



# Silicon: the gulf between crystalline and amorphous

Expert Opinion

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comments to pss.rapid@wiley-vch.de or to the author. The text by D. A. Drabold refers to the Rapid Research Letter by F. Kail et al., published in this issue of Phys. Status Solidi RRL 5(10–11), 361–363 (2011).

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It can be said that the history of solid state physics began with the discovery of crystalline order from diffraction studies in the early years of the 20th century. Crystalline order produces X-ray, neutron or electron diffraction patterns with a tremendous amount of information: in an ideal case the data approximates a palisade of Dirac  $\delta$ -functions. The precisely defined peak locations and intensities measured over large ranges in real or momentum space have led to repeated breakthroughs in science. As recently as 2009, the Nobel Prize in Chemistry [1] was awarded to Ramakrishnan, Steitz and Yonath for their work in Protein Crystallography. From the viewpoint of materials science their work is marvelous – growing single crystals of proteins, and essentially uniquely determining the positions of order  $10^5$  atoms in the unit cell!

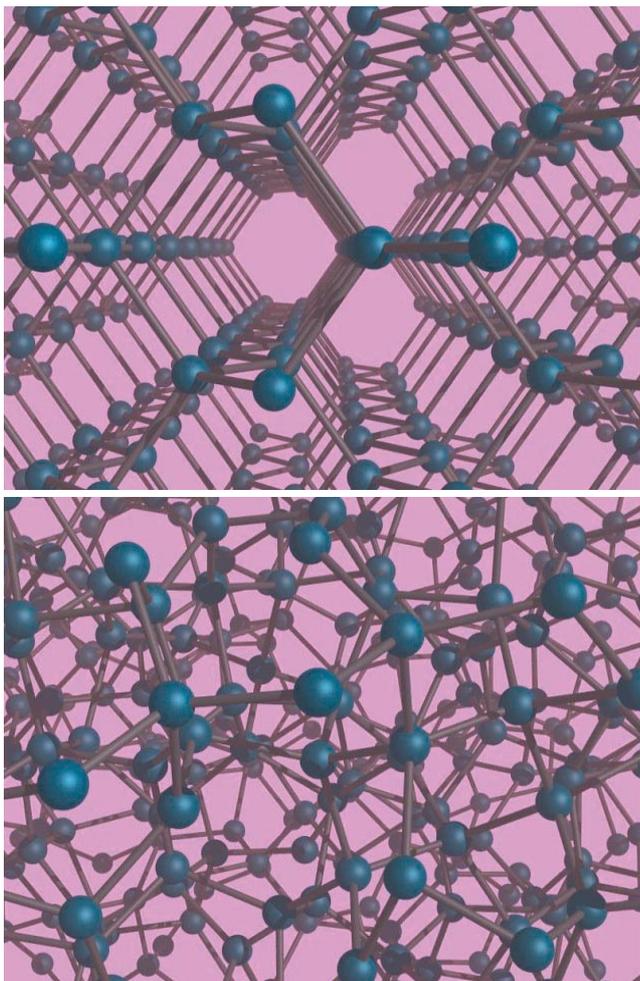
Unfortunately, these tools are not so effective for scientists studying disordered materials: amorphous solids, glasses and polymers. Here, diffraction data is “blurred” by the lack of long-range order: structure factors and radial distribution functions (RDFs) are smooth, and typically the spatial correlations decay away after about 1 nm, depending on the system under study [2]. Thus, diffraction offers only an essential sum rule that realistic models must reproduce – not information adequate to directly invert the structure from experimental information [3].

In this context, the recent Rapid Research Letter of Kail and coworkers [4] provides a helpful means to gauge the credibility of computer models. Kail et al. undertook a systematic experimental study of the archetypal amorphous

semiconductor, amorphous silicon (a-Si), technologically important for thin-film transistor and photovoltaic applications (see Fig. 1 [5]). They grew about 20 samples of a-Si, fabricated in various ways, and then used Differential Scanning Calorimetry (DSC) to estimate the crystallization enthalpy of samples. This provided a direct comparison of the energetics of the various samples to crystalline Si (diamond). The paper reveals several points of basic interest:

First, consistent with a hypothesis of Beeman, Tsu and Thorpe [6], it appears that there is a clearly defined “configurational energy gap” between diamond and optimally relaxed a-Si, and furthermore, the magnitude of this structural energy difference is about  $E_g \sim 240$  J/g (in other units, of order 0.07 eV/atom). Despite a fairly extensive exploration of samples, no smaller gap could be found. One concludes that there is *not* a continuum of homogeneously amorphous structures with energies increasing from diamond. For experts on a-Si: samples with similar energies near the best attainable were grown using chemical vapor deposition with or without a “Hot Wire”.

Secondly, the paper emphasizes the diverse nature of a-Si materials: here we have 20 samples with recrystallization enthalpies varying by more than a factor of two, but any of which might be identified as a-Si from diffraction measurements. Studies of medium range order have uncovered topological differences beyond pair-correlations (e.g. diffraction measurements) that also show variations in samples understood to be a-Si:H [7]. All such work helps



**Figure 1** (online colour at: [www.pss-rapid.com](http://www.pss-rapid.com)) Views of silicon in the diamond structure (top) and a model of amorphous silicon (bottom) [5]. The Rapid Research Letter of Kail and coworkers [4] quantifies the energy difference between the two structures, and suggests the existence of amorphous structures only above a configurational energy gap separating the crystalline and amorphous states.

to understand these important materials in a more subtle way; in the case of the RRL, highlighting the significant variation in crystallization enthalpy.

Finally, this paper provides an important practical check on the validity of computer models and the energy functionals used to evaluate the models. At present, modelers create structures, and compare to the available experiments, typically including diffraction (from X-rays, neutrons or electrons), spectroscopy (electronic, optical, magnetic, vibrational). Now, for a-Si, there is another test that candidate models must pass: they should have energies in the range of 0.07 eV/atom to ~0.15 eV/atom above diamond.

Two earlier calculations overestimate this energy for topologically similar models, giving 0.34 eV/atom with Keating Springs [8] and 0.17 eV/atom [9] with FIREBALL [10], a local basis density functional code employing the local density approximation. These energies must be compared with care owing to the tendency of density functional theory in the local density approximation to exaggerate cohesive energies, and other computational details as well.

For this well characterized set of samples, it would also be of interest to see how or if spectroscopic properties correlate with the configurational energy (for example, the Urbach energy [11], characterizing the decay of electronic bandtails, is often interpreted as a measure of structural disorder; I wonder if crystallization enthalpy is correlated with the Urbach parameter). Additional studies of this type would be of considerable value for other disordered materials.

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