

Extended x-ray-absorption fine-structure study of hydrogenated amorphous silicon-germanium alloys. I. Analysis based on spherical waves of photoelectrons

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(Received 23 November 1987)

In conventional EXAFS (extended x-ray-absorption fine-structure) analyses, reliable structures are obtained with different values of absorption-edge energy E_0 for different neighboring atoms. It is shown in this study that the Ge K -edge EXAFS resulting from the Ge—Ge and Ge—Si bonds in hydrogenated amorphous Si-Ge alloys can be excellently explained by a unique E_0 value provided that a newly developed formula based on the spherical wave functions of photoelectrons is employed. The E_0 value is just at the steepest point in the experimental edge-jump curve. With the conventional formula the adjusted E_0 values for the Ge—Ge and Ge—Si bonds differ by 7 eV at maximum, and in addition they deviate by 3 eV at least from the steepest point.

I. INTRODUCTION

EXAFS (extended x-ray-absorption fine-structure) oscillations have been analyzed using the curve-fitting method,¹⁻³ in which the interatomic distances, the number of atoms, and the Debye-Waller factors for each coordination shell are the fitting parameters. Sometimes the absorption-edge energy E_0 is also treated as a fitting parameter to obtain the best fit. Significant progress in this method's accuracy has been achieved with the fine-adjustment technique based on model compounds (FABM) technique.³ In this FABM technique, reliable estimations of crystal structures for unidentified compounds can be obtained if the same correlation between the E_0 and interatomic distance R are obtained from the unidentified and model compounds.

It should be noted that an optimum E_0 inevitably results in a different value for each shell in the FABM technique. It is also noteworthy that the E_0 value is by no means an adjusting parameter and must have the same value for individual bonds.

Model compounds with clearly identified structures are required to have the same E_0 -to- R correlation as in the

case of unidentified compounds. It is difficult, for example, to obtain such compounds for a -Si_{1-x}Ge_x:H alloys, in which Si and Ge atoms form a random solid solution throughout the entire compositional range. Thus the validity of the FABM technique is extremely limited. This is why a well-grounded and universal technique for EXAFS analysis is required.

The purpose of this report is to show that EXAFS oscillation caused by two coordination shells can be analyzed with the same E_0 value for each bond. In addition, it is clarified that model compounds are not necessary if a new formula based on the spherical wave functions of emitted photoelectrons is employed. An experimental Ge K -edge EXAFS for a -Si_{0.62}Ge_{0.38}:H has been used for the present study. In Sec. II computational procedures are presented. In Sec. III results are given and the E_0 problem in conventional analyses is discussed.

II. COMPUTATIONAL PROCEDURES

Some formulas based on spherical waves for a single scattering process have been independently developed.⁴⁻⁶ The K -edge EXAFS $\chi(k)$ for nonpolarized x rays in a single scattering process is described by the following final expression:⁶

$$\chi(k) = -\text{Im} \left[\sum_{j \neq 0, l} (2l+1) \exp(2i\delta_1^0 + i\delta_1^j) \sin(\delta_1^j) \{ l(l+1) [h_l^{(1)}(\rho_j)/\rho_j]^2 + [lh_l^{(1)}(\rho_j)/\rho_j - h_{l+1}^{(1)}(\rho_j)]^2 \} \right], \quad (1)$$

where ρ_j is given by $\rho_j = kr_j$, with k the wave number of the photoelectrons, and r_j the distance of the j th scattering atom from the absorbing atom. The δ_1^0 is the p -wave phase shift of the photoelectron at absorbing atoms, δ_1^j is the phase shift of the l th partial wave at the j th scattering atoms, and $h_l^{(1)}(\rho_j)$ is the spherical Hankel function of

the first kind of order l . If we take only the first term in the following asymptotic expansion for $\rho \rightarrow \infty$,

$$h_l^{(1)}(\rho) \cong (-i)^{l+1} \frac{e^{i\rho}}{\rho} \left[1 + i \frac{l(l+1)}{2\rho} + \dots \right], \quad (2)$$

the l summation in Eq. (1) can be expressed with the backscattering amplitude $f_j(\pi)$:

$$\chi(k) = -\text{Im} \left[\sum_{j \neq 0} f_j(\pi)(2l+1) \times \exp[2i(\delta_1^0 + kr_j)] / kr_j^2 \right]. \quad (3)$$

This asymptotic equation corresponds just to a conventional formula.^{7,8}

The experimental EXAFS was fitted with the following parameters: the Ge—Ge bond length, the Ge—Si bond length, and the coordination ratio $N_{\text{Ge}}/(N_{\text{Ge}} + N_{\text{Si}})$, where N_{Ge} and N_{Si} are the coordination numbers of Ge and Si atoms around a Ge atom. In the fitting the bond lengths and coordination ratio were varied by 0.005 Å and 0.05, respectively.

The physical quantities used to calculate Eqs. (1) and (3) were obtained as follows. The phase shifts of the photoelectron at the absorbing atom were taken from the numerical tables given by Teo and Lee⁹ with Herman and Skillman wave functions.¹⁰ The phase shifts for the scattering atom ($l=0-12$) were calculated with a program developed by Pendry¹¹ from core-state wave functions.¹⁰ The effect of thermal vibration of scattering atoms was included in thermal Debye parameter B .⁶ The B factor at room temperature was estimated at 0.31 and 0.30 Å² for Ge and Si atoms, respectively, from the characteristic Debye temperature for crystals for each element.^{12,13} The effect of inelastic scattering of photoelectrons was included in a form $\exp(-2r/\lambda)$, where r is the interatomic path length and λ is the mean free path. For the mean free path, the escape depth of crystalline germanium measured by Gant and Monch¹⁴ was used.

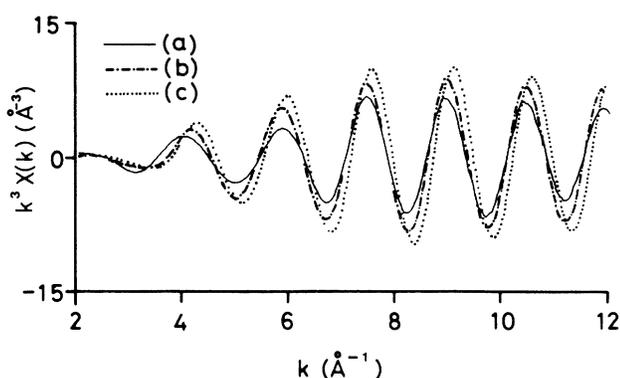


FIG. 1. Comparison of theoretical and experimental EXAFS for $a\text{-Si}_{0.62}\text{Ge}_{0.38}\text{:H}$. The total coordination number around a Ge atom is assumed to be 4 in (b) and (c). (a) Experimental Ge K EXAFS. The energy of absorption edge E_0 is taken at the steepest point in the edge jump. (b) Theoretical EXAFS calculated using Eq. (1) for the Ge coordination ratio, 0.4, and the bond lengths, 2.46 Å for Ge—Ge and 2.41 Å for Ge—Si. (c) Theoretical EXAFS calculated using Eq. (1) for the Ge coordination ratio, 0.4, and the bond lengths, 2.45 Å for Ge—Ge and 2.37 Å for Ge—Si.

III. RESULTS AND DISCUSSION

A. Analysis based on spherical waves of photoelectrons

The x-ray-absorption coefficient for $a\text{-Si}_{0.62}\text{Ge}_{0.38}\text{:H}$ was measured.¹⁵ The experimental Ge K -edge EXAFS is shown by the solid line in Fig. 1. The photoelectron wave number as the abscissa is converted from the x-ray energy via an absorption-edge energy of 11.109 keV defined as the steepest point in the experimental absorption curve. The $\chi(k)$ was multiplied by k^3 to intensify the amplitude at higher k values. Good fitting with a theoretical curve was realized at the Ge coordination ratio, 0.4, and the bond lengths, 2.46 Å for Ge—Ge and 2.41 Å for Ge—Si as shown by the dash-dotted line in the figure. As for the phase and period of the EXAFS, the solid line is in good agreement with the dash-dotted line over a range of k from 4.5 to 12 Å⁻¹.

The Ge K -edge EXAFS for $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ has been analyzed by Minomura *et al.*¹⁶ and Incoccia *et al.*¹⁷ However, their results, although generally excellent, contain some ambiguities because of the lack of model compounds.

Incoccia *et al.* have used the conventional formula and extracted the backscattering amplitude and the phase shift for the Ge—Ge and Ge—Si bonds from experiments on $a\text{-Ge:H}$ and $a\text{-Si}_{0.93}\text{Ge}_{0.07}\text{:H}$. The E_0 value in that work was taken at the inflection point at the edge jump. It was concluded that the Ge—Ge bond length and the Ge—Si bond length were 2.45 and 2.37 Å, respectively, for $x=0.37-0.72$.

The Ge—Ge bond lengths in Incoccia's and the present authors' results were very close. However, the Ge—Si bond lengths differed by 0.04 Å. The EXAFS calculated by using Eq. (1) with Incoccia's results are shown by the dotted line in Fig. 1. The Ge coordination ratio was assumed to be 0.4. The dotted line is considerably different from the solid one for a whole range of the wave number k . The E_0 value alone cannot account for this

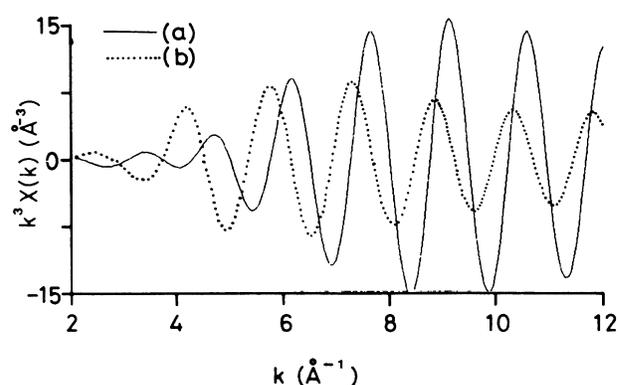


FIG. 2. Theoretical EXAFS for two extreme cases: (a) The Ge atom is surrounded by Ge atoms only (solid line) and (b) the Ge atom is surrounded by Si atoms only (dashed line). The total of coordination number around the Ge atom is assumed to be 4.

discrepancy. Thus, it is unfortunately difficult to explain the experiment with Incoccia's results.

The theoretical EXAFS for two extreme cases are shown in Fig. 2. One is the EXAFS when the absorbing Ge atom is surrounded only by Ge atoms (solid line). The other case is obtained when it is surrounded only by Si atoms (dotted line). The Ge—Ge bond length and the Ge—Si bond length were set to be 2.46 and 2.41 Å, respectively. The phase difference for these two cases increased at a low k value. Because the phase and period of EXAFS oscillation is sensitive to a slight change of coordinating atom, determination of the coordination ratio was highly accurate in the a -Si_{1-x}Ge_x:H case.

The EXAFS oscillation when the Ge coordination ratio is 0.3 (dotted line), 0.4 (solid line), and 0.5 (dash-dotted line) is shown in Fig. 3. The Ge—Ge bond length and the Ge—Si bond length were set to be 2.46 and 2.41 Å, respectively. It is clearly easy to distinguish one spectrum from another. Thus, the accuracy of the coordination ratio is within 0.05.

As for the amplitude of the EXAFS, it is hard to say that good agreement has been attained. The amplitude is affected by the thermal vibrations of atoms and the inelastic scattering of photoelectrons. In the present analysis, Debye parameters B_{293} for crystals at room temperature were employed. Strictly speaking, the B_{293} values for crystals are invalid for amorphous material. Incoccia *et al.* have also discussed Debye-Waller factors σ^2 for the Ge—Ge bond and the Ge—Si bond. It was concluded in that paper that the σ^2 for both bonds have almost the same value and do not change with the Ge concentration. Accordingly, in the case of a -Si_{1-x}Ge_x:H, the B value for crystals is valid unless it is necessary to determine the absolute coordination number, N_{Ge} or N_{Si} . Additionally, the effect of the inelastic scattering of photoelectrons should be the same for the Ge—Ge bond and the Ge—Si bond. It must be emphasized that the fine adjustment of the phase and period of EXAFS oscillation as employed in the present analysis can provide accurate short-range structures, except for the absolute coordination number.

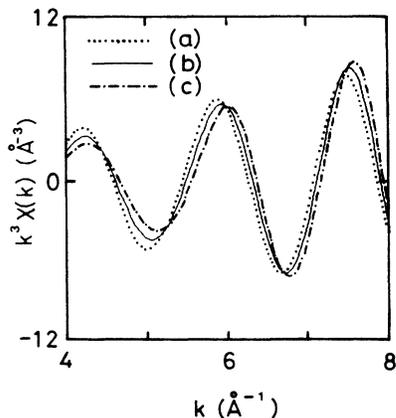


FIG. 3. Change in EXAFS with a Ge coordination ratio of (a) 0.3 (dotted line), (b) 0.4 (solid line), and (c) 0.5 (dash-dotted line).

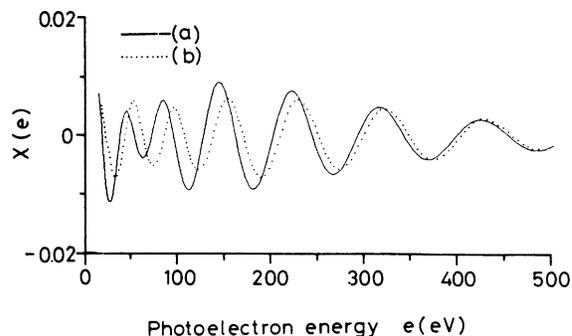


FIG. 4. Comparison of theoretical EXAFS for Ge—Ge bond whose bond length is 2.46 Å. (a) Calculated using Eq. (1). (b) Calculated using Eq. (3).

B. E_0 problem

It has been pointed out that the optimum E_0 in conventional analyses with or without the use of model compounds have different values for each bond.³ The optimum E_0 for Ge—Ge and Ge—Si bonds, which is derived from the analytic property of asymptotic Eq. (3), is estimated below.

The EXAFS oscillation due to the Ge—Ge bond calculated by using Eq. (1) is represented by the solid line in Fig. 4. The dotted line shows the result obtained through the use of Eq. (3). The Ge—Ge bond length was 2.46 Å in both cases. The EXAFS oscillation for the dotted line is quite different from that for the solid line, especially at a low energy. The phase difference in both cases is ~ 12 eV and ~ 3 eV at a photoelectron energy of 100 and 500 eV, respectively.

The EXAFS oscillation due to the Ge—Si bond calculated by using Eq. (1) is represented by the solid line in Fig. 5. The dotted line shows the same calculated by using Eq. (3). The Ge—Si bond length was set to be 2.41 Å. The phase difference for these two cases is ~ 5 eV and ~ 3 eV at a photoelectron energy of 100 and 500 eV, respectively.

It should be noted that the phase difference in Fig. 4 and Fig. 5 is not constant and increases as the photoelectron energy becomes small. It is because the second term

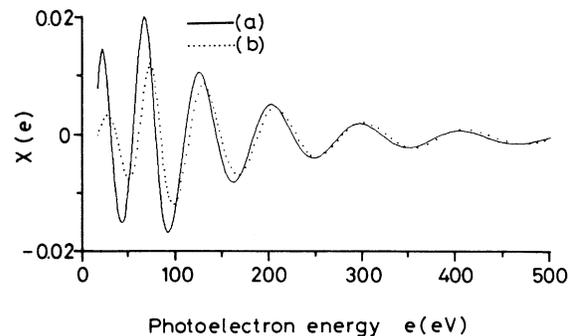


FIG. 5. Comparison of theoretical EXAFS for Ge—Si bond when the Ge—Si bond length is 2.41 Å. (a) Calculated using Eq. (1). (b) Calculated using Eq. (3).

of the asymptotic expansion in Eq. (2), $l(l+1)/2\rho$, depends on the photoelectron energy and the interatomic distance. The term $l(l+1)/2\rho$ cannot be neglected for photoelectron energy up to 500 eV when the Ge—Ge bond length is 2.46 Å and the Ge—Si bond length is 2.41 Å. Asymptotic Eq. (3) is valid for a more distant electron path: for a Cu—Cu bond whose interatomic distance is 5.11 Å, Eq. (3) almost agrees with Eq. (1) down to 100 eV of the photoelectron energy.⁶

The absorption coefficient near the Ge *K* edge for α -Si_{0.62}Ge_{0.38}:H is shown in Fig. 6. The arrow A shows the E_0 value employed in the present analysis. Arrows B and C show the optimum E_0 in Eq. (3) for Ge—Ge and Ge—Si bonds at the photoelectron energy of 100 eV, respectively. Clearly, the arrows B and C are out of the edge region. Maximum discrepancy of optimum E_0 for the Ge—Ge and the Ge—Si bonds are ~ 7 eV at a photoelectron energy of 100 eV. Although it has not been confirmed that the point of steepest change corresponds to the absorption edge, only one value of energy is allowed to be the absorption edge. Nevertheless, the optimum E_0 in Eq. (3) requires an E_0 for each Ge—Ge and Ge—Si bond, which contradicts the uniqueness of E_0 .

In curve-fit analyses with Eq. (3), the best fit is realized with the different values for each bond: Maximum discrepancy is 22.27 eV for the Mo—S and Mo—Fe bonds.³ However, as pointed out above, the optimum E_0 cannot be uniquely defined over a wide range of photoelectron energy even if only the Ge—Si bond is concerned. So real structures cannot be obtained with Eq. (3) no matter how the E_0 value for each bond is optimized.

IV. CONCLUSIONS

The absorption-edge energy E_0 is the most fundamental quantity in EXAFS analyses because it defines the wave number of emitted photoelectrons. However, in conventional analyses, the E_0 results in different values

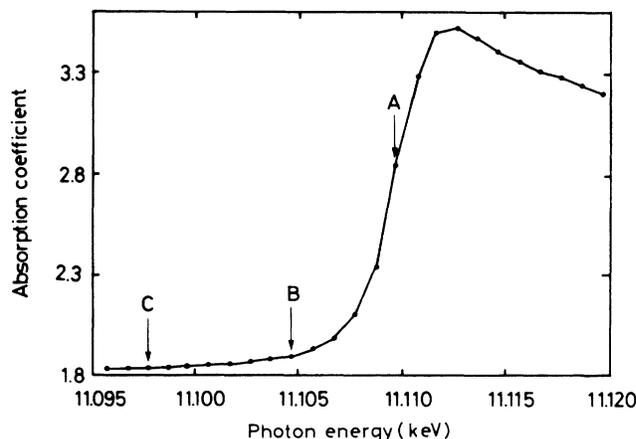


FIG. 6. The absorption coefficient near the Ge *K* edge for α -Si_{0.62}Ge_{0.38}:H. The absorption-edge energy E_0 in the present analysis is shown by arrow A. Arrows B and C show the optimum E_0 values in Eq. (3) for Ge—Si and Ge—Ge bonds at a photoelectron energy of 100 eV, respectively.

for neighboring atoms. We have shown that the EXAFS oscillation due to the Ge—Ge and Ge—Si bonds can be analyzed with a unique E_0 value provided that the EXAFS formula based on spherical wave functions of photoelectrons is employed.

ACKNOWLEDGMENTS

We are grateful to Dr. T. Shimada of Hitachi, Ltd. for fruitful discussions and continuous encouragement throughout this work. We would also like to thank Dr. M. Nomura of the Photon Factory at the National Laboratory for High-Energy Physics in Tsukuba, Japan, for experimental assistance and useful discussions on EXAFS.

- ¹S. P. Cramer, K. O. Hodgson, E. I. Stiefel, and W. E. Newton, *J. Am. Chem. Soc.* **100**, 2748 (1978).
- ²B.-K. Teo, R. G. Shulman, G. S. Brown, and A. E. Meixner, *J. Am. Chem. Soc.* **101**, 5624 (1979).
- ³B.-K. Teo, M. R. Antonio, and B. A. Averill, *J. Am. Chem. Soc.* **105**, 3751 (1983).
- ⁴W. L. Schaich, *Phys. Rev. B* **29**, 6513 (1984).
- ⁵S. J. Gurman, N. Binstead, and I. Ross, *J. Phys. C* **17**, 143 (1984).
- ⁶A. Fukuhara and H. Kajiyama (unpublished).
- ⁷D. E. Sayers, E. A. Stern, and F. W. Lytle, *Phys. Rev. Lett.* **27**, 1204 (1971).
- ⁸P. A. Lee and J. B. Pendry, *Phys. Rev. B* **11**, 2795 (1975).
- ⁹B.-K. Teo and P. A. Lee, *J. Am. Chem. Soc.* **101**, 2815 (1979).
- ¹⁰F. Herman and S. Skillman, in *Atomic Structure Calculations*

(Prentice-Hall, Englewood Cliffs, 1963).

- ¹¹J. B. Pendry, *J. Phys. C* **4**, 2501 (1971); **5**, 2567 (1972); the program, is listed by J. B. Pendry, in *Low-Energy Electron Diffraction* (Academic, New York, 1974).
- ¹²*International Tables for X-Ray Crystallography III*, edited by K. Lonsdale *et al.* (Kynoch, Birmingham, 1962).
- ¹³*American Institute of Physics Handbook*, 3rd ed. (McGraw-Hill, New York, 1972).
- ¹⁴H. Gant and W. Monch, *Surf. Sci.* **105**, 217 (1981).
- ¹⁵Y. Nishino, S. Muramatsu, and H. Kajiyama, following paper, *Phys. Rev. B* **38**, 1942 (1988).
- ¹⁶S. Minomura, T. Tsuji, M. Wakagi, T. Ishidate, K. Inoue, and M. Shibuya, *J. Non-Cryst. Solids* **58-60**, 541 (1983).
- ¹⁷L. Incoccia, S. Mobilio, M. G. Proietti, F. Fiorini, C. Giovannella, and F. Evangelisti, *Phys. Rev. B* **31**, 1028 (1985).