RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 5 15 FEBRUARY 1988-I

Structure of Si—Ge amorphous-semiconductor heterojunctions

F. Sette
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

B. Abeles and L. Yang
Exxon Research and Engineering Co., Annandale, New Jersey 08801

A. A. Mac Dowell, C. H. Richardson, and D. Norman
SERC Daresbury Laboratory, Warrington WA4-4AD, United Kingdom

(Received 29 October 1987)

We determined by extended x-ray-absorption fine structure (EXAFS) that the interfaces in hydrogenated amorphous Si—Ge superlattices are atomically abrupt and the interface atoms are bound on average to two Si and two Ge atoms. The Si—Ge interface bond distance is 2.40 ± 0.02 Å, equal to the average of the bulk distance values for Si and Ge. The experiment was performed at the Si K edge and the EXAFS was monitored by Si $K\alpha$ soft x-ray fluorescence detection. This innovative approach allows for EXAFS studies of *buried* and *oriented* interfaces and offers new opportunities in structural studies of interfaces.

The observation of new electronic phenomena in amorphous semiconductor superlattices such as quantum size effects,[1] enhanced photoluminescence,[2] and electroabsorption,[3] has focused a large experimental effort to understand the properties of these systems and their dependence on the details of the potential across the quantum well.[4] A strong dependence of the optoelectronic properties of these materials on the growth parameters has attracted interest on the possibility of tailoring the amorphous semiconductor superlattice to match particular device applications. Moreover, the growth mechanism has been widely recognized as important in determining the interface morphology and the nature of the defects across the superlattice. Further advances in the fundamental understanding and in the application of amorphous superlattices to devices requires detailed knowledge of the atomic structure of the interface. We report results of extended x-ray-absorption fine-structure (EXAFS) experiments on the interface structure of hydrogenated amorphous Si—Ge semiconductor multilayers. We find the Si—Ge interface to be atomically abrupt. This result, directly derived from our microscopic structural analysis, substantiates the interpretation of the optoelectronic properties of these superlattices.

Our study was performed at the Si K edge absorption threshold and the EXAFS signal was measured monitoring the Si $K\alpha$ soft-x-ray fluorescence yield (SXFY). This novel approach to study interface structures by EXAFS, has various innovations with respect to previous attempts carried out by Auger-electron detection.[5,6] In particular, by monitoring the SXFY signal the detection sensitivity is increased[7] and the experiment is not surface sensitive.[8] Accordingly, this technique allows the study of buried interfaces, does not require sample growth and characterization tools in the spectroscopy chamber, and there are no interface structure alterations, as in surface sensitive measurements, induced by the proximity of the surface to the interface (surface contamination or reconstruction). Furthermore, by detecting photons, there is no exponential decay of the interface signal on the same scale of distances of typical interface thicknesses as in the case of electron detection. This property allows for a direct and quantitative analysis of the amplitudes of different atom pairs and enables a precise description of the interface morphology in terms of bond counting. Such an improvement on EXAFS studies of interfaces is of general character and of critical importance in deriving the conclusions described here on the amorphous Si—Ge interface.

The EXAFS experiments were performed on the surface EXAFS (SEXAFS) beam line at the Daresbury synchrotron radiation facility.[9] The double-crystal monochromator used InSb(111) crystals. The Si $K\alpha$ signal was measured with a custom-made proportional counter.[10] The hydrogenated amorphous Si—Ge superlattices were grown by plasma-assisted chemical vapor deposition[1] using SiH_4 gas for the a-Si:H layers and 10% GeH_4 in H_2 for the a-Ge:H layers. The plasma was interrupted for several seconds after the completion of each layer to allow sufficient time for the gas exchange. The substrates were c-Ge covered with 200 Å of a-Ge:H and the superlattices were terminated with a 200-Å a-Ge:H top layer to prevent contamination. In our multilayers the a-Ge:H film thickness was kept constant at 7 Å and each sample had a different a-Si:H layer thickness (1.05, 2.10, 4.20, and 20.0 Å.) The total amount of a-Si:H varied between 50 and 60 Å. The sample growth was monitored with *in situ* optical reflectance methods.[11] The H concentration in the superlattices was 10% in atomic content.

In Fig. 1 we report the Si K-edge EXAFS signal after background subtraction and transformation in momentum space, measured in Si—Ge superlattices of different Si film thicknesses. The experimental data for different samples show a noticeable variation with Si film thickness. For the thin ($\simeq 1$ Å) Si film, the spectrum shows a broad envelope with a maximum at $k \simeq 7$ Å^{-1} whereas the 20-Å-thick sample shows a reduced amplitude with increased

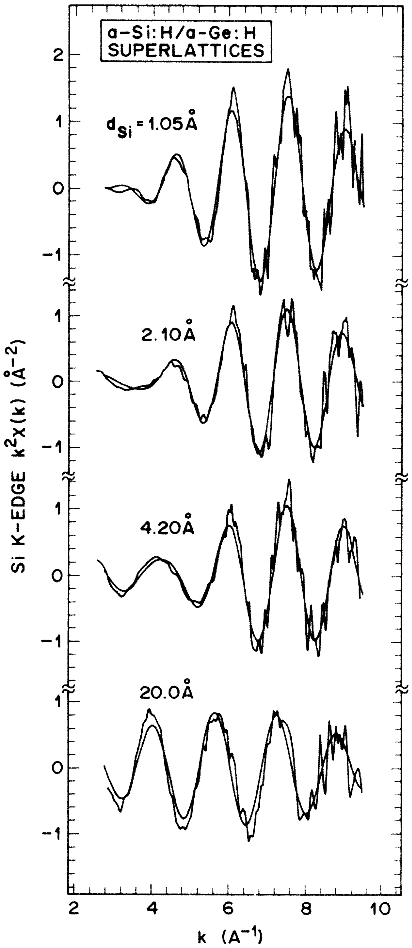

FIG. 1. Si K edge $k^2\chi(k)$ (EXAFS) data after background removal and transformation in momentum space for a-Si:H/a-Ge:H superlattices of periods 1.05 Å Si+7 Å Ge, 2.1 Å Si+7 Å Ge, 4.20 Å Si+7 Å Ge, and 20.0 Å Si+7 Å Ge, respectively. The data have been fitted (smooth line) with a linear combination of Si–Si and Si–Ge bonds using the parameters of Table I as explained in the text.

intensity in the lower-k region of our data range. The spectra of Fig. 1 also show a noticeable variation in the phase of the leading frequency with Si film thickness. Both observations are direct evidence of changes in the relative concentration of the atomic species bound to Si. It is expected that at small Si film thicknesses ($d_{\mathrm{Si}} \simeq 1$ Å) most of the Si atoms are bound to Ge while the Si–Si bond concentration becomes dominant in samples with larger Si layer thicknesses ($d_{\mathrm{Si}} > 4$ Å). The above experimental observations are consistent with the calculated differences in the total phase-shift and amplitude function of Si–Si and Si–Ge atom pairs.[12]

The substantial changes between the backscattering properties of Si and Ge atoms allow for a very good fit of the EXAFS data and provide a reliable deconvolution of the relative fractions of the Si–Ge and Si–Si bonds in the different samples. Using standard Fourier filtering procedures, it is possible to isolate the signal arising from the first-neighbor shell of the Si atom.[13] This oscillation is fitted with a linear combination of two oscillations representing the Si–Si and the Si–Ge bonds which are obtained, respectively, from the experimental first-shell EXAFS data of Si in bulk Si and P in bulk GaP.[13] After the determination of the distances and Debye-Waller factor differences between the standards and our samples, the two parameters which are different in the fit of different Si–Ge superlattices are the amounts of the Si–Si and Si–Ge bond fractions compared to the respective standard.

TABLE I. Summary of EXAFS results for Si–Ge superlattices.

d_{Si} (Å)	$R_{\mathrm{Si-Si}}$ (Å)	$N_{\mathrm{Si-Si}}$	$R_{\mathrm{Si-Ge}}$ (Å)	$N_{\mathrm{Si-Ge}}$
1.05	2.34 ± 0.03	0.5 ± 0.1	2.40 ± 0.02	3.6 ± 0.2
2.10	2.34 ± 0.03	1.1 ± 0.1	2.40 ± 0.02	2.9 ± 0.2
4.20	2.35 ± 0.02	2.0 ± 0.2	2.39 ± 0.02	2.1 ± 0.2
20.0	2.35 ± 0.02	3.6 ± 0.2	2.40 ± 0.03	0.5 ± 0.1
∞	2.35 ± 0.01	4.0 ± 0.2		

This procedure allows for proper and independent determination of the Si–Si and Si–Ge distances, the total Si coordination, and the Si–Si and Si–Ge bond fractions ($N_{\mathrm{Si-Si}}, N_{\mathrm{Si-Ge}}$) in the various superlattices. Results are reported in Table I and the best fit (sum of Si–Si and Si–Ge contributions) is superimposed to the EXAFS data of Fig. 1. The absolute values of the Si–Ge interface bond distance and of the Si–Si bond distance are, respectively, $R_{\mathrm{Si-Ge}} = 2.40 \pm 0.02$ Å and $R_{\mathrm{Si-Si}} = 2.35 \pm 0.02$ Å. The difference ΔR between $R_{\mathrm{Si-Ge}}$ and $R_{\mathrm{Si-Si}}$ is determined to a higher precision where $\Delta R = 0.05 \pm 0.015$ Å. No changes in distance are observed at different Si layer thicknesses. The Si–Ge bond distance corresponds to the average between the Ge–Ge and Si–Si bonds in bulk Ge (2.45 Å) and in bulk Si (2.35 Å). Such simple relations between the observed $R_{\mathrm{Si-Ge}}$ and $R_{\mathrm{Si-Si}}$ distances and the corresponding bulk values highlights the local nature of the Si–Ge and Si–Si covalent bonds in the amorphous network, where each bond distance is not visibly affected by the nature of the remaining atoms bound to the considered Si atom. This result is similar to the findings of a Ge K-edge EXAFS study in a large range of bulk hydrogenated $\mathrm{Ge}_x\mathrm{Si}_{1-x}$ alloys, where the Ge–Si distance was measured to be 2.38 Å.[14]

The Si atoms of our samples have a total coordination of 4 ± 0.3 first neighbors. The fraction of Si–Si and Si–Ge bonds observed at different Si layer thicknesses and reported in Table I are shown in Fig. 2 as a function of nominal Si layer thickness d_{Si} and d_{Si}^{-1}. These data show that for $d_{\mathrm{Si}} = 4$ Å, the Si atoms have, on average, an equal number of Si and Ge neighbors. This film thickness corresponds to a total amount of Si approximately equal to two monolayers. Therefore an equal number of Si homobonds and heterobonds at this Si film thickness directly implies that the Si–Ge interface is atomically abrupt. Accordingly, any Si–Si clustering or Si–Ge alloying can be ruled out because it would result in a larger fraction of Si–Si or Si–Ge bonds. Our interpretation is substantiated by the further observation that the Si bond fractions are linear in d_{Si} for $d_{\mathrm{Si}} \leq 4$ Å, and in d_{Si}^{-1} for Si film

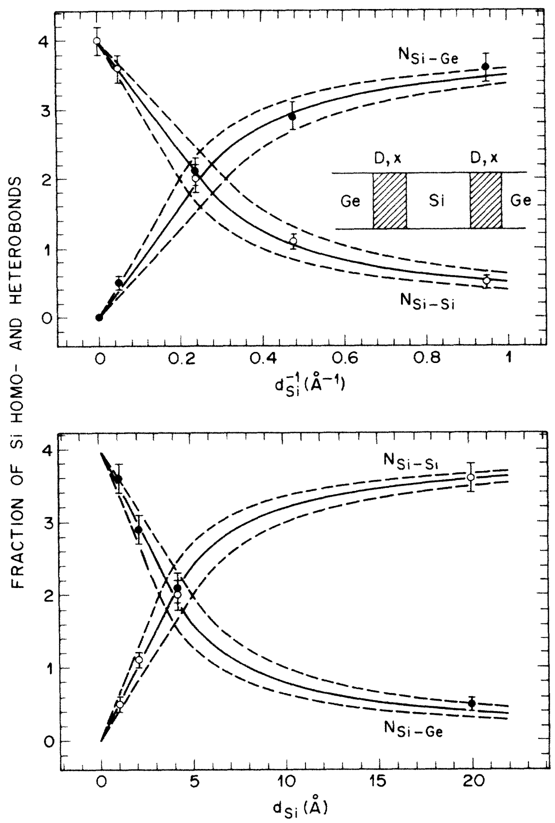

FIG. 2. Interpolation of the $N_{\text{Si-Si}}$ (open circles) and $N_{\text{Si-Ge}}$ (solid circles) data of Table I obtained using Eq. (1) with $D=2$ Å and $x=0.5$ as a function of d_{Si} and d_{Si}^{-1} (solid lines). Dashed lines are obtained allowing ±20% variation on the best values of the slopes.

thicknesses larger then 4 Å. This linear behavior can be understood with an interface continuum model where Si and Ge amorphous layers are separated by an interface region of composition $\text{Si}_x\text{Ge}_{1-x}$ and thickness D. Within this model, pictorically shown in Fig. 2, variations of $N_{\text{Si-Si}}$ and $N_{\text{Si-Ge}}$ with the Si film thickness d_{Si} are expressed by

$$\begin{aligned} N_{\text{Si-Si}} &= \frac{2xd_{\text{Si}}}{D} \quad \text{for } d_{\text{Si}} \le 2D \ , \\ N_{\text{Si-Si}} &= 4 + \frac{8D}{d_{\text{Si}}}(x-1) \quad \text{for } d_{\text{Si}} \ge 2D \ , \qquad (1) \\ N_{\text{Si-Ge}} &= 4 - N_{\text{Si-}Si} \ . \end{aligned}$$

According to Eq. (1), it is possible from our data to estimate D and x by determining the slopes in the two data regions, which are linear in d_{Si} and d_{Si}^{-1}. Allowing for a ±20% variation in the slope determinations (dashed lines in Fig. 2), we derive $D=2\pm0.5$ Å and $x=0.5\pm0.15$. These two values confirm our previous conclusions and describe the abruptness of the interface by a monolayer region of Si atoms ($D=2$ Å) coordinated, on average, with two Si and two Ge atoms ($x=0.5$). This result relies on the ability of the present SXFY technique to directly measure the absolute fraction of bonds in different samples. In particular, the linearity observed in Fig. 2 shows that the interface region EXAFS signal is homogeneously weighted, and effects associated with short escape distances, as in the case of electron detection, are not important.

In the present study we demonstrated that in our Si–Ge amorphous interfaces the material discontinuity is atomically abrupt. This result is in agreement with previous conclusions reached from the interpretation of Raman scattering experiments on Si–Ge superlattices.[15] This has important implications for amorphous semiconductor superlattice applications because it confirms the possibility of synthesizing superlattices with short periods. The ability of controlling the interface stoichiometry at the monolayer level allows for tailoring of the energy gap of the superlattice. The results presented here were obtained by an innovative approach on EXAFS experiments which is well suited for studies of buried interfaces in amorphous and crystalline materials with absorption lines in the soft x-ray region.

We wish to acknowledge E. E. Chaban, P. Petrie, and the staff at Daresbury for effective and invaluable technical assistance.

---

[1] B. Abeles and T. Tiedje, Phys. Rev. Lett. **51**, 2003 (1983); C. R. Wronski, P. Persans, and B. Abeles, Appl. Phys. Lett. **49**, 569 (1986).

[2] T. Tiedje, B. Abeles, and B. G. Brooks, Phys. Rev. Lett. **54**, 23 (1985).

[3] C. B. Roxlo and B. Abeles, Phys. Rev. B **34**, 2522 (1986).

[4] See references in *The Proceedings of the 11th International Conference on Amorphous and Liquid Semiconductors, Rome, 1985,* edited by F. Evangelisti and J. Stuke (North-Holland, Rome, 1985); Proceedings of the International Conference on Amorphous and Liquid Semiconductors, Prague, 1987 (unpublished).

[5] F. Comin, J. E. Rowe, and P. H. Citrin, Phys. Rev. Lett. **51**, 2402 (1983); F. Comin, J. Vac. Sci. Technol. A **3**, 930 (1985).

[6] J. Stöhr, R. Jaeger, A. Rossi, T. Kendelewicz, and I. Lindau, Surf. Sci. **134**, 813 (1983).

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

[8] F. Sette, S. J. Pearton, J. M. Poate, J. E. Rowe, and J. Stöhr, Phys. Rev. Lett. **56**, 2637 (1986).

[9] A. A. Mac Dowell, D. Norman, and J. B. West, Rev. Sci. Instrum. **57**, 2667 (1986).

[10] D. A. Fischer, J. B. Hastings, F. Zaera, J. Stöhr, and F. Sette, Nucl. Instrum. Methods A **246**, 561 (1986).

[11] L. Yang and B. Abeles, Appl. Phys. Lett. (to be published).

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

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

[14] L. Incoccia, S. Mobilio, M. G. Proietti, P. Fiorini, C. Giovannella, and F. Evangelisti, Phys. Rev. B **31**, 1029 (1985).

[15] P. D. Persans, A. F. Ruppert, B. Abeles, and T. Tiedje, Phys. Rev. B **32**, 82 (1985).