

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 experimental XAFS signals are Fourier-transformed (FT) with a Hamming window in the range 4 to 18 \AA^{-1} . For the 300 nm thick films the evolution of FT with the temperatures (23K, 200K and room temperature (RT)) are presented in Fig.1. The large peak at 3.03 \AA is the contribution from the first shell of Bi neighbors within the layer. The intensities of the main peak are very large compared to other peaks at all temperatures. There is a second peak around 3.6 \AA which is close to the first inter atomic distance between layers. The peak dumps with increasing temperature and disappears at RT, suggesting that the peak originates from interlayer correlation.

Fig.2 shows FT of the 0.5 nm thick films. Some peaks exist in the shorter distance region compared to the main peak. There is possibility that they are originated from

Bi_2O_3 or BiCl_3 . But bond lengths are 2.40 and 2.48 \AA for Bi-O and Bi-Cl, respectively, so they may be suspected peaks. The main peak locates at 2.97 \AA , which is shorter than that of the 300 nm thick film. It is interesting that the peak originated from the interlayer correlation disappears.

The results of EXAFS indicate slight shrinkage of covalent bond within the layer and the disappearance of interlayer correlation.

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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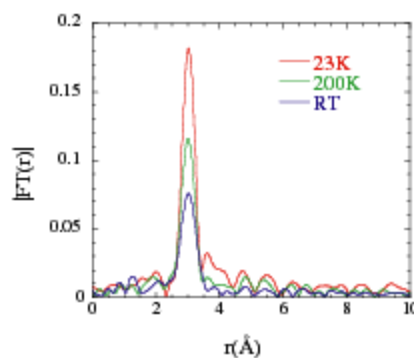


Fig. 1 Fourier transform of $k\chi(k)$ for the 300 nm thick films at 23K, 200K and RT.

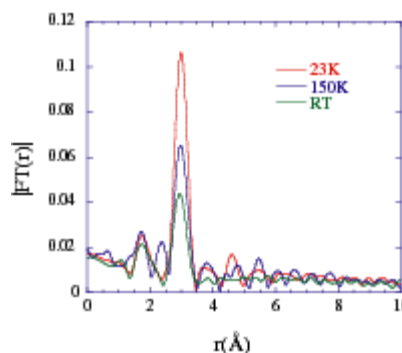


Fig. 2 Fourier transform of $k\chi(k)$ for 0.5 nm thick films at 23K, 150K and RT.