Comment on "Defects in Amorphous Silicon: A New Perspective"

For nearly twenty years it has been universally believed that the dominant spin-resonant defect D in amorphous Si (a-Si) is a threefold-coordinated atom with a dangling bond similar to that present on unreconstructed (111) natural cleavage surfaces of crystalline Si. In a recent Letter[1] Pantelides has challenged this assumption with a model that asserts that threefold- and fivefold-coordinated atoms are energetically conjugate primitive bulk defects. He concludes that the available *static* evidence (such as the interpolated equilibrium crystalline energy per atom as a function of coordination number and the spin-resonance parameters) actually favors the fivefold-coordinated model over the threefold. Here I mention *kinetic* evidence which does indeed favor the conventional model.

On mechanical grounds the energies per atom in the graphite, diamond, and metallic crystal structures and the spin-resonance parameters of defects in c-Si, which are said by Pantelides to favor fivefold-coordinated defects, are not entirely relevant. a-Si is not in equilibrium, and the defects which are present in evaporated films occur not to minimize the free energy but rather because the films are prepared kinetically by vapor deposition at atmospheric pressure and room temperature. For qualitative purposes we can regard the defects as produced by remnant pressure fluctuations. These nonequilibrium fluctuations are retained as a memory effect related to the gas state, which would be stable at room temperature only at very large negative pressure (hydrostatic tension). Thus a residual or remnant negative-pressure fluctuation[2] is inherently more probable than a positive-pressure fluctuation, although both are equally likely on energetic grounds alone.

The negative-pressure fluctuation required to produce graphite Si (threefold coordinated) is -70 kbar, according to theoretical estimates.[3] The positive pressure required to produce (sixfold coordinated) metallic Si is $+125$ kbar.[3] a-Si, like all known nonequilibrium solids (except those prepared by quenching from high pressure), has an absolute density less than that of its equilibrium counterpart.[4] Regardless of how we partition this density deficit (which is typically 5%–10%, compared to 3-at.% defect density in nonhydrogenated a-Si),[4,5] its presence indicates memory of the negative pressure[6] required to stabilize the vapor phase at room temperature. A large part of the density deficit is probably concentrated at the submicrocrystalline grain boundaries[5] which have recently been imaged by high-resolution electron microscopy.[7] Incomplete reconstruction of (111)-type grain boundaries produces atoms with unpaired spins at little cost in energy ($\simeq 5\times 10^{-2}$ eV compared to $\simeq 5$ eV for bulk bonding defects). No corresponding low-energy kinetic mechanism to produce large positive-pressure fluctuations, local compaction, and fivefold-coordinated bulk atoms has been proposed.[1] By Ockham's razor there is no logical basis for postulating high-energy fivefold-coordinated bulk point defects as likely candidates for D in a-Si once the ready availability of native internal surfaces as threefold-coordinated defect sites is recognized.[5]

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[5] J. C. Phillips, Phys. Rev. Lett. **42**, 1151 (1979), and J. Non-Cryst. Solids **43**, 37 (1981), and Phys. Status. Solidi (b) **101**, 473 (1980). These papers contain detailed discussions, supported by indirect evidence, of the effect of cluster formation, surface or grain boundary reconstruction, and hydrogenation on defect density. Direct evidence for many features of the discussion is reported in J. C. Phillips, J. C. Bean, B. A. Wilson, and A. Ourmazd, Nature (London) **325**, 121 (1987).

[6] This remnant negative internal pressure has been estimated to be about -30 kbar in a-Si by S. Veprek, private communication and unpublished.

[7] Phillips, Bean, Wilson, and Ourmazd, in Ref. 5. Note that there is no need for fivefold-coordinated atoms at intergranular contacts, which can be made entirely by deformed tetrahedrally coordinated atoms.