Phase transitions of bismuth clusters

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Abstract

X-ray diffraction patterns, extended X-ray absorption fine structure, and optical absorption coefficients were measured in order to investigate the size-dependence of structural and optical phase transitions of bismuth clusters. Contrary to the case of 15-nm thick films, peaks due to crystalline Bi were not observed in X-ray diffraction patterns of as-deposited 0.5-nm thick films. Optical absorption coefficients of the 0.5-nm thick films are small compared with those of 100-nm thick films, and an optical gap appears in the 0.5-nm thick films. These results show directly the phase transition of bismuth clusters from semi-metallic nanocrystalline to semiconducting amorphous-like clusters with decreasing size.

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1. Introduction

Rhombohedral bismuth has a layer structure and the Bi atoms are incorporated into two-dimensional networks of puckered six-fold rings, the bonding between the three-fold co-ordinated atoms being mainly covalent. Adjacent layers are situated at distances larger than the covalent intra-layer bond length but shorter than the van der Waals distance.

It is well known that small clusters of atoms will have local structures and properties different from their elemental crystalline equilibrium values [1]. Raman-scattering measurements of clusters of bismuth exhibit a phase transition from rhombohedral Bi nanocrystalline to amorphous-like clusters depending on the cluster size [2]. They also suggest that amorphous clusters are semiconducting and the covalent interactions increase with decreasing size.

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

2. Experimental

Bismuth of 99.999% purity was slowly deposited onto substrates from a tungsten boat. The Bi thin film was discontinuous with isolated island formation. Then, NaCl or KBr of 99.99% purity was deposited to cover the Bi islands. By repeating these procedures, a sample of Bi clusters isolated in an alkali–halide matrix was obtained. Alkali halides such as NaCl and KBr are good materials to confine Bi clusters, because their melting points are high enough that they can isolate the clusters at high temperature without any reaction with Bi, and they are easy to be pressed into pellet form. NaCl and KBr were used for X-ray and optical measurements, respectively, because NaCl has a low absorption of X-rays and KBr is transparent in wide optical spectrum band.
The size of the islands was adjusted 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. As mentioned above the Bi clusters are formed in thin films, and samples are represented by their average thickness of the Bi films in this paper.

Multi-layers of Bi and NaCl were pressed into pellet form in order to prevent aggregation of Bi atoms in a heat treatment at 300 °C. EXAFS measurements were carried out for the pellets, using the spectrometer installed at BL-7C and 12C of the Photon Factory (PF) in the National Laboratory for High Energy Physics (KEK), Tsukuba, Japan. X-ray absorption spectra were measured for the Bi L$_{III}$-edge (13.404 keV). The intensities of the incident beam and the transmitted beam were monitored by ionization chambers. To obtain EXAFS oscillations $\gamma(k)$ from the observed absorption spectra, the standard procedures were performed using XANADU [3].

Samples for XRD measurements were prepared by powdering the pellets of the multi-layers of Bi and NaCl. XRD patterns were measured using an X-ray diffractometer (Rigaku RINT 2200) with Cu K$\alpha$ radiation.

The optical transmittances were measured for the Bi clusters isolated in KBr matrices by an optical system composed of light source, a chopper, a monochromator (Acton SP275), detectors and a lock-in amplifier (EG&G 7260) in this order in the optical path. A halogen lamp was used as the light source. The monochromatic light was detected by a PbS detector and a photomultiplier.

All measurements were performed at room temperature.

3. Result

Fig. 1(a) and (b) shows the diffraction patterns due to the as-deposited multi-layers of Bi and NaCl where the thicknesses of the Bi layers were 15 and 0.5 nm, respectively. All of the patterns due to the 15-nm thick films can be explained as a rhombohedral Bi system and a face centered NaCl system. In contrast to the patterns of the 15-nm thick films there are only peaks due to the NaCl in those of the 0.5-nm thick films. Differences between two patterns are seen clearly around 40°.

Fig. 2(a) and (b) presents the diffraction patterns of the samples which were heated up to 300 °C. (The melting point of the crystalline Bi is 271 °C.) The patterns of the

![Fig. 1. XRD patterns for the as-deposited multi-layers of Bi and NaCl where the thicknesses of the Bi layers were 15 and 0.5 nm. The inset shows the region where differences are clear.](image-url)
15-nm thick films are the same as the as-deposited samples. In the case of the 0.5-nm thick films peaks of Bi crystals appear, implying that there are Bi nanocrystals. The no observation of the peaks originated from the crystalline Bi in Fig. 1(b) and the appearance of the peaks in Fig. 2(b) suggest that the clusters of the 0.5-nm thick films are amorphous.

The $k\chi(k)$ data for the as-deposited Bi films are reported in Fig. 3(a) and (b). The differences of EXAFS functions between the 15-nm thick films and the 0.5-nm thick films are evident; they are direct manifestations of the change of the local structure. Fig. 4(a) and (b) presents the $k\chi(k)$ data of the films after the heat treatment. The patterns of the 15-nm thick films are the almost same as the as-deposited samples. In the case of the 0.5-nm thick films the patterns look like to those of the 15-nm thick films, confirming the result of the X-ray diffraction measurements.

Fig. 5 presents a representative set of curves for the optical absorption coefficients of two thickness films. Those of the crystalline Bi are shown by open circles and triangles [4,5]. Several characteristics can be seen by examining the absorption data by itself. In 100-nm thick films $\alpha$ rises to a plateau above 2 eV. The values of $\alpha$ above 1.9 eV and extrapolation to the lower energy side are close to those of the crystalline Bi. On the other hand the absorption coefficients of the 0.5-nm thick films are close to zero around 0.6 eV and increase linearly with photon energy.

4. Discussion

The absorption coefficient occurring at photon energies corresponding to the band gap energy $E_g$ is often well described by Tauc law

$$\alpha h = (h - E_g)^2$$

where $h$ is photon energy [6]. Such an empirical definition of $E_g$ is based on the observation for the majority of amorphous semiconductors. Fig. 6 shows a plot of $(\alpha h)^{1/2}$ vs $h$ of the 0.5-nm thick films. As seen in the figure the plot lies on the straight lines, so the optical gap can be deduced by extrapolation of the straight lines. The values of $E_g$ is about 0.4 eV, implying that the films are semiconductors.

Fourier transforms of $k\chi(k)$ data give useful information to estimate bond length. Unfortunately we do not discuss the bond length, because we cannot get reliable Fourier transforms for the as-deposited 0.5-nm thick films at this

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**Fig. 2.** XRD patterns for the multi-layers of Bi and NaCl which were heat treated at 300 °C. The inset shows the region where differences are the clear.
stage. Preliminary Fourier transform data show that the bond length between Bi atoms is shorter than that of the 15-nm thick films.

Our results of the XRD patterns and the optical absorption coefficients for the as-deposited Bi films exhibit a phase transition from semi-metallic nanocrystalline to semiconducting amorphous clusters with decreasing size. The semi-metallic nature of the rhombohedral Bi is attributed to the overlap between the back lobes of orbitals in adjacent layers, and the semiconducting nature of amorphous Bi is attributed to the loss of this overlap [7]. We suppose following mechanism of the phase transition. Even if the clusters are small, the three-folded covalent bonds are...
similar with those of the crystal and the layer structure is reserved. But the amorphization of the 0.5-nm thick films results in the disappearance of the interlayer correlation and the loss of the overlap between the orbitals in the adjacent layers, which gives rise to the semiconducting nature.

The heat treatment brings about the crystallization of the Bi clusters in the 0.5-nm thick films, but the intensities of the XRD peaks are weaker than those of the 15-nm thick films. When the intensities are normalized by those of the peaks of NaCl, the intensities of the 0.5-nm thick films are about half of those of the 15-nm thick films. In the thin films size distribution of the Bi clusters is widespread [8]. We guess that some parts of the clusters in the 0.5-nm thick films crystallize with the heat treatment.

5. Conclusion

The studies of XRD, EXAFS and the optical absorption coefficients have been performed. The results suggest that the phase transition occurs from the semi-metallic crystalline to the semiconducting amorphous clusters with decreasing size. The loss of the overlap between the orbitals in adjacent layers, which is accompanied with the amorphization of the small clusters, gives rise to the semiconducting nature.

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References