VOLUME 56, NUMBER 24 PHYSICAL REVIEW LETTERS 16 JUNE 1986

Local Structure of S Impurities in GaAs

F. Sette, S. J. Pearton, J. M. Poate, and J. E. Rowe
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

and

J. Stöhr
IBM Almaden Research Center, San José, California 95120

(Received 25 February 1986)

The local structure of S implanted in GaAs has been determined by extended x-ray-absorption fine structure by monitoring of the S $K\alpha$ fluorescence yield. The S first-neighbor shell shows a significant static broadening compared to the S second- and third-neighbor shells. This indicates two S configurations of approximately equal population: (1) substitutional S on an As site and (2) a complex formed by S on an As site and an As vacancy on the second-neighbor shell with a S–first-neighbor distance relaxation of 0.14 ± 0.04 Å. The two-site configuration explains the disparity between implanted S concentration and net electrical activity.

PACS numbers: 61.10.Lx, 61.70.Bv, 78.50.Ge, 78.70.Dm

The physical properties of highly doped III-V semiconductors ($\geqslant 10^{18}$ atoms/cm^3) have attracted much interest.[1] A continuing problem for n-type III-V semiconductors is the formation of donor-related defects which drastically change the expected physical properties of these systems. Typical defect-induced features are persistent photoconductivity and saturation of the electrical activity with increasing dopant concentration.[2] Various models of the local structure for defect centers have been proposed, but so far, the geometrical structure of the impurity atom has not been measured directly. We report here bond distances and numbers of atoms in the atomic shells surrounding a prototypical donor, S in GaAs, obtained by measuring the extended x-ray-absorption fine structure (EXAFS) signal from the $1s$ core level of the S impurity atom.[3] The EXAFS spectra were measured by detection of the impurity $K\alpha$ soft-x-ray fluorescence yield (FY). Our studies cover the concentration range between 2×10^{19} and 2×10^{20} S-atoms/cm^3.

The experiments were performed with use of synchrotron radiation at the Stanford Synchrotron Radiation Laboratory. The fluorescence detector, used to monitor the S $K\alpha$ FY, was a custom-made energy-dispersive proportional counter with a 125-μm Be window and an energy resolution of ≈ 800 eV FWHM.[4] The samples were prepared by implanting 100-keV ^{32}S ions into undoped GaAs $\langle 100\rangle$. Annealing was performed in a flowing As-H$_2$ ambient at temperatures in the 700–900 °C range. The depth profiles of S were measured by secondary-ion mass spectrometry and the electrical activity of the S was determined by Hall effect and electrochemical capacitance-voltage (C-V) profiling. In accordance with previous results,[5] we found a saturation electron density of $\approx 5\times10^{18}$/cm^3, which is at least an order of magnitude less than the implanted S concentration. Remnant damage was studied by ion channeling; samples showed a high degree of crystallinity after annealing, with backscattering yields ($\approx 4\%$) close to those of virgin GaAs.

In Fig. 1 we show the S (K edge) photoabsorption spectra and the EXAFS signal in k space of two GaAs samples which were implanted with S to doses of 1×10^{15} and 1×10^{16} atoms/cm^2 and annealed at 900 °C. The mean concentrations ($\bar{n} = 2\times10^{19}$ atoms/cm^3 and $\bar{n} = 2\times10^{20}$ atoms/cm^3, respectively) were calculated with the assumption of Gaussian-type implantation distributions in agreement with secondary-ion mass-spectrometry measurements. Measurements of the S KLL Auger electrons, with escape depth of ≈ 30 Å, showed no enrichment of S at the surface.[6] The S atoms were distributed over a mean depth of ≈ 5000 Å from the surface. On the 2×10^{19}-atoms/cm^3 sample, the S K-edge signal-to-background ratio is 220%. EXAFS experiments can be performed with signal-to-background ratios of 10%.[4,6] The S $K\alpha$ absorption length in GaAs is ≈ 1 μm. The detection sensitivity limit of soft-x-ray–FY EXAFS can therefore can be calculated to be $(10\%/220\%)\times[(0.5\ \mu\text{m})/(1\ \mu\text{m})]\times(2\times10^{19}\ \text{atoms/cm}^3)$, i.e., 5×10^{17} atoms/cm^3 for S impurities in GaAs. Similar arguments apply to other impurities, such as Si, P, Cl, and Ar, with K edges in the soft x-ray region.

In Fig. 2 we show the Fourier transform $|F(r)|$ of the data reported in Fig. 1. Three peaks arise from the first three atomic-coordination shells around S which are analyzed by use of experimental phase shifts and backscattering amplitudes[3] from GaS, GeS$_2$, and CuGaS$_2$. Inconsistencies in bond length due to differences between Cu, Ga, and Ge phase shifts and backscattering amplitudes were less than ± 0.01 Å. The peaks in Fig. 2 arise from Ga and As neighbors and not from other S atoms as revealed by the k-space maximum of the backscattering amplitude.[7] Each

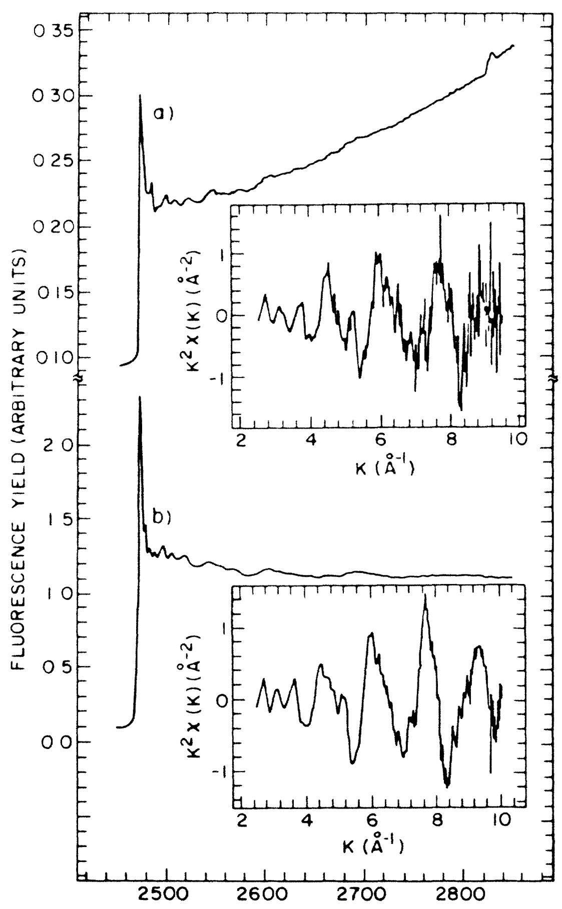

FIG. 1. S (K edge) photoabsorption spectrum and EXAFS signal after background removal, transformation to k space, and multiplication by k^2 (insets) for S implanted in GaAs ⟨100⟩ at 100 keV and annealed at 900 °C. (a) $\bar{n}=2\times10^{19}$ S-atoms/cm^3; (b) $\bar{n}=2\times10^{20}$ S-atoms/cm^3.

bond distance and number of neighbors was obtained by fitting the backtransformed data of the shell with the amplitude and phase obtained from the first-neighbor shell of each standard. The Fourier transformation interval was chosen to be 2.5–10 Å^{-1}. No appreciable changes were observed in the $|F(r)|$ function by reducing this interval to 4.0–10 Å^{-1}.

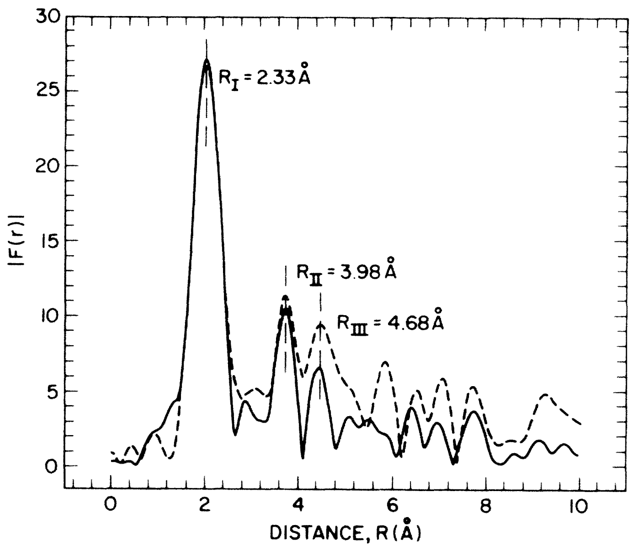

FIG. 2. Fourier-transform magnitude $|F(r)|$ of the EXAFS signal shown in the inset of Fig. 1 (solid line, 2×10^{20} S-atoms/cm^3; dashed line 2×10^{19} atoms/cm^3). Bond distances obtained from the one-shell analysis of the first three shells around the S atom are indicated.

The S first-neighbor-shell distance is 2.33 ±0.03 Å for samples annealed at temperatures above 700 °C and $\bar{n}$ ranging between 2×10^{19} and 2×10^{20} atoms/cm^3. This distance is 0.12 Å shorter than in GaAs (2.445 Å). However, the S second- and third-neighbor-shell distances (3.98 ±0.03 and 4.68 ±0.03 Å) are identical with GaAs (3.990 and 4.679 Å). These results demonstrate that the S atoms are substitutional and rule out models with interstitial or clustered S atoms behaving as nonelectrically active defects.[2] The contraction of the S first-neighbor distance may be expected because the S—Ga or S—As bonds are typically ≈ 0.15 Å shorter than the Ga–As bond; however, the first-neighbor-shell EXAFS parameters show some anomalies with respect to those of the outer shells. The number of first-shell neighbors is 2.6 instead of 4 as expected for substitutional S atoms and the first-neighbor-shell Debye-Waller factor is physically too large when compared with that of the second- and third-neighbor shells. Another unusual feature is the width of the first-neighbor-shell peak in the $|F(r)|$ transform function which has FWHM 0.13 Å wider than the second- and third-neighbor-shell widths. This point is illustrated in Fig. 3 for the data of the 2×10^{20}-atoms/cm^3 sample. A first-neighbor shell wider than

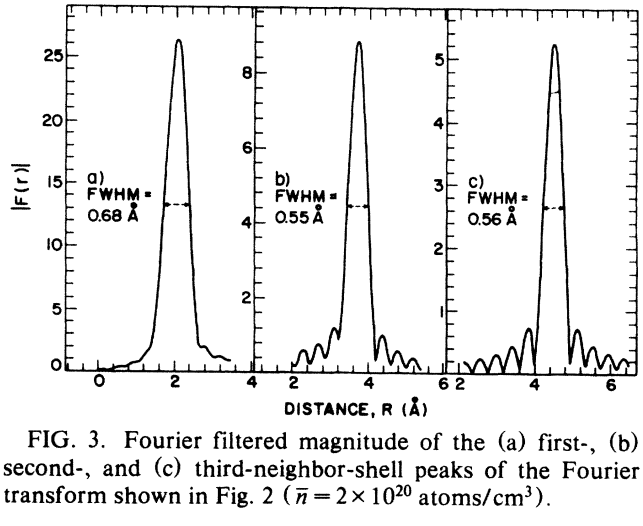

FIG. 3. Fourier filtered magnitude of the (a) first-, (b) second-, and (c) third-neighbor-shell peaks of the Fourier transform shown in Fig. 2 ($\bar{n}=2\times10^{20}$ atoms/cm^3).

the outer shells means that there are interactions affecting the local structural configuration of the atoms closer to the S but not the position of the S with respect to the rest of the lattice. We checked this idea by comparing the widths of the first-, second-, and third-neighbor-shell Fourier-transformed EXAFS peaks in the $|F(r)|$ of Ga and As in GaAs.[8] In this system second- and third-neighbor-shell peak widths are 0.55 Å FWHM, consistent with our results, but the first-neighbor-shell width is 0.45 Å FWHM, which is 0.23 Å narrower than our case.

This effect cannot be explained by a single substitutional site for the S atoms but it can be explained by two different substitutional configurations which are characterized by different first-neighbor relaxations and by relatively unperturbed second- and third-neighbor shells. The two S site configurations are (1) $\approx 50\%$ of S atoms on As sites with 4 Ga first neighbors at 2.43 ±0.04 Å (S_{As}) and (2) $\approx 50\%$ of S atoms on As sites with an As vacancy on the second-neighbor shell and 4 Ga first neighbors at 2.31 ±0.04 Å (S_{As}, V_{As}). The first-neighbor-shell filtered experimental data and the least-squares best fits with one and two configurations (dashed and solid line, respectively) are reported in Fig. 4. The fit with two configurations decreased the statistical χ^2 and residual values by a factor of 30. The two configurations have equal concentration to within ±20%, each with 4 nearest-neighbor atoms and bond distances of 2.31 and 2.43 Å. The uncertainty on these distances is given conservatively as ±0.04 Å. Another conclusive aspect of this model is that the Debye-Waller factors of the two configurations are the same as for the S second- and third-neighbor shells and the GaS standard to within 10%, whereas the single-configuration fit requires an anomalously large and unphysical Debye-Waller factor.

Our EXAFS results show that the S is on the As site with or without an As vacancy on the second shell [S_{As} or (S_{As}, V_{As})]. A missing As atom on the second-neighbor shell implies four broken bonds, one on a Ga atom of the first-neighbor shell, two on two Ga atoms of the third-neighbor shell, and one on a Ga atom on the fifth-neighbor shell. Therefore the As vacancy is a weak perturbation on the eleven second-neighbor-shell As atoms and on ten of the twelve third-neighbor-shell Ga atoms, which do not have broken bonds. However, the first-neighbor-shell Ga atom with a broken bond will cause a contraction of the average S-Ga distance. Therefore we assign the value of 2.31 ±0.04 Å to the S—Ga bond of this complex. Moreover the remaining eleven bonds between the first-neighbor-shell Ga and second-neighbor-shell As constrain the S first-neighbor shell so that the S atom is close to a substitutional site and the second- and third-neighbor S shells are relatively unperturbed with respect to the GaAs lattice.

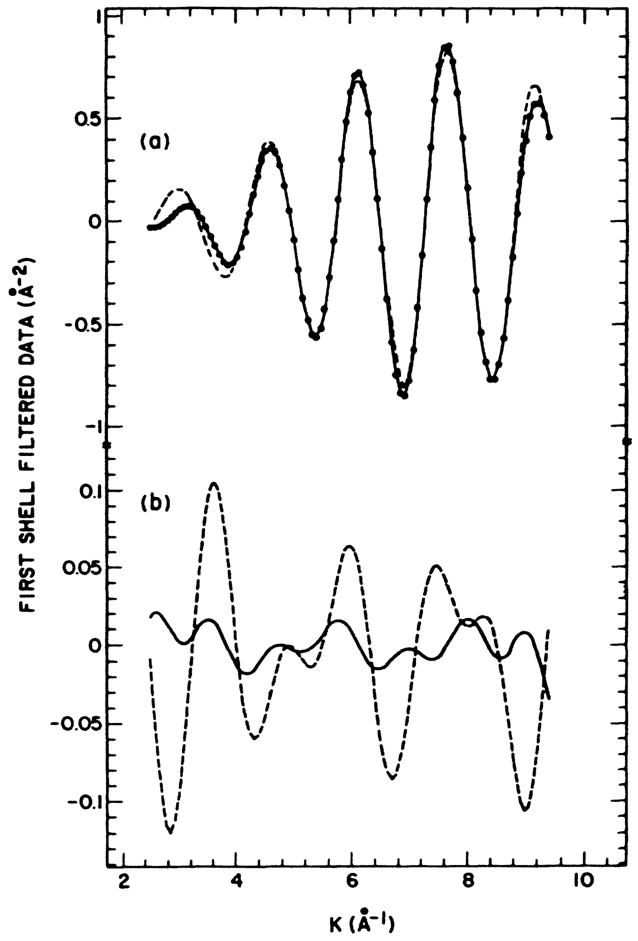

FIG. 4. S first-neighbor-shell filtered data (dots) with one- and two-configuration fits for the $\bar{n} = 2 \times 10^{20}$-atoms/cm^3 S-doped GaAs sample. The fits were obtained using GaS first-neighbor-shell model amplitude and phase shift: (a) One-configuration fit with $R = 2.33$ Å and 2.6 neighbors (dashed line) and two-configuration fit with $R_1 = 2.31$ Å, $R_2 = 2.43$ Å and 4 neighbors (solid line); (b) residual differences between the first-neighbor-shell filtered data and the one-configuration fit (dashed line) or the two-configuration fit (solid line). Note the change in vertical scale from (a) to (b).

It could be argued that the S is equally distributed on As (S_{As}) (unrelaxed configuration, S—Ga bond 2.43 Å) and Ga (S_{Ga}) (relaxed configuration, S—As bond 2.31 Å) sites. However, this arrangement is ruled out by specific lattice-site-location measurements performed on implanted samples similar to ours, using the channeling technique, which show S to be uniquely on As sites.[9] Moreover, electrical activity would not saturate in the $S_{Ga} + S_{As}$ model as S_{Ga} is a double donor. In contrast, electrical-activity measurements are consistent with the As-vacancy model where the (S_{As}, V_{As}) complex is an acceptor[5] that will compensate the donor S_{As}. Therefore, with two species present in roughly equal amounts, the concentration of net electrically active sites (i.e., uncompensated donors) should be much smaller than the total S-atom concentration. Indeed there are experimental observations which show that the electrical activity changes when the V_{As} concentration is altered. The electrical activity of donors decreases when GaAs crystals are grown under As-deficient conditions[5] (i.e., an increase in V_{As}). Moreover, when our samples are coimplanted with As to the same dose and range (i.e., a decrease in V_{As}) the electrical activity increases.

In this work we have demonstrated that EXAFS measurements using soft-x-ray FY detection are a powerful tool for the determination of the local defect environment of impurities in semiconductors. Such information is crucial for a complete description of these systems. We have shown that the structure of implanted S can be correlated with the electrical properties of S-doped GaAs.

We wish to acknowledge useful discussions and support from our colleagues at AT&T Bell Laboratories. We also wish to thank the staff at the Stanford Synchrotron Radiation Laboratory, which is supported by the Office of Basic Energy Sciences of the U.S. Department of Energy and the Division of Materials Research of the National Science Foundation.

---

[1] See, for example, *New Developments in Semiconductor Physics,* edited by F. Beleznay, G. Ferenczi, and J. Giber (Springer-Verlag, Berlin, 1980); *Ion Implantation and Beam Processing,* edited by J. S. Williams and J. M. Poate (Academic, New York, 1984).

[2] D. V. Lang, in *Deep Levels in Semiconductors,* edited by S. Pantelides (Gordon and Breach, New York, 1985).

[3] P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Rev. Mod. Phys. **53**, 769 (1981).

[4] J. Stöhr, E. B. Kollin, D. A. Fisher, J. B. Hastings, F. Zaera, and F. Sette, Phys. Rev. Lett. **55**, 1468 (1985).

[5] C. M. Wolfe and G. E. Stillman, Appl. Phys. Lett. **27**, 564 (1975).

[6] P. H. Citrin, J. E. Rowe, and P. Eisenberger, Phys. Rev. Lett. **28**, 2299 (1983).

[7] B. K. Teo and P. A. Lee, J. Am. Chem. Soc. **101**, 2815 (1979).

[8] J. C. Mikkelsen and J. B. Boyce, Phys. Rev. B **28**, 7130 (1983). The same results are found for germanium; E. A. Stern, B. A. Bunker, and S. M. Heald, Phys. Rev. B **21**, 5521 (1980).

[9] R. S. Bhattacharya, A. K. Rai, Y. K. Yeo, P. Pronko, and Y. S. Park, Nucl. Instrum. Methods **209/210**, 637 (1983); R. S. Bhattacharya, P. Pronko, and S. C. Ling, Appl. Phys. Lett. **42**, 880 (1983).