EXAFS Study of Semimetal-Semiconductor Transition of Bismuth Clusters

H. Ikemoto*, T. Miyanaga†, S. Yoshida* and J. Sogoh*

*Faculty of Science, University of Toyama, Toyama 930-8555, Japan
†Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan

Abstract. Extended X-ray absorption fine structure (EXAFS) measurements of bismuth clusters in the temperature range of 23 -300 K have been performed using synchrotron radiation in order to investigate the size dependent phase transition. The inter-atomic distances around 3.0 Å and 3.6 Å are attributed to the nearest neighbors within the layer and between layers, respectively. EXAFS functions were analysed by the curve fitting method within a symmetric distribution approximation. The nearest neighbor distance of the 0.5 nm thick films is shorter than that of the 300 nm thick films at all the temperatures, which is related to the reduction of the inter-layer correlation.

INTRODUCTION

In the rhombohedral phase, Bi atoms are incorporated into two-dimensional networks, and adjacent layers are situated at distances larger than the covalent intralayer bond length but shorter than the van der Waals distance. The semimetallic nature of rhombohedral Bi is attributed to the overlap between the back lobes of orbitals in adjacent layers, and the semiconducting nature of bulk amorphous Bi is attributed to the loss of this overlap [1].

Raman-scattering measurements of Bi clusters exhibit a phase transition from nanocrystalline rhombohedral Bi to amorphous-like clusters depending on cluster size [2]. They also suggest that amorphous clusters are semiconducting and covalent interactions increase with decreasing size.

In the present study we report results of extended X-ray absorption fine structure (EXAFS) for Bi clusters in order to study local structural changes in the phase transition.

EXPERIMENTAL

Thin layers of Bi and layers of NaCl were deposited alternately onto glass substrates from tungsten boats. The thin Bi films were discontinuous with isolated island formation, so that a sample of Bi clusters isolated in NaCl matrix was obtained. The size of the islands was changed by controlling the thickness deposited on the substrates, which was monitored with a quartz oscillator. The thickness ratio of the Bi and the matrix is about 1:20. Samples are represented by their average thickness of the Bi thin films in this paper.

EXAFS measurements were carried out at the BL12C in the Institute for Structure Material Science's Photon Factory (KEK-PF) using a Si(111) double crystal monochromator. X-ray absorption spectra were measured for the Bi L_{III}-edge (13.404 keV). The incident and transmitted X-rays were monitored by ionization chambers.

One of the most difficult problems in EXAFS analysis is the extraction of absorption by hypothetically isolated atoms [3]. The extraction needs information on maxima and minima of the absorption coefficients. It is difficult to define their location in the case of room temperature data of the 0.5 nm thick films. So we specified the k points which were determined in the absorption coefficients at 23 K.

Fourier transforms (FT) were performed with a k-range of 4.0 -18.0 Å^{-1}. To reduce ripples, a Hanning window function was used for truncation of the k-range. The peaks were Fourier filtered with $r = 2.58$ - 3.35 Å for the first shell. The curve fitting analyses were carried out in the k-space with range of 7.0 - 16.0 Å^{-1}. The coordination number, interatomic distance and Debye-Waller factor were used as fitting parameters in the curve-fitting procedure. In temperature dependent analysis for such a small cluster system third order cumulant should be taken into account, because an asymmetric distribution is expected. But as the first stage of the EXAFS analysis of the Bi cluster, we assumed that the third order cumulant was zero in this paper. Phase shift and amplitude functions obtained from FEFF8.2 [4] were used in the EXAFS analyses.
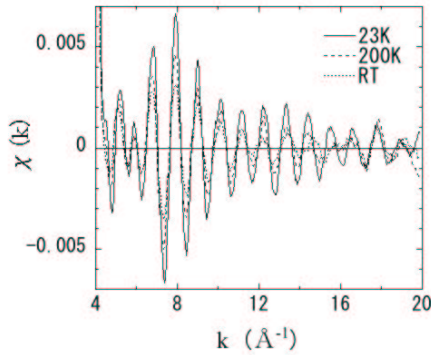
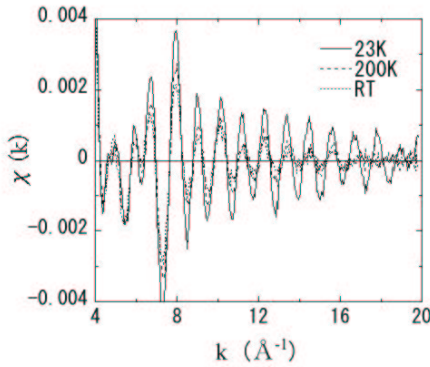**FIGURE 1.** $\chi(k)$ for the 300 nm thick films measured at different temperatures.

FIGURE 3. Fourier transform of $k\chi(k)$ for the 300 nm thick films at different temperatures.

FIGURE 2. $\chi(k)$ for the 0.5 nm thick films measured at different temperatures.

RESULTS

The EXAFS $\chi(k)$, as a function of wave number k, for several measuring temperatures of the 300 and 0.5 nm thick films are shown in Figs. 1 and 2, respectively. The oscillations of $\chi(k)$ are observed up to 20 Å^{-1}. Phases of $\chi(k)$ for all temperatures are coincident and increasing temperatures simply attenuates the amplitude of the EXAFS signal, indicating success of evaluations of $\chi(k)$.

FT of $k\chi(k)$ data and their temperature variations give useful information to consider origins of the peaks of the FT. Figure 3 shows the variations of the FT for the 300 nm thick films with the temperatures. The peaks around 3.0, 4.5 and 5.4 Å are the contributions from the first, second and third shells of Bi neighbors within the layer in consideration of atomic distances for the rhombohedral Bi. The intens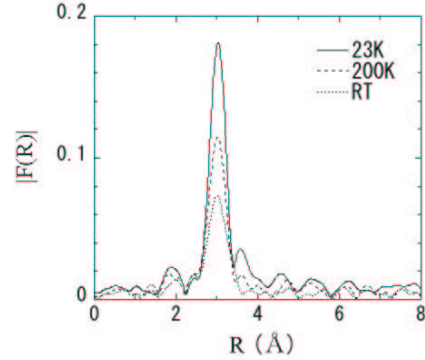ities of the main peak are very large compared to other peaks at all temperatures. There is a second peak around 3.6 Å which is close to the nearest inter atomic distance between layers. The reduction of the peak with increasing temperature indicates that the peak originates from interlayer correlation.

Figure 4 shows FTs of the 0.5 nm thick films. The amplitudes of the 0.5 nm thick films are weak compared to those of the 300 nm thick films. It is interesting that the peak originating from the interlayer correlation is very weak in the case of the 0.5 nm thick films.

One-shell (Bi-Bi) curve fitting analysis to the Fourier-filtered $\chi(k)$ gives the structural parameters. The coordination numbers of the 0.5 nm thick films is 1.4 ± 0.2 when the coordination number is scaled by that of the 300 thick films. The coordination number of the 0.5 nm thick films is unreliable, because the coordination number implies that the 0.5 nm thick films are composed of small molecules in spite of the small difference of the interatomic distances against that of the 300 nm thick films. In cluster systems, atoms at the cluster surface are not negligible and the reduction of the mean free path of excited electrons must be considered. Our analysis is the state of art at this stage.

Figure 5 shows the temperature variations of the nearest neighbor distance. At all measured temperatures the nearest neighbor distances of the 0.5 nm thick films are shorter than those of the 300 nm thick films. The distances for both samples shorten with increasing temperatures.

Figure 6 shows the temperature variations of the Debye-Waller factor. The difference between two samples is small, but there is a tendency that the Debye-Waller factors of the 0.5 nm thick films are smaller than those of the 300 nm thick films.
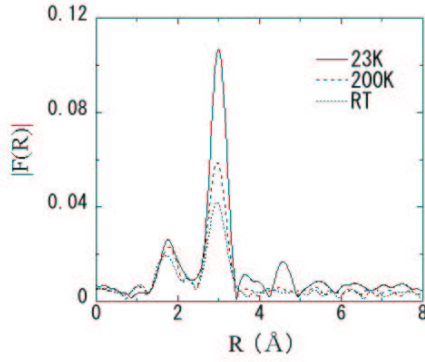
FIGURE 4. Fourier transform of $k\chi(k)$ for the 0.5 nm thick films at different temperatures.

FIGURE 5. Temperature variations of the nearest neighbor distances for the 300 and 0.5 nm thick films.

DISCUSSION

In comparison with the 300 nm thick films the 0.5 nm thick films are characterized by the shorter nearest neighbor distance and the reduction of the inter-layer correlation. Since the overlap between the back lobes of orbitals in adjacent layers gives weakening of the covalent bonds within the layer, the two characters are closely related. The reduction of the interlayer correlation decreases the overlap between the orbitals in adjacent layers, which strengthens the covalent bonds and gives rise to the bond shrinkage. The smaller Debye-Waller factor for the 0.5 nm thick films than that of the 300 nm thick films supports the bond shrinkage in the small clusters. The bond shortening of the 300 nm thick films with increasing temperature may be induced by the loss of the overlap by thermal vibration. There is a possibility that the bond length shortening is an artifact of the analysis without accounting for the effect of the asymmetric distribution (the third order cumulant). For more detailed analysis the asymmetric distribution effect would be taken into account in the next stage.

FIGURE 6. Temperature variations of the Debye Waller factors for the 300 and 0.5 nm thick films.

CONCLUSION

The EXAFS study of 300 and 0.5 nm thick films has been performed at several measuring temperatures within the limit of symmetric bond length distribution. The curve fitting analysis and the FT of EXAFS indicate slight shrinkage of covalent bonds within the layer and the disappearance of interlayer correlation in the 0.5 nm thick films. The loss of the overlap between the orbitals in adjacent layers induces the shrinkage.
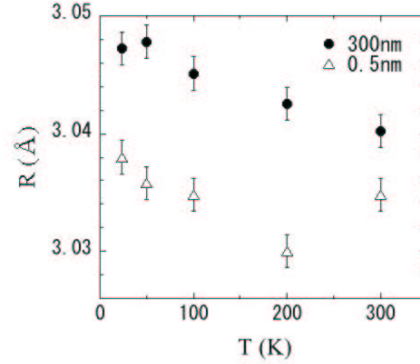
REFERENCES

1. N. F. Mott and E.A. Davis, *Electronic Progress in Non-Crystalline Materials, Second Edition*, Clarendon Press, Oxford, 1979, p 413.
2. M.G. Mitch, S.J.Chase, J. Fortner, R.Q. Yu, and J. S. Lannin, *Phys. Rev. Lett.* **67**, 875-878 (1991).
3. H. Sakane, T. Miyanaga, I. Watanabe, N. Matsubayashi, S. Ikeda, and Y. Yokoyama, *Jpn. J. Appl. Phys.* **22**, 4641-4647 (1993).
4. A.L. Ankudinov, B. Ravel, J.J. Rehr, and S.D. Conradson, *Phys. Rev.* **B58**, 7565-7576 (1998).