PHYSICAL REVIEW B VOLUME 40, NUMBER 11 15 OCTOBER 1989-I

Neutron-diffraction study of the structure of evaporated pure amorphous silicon

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(Received 30 January 1989)

A neutron-scattering measurement was performed on pure amorphous Si. The radial distribution function was derived from the wide momentum-transfer range spectra. These data are compared to theoretical models in the 0–10-Å real-space interval.

Despite more than 15 years of investigation, one of the main problems concerning amorphous silicon remained the determination of its microscopic structure. Since Polk[1] made the first so-called continuous-random-network (CRN) model in 1971, many models have been constructed in different ways.[2–17] In the relaxed CRN models the Keating, the Stillinger-Weber, the Weber bond-charge potential, and the Lifson-Warshel force field were used as assumptions for the interatomic interaction to minimize the total energy. Four models[13–16] were obtained by molecular-dynamics techniques. The number of atoms they contain varies from several tens to hundreds. To eliminate the surface effects some of these models satisfy periodic boundary conditions. The radial distribution function (RDF) calculated from the above theoretical models was compared to neutron scattering data on amorphous Ge,[18] since experimental information on pure silicon is rather limited. There were experimental structural studies made on *a*-Si using electron,[19,20] x-ray,[21] and Raman[22] diffractions, but still the elastic neutron-scattering technique provides the most fundamental information about the structure. While various types of neutron measurements[23–27] have been carried out on hydrogeneted amorphous silicon, so far there are no such structural data available for pure *a*-Si in real space. Recently Fortner and Lannin communicated information of RDF in the range of 1–7 Å on sputtered samples from a neutron study and presented a careful determination of bond-angle distribution in amorphous silicon.[28]

In this report we present RDF for pure evaporated *a*-Si obtained from high-momentum-transfer neutron-diffraction measurements lending direct support for the theoretical models cited in Refs. 1–17.

The 0.45-g nearly pure evaporated amorphous Si sample has been prepared in the Central Research Institute for Physics, Budapest. Using a 6-kW *e*-beam gun in a VARIAN VT-460 oil-free evaporator of 5×10^{-6} Pa pressure the evaporation speed was 0.4–0.5 nm/sec. The deposition was carried out from semiconductor grade Si source material onto polished Ta substrate at room temperature. The deposited layer was removed mechanically from the substrate. In order to minimize the sample contamination by hydrogen a 24-h annealing of the sample at 400 °C was performed in a vacuum of 10^{-4} Pa. The *a*-Si was checked by x-ray diffraction in a Guinier camera with a quartz monochromator and photographic registration. The *a*-Si layers were tested after each deposition; the total amount of the sample was provided in 20 cycles including the deposition process and testing. The x-ray data did not show any sign of crystallinity, and the diffraction patterns were qualitatively similar to the previously published data on amorphous silicon.[21]

Neutron-diffraction experiments were performed at the 7C2 spectrometer installed on the hot source of the reactor Orphee at Saclay. A 640-cell position-sensitive detector provides the whole spectrum covering a 128° angle with resolution of 0.2° in a single measurement. Using an incident wavelength of $\lambda=0.706$ Å, a large momentum-transfer range from 0.5 to 16 $Å^{-1}$ was covered. In order to minimize the background the sample was packed into a vanadium container of 20 μm thickness. Corrections have been applied for background, absorption, and multiple scattering. As a result, statistical error remained below 1% for the whole spectrum. A residual concentration of hydrogen of 1.95% was measured. In spite of this low concentration, particular attention has been given to carrying out the inelastic correction[29] for the very high incoherent scattering from hydrogen.

The measured structure factor of *a*-Si is shown in Fig. 1. The small increase in low-angle intensity is due to scattering by large-scale heterogeneities in the sample,[30] and thus has no effect on local order. A pronounced first sharp diffraction peak[31] is noticed at $Q_1=2.0$ $Å^{-1}$, then the usual liquid-type structure factor is recorded. The pair correlation function has been calculated by a Fourier transformation procedure of this $S(Q)$. The RDF is displayed in Fig. 2. A marked prepeak appears systematically at around 1.8 Å in the data treatment, therefore no special smoothing was applied before the first-neighbor peak (except the inverse Fourier transformation). Due to the fact that the structure factor still shows important oscillations until 16 $Å^{-1}$, which is the maximum momentum transfer that has been measured (Fig. 1), particular

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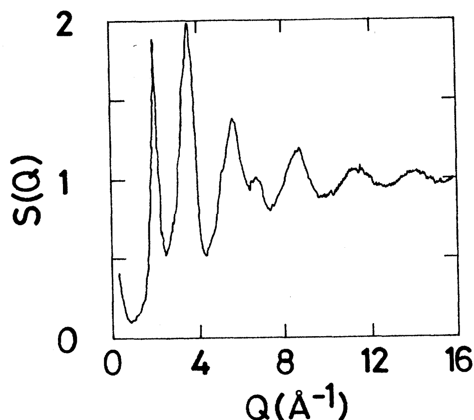


FIG. 1. Measured structure factor of pure evaporated a-Si after background, absorption, and multiple-scattering corrections.

care should be taken in a physical interpretation of the bumps in the $r < 2.1$ Å range of the radial distribution function (they may be connected with Fourier transformation artifacts). The maximum position of first- and second-neighbor peaks are 2.34 and 3.84 Å, respectively. The first two distances are very close to data derived by Moss and Graczyk.[19] The full width of the first-neighbor peak is 0.26 Å at half maximum, which is greater than the value measured by electron diffraction.[19]

The above experimental data can be used for comparison with theoretical simulations of the a-Si structure. We have chosen two advanced models based on different approaches. First Car and Parinello's calculations[15] are considered. This model based on a molecular-dynamics technique contains a relatively low number of atoms (54 atoms), however it seems to be one of the most realistic computer simulations since it generates structural defects on relaxing the atoms. In Fig. 3(a) the calculated RDF is

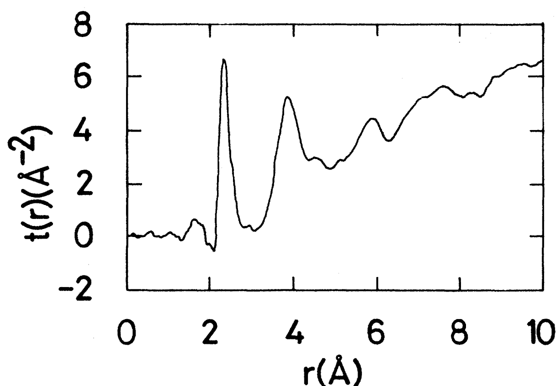
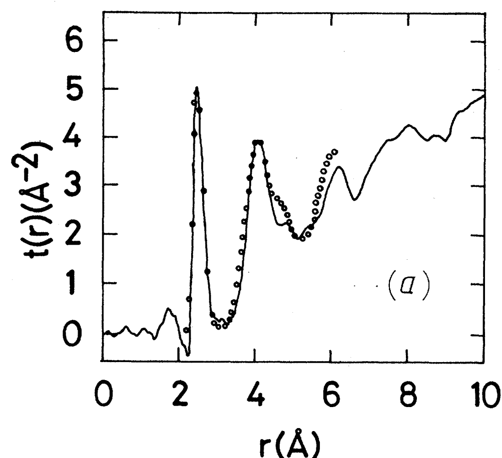
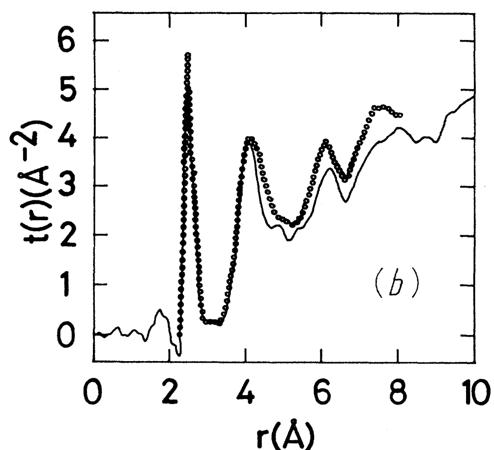


FIG. 2. The measured radial distribution function, $t(r) = 4\pi\rho r g(r)$, where $\rho_{Si} = 0.054$ atoms/Å^3 is the density and $g(r)$ is the pair correlation function.





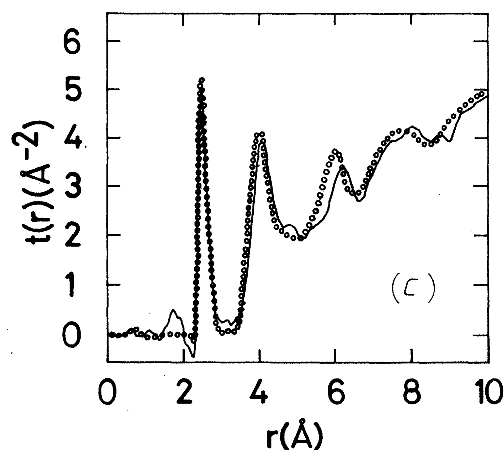


FIG. 3. Measured radial distribution function of a-Si (solid lines) compared to theoretical models (open circles): (a) Ref. 15, (b) Ref. 11, and (c) amorphous Ge measurement (Ref. 18). Each RDF is scaled to the Ge data with density $\rho_{Ge} = 0.03975$ atoms/Å^3 and the maximum position of the first-neighbor peaks $r_1 = 2.463$ Å.

compared to our measured pattern and a good agreement can be seen in the 2–6-Å range, as given by the model curve. The first- and second-neighbor peaks are in perfect coincidence; even the small shoulder at ∼4.5 Å corresponding to the third-neighbor correlation is reproduced.

On the other hand, the model of Wooten *et al.*[11] was selected for comparison because of its large size ($V=16.3^3$ Å^3). It operates with 216 Si atoms and uses periodic boundary conditions. In contrast to the previous case, this model yields comparison for a wider real-space interval (within 0–8 Å). The calculated RDF gives an excellent fit [Fig. 3(b)] for the first-neighbor peak and the general shape of the radial distribution curve is well described. At the same time some details, i.e., the third-neighbor correlation enhancement at ∼4.5 Å, are hindered.

Most of the *a*-Si models have so far been compared to the *a*-Ge measurement.[18] In Fig. 3(c) we reproduced the RDF of *a*-Ge together with our *a*-Si data. The silicon RDF is scaled to the Ge data with $\rho_{\mathrm{Ge}}=0.03975$ atoms/Å^3 and with a 2.463-Å first-neighbor distance. The positions of the second and third large maximums do not coincide, e.g. a shift of 0.2 Å appears between the peak positions of the third maximums in Fig. 3(c). Whether these small discrepancies are only a kind of error due to data treatments, or have a physical meaning, needs further investigations.

In conclusion, we have experimentally determined the radial distribution function for pure amorphous silicon. In this way a direct comparison can be made in real space with structure simulations as well as the measured RDF of *a*-Ge which has been used so far for analyzing the *a*-Si models. Our preliminary comparison seems to confirm the two recent calculations we have chosen, showing that both give rather realistic descriptions of the amorphous silicon structure.

One of us (S.K.) is indebted to Professor B. Vasvári (Technical University of Budapest) for his support in this work.

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