Phase Diagram of Silicon from Atomistic Simulations

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In spite of being one of the most extensively studied materials, the phase diagram of silicon is not accurately known. Many phases of silicon have been identified[1], of which at least six are thermodynamically stable in some range of temperatures and pressures, while others are found to be metastable. Phase transitions between stable allotropes of silicon generally occur at rather extreme conditions of temperature and/or pressure, and this is mostly why the phase diagram of this material is only scantly known. For example, the melting temperature at zero pressure is measured to be 1687 K, while the transition from diamond (the stable phase at ambient conditions) to the β-Sn phase (the first phase to become stable under application of pressure) occurs at a pressure in the range of 10 to 12 GPa at low temperatures.

Our objective has been to obtain from simulation studies the phase diagram of silicon, and to compare our results with what is known experimentally of the phase diagram of this material. Recent developments in the theory of simulation now allow one to calculate free energies more efficiently, and to obtain them in large temperature or pressure ranges from a single simulation[2,3]. Furthermore, techniques have also been developed for directly integrating the Clausius-Clapeyron equation, leading directly to the phase boundaries of two phases known to be in coexistence[4]. These techniques facilitate enormously the calculation of phase diagrams of complex materials from simulation, and in this study we obtain the phase diagram of silicon in a temperature range from zero to above the melting point and a range of pressures from -5 to 20 GPa. This range covers four phases (diamond, β-Sn, a clathrate phase, and the melt). We have mapped the five phase boundaries encountered in this region of the phase diagram, and have approximately located the temperature-pressure coordinates of the two triple points. Our calculated phase diagram can be seen in Figure 1. Our simulations employed the tight binding[5] model of Lenosky *et al.*[6], which has been shown[7] to describe the structural and thermal properties of silicon with an accuracy comparable to that of first principles calculations. All simulations were undertaken employing the Trocadero code[8]. A more extended description of our results can be found in refs. [7, 9]

Good agreement has been found between our theoretical prediction of the Silicon phase diagram, and what is experimentally known. This study shows that the recently developed tools at our disposal make possible the efficient calculation of phase diagrams of complex materials from simulation.

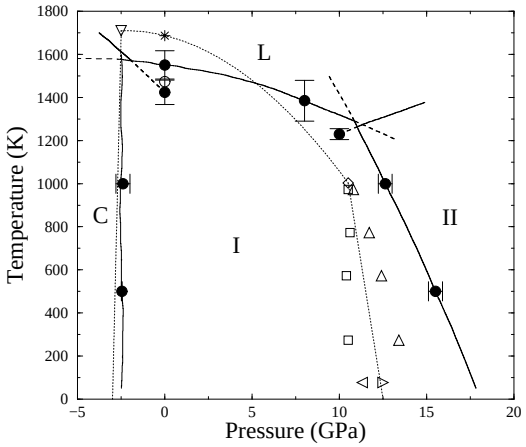

Figura 1. Calculated silicon phase diagram. The continuous and dashed lines are the results of our calculations; continuous lines are phase boundaries separating phases that are thermodynamically stable, while dashed lines separate phases that have become metastable. Uncertainty bounds were estimated at specific points of the phase diagram (indicated by filled circles), and are provided as error bars on the plot. For comparison, a schematic phase diagram summarising the experimental data is shown in dotted lines, and experimental data at specific points is shown in the form of empty simbols. The asterisc corresponds to the zero pressure melting point of the diamond phase (Silicon I), which is 1687 K; the circle is the zero-pressure melting point of the clathrate phase (C), at 1473 K; the squares and triangles are observed transition pressures from phase I to phase II (β-Sn); the diamond is the experimentally estimated location of the I-II-L triple point, and the inverted triangle is the experimentally estimated position of the I-C-L triple point.

[1] Hull, R. (Ed.) *Properties of Crystalline Silicon* (Inspec, London 1999).
[2] M. Watanabe and W. P. Reinhardt, Phys. Rev. Lett. **65**, 3301 (1990).
[3] M. de Koning, A. Antonelli and S. Yip, Phys. Rev. Lett. **83**, 3973 (1999).
[4] M. de Koning, A. Antonelli and S. Yip, J. Chem. Phys. **115**, 11025 (2001).
[5] C. M. Goringe, D. R. Bowler and E. R. Hernández, Rep. Prog. Phys. **60**, 1447 (1997).
[6] T. J. Lenosky, *et al.*, Phys. Rev. B **55**, 1528 (1997).
[7] M. Kaczmarski, R. Rurali, R. and E. R. Hernández, Phys. Rev. B **69**, 214105 (2004).
[8] R. Rurali and E. R. Hernández, Comput. Mat. Sci. **28** 85 (2003).
[9] M. Kaczmarski, O. N. Bedoya Martínez and E. R. Hernández, Phys. Rev. Lett. (accepted).