

EXAFS Study of Semimetal-Semiconductor Transition of Bismuth Clusters

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Introduction

Raman-scattering measurements of bismuth clusters exhibit a phase transition from rhombohedral Bi nanocrystalline to amorphouslike clusters depending on cluster size[1]. They also suggest that amorphous clusters are semiconducting and covalent interactions increase with decreasing size.

The Raman studies are good tools but indirect evidences for the transition. So it is very important to investigate the structure to reveal the mechanism of the phase transition. In the present study we report results of extended X-ray absorption fine structure (EXAFS) of Bi clusters.

Experimental

Bismuth of 99.999 % purity was slowly deposited onto the substrates from a tungsten boat. The Bi film was discontinuous with isolated island formation. Then, NaCl of 99.99 % purity was deposited to cover the Bi islands. By repeating these procedures, a sample of Bi clusters isolated in the NaCl matrix was obtained. Since the Bi clusters are formed in thin films, samples are represented by their average thickness of the Bi thin films in this report.

EXAFS measurements were carried out for the Bi clusters isolated in the NaCl matrix, using the spectrometer installed at BL-12C of the Photon Factory (PF). X-ray absorption spectra were measured for Bi L_{III}-edge (13.404 keV). The intensity of incident beam and the transmitted beam were monitored by ionization chambers.

Result and Discussion

The XAFS $\chi(k)$, as a function of wave number k , for several temperatures of the 0.5 nm thick film are shown in Fig. 1. The phases in oscillations of $\chi(k)$ are observed up to 20 \AA^{-1} . If the phase difference between XAFS of different temperatures is negligible, then increasing temperatures simply attenuates the amplitude of the XAFS signal and the XAFS will have zero crossing at the same wave number where the background must pass through the absorption data itself. The temperature variations indicate success of evaluations of $\chi(k)$.

Figure 2 shows Fourier transform of $k\chi(k)$ of the 0.5 and 300 nm thick films at 23K. As can be noted in Fig. 2, the major contribution to the XAFS is from the first shell. The large peaks around 3.0 \AA are the contribution from the first shell of Bi neighbors within a layer. The peaks locate at 3.03 and 2.97 \AA for the 0.5 and 300 nm

thick films, respectively. The shift of first peak indicates shrinkage of covalent bond with decreasing size. There is a second peak around 3.6 \AA in 300 nm thick films. The peak dumps with increasing temperature, suggesting that the peak originates from interlayer correlation. It is not observed in the 0.5 nm thick film. The disappearance of the peak around 3.6 \AA suggests loss of interlayer interaction. We suppose that the loss of the overlap between the orbitals in adjacent layers gives rise to the bond shrinkage and the semiconducting nature.

References

[1] M. G. Mitch, S.J.Chase, J Fortner, R.Q. Yu, and J. S. Lannin, Phys. Rev. Lett., 67 (1991) 875-878

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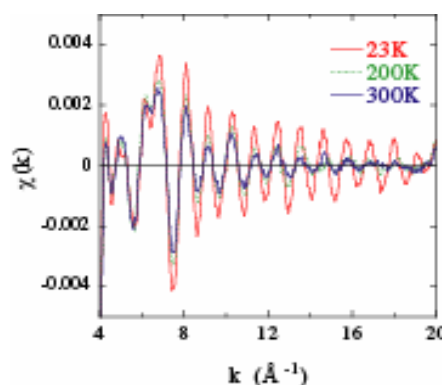


Fig. 1 $k\chi(k)$ for the 0.5 nm thick film measured at several temperatures.

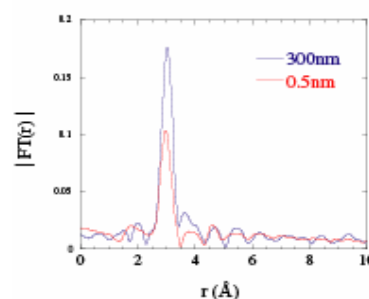


Fig. 2 Fourier transform of $k\chi(k)$ for the 0.5 and 300 nm thick films measured at 23K.