its ability to show various electronic behaviors that are relevant to numerous fields of cutting-edge applications. It is not a pollutant and, therefore, an ideal candidate to replace the actual materials in photovoltaics, such as compounds based on the arsenic and heavy metals. However, conventional diamond-like Si is an indirect gap semiconductor and cannot absorb solar photons directly. This justifies intensive theoretical and experimental research for the direct-bandgap forms of silicon. Our recent high-pressure studies of the chemical interaction and phase transformations in the Na-Si system, revealed a number of interesting routes to new and known silicon compounds and allotropes. The pressure-temperature range of their formation is suitable for large-volume synthesis and future industrial scaling. The variety of properties observed (e.g. quasi-direct bandgap of open-framework allotrope Si_{24}) allows us to suggest future applications.

Keywords: silicon allotropes, high pressure

1. Introduction

The application of high pressure for materials synthesis, both in industry and science, have been traditionally limited to superhard materials [1,2], e.g. diamond [3], cubic boron nitride cBN [4], diamond-forming carbon-metal systems [5,6], nano-cBN [7], nano-diamond [8], cBC_5 [9], γ-B_{28} [10], $B_{13}N_2$ [11], B_6O [12,13], high-pressure B_2O_3

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[14,15]. Our recent results allowed us to overcome this "restriction" and to give a new dimension for design of high-pressure materials [16,17] at pressures accessible for large-volume industrial scaling.

Silicon is essential for today's electronics, in particular in optoelectronics. For this reason many attempts have been made to design a silicon allotrope with direct gap that could efficiently absorb and emit light. Ideal material should have optically allowed direct bandgap [18], close direct & indirect gaps of absolute values from 1 to 2 eV in order to have highest efficiency of cells, and high light absorption in thin films [19,20]. Three principal methodologies may be employed for this, i.e. (1) nanostructuring, (2) low-dimensional materials (silicene, thin films) and (3) new crystal structures, both dense and open-framework [21-24]. The last approach has been explored mainly by *ab initio* metadynamical studies. In this paper our recent achievements in synthesis of silicon allotropes will be described. They imply new chemical routes that combine both soft chemistry and high-pressure techniques.

In this paper the recent achievements in synthesis and bandgap engineering of silicon allotropes will be described. They imply new chemical routes that combine both soft chemistry and various high-pressure techniques.

2. Synthesis of dense tetrahedrally-coordinated silicon allotropes

Three dense silicon phases are believed to be stable/metastable below 10 GPa (industrial domain) [25,26]. The crystal forms that exist below 16 GPa have tetrahedral coordination. Fig. 1a shows the relative transformations at pressures below 12 GPa. Only three phases can be obtained/recovered at ambient conditions. All represented transformations (Fig. 1a) have been reproduced in our experiments, both *ex situ* (high-pressure room-temperature synthesis of Si-III in Paris-Edinburgh cell using boron-epoxy gasket and sintered diamond anvils) and *in situ* (observation of Si-IV during heating of Si-III in high-temperature cell for conventional diffractometry). However, room-temperature synthesis is not efficient, since the pressures required for structural changes in silicon are higher than industrially accessible.
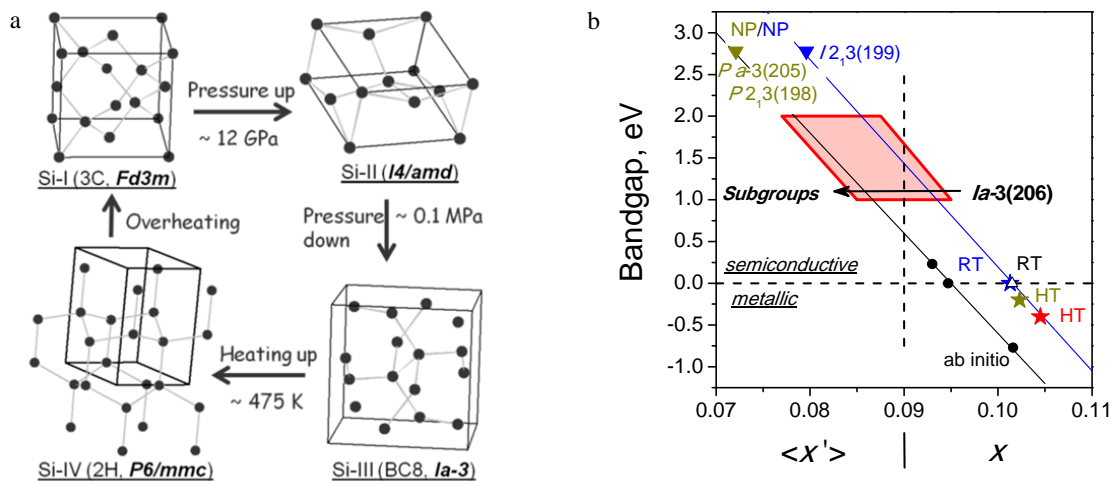

Fig. 1. (a) Direct phase transformations between dense Si forms. (b) Bandgap of Si-III (BC8) as a function of order parameter, atomic coordinate (x,x,x). Solid and dashed lines are given as guides for eyes. Symbols show *ab initio* predictions (●) and experimental values (our data - ★, our refinement of data from [32] - ▼, [25] Δ). HT and RT indicate the high-temperature and room-temperature syntheses respectively.

In the case of diamond silicon (Si-I) the bandgap engineering by nanostructuring [27] is possible. However, the most interesting is exotic Si-III (BC8) phase. In a pure polycrystalline state (with strained lattice) it can be obtained by decompression from above 15 GPa without heating [28] or from pressures above 10 GPa with heating [29]. It is a semimetallic allotrope, whose gap was predicted to open by (1) the change of structural order parameter, the *x* of Wyckoff position 16*c* with (x,x,x) unit cell coordinates in *Ia*-3 space group (No 206) [30], or (2) the grainsize of Si-

III clusters [31]. Moreover, very recently the nanoparticles of BC8 cubic silicon obtained by a mean of colloidal chemistry were claimed in ref. [32]. The bandgap measured by absorption in visible region was found to be of ~2.8 eV [32], slightly higher than predicted by *ab initio* calculations for the same grainsize [31].

Our results on Na-Si interactions at HPHT conditions using the large-volume multianvil press in conjunction with synchrotron radiation at the ID06 beamline of the ESRF, have indicated the possibility of obtaining pure polycrystalline strain-free Si-III grains up to 500 µm at pressures as low as 9.5 GPa in the Na-Si system. At lower pressure this phase was also often observed (at least down to 7 GPa in Na-Si system), but pure grains cannot be easily extracted. In a number of samples obtained in our experiments by variation of chemical conditions, Rietveld refinement give x from 0.101 to 0.105. The lowest x corresponds to the sample obtained at room temperature (~13 GPa in our experiments using Paris-Edinburgh cell at IMPMC, 40% yield of Si-III). At the same time the nanoparticles [32], the PXRD pattern may be adjusted to original cubic *Ia*-3 space group using structureless full-profile LeBail analysis, however the pattern shows quite different intensities from theoretical ones. Our attempts to adjust the intensities to experimental one using Rietveld analysis, led to the value of $<x>$ as low as of ~0.088. However, not all the intensities are in reasonable agreements, moreover, very short Si-Si bonds appear (17% shorter as compared to expected ~2.4 Å). To avoid these discrepancies, we tried to refine the structure using cubic subgroups of *Ia*-3 space group. The obtained mean values of $x's$ are between 0.070 and 0.088, representing the analogue of x in the original structure, now for 2 or 4 sublattices of Si with more reasonable interatomic distances. More detailed study of this crystallographic point is required. Anyway, one can easily see the possibility of vary x by the methods of synthesis. So, the grainsize may be considered a crucial point for impact on order parameter x (or $<x>$), crystal structure stability (similar to nano polymorphism of TiO_2 [33] or stability of nanostructured high-pressure form of ZnO [34,35]) and, mostly important, on the bandgap.

Fig. 1b shows the relative position in the order parameter x - bandgap E_g coordinates of Si-III nanoparticles [32] vs polycrystalline materials synthesized at high-pressure by direct transformation & in chemical systems (Na-Si in our case). A solid line connects the *ab initio* points [30] (black circles); although the "extrapolated values" may be quite different from true *ab initio* values, the general tendency of gap opening with decreasing x can be clearly seen. The experimentally known values are represented by colored triangles (data of other authors, solid triangles show our refinement using structural models described above) and stars (our data). One can see that, although displaced, the experimental and *ab initio* dependencies of bandgap on x (or $<x>$) have very similar slopes (here we can note that usually DFT calculations often lead to underestimated band gap values, which give even more relevance to the tendency shown on Fig. 1b). So, now semimetallic polycrystalline and semiconductive wide-bandgap semiconductive nanoparticles are known for Si-III. The use of high-pressure chemical reactions seem to be quite promising to fulfill the "gap" of materials with intermediate (direct) bandgaps (especially close to 1-2 eV) by playing the grainsize through the kinetics dependent on *p-T*-time regime and chemical environments.

3. Synthesis of open-framework silicon allotropes

As it has been already mentioned above, high-pressure is a newly proposed route to the new and known compounds in the Na-Si system [17,36] (Zintl phase Na_4Si_4 and intermetallic clathrates Na_8Si_{46}, $Na_{24+x}Si_{136}$ and Na_4Si_{24}); while the pressure-temperature range of their formation (3-8 GPa) is suitable for large-volume synthesis and future industrial scaling. Moreover, sodium removal at T > 700 K from the common $Na_{24-x}Si_{136}$ [37] or its high-pressure form $Na_{24+x}Si_{136}$ leads to the "clathrate" allotrope Si_{136} (Fig. 2b) with quasidirect bandgap [38] of ~2 eV [39]. In our high-temperature experiments we observed the sodium escape from the structure within 1h (at ~775 K). Unfortunately, the direct electron transitions at Γ point are not allowed by the cubic symmetry and this silicon form is not a good candidate for photovoltaic applications.

In a similar way, sodium removal from Na_4Si_{24} [17] by heating in vacuum leads to a new allotrope of silicon with zeolite structure, orthorhombic o-Si_{24} [16] (Fig. 2b). In this case the required temperature is remarkably lower, ~400 K. The zeolite silicon framework deform during this process (+6% along *a*-axis and -3% along *b*- and *c*-axes), but, in general, the silicon framework remains the same (zeolite CAS). The quasi-direct bandgap of ~1.35 eV (Fig. 2b) with allowed direct electronic transitions due to orthorhombic symmetry (*Cmcm* space group) permits consideration of this material for future photovoltaic applications.
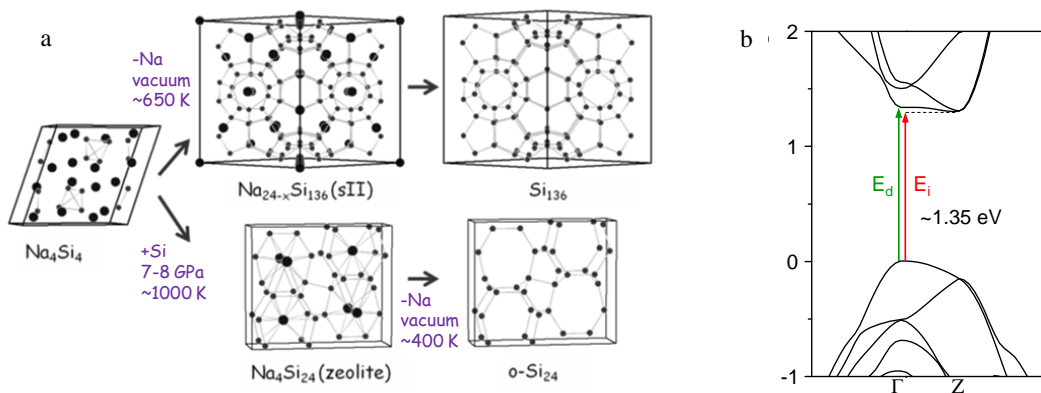
Fig. 2. (a) Chemical routes to clathrate silicon allotropes (small ball represent silicon atoms, large balls - sodium). Top: Synthesis below 0.1 MPa (in vacuum) [37], bottom: combined synthesis at ~8 GPa (Na_4Si_4+Si) and in vacuum [16,17]. (b) The direct and indirect band gaps are close to 1.35 eV [16], the ideal theoretical value for maximal solar cell efficiency.

As for the possible bandgap engineering of o-Si_{24}, it is interesting to note that under uniaxial strain along the *c*-axis the gap is expected to become truly direct [16] (Fig. 3a). The change of *c*-parameter can be made not only by mechanical deformation of a crystal, but also by intercalation of atoms or molecules in the voids. For example, alkali and alkali earth metals, while intercalated, cause the contraction of lattice along the *c*-direction (Fig. 3b). In the case of the metals, the resulting crystal become metallic, but in other cases (noble gases, simple molecules) one may expect to observe the predicted indirect-direct transition in zeolite silicon framework.
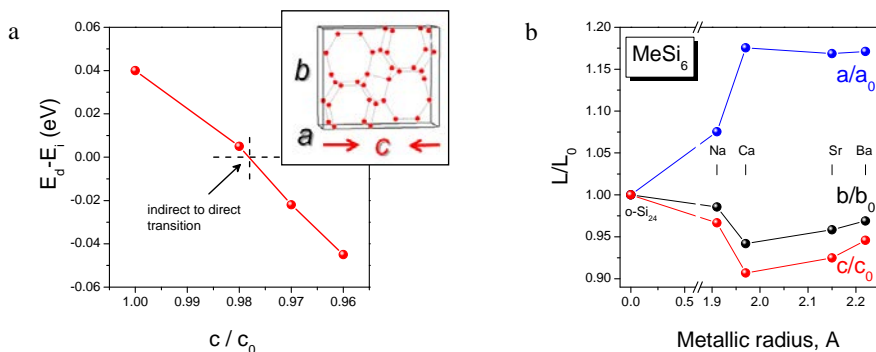

Fig. 3. (a) Difference between direct and indirect bandgaps in o-Si_{24} under uniaxial strain (compression along *c*-axis). (b) Relative lattice parameters of o-Si_{24} framework as a function of intercalated atom size (metallic radii) [40-42].

4. Conclusions

Finally, chemical interactions and phase transformations in the Na-Si system are very promising for the elaboration of various allotropes of silicon, Si-III (BC8) and zeolite o-Si_{24}, in the form of well crystallized polycrystalline grains of high purity. High pressure chemical routes seem also quite promising, by varying *p-T*-time-concentration protocols, for nanostructuring of silicon forms. The bandgap engineering of silicon materials is, thus, possible using high-pressure techniques.

Acknowledgements

References

[1] Kurakevych OO. Superhard phases of simple substances and binary compounds of the B-C-N-O system: from diamond to the latest results (a review). J Superhard Mater 2009;31:139-57.

[2] Kurakevych OO, Solozhenko VL. High-pressure route to superhard boron-rich solids. High Press Res 2011;31:48-52.

[3] Bundy FP, Hall HT, Strong HM, Wentorf Jr. RH. Man made diamonds. Nature 1955;176:51-55.

[4] Wentorf Jr. HR. Cubic form of boron nitride. Chem Phys 1957;26:956-60.

[5] Novikov NV. New trends in high-pressure synthesis of diamond. Diamond Relat Mater 1999;8:1427–32.

[6] Kurakevych OO, Le Godec Y, Strobel TA, Kim DY, Crichton WA, Guignard J. High-pressure and high-temperature stability of antifluorite Mg_2C by in situ x-ray diffraction and ab initio calculations. J Phys Chem C 2014;118:8128-33.

[7] Solozhenko VL, Kurakevych OO, Le Godec Y. Creation of nanostuctures by extreme conditions: High-pressure synthesis of ultrahard nanocrystalline cubic boron nitride. Adv Mater 2012;24:1540-44.

[8] Irifune T, Kurio A, Sakamoto S, Inoue T, Sumiya H. Ultrahard polycrystalline diamond from graphite. Nature 2003;421:599-600.

[9] Solozhenko VL, Kurakevych OO, Andrault D, Le Godec Y, Mezouar M. Ultimate metastable solubility of boron in diamond: Synthesis of superhard diamond-like BC_5. Phys Rev Lett 2009;102:015506.

[10] Oganov AR, Chen J, Gatti C, Ma Y, Ma Y, Glass CW, Liu Z, Yu T, Kurakevych OO, Solozhenko VL. Ionic high-pressure form of elemental boron. Nature 2009;457:863-67.

[11] Kurakevych OO, Solozhenko VL. Rhombohedral boron subnitride, $B_{13}N_2$, by X-ray powder diffraction. Acta Crystallogr Sect C 2007;63:i80-i82.

[12] Hubert H, Garvie LAJ, Devouard B, Buseck PR, Petuskey WT, McMillan PF. High-pressure, high-temperature synthesis and characterization of boron suboxide (B_6O). Chem Mater 1998;10:1530-37.

[13] Kurakevych OO, Solozhenko VL. Experimental study and critical review of structural, thermodynamic and mechanical properties of superhard refractory boron suboxide B_6O. J Superhard Mater 2011;33:421-28.

[14] Prewitt CT, Shannon RD. Crystal structure of a high-pressure form of B_2O_3. Acta Crystallogr Sect B 1968;24:869-74.

[15] Solozhenko VL, Kurakevych OO, Le Godec Y, Brazhkin VV. Thermodynamically consistent p-T phase diagram of boron oxide B_2O_3 by in situ probing and thermodynamic analysis. J Phys Chem C 2015;119:20600-05.

[16] Kim DY, Stefanoski S, Kurakevych OO, Strobel TA. Synthesis of an open-framework allotrope of silicon. Nat Mater 2015;14:169–73.

[17] Kurakevych OO, Strobel TA, Kim DY, Muramatsu T, Struzhkin VV. Na-Si clathrates are high-pressure phases: A melt-based route to control stoichiometry and properties. Cryst Grow Des 2013;13:303-07.

[18] Zhang P, Crespi VH, Chang E, Louie SG, Cohen ML. Computational design of direct-bandgap semiconductors that lattice-match silicon. Nature 2001;409:69-71.

[19] Archer MD, Bolton JR. Requirements for ideal performance of photochemical and photovoltaic solar energy converters. J Phys Chem A 1990;94:8028-36.

[20] Botti S, Flores-Livas JA, Amsler M, Goedecker S, Marques MAL. Low-energy silicon allotropes with strong absorption in the visible for photovoltaic applications. Phys Rev B 2012;86:121204.

[21] Lee I-H, Lee J, Oh YJ, Kim S, Chang KJ. Computational search for direct band gap silicon crystals. Phys Rev B 2014;90:115209.

[22] Wang Q, Xu B, Sun J, Liu H, Zhao Z, Yu D, Fan C, He J. Direct band gap silicon allotropes. J Amer Chem Soc 2014;136:9826-29.

[23] Xiang HJ, Huang B, Kan E, Wei S-H, Gong XG. Towards direct-gap silicon phases by the inverse band structure design approach. Phys Rev Lett 2013;110:118702.

[24] Mujica A, Pickard CJ, Needs RJ. Low-energy tetrahedral polymorphs of carbon, silicon, and germanium. Phys Rev B 2015;91:214104.

[25] Wentorf RH, Kasper JS. Two new forms of silicon. Science 1963;139:338-39.

[26] Besson JM, Mokhtari EH, Gonzalez J, Weill G. Electrical properties of semimetallic silicon III and semiconductive silicon IV at ambient pressure. Phys Rev Lett 1987;59:473-76.

[27] Delerue C, Allan G, Lannoo M. Optical band gap of Si nanoclusters. J Luminescence 1998;80:65-73.

[28] Hu JZ, Merkle LD, Menoni CS, Spain IL. Crystal data for high-pressure phases of silicon. Phys Rev B 1986;34:4679-84.

[29] Demishev SV, Lunts DG, Nekhaev DV, Sluchanko NE, Samarin NA, Brazhkin VV, Lyapin AG, Popova SV, Mel'nik NN. Structural relaxation of the metastable Kasper phase of silicon. JETP 1996;82:1159-67.

[30] Malone BD, Sau JD, Cohen ML. Ab initio survey of the electronic structure of tetrahedrally bonded phases of silicon. Phys Rev B 2008;78:035210.

[31] Wippermann S, Vörös M, Rocca D, Gali A, Zimanyi G, Galli G. High-pressure core structures of Si nanoparticles for solar energy conversion. Phys Rev Lett 2013;110:046804.

[32] Ganguly S, Kazem N, Carter D, Kauzlarich SM. Colloidal synthesis of an exotic phase of silicon: The BC8 structure. Amer Chem Soc 2014;136:1296-99.

[33] Gałyńska M, Persson P. Emerging polymorphism in nanostructured TiO$_2$: Quantum chemical comparison of anatase, rutile, and brookite clusters. Int J Quant Chem 2013;113:2611-20.

[34] Baranov AN, Kurakevych OO, Tafeenko VA, Sokolov PS, Panin GN, Solozhenko VL. High pressure synthesis and luminescent properties of cubic ZnO/MgO nanocomposites. J Appl Phys 2010;107:073519.

[35] Solozhenko VL, Kurakevych OO, Sokolov PS, Baranov AN. Kinetics of the wurtzite-to-rock-salt phase transformation in ZnO at high pressure. J Phys Chem A 2011;115:4354-58.

[36] Jouini Z, Kurakevych OO, Moutaabbid H, Le Godec Y, Mezouar M, Guignot N. Phase boundary between Na-Si clathrates of structures I and II at high pressures and high temperatures. J Superhard Mater 2016;38:66-70.

[37] Kasper JS, Hagenmul P, Pouchard M, Cros C. Clathrate structure of silicon and Na$_x$Si$_{136}$ (x=11). Science 1965;150:1713-14.

[38] Connétable D. First-principles calculations of carbon clathrates: Comparison to silicon and germanium clathrates. Phys Rev B 2010;82:075209.

[39] Gryko J, McMillan PF, Marzke RF, Ramachandran GK, Patton D, Deb SK, Sankey OF. Low-density framework form of crystalline silicon with a wide optical band gap. Phys Rev B 2000;62:R7707-10.

[40] Wosylus A, Prots Y, Burkhardt U, Schnelle W, Schwarz U. High-pressure synthesis of the electron-excess compound CaSi$_6$. Sci Techn Adv Mater 2007;8:383-88.

[41] Wosylus A, Prots Y, Burkhardt U, Schnelle W, Schwarz U, Grin Y. High-pressure synthesis of strontium hexasilicide. Zeits Natur 2006;61:1485-92.

[42] Yamanaka S, Maekawa S. Structural evolution of the binary system Ba-Si under high-pressure and high-temperature conditions. Zeits Natur 2006;61:1493-99.