but interior ones do not.

The full O_2-C potential gives results qualitatively similar to those calculated with use of the spherically symmetric expression except that the O_2-C anisotropies cause the O_2 molecules to lie flat on the substrate and the triangular structure is distorted by the anisotropy. Some results for this case are given in parentheses in Table I. For $N \leqslant 6$, $T_O \simeq 4$ K; and for $N = 7$, $T_O \simeq 6$ K. In the plastic crystallite phase, $T_O \leqslant T < T_M$, the O_2 molecules relax from the distorted configurations to 2D structures constructed by connecting equilateral triangles. This is caused by the O_2 rotations averaging out the anisotropies responsible for the distortion. There is no indication of registry.

To summarize our work on infinite O_2 monolayers, it is significant that the nearest-neighbor separation agrees to within 3% of experiment and is almost exactly the same for those calculations on bulk β-O_2 that used the English-Venables potential.[6] This, coupled with our determination of an equilateral-triangular lattice and O_2 orientations perpendicular to the substrate, supports the view that 2D monolayers have the same character as the densest, packed plane of bulk O_2. Depending on the strength of the O_2-C anisotropy, a possible new low-density state at $\rho \simeq 1.29$ is also predicted, where the O_2 lay flat on the substrate.[10]

In the fractional-monolayer $\rho \ll 1$ region, our 2D-cluster model gives structures, nearest-neighbor distances, orientations, melting temperatures, etc., that are consistent with experiment.[1-4,10] Particularly unusual are the well-defined orientational order-disorder transitions into a plastic crystallite phase. Our results indicate that monolayer O_2 will gasify at $T \simeq 55$ K.

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[10] We have just learned of heat capacity and x-ray scattering data, to be published by O. Vilches and by R. J. Birgeneau and P. Stephens, which agrees qualitatively and quantitatively with our predicted low-density "laying flat" state. This contradicts earlier experiments (Ref. 1). There is also new evidence that the δ-phase melting line approaches $\rho = 0$ at $T \simeq 25$ K as we predict; see Fig. 1.

Structure of Amorphous Silicon and Silicon Hydrides

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Neutron scattering measurements have been made on pure, hydrogenated, and deuterated samples of amorphous silicon (a-Si) in the wave-vector range 0.007–8.75 Å^{-1}. Small-angle data indicate structures in the samples of average radius of gyration as large as 270 Å. Large-angle data show that for the concentrations we have measured (14%), the structure of a-Si is not altered by the incorporation of large amounts of H or D. The silicon-hydrogen and silicon-deuterium partial structure factors have also been obtained.

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Amorphous silicon (a-Si) and hydrogenated a-Si have received considerable attention very recently.[1] This has been motivated by recent interest in the general subject of amorphous materials as well as by the discovery that incorporation of hydrogen changes the conductivity of a-Si by several orders of magnitude.[2] Work in this area has also been motivated by the potential applications of chemically modified *a*-Si to photovoltaic solar-energy conversion.[3] In spite of this widespread interest, to our knowledge no previous detailed structural studies have been performed. Small-angle x-ray scattering[4,5] has been used to obtain information on void sizes, but gives no information on the hydrogen because of its small cross section. Structural information is crucial for any understanding of the electronic properties of the material.[4] We report here an extensive structural study of *a*-Si and of hydrogenated and deuterated *a*-Si, using neutron scattering.

We observe very intense small-angle scattering indicative of the existence of large voids. A comparison of both small- and large-angle scattering from pure *a*-Si with hydrogenated and deuterated *a*-Si indicates that the microscopic structure of the silicon is not modified by the incorporation of large amounts (14%) of hydrogen or deuterium. From the large-angle (wave-vector range 0.2–8.75 Å^{-1}) scattering, detailed information on the silicon-hydrogen correlation function is obtained. This correlation function is found to be in qualitative agreement with recent computer simulation studies.[5]

Neutron diffraction measurements provide fundamental information on the structural properties of materials that may not be obtained with x rays. In particular, hydrogen is a strong neutron scatterer but transparent to x rays, so that neutron scattering is a particularly powerful tool for the study of hydrogenated materials. In the case of hydrogenated *a*-Si, neutron scattering provides a unique tool to measure directly the silicon-hydrogen partial structure by isotopically substituting deuterium for hydrogen. This isotopic substitution results in large changes in the neutron scattering amplitudes.

The samples (~ 3 g each) were prepared using high-rate magnetron sputtering techniques. A Varian S-gun dc sputtering source with 99.9995% Si target was used to deposit samples on glass substrates at 200–250 °C. All depositions were made using 10 mTorr Ar for the sputtering. The hydrogenated and deuterated samples were reactively sputtered by the introduction of an additional 1.0 mTorr of the appropriate gas during the sputtering. The samples were removed from the glass substrates and packed in thin-walled vanadium containers (diameter, 0.635 cm; length, 4 cm) in a dry nitrogen glove box. The concentration of hydrogen or deuterium (14 ± 3 at.%) was determined from gas evolution studies of part of each sample. In combination with infrared reflectivity measurements, the gas pressure in a calibrated cell at constant warmup rate can be used to determine the kinetics of decomposition as well as total atomic fraction of gas.[6] Qualitatively, it was found that the gases are bound to silicon as both SiH_2 (SiD_2) and SiH (SiD) centers. Quantitative measurements of the relative amounts of each type of center were not possible because of poor infrared spectra inherent in powdered samples.

Neutron scattering measurements were performed at the University of Missouri Research Reactor (MURR) on two different double-axis spectrometers as well as the small-angle neutron-scattering spectrometer (SANS) using incident neutron wavelengths of $\lambda = 1.052$, 4.07, and 4.75 Å. The combined measurements cover a wave-vector range from $k = 0.007\ \text{Å}^{-1}$ to $k = 8.75\ \text{Å}^{-1}$. Since differences between the intensities of scattered neutrons from the different samples was required, measurements were performed on several short runs rather than on single long runs. In this manner we were able to verify the repeatability of different runs on the same sample. The relative efficiency of the beam monitors to the scattering detector was determined at 1.052 and 4.07 Å using a vanadium standard on the double-axis instruments. The effect of multiple scattering and self-shielding on the measured vanadium intensities were calculated using the Monte Carlo code of Copley[7] and results were checked for consistency with self-shielding corrections using the procedure of Mildner, Carpenter, and Pelizzari.[8] After these corrections, the small- and large-angle scattering data from the double-axis spectrometers were joined with the SANS data by applying a scale factor in the region of overlap. In this fashion a unified absolute measure of the structure factor was obtained from $k = 0.007\ \text{Å}^{-1}$ to $k = 8.75\ \text{Å}^{-1}$.

Figure 1 shows the experimentally measured intensity I of scattered neutrons versus momentum transfer in the region below 0.055 Å^{-1} for hydrogenated and deuterated *a*-Si. The momentum-transfer range reported here extends at least one order of magnitude to lower k than previous measurements using x-ray scattering techniques. If we assume that the small-angle scattering is due to an isotropic mixture of isolated particles of average radius of gyration, R_G (an oversimplification for our samples), the intensity for $k \to 0$ is given by

$$I = I_0 \exp(-\tfrac{1}{3}k^2 R_G^2). \quad (1)$$

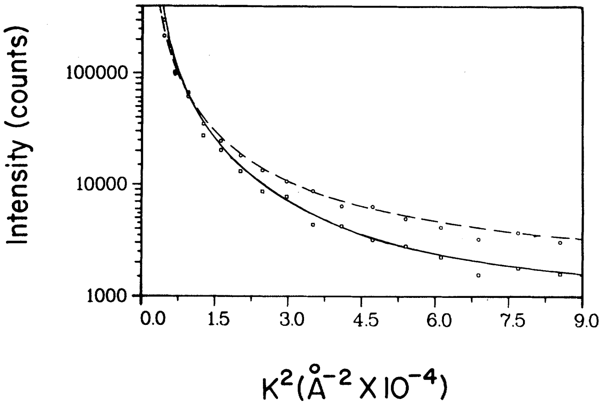

FIG. 1. Guinier plot of the low-angle neutron-scattering intensity data for wave vectors below 0.055 $Å^{-1}$. Circles, hydrogenated *a*-Si; squares, deuterated *a*-Si. The lines are fits to the experimental points.

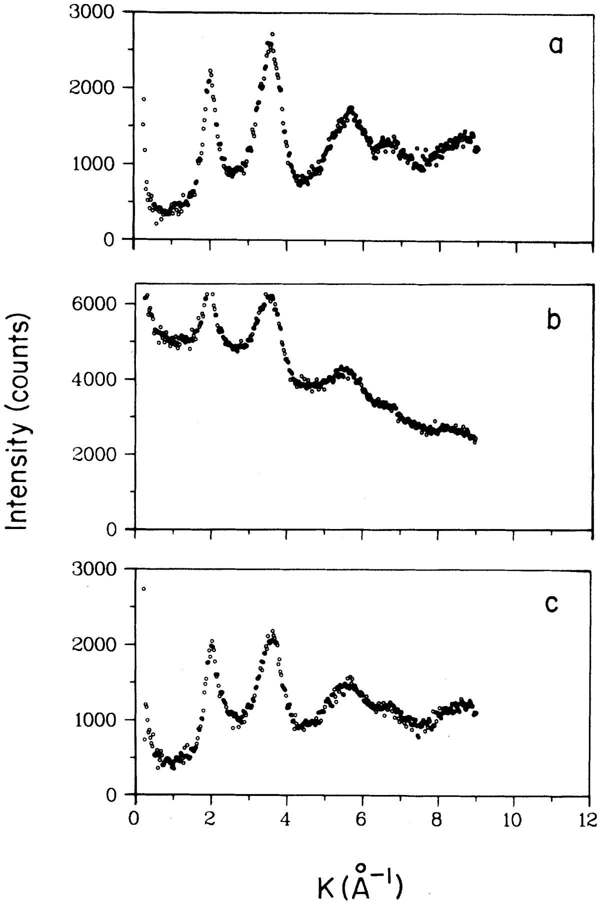

FIG. 2. Large-angle neutron scattering intensities for (a) pure *a*-Si, (b) hydrogenated *a*-Si, and (c) deuterated *a*-Si.

The radius of gyration obtained in this manner from the Guinier plot shown in Fig. 1 for the hydrogenated sample is $R_G \sim 270$ Å. This value is an upper limit for the largest scattering centers in the sample and is a factor of 5 greater than the largest voids reported in Refs. 9 and 10 which used, respectively, evaporated and glow-discharge–produced *a*-Si. However, Refs. 9 and 10 disagree considerably on the void distributions and our determination may be a reflection of the different sample-preparation technique. Since the intensity of scattering from voids is proportional to the square of the mean scattering length of the material surrounding the void, scattering from voids surrounded by D (deuterium has a positive scattering length) should be more intense than for similar voids in the SiH (since hydrogen has a negative scattering length). We in fact observe the opposite situation: The hydrogenated material scatters more intensely than the deuterated material. One possible explanation for this reversed situation is that there are large surface areas within the sample covered with hydrogen (deuterium). Since hydrogen has a negative scattering length, neutrons are subjected to a far more pronounced fluctuation in the mean scattering density as they traverse a surface covered by hydrogen rather than by deuterium. However, for void structures which are very large (where the volume scattering dominates over the surface scattering) one might expect to observe a crossing over to more intense scattering from the deuterated sample relative to the hydrogenated sample. We have performed a computer simulation of the scattering by spherical voids covered with H or D which shows such a crossover effect. This effect is due to the fact that the scattering from very large voids is proportional to the square of the contrast with the average bulk medium while the scattering from small voids is more sensitive to local fluctuations. Such a crossover is observed at about 0.008 $Å^{-1}$, which corresponds to spatial structures of characteristic dimension of order 800 Å. The difference between the SiH and SiD data indicates therefore that there are voids which may be covered by H and D, and/or large areas of grain boundaries in which hydrogen or deuterium reside. The crossover at very low wave vectors between the SiH and SiD data is real and arises from the fact that H and D have scattering lengths of opposite sign.

Figure 2 shows the experimental large-angle scattering from *a*-Si, hydrogenated *a*-Si, and deuterated *a*-Si. The large decaying background for the hydrogenated sample is due to the large incoherent scattering of the hydrogen ($\sigma_i = 80$ b). If the scattering by the pure sample is subtracted from the hydrogenated one, an almost structureless curve is obtained which can be fitted by a Debye-Waller form as expected for purely incoherent scattering. The contribution from the purely coherent scattering of the hydrogen can then be obtained by subtracting this computed incoherent scattering from the experimental data.

The scattering intensity from a binary system is given by

$$I_{\alpha\beta}(k) = a_\alpha^2 \chi_\alpha S_{\alpha\alpha}(k) + Q a_\alpha a_\beta \chi_\alpha \chi_\beta S_{\alpha\beta}(k) + a_\beta^2 \chi_\beta S_{\beta\beta}(k), \quad (2)$$

where α and β refer to the species α and β in the binary system, a is their respective scattering length, χ is the concentration, and S is the structure factor. If the concentration χ_β is small (~0.14) as is the case for the hydrogenated and deuterated sample, the third term in Eq. (2) is small and hence can be neglected. The silicon-hydrogen and silicon-deuterium partial structure factors ($S_{\alpha\beta}$) can be obtained by taking the differences between the coherent structure factor of the a-Si ($S_{\alpha\alpha}$) and of the hydrogenated and deuterated a-Si (see Fig. 3). These three differences have been scaled by the appropriate scattering lengths (*no adjustable parameters*). The curves lie on top of each other, indicating that the difference function is a meaningful physical quantity. This also shows that for the concentration we have measured (14%), the structure of a-Si is not altered by the incorporation of large amounts of hydrogen or deuterium. In fact, a comparison of this difference with independent computer simulation of the silicon-hydrogen structure factor shows striking similarities.[5]

The experimentally determined structure factor $S_{\alpha\beta}(k)$ can be directly related to the silicon-silicon or silicon-hydrogen pair correlation function $g_{\alpha\beta}(r)$ with use of

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + 4\pi(\rho_\alpha\rho_\beta)^{1/2} \times \int_0^\infty [g_{\alpha\beta}(r) - 1][(\sin kr)/kr] r^2 dr. \quad (3)$$

The pair correlation function $g_{\alpha\beta}(r)$ is the probability of finding an atom of type α at a distance r from a fixed atom of type β at the origin. We should stress at this point that the pair correlation function $g_{\alpha\beta}(r)$ is the fundamental quantity that defines the structure of the material. Any structural model of a-Si which is used to predict electronic and optical properties should be capable of generating an $S_{\alpha\beta}(k)$ consistent with these experimental results. A detailed comparison of our measured neutron partial structure intensities with computer simulated partial structure factors based on a relaxational model[5] indicates that about half of the hydrogen (deuterium) is incorporated in the bulk and the remainder is on surfaces.

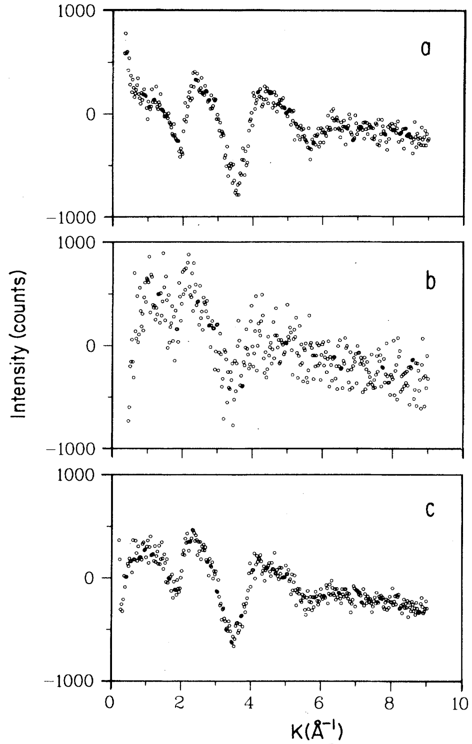

FIG. 3. Differences of coherent structure factors of the three samples: (a) SiD-Si, (b) SiD-SiH, and (c) Si-SiH.

In summary, we have performed the first structural studies of pure, hydrogenated, and deuterated amorphous silicon, using neutron scattering. Our results indicate the existence of large areas of surface covered by hydrogen (deuterium) as well as voids possibly covered by hydrogen (deuterium). We also find that the incorporation of 14% hydrogen (deuterium) into a-Si does not significantly alter the bulk structure of the silicon. The silicon-hydrogen and silicon-deuterium partial structure factors can be obtained from these measurements and the intensities of these measured partial structure factors scale in agreement with the known scattering lengths of hydrogen, deuterium, and silicon.

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