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# Lattice distortions for arsenic in single-crystal silicon

A. Erbil,[*] W. Weber,[†] G. S. Cargill III, and R. F. Boehme
*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*
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Extended x-ray-absorption fine-structure measurements for 0.1, 0.7, and 7 at.% arsenic impurities in single-crystal silicon yield As-to-Si nearest-neighbor distances of 2.41 ± 0.02 Å, which are 0.06 Å (2.5%) greater than the Si-to-Si distance in pure silicon. Next-nearest-neighbor distances are 3.85 ± 0.02 Å, only 0.01 Å (0.3%) greater than the corresponding Si-to-Si distance.

The controlled doping of semiconductors by selected impurities is of scientific and technological interest. Fundamental understanding of solubilities and electronic properties of impurities in semiconductors requires precise information on locations of the impurities in the host lattice and on lattice distortions caused by the impurities.[1,2] More knowledge in these areas may permit better control of impurity incorporation and doping in semiconductor devices. Extended x-ray-absorption fine-structure (EXAFS) spectroscopy is a useful method for characterizing lattice distortions around impurity atoms, because EXAFS probes one particular element at a time and provides information about the number, distance, and chemical identity of its neighbors.[3]

Here we report the first experimental determination of local lattice distortions for arsenic as a dopant impurity in single-crystal silicon.[4] EXAFS measurements were made for three different As-in-Si samples. One was a 0.1 at.% As sample, bulk doped during crystal growth. Other samples with 0.7% and 7% As were prepared by 100-keV As ion implantation with doses of $6\times10^{15}$ and $6\times10^{16}$ $\mathrm{cm}^{-2}$ respectively, followed by laser annealing[4,5] using a frequency-doubled Nd:YAG $Q$-switched laser. Arsenic in these two samples is in a 2000-Å-thick near-surface layer. 0.7% and 7% represent the average arsenic concentrations at depths which are responsible for the observed EXAFS for the two ion-implanted samples. Alpha-particle backscattering and channeling measurements for the 0.7% sample are shown in Fig. 1. Channeling data for all three samples are consistent with > 90% of the arsenic atoms being in substitutional sites.[5,6]

The crystalline compound SiAs was the standard for determining the total phase function $\phi^{\text{As-Si}}(k)$ and the nearest-neighbor envelope function $\chi^{\text{As-Si}}_{\text{NN,env}}(k)$ for As-Si pairs, which were needed to evaluate EXAFS measurements for the As-in-Si samples. From reported uncertainties in lattice parameters and atom positions for SiAs,[7] uncertainty in the average As-Si distance should be less than 0.01 Å. The total phase function $\phi^{\text{As-As}}(k)$ and the envelope functions for As-As nearest neighbors $\chi^{\text{As-As}}_{\text{NN,env}}(k)$ and next-nearest neighbors $\chi^{\text{As-As}}_{\text{NNN,env}}(k)$ were obtained from EXAFS measurements on crystalline germanium, with small corrections made for going from germanium to arsenic.[8]

EXAFS measurements were made at the Cornell High Energy Synchrotron Source (CHESS). Fluorescence detection[9] was used for the 0.1% sample, and total yield detection[10] was used for the 0.7% and 7% samples and for SiAs. The EXAFS function $\chi(k)$ for the 0.7% sample is shown in Fig. 2, together with $|\Phi_2(r)|$, which was obtained by Fourier transformation of $k^2\chi(k)$. The subscript $n$ of $\Phi_n(r)$ denotes the exponent of $k$ employed in the Fourier transform, e.g., $k^n\chi(k)$. The sharp first, second, and third neighbor peaks in $|\Phi_2(r)|$ at positions very close to those expected for a silicon lattice confirm, in agreement with channeling measurements, that most arsenic atoms occupy substitutional sites for all three As-in-Si samples.

Quantitative information on local structure around arsenic atoms was obtained by fitting calculated model functions $\chi_{\text{cal}}(k)$ to the corresponding experimental functions $\chi_{\text{NN}}(k)$ and $\chi_{\text{NNN}}(k)$ obtained by back-transforming nearest-neighbor and next-nearest-neighbor regions of $\Phi_0(r)$ using the window functions shown in Fig. 2. $\chi_{\text{cal}}(k)$ included both As-Si and As-As pairs, and the total coordination number $N_{\text{As-Si}}+N_{\text{As-As}}$ was fixed at 4 for nearest neighbors and at 12 for next-nearest neighbors. The contribution from As-As pairs was too small to permit accurate determinations of the As-As distance even for the 7% sample. For definiteness and to aid in sample-to-sample comparisons $r_{\text{As-As}}$ was fixed at 2.45 Å in nearest-neighbor fitting for all three samples. This is a physically reason-

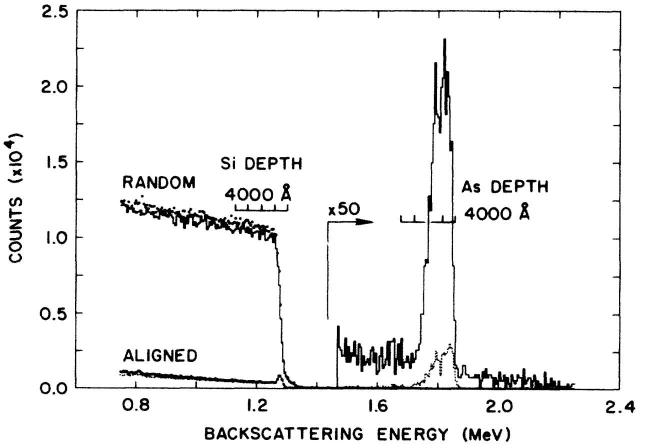

FIG. 1. Backscattering measurements for random and ⟨100⟩ aligned orientations taken with 2.3-MeV $\alpha$ particles. The solid and dashed lines are for the 0.7% As-in-Si sample, and the dots are for an undoped silicon crystal.

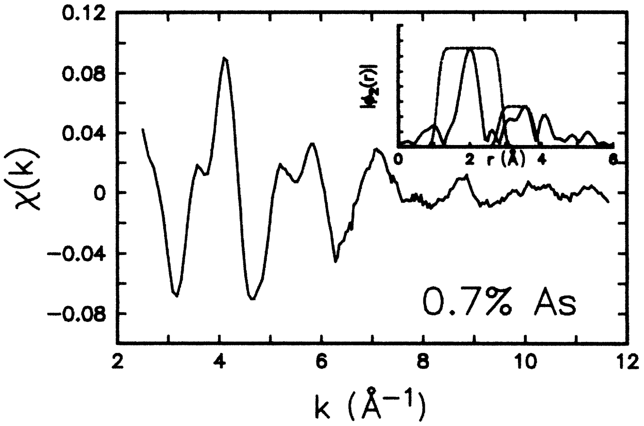

FIG. 2. EXAFS functions $\chi(k)$ and $|\Phi_2(r)|$ for 0.7% As-in-Si sample. Window functions used in extracting $\chi_{NN}(k)$ and $\chi_{NNN}(k)$ are shown as dashed lines.

TABLE I. Parameters obtained from fits to EXAFS data, except value given in *italics*, which was assumed in the analyses. $x_{Si}^{NN}$ and $x_{Si}^{NNN}$ are chemical compositions of As nearest-neighbor and next-nearest-neighbor environments. $\varepsilon^{NN}$ and $\varepsilon^{NNN}$ are strains for As-Si nearest- and next-nearest-neighbor distances with respect to the corresponding distances in crystalline silicon.

| Sample | $x_{Si}^{NN}$ | $x_{Si}^{NNN}$ | $\varepsilon^{NN}$ | $\varepsilon^{NNN}$ |
|---|---|---|---|---|
| 0.1% | 1.00<br>±0.09 | *1.0* | 0.022<br>±0.009 | 0.0016<br>±0.005 |
| 0.7% | 1.09<br>±0.09 | 0.95<br>±0.17 | 0.027<br>±0.007 | 0.0047<br>±0.007 |
| 7% | 0.91<br>±0.06 | 0.72<br>±0.11 | 0.025<br>±0.008 | 0.0013<br>±0.006 |

able value which is twice the tetrahedral covalent radius predicted by Van Vechten and Phillips.[11] Results are shown in Fig. 3 for the As-to-Si distance $r^{NN} = r_{As\text{-}Si}$, and results are given in Table I for the chemical composition of the As nearest-neighbor environment, expressed in terms of $x_{Si}^{NN} = N_{As\text{-}Si}/4$. Standard deviations were calculated for each of the structural parameters determined by linearized least-squares fitting.[12] These error estimates shown in Fig. 3 and in Table I correspond to the range of values which increase the mean-square fitting error $\sum[\chi_{NN}(k_i) - \chi_{cal}(k_i)]^2$ by no more than 100%.

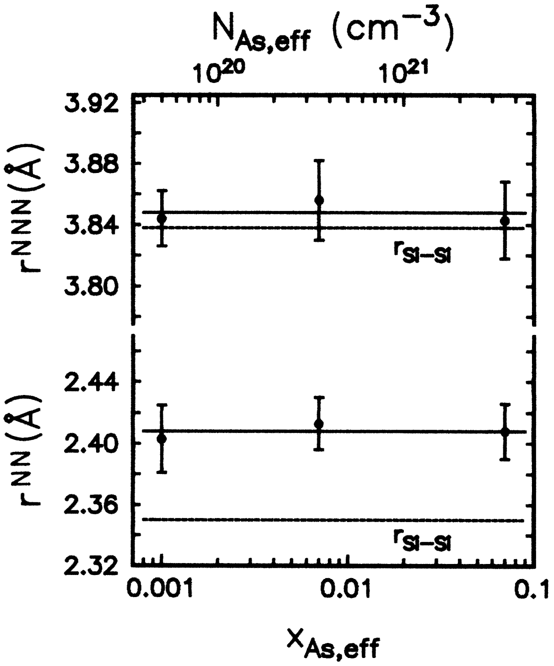

FIG. 3. Nearest-neighbor distances $r^{NN}$ and next-nearest-neighbor distances $r^{NNN}$ for As atoms in three As-in-Si samples. Both atom fractions $x_{As,eff}$ and concentrations $N_{As,eff}$ are indicated. The solid horizontal lines represent the average values of $r^{NN}$ and $r^{NNN}$, and the dashed horizontal lines represent the corresponding distances for crystalline silicon.

For fitting the next-nearest-neighbor regions, the As-Si envelope function was taken from measurements for the 0.1% sample, assuming for this most dilute sample that all 12 next-nearest neighbors of each As atom are Si atoms. The total coordination number $N_{As\text{-}Si} + N_{As\text{-}As}$ was fixed at 12. For definiteness it was assumed for next-nearest neighbors that $r_{As\text{-}Si} = r_{As\text{-}As}$. Results for $r^{NNN}$ are given in Fig. 3. Results for $x_{Si}^{NNN} = N_{As\text{-}Si}/12$ are given in Table I,[13] together with the "strains" $\varepsilon^{NN}$ and $\varepsilon^{NNN}$ for As-Si nearest-neighbor and next-nearest-neighbor distances with respect to the corresponding distances $r_{xtl,Si}$ in crystalline silicon: $\varepsilon = (r_{As\text{-}Si} - r_{xtl,Si})/r_{xtl,Si}$. Both for nearest neighbors and for next-nearest neighbors other fitting procedures, e.g., allowing $r_{As\text{-}Si}$ and $r_{As\text{-}As}$ to vary independently, give results which are consistent with those of Fig. 3 and Table I, but with about twice the error estimates and with more variation among results for the three different samples.

The As-Si nearest-neighbor distance determined in these measurements, 2.41 ± 0.02 Å, is 0.06 Å greater than the usual Si-Si distance but is consistent with the sum of tetrahedral covalent radii for As (1.225 Å) and Si (1.173 Å), described by Van Vechten and Phillips[11] as appropriate for estimating lattice distortions produced by *isovalent* impurities. Parameter-free self-consistent Green's function calculations by Scheffler[14] predicted an expansion of 0.03 ± 0.01 Å. Calculations by Kraut and Harrison[15] using a tight-binding theory predicted an As—Si bond length of 2.315 Å, which is 0.1 Å smaller than the observed value and corresponds to nearest neighbors relaxing *inward* by 0.03 Å. The only other experimental measurements concerning lattice distortion caused by arsenic in silicon have been lattice parameter measurements,[16] which are sensitive only to the average lattice expansion or contraction.

The EXAFS measurements show that most of the misfit for arsenic in silicon is taken up in the nearest-neighbor shell $\varepsilon^{NN} = 0.025 \pm 0.008$ with very little change in next nearest-neighbor distances, $\varepsilon^{NNN} = 0.0025 \pm 0.006$. These results from Fig. 3 and Table I provide a test for theories of bond lengths, lattice distortions, and lattice parameter changes for substitutional impurities in tetrahedral semiconductors.[14,15,17] Another important result from the present work is an upper limit of ±0.03 Å on the change in nearest-neighbor As-Si bond lengths for materials with from 0.1% As to 7% As, whereas a larger change might be expected from "electronic strain"[18] in going from a carrier concentration of $5\times10^{19}$ to $\sim3\times10^{21}$ electrons/cm$^3$.

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[*] Present address: Georgia Institute of Technology, School of Physics, Atlanta, GA 30332.

[†] Present address: Siemens Research Laboratories, Otto Hahn Ring 6, D-8000 Munich 83, West Germany.

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