Coordination of Arsenic Impurities in Amorphous Silicon-Hydrogen Alloys

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We have determined the coordination of arsenic impurities in amorphous silicon-hydrogen alloys prepared by plasma decomposition of silane-arsine mixtures. From analysis of the extended x-ray absorption fine structure (EXAFS) on the arsenic K-shell absorption, we find at low arsenic concentrations that an average of two arsenic atoms in ten are fourfold coordinated with silicon. This is the first direct evidence for the occurrence of substitutional doping in an amorphous semiconductor.

A current focus of interest in the field of amorphous semiconductors is the question of substitutional doping. It has long been argued that in these materials there would be local structural relaxation around impurities so as to satisfy their bonding requirements. Recently, however, effects characteristic of substitutional doping have been observed when group-III[1] and -V[1,2] impurities have been incorporated in thin films of amorphous "silicon" prepared by plasma decomposition of silane. Specifically, the dopants phosphorus, boron, and arsenic produce large conductivity changes and yield the sign of the thermopower expected by analogy with crystalline silicon. In addition, changes in electronic properties indicative of a transition from doping to alloying behavior are observed as a function of increasing impurity concentration in the case of arsenic.[2] These observations, however, though highly indicative of true substitutional doping, are circumstantial. Furthermore, if the doping is in fact substitutional, there is the question of what fraction of the impurities is incorporated in a fourfold-coordinated environment. Previous estimates[3] have been based on a specific model for impurity incorporation and a defect-state derived from field-effect measurements, both of which have recently been called into question.[4,5] Thus at present no acceptable estimate exists of the electrically active fraction for any of the known dopants. It is clear that a direct measurement of the local coordination of the impurity is an essential contribution toward resolving these issues. To this end we present and analyze extended x-ray absorption fine structure (EXAFS)[6] and hydrogen-evolution data on amorphous films deposited from silane-arsine mixtures.

Our major result is that we observe an increase of ~0.2 in the coordination of arsenic on decreasing the arsenic content from alloy (~12 at.%) to doping (~1 at.%) concentrations. At alloy concentrations we find that arsenic has significantly fewer than three silicon nearest neighbors. This deficit is explained through hydrogen-evolution measurements which indicate atomic percentages of hydrogen in all samples in excess of 13%. These results lead us to conclude that these materials are properly described as doped silicon-hydrogen *alloys*. In the doping regime, we show that approximately two in ten of the arsenic atoms are fourfold coordinated with silicon in a local environment that does not possess long-range order. The observed changes in electronic properties are correlated with the onset of fourfold coordination for the arsenic atoms. This is the first direct evidence for the occurence of substitutional doping in an amorphous semiconductor.

EXAFS measurements were performed at the Stanford synchrotron radiation project on amorphous compositions in the Si-H:As system and on single-crystal SiAs. The amorphous samples were deposited in thicknesses ~20–50 μm onto aluminum foil from mixtures of silane and arsine diluted to 10% in argon. Details of the deposition system have been described elsewhere.[7] The substrate temperature during deposition, T_s, was 235°C for all samples except two: A 1% AsH_3/SiH_4 sample was deposited onto a substrate at 25°C and the 100% AsH_3 material was deposited onto a substrate at 127°C. The hydrogen content was obtained by measuring the volume of gas (determined to be hydrogen using a residual-gas analyzer) released on heating weighed samples to crystallization. Crystalline silicon arsenide was grown by the vertical Bridgman-Stockbarger technique. Samples thicknesses calculated to give the optimum signal-noise ratio were prepared by stacking coated foils in the case of the amorphous materials, and by cleaving in the case of the c-SiAs. A ⟨111⟩ channel-cut Si crystal was used in the monochromator, electron-beam energies

TABLE I. Composition of samples deposited from silane-arsine mixtures.

% AsH_3 in mixture	Substrate temperature T_s (°C)	Atomic percent arsenic	Atomic percent hydrogen	Atomic percent silicon
0.5	235	0.9	13.2	85.9
1.0	235	1.7	13.6	84.7
5.0	235	6.0	15.6	78.4
10.0	235	11.7	17.6	70.7
1.0	25	2.6	34.6	62.8

were ~3.7 GeV, and copper and nickel foils were used both to calibrate photon energy and to check for the absence of second-order beams. All experiments were performed with samples immersed in helium gas at (77.5 ± 0.3)°K to reduce thermal broadening of the radial distribution function.

The first information extracted from the x-ray absorption measurements was the arsenic concentration. This was obtained from the measured K-edge–absorption steps using the tabulated change in arsenic scattering cross section, the sample thickness and density, and the measured hydrogen content. The results of these determinations are shown in Table I. We note that the hydrogen contents are similar in magnitude to those reported by other workers,[8,9] and are far too large to permit the material to be called a-Si. As we shall discuss later, the hydrogen is bonded, indicating that we are dealing with a true silicon-hydrogen alloy.

Secondly, using procedures which have been described in detail elsewhere,[10] we extracted the EXAFS on the arsenic K-shell absorption as a function of final-state electron momentum, k, and Fourier transformed it into real space. The resultant complex transform, $\varphi(r)$, is shown in Fig. 1 for the 1.7-at.%-As material, c-SiAs, and the material deposited from pure arsine. All the data were reduced in a similar manner. Considering the data in Fig. 1, we note firstly that the structure at $r \sim 0.5$ Å is an artifact of the data-reduction process. Secondly, the complete absence of structure beyond 3 Å in all amorphous samples is strong evidence for the lack of order extending beyond first nearest neighbors about the arsenic sites—specifically, the second-nearest-neighbor distribution must be at least 0.2 Å broader than the first.

The Fourier transform, $\varphi(r)$, of the EXAFS on K-shell absorption can be expressed[10] as a sum

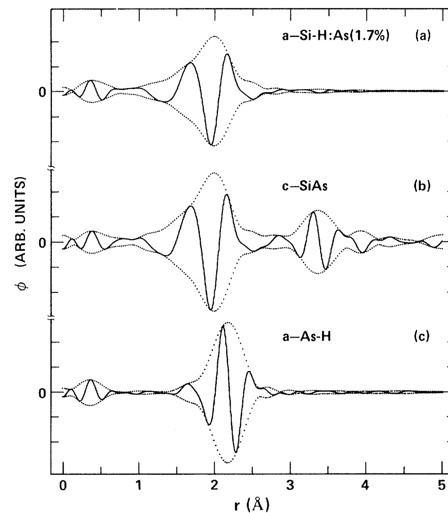

FIG. 1. The real part (solid line) and the magnitude of the Fourier transform $\varphi(r)$ of the EXAFS on the As K-shell absorption in (a) 1.7 at.% As in amorphous Si-H, (b) c-SiAs, and (c) amorphous As-H. The vertical units are arbitrary, but identical for each set of data. The data were all transformed using a square window with k between 3.75 and 13.85 Å^{-1}, broadened by a Gaussian $\sigma_w = 0.7$ Å^{-1}.

of contributions, ξ, from each shell of atoms surrounding the excited atom:

$$\varphi(r) = \sum_\alpha \int_0^\infty dr' \, (r')^{-2} p_\alpha(r') \xi_\alpha(r - r'), \tag{1}$$

where $r > 0$ and p_α is the radial distribution function of atomic species α about the excited atom. As in x-ray and neutron diffraction studies, φ is a radial distribution function modified by convolution with a peak function, ξ. $\xi(r)$ is a complicated function involving the complex t matrix of the scattering atom, the final-state electron lifetime, and the initial phase shift due to the excited-atom potential. In addition, ξ is a function of the manner in which the finite range of the k-space data is treated. In order to enable direct comparison among the data from different samples, we have used in each case the same square window, $k = 3.75$–13.85 Å^{-1}, Gaussian broadened with $\sigma_w = 0.7$ Å^{-1}. ξ is insensitive, however, to changes in crystal structure, local bonding, thermal effects, etc. The analysis in this case was performed in two stages. Firstly the $\varphi(r)$ for the 1.7-at.%-As sample was compared with the $\varphi(r)$ of the c-SiAs, using a synthesis technique described in detail elsewhere.[10] For the purposes of this comparison we assumed that there was a single peak in the radial distribution function in the amorphous sample corresponding to silicon

nearest neighbors and we used the published structure for c-SiAs.[11] In the case of the crystalline sample, we determined the orientation relative to the polarization of the x-ray beam and used the appropriate $\cos^2\theta$ correction in the analysis. In order to quantify the comparison, we have defined a reliability index by analogy with x-ray and neutron scattering:

$$R = \frac{\sum\{|\mathrm{Re}(\varphi_0 - \varphi_m)| + |\mathrm{Im}(\varphi_0 - \varphi_m)|\}}{\sum\{|\mathrm{Re}\varphi_0| + |\mathrm{Im}\varphi_0|\}}, \qquad (2)$$

where φ_0 is the experimentally determined EXAFS real-space function, φ_m is the model function simulated from the 1.7-at.%-As-sample data, and the sum is over all the data points with r between 1.0 and 2.6 Å. The result of this comparison is an R value of 0.037. In view of this excellent agreement, we conclude that the assumption of a single silicon nearest-neighbor peak in the 1.7-at.%-As sample is correct and we determine the coordination number to be 2.80 ± 0.04 silicon atoms at a mean distance of 2.38 ± 0.01 Å. This procedure yields ξ_{Si}, the peak function for a silicon scatterer. ξ_{As} was obtained from the material deposited from pure AsH_3 on the assumption that the coordination number is 3, the same as for the other forms of a-As.[12] We note, however, that the precise value of this coordination number does not influence the analysis in the cases considered.

The radial distribution functions in the other samples were then extracted using these ξ's. The results of this analysis for the high-T_s and low-T_s samples are shown as the open and closed circles, respectively, in Fig. 2. The silicon nearest-neighbor distance is unchanged to within 0.002 Å in each case. The reliability indices for these results, with the exception of the 1% sample, are ~0.04 and show no systematic change with concentration. The error bars represent values obtained by allowing compensating changes in broadening and amplitude so as to cause a 5% increase in the reliability index. Note that only ξ_{Si} has been used in these syntheses. An estimate of the possible fraction of As-As bonds was obtained by subtracting a 5% ξ_{As} from the experimental result for the 12-at.%-As sample and performing a new synthesis. The result was both a worsening of the reliability index by 5% and systematic fluctuations in the deviation as a function of r. We conclude that As-Si bonds are energetically preferred over As-As bonds. The two most important features of these results, however, are the monotonic decrease in arsenic co-

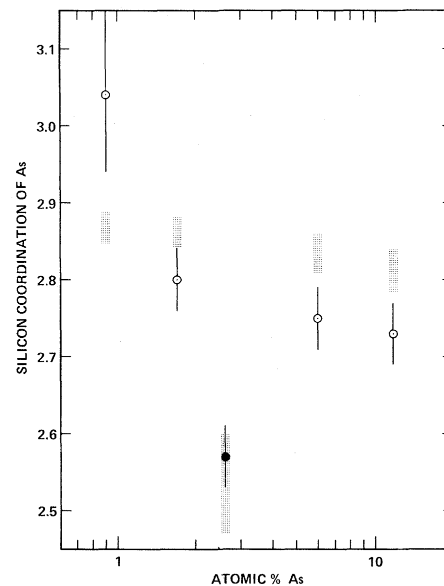

FIG. 2. Silicon coordination of arsenic as a function of arsenic concentration in amorphous Si-H:As compounds: Points represent values determined from EXAFS; shaded bars represent range of values predicted from hydrogen content (see text).

ordination with increasing arsenic concentration and the fact that at high concentrations the coordination number is less than 3—the lowest valency of arsenic.

At this juncture we consider the effect of hydrogen on the EXAFS results. Hydrogen has a negligible scattering cross section[13] in the electron energy range investigated. Thus it will effectively reduce the measured coordination if it is bonded to the arsenic. To quantify this reduction, we must make some assumptions concerning both the bonding to and the distribution of hydrogen between arsenic and silicon. Firstly, since we observe strong infrared absorption bands in these samples corresponding to bonded hydrogen (the As-H and Si-H frequencies are too close to differentiate), we assume that essentially all the incorporated hydrogen is bonded to either Si or As. Secondly, we consider two simple models for the distribution, equal probability per atom and equal probability per bond. We have represented the range of reduced coordinations predicted by these models by the shaded bars in Fig. 2, the lowest value being that predicted by the "per atom" model.

Commenting firstly on the high-arsenic-concentration (≥2%) region, we see that the "per atom" model produces an absolute value closely comparable to the measured coordination number

for the high–substrate-temperature samples. We also note that the model values parallel the systematic decrease in coordination with increasing arsenic concentration and account very well for the reduced coordination in the sample deposited at 25°C. Secondly we see that, at the lowest arsenic concentration, the measured coordination number is 0.2 ± 0.1 higher than that predicted from the "per atom" model. Since there is no evidence to suggest a change in the manner in which hydrogen is bonded at low arsenic concentrations, we interpret this difference as an increase in the total coordination of the arsenic. We conclude that we are observing approximately 20% of the arsenic atoms fourfold-coordinated with silicon.[14] The onset of fourfold coordination as the arsenic concentration is reduced coincides with the enhancement in electrical conductivity. This is analogous to substitutional doping in crystalline semiconductors—except for the absence of long-range order.

To summarize, we have shown firstly that the material plasma-deposited from silane-arsine mixtures contains hydrogen in excess of 13 at.% and is properly described as a doped silicon-hydrogen alloy. Secondly, we have demonstrated directly that the environment of arsenic is disordered at the second-nearest-neighbor position and deduced that As-Si bonds are energetically preferred over As-As bonds. Finally, we have found an increase in the arsenic coordination at low arsenic concentrations that parallels the sharp increase in the electrical conductivity, thus providing direct evidence for the concept of substitutional doping in an amorphous semiconductor.

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[1]W. E. Spear and P. G. LeComber, Solid State Commun. 17, 9 (1975).

[2]J. C. Knights, Philos. Mag. 34, 663 (1976).

[3]P. G. LeComber and W. E. Spear, in *Structure and Excitations in Amorphous Solids*, AIP Conference Proceedings No. 31, edited by G. Lucovsky and F. L. Galeener (American Institute of Physics, New York, 1976), p. 284.

[4]J. C. Knights, D. Biegelsen, and I. Solomon, Solid State Commun. 22, 133 (1977).

[5]C. R. Wronski and D. E. Carlson, to be published.

[6]EXAFS has been discussed at length in the literature. See, for example, F. W. Lytle, D. E. Sayers, and E. A. Stern, Phys. Rev. B 11, 4825 (1975); E. A. Stern, D. E. Sayers, and F. W. Lytle, Phys. Rev. B 11, 4836 (1975).

[7]J. C. Knights, in *Structure and Excitations of Amorphous Solids*, AIP Conference Proceedings No. 31, edited by G. Lucovsky and F. L. Galeener (American Institute of Physics, New York, 1976), p. 284.

[8]H. Fritzsche, in Proceedings of the Seventh International Conference on Amorphous and Liquid Semiconductors, Edinburgh, Scotland, June, 1977 (Taylor and Francis, London, to be published).

[9]M. Brodsky, M. A. Frisch, J. F. Ziegler, and W. A. Landford, Appl. Phys. Lett. 30, 561 (1977).

[10]T. M. Hayes, P. N. Sen, and S. H. Hunter, J. Phys. C 9, 4357 (1976).

[11]T. Wadsten, Acta Chem. Scand. 19, 1232 (1965).

[12]H. Krebs and R. Steffen, Z. Anorg. Allg. Chem. 327, 224 (1964).

[13]P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Phys. Rev. Lett. 36, 1346 (1976).

[14]The occurrence of arsenic coordination higher than four is rare in general, and especially unlikely in semiconducting glass. See, for example, A. F. Wells, *Structural Inorganic Chemistry* (Oxford Univ. Press, London, 1962), 3rd ed., pp. 662–683.