Medium-Range Order in the Scientific Court

Jeffrey S. Lannin has written a splendid popular article on short- and medium-range order in elemental amorphous semiconductors (July 1988, page 28). It is a pity, however, that for want of space he has left his readers with the impression that not much is known (except very indirectly) about medium-range order. I described large clusters in amorphous binary and ternary alloys in my February 1982 PHYSICS TODAY article (page 27), and that work on Ge(S,Se) alloys has since been extended[1] to Si(S,Se,Te) alloys, where chains instead of planes are the dominant structural units.

In the elemental material of greatest technological interest, amorphous Si, we need no longer rely on inadequately equilibrated (only poorly relaxed) computer models such as that shown in Lannin's figure 1. Tremendous advances in sample preparation methods, together with continuing refinements in instrumentation and image analysis, have made it possible to obtain directly pictures of the atomic structure of this material by high-resolution electron microscopy.[2] These show, as Lannin remarks, that the structure of amorphous Si deposited at room temperature varies significantly depending on the substrate used. The range, however, always includes large clusters with close-packed ⟨111⟩ atomic planes similar to those of the crystal and with cluster diameters between 15 and 30 Å. Such exciting results pose a challenge to those doing research on amorphous conductors. They can meet this challenge by using indirect methods such as nuclear quadrupole and Raman scattering spectroscopy together to identify parallel but complementary chemical trends in site and bond populations in alloys.[1]

References

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2. J. C. Phillips, J. C. Bean, B. A. Wilson, A. Ourmazd, Nature **325**, 121 (1987).

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LANNIN REPLIES: I chose not to discuss binary group 4-6 systems because there is currently considerable debate regarding their structure, both among those favoring different noncrystalline models and among those such as J. C. Phillips, who posit crystal-like molecular fragments.

The evidence for structural correlations that are *not* crystal-like is quite strong in amorphous Si (or Ge). Radial distribution functions do not provide an indication of higher-neighbor crystalline angular correlations. The wide distribution of bond angles (and their sensitivity to preparation conditions) cannot be accounted for by microcrystalline-type models without the resulting structures' having a large fraction of noncrystalline regions (in contrast to Phillips's reference 2). It appears that only specifically prepared films of Si deposited on crystalline Si substrates, or at high temperature, yield possible crystal-like features in electron microscopy. These latter films are clearly uncommon and do not "always" support microcrystalline order in amorphous films, but in fact suggest the opposite. Similarly, EXAFS studies of high-temperature Ge films made near the crystallization point suggest a mixture of approximately 20% of 10-Å microcrystallites and 80% of an amorphous phase, whereas in films made at lower temperatures no microcrystallites are observed.[1] This indicates that microcrystalline models cannot logically describe the amorphous state. Raman scattering measurements in microcrystalline Si of average diameter 35 Å exhibit a spectral form qualitatively quite different from that of amorphous Si.[2] Current theoretical models such as the one[3] shown in figure 1 of my article provide a reasonable first-order description of actual amorphous Si and Ge films whose structures are kinetically limited.

References

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Correction

May, page 13—The letter by Richard Feynman published in David Goodstein's letter was from box 1.5 of the Richard P. Feynman papers at the California Institute of Technology Archives, and permission to publish was courtesy of the archives. ■