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Volume plasmon of bismuth nanoparticles

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ABSTRACT

This paper reports the measurements of the bulk plasmon of Bi nanoparticles supported by a SiO_2 matrix using electron energy-loss spectroscopy. The blue shifts of plasmon peak in small particles were observed. However, the degree of shift was much smaller than the previous study in the literature and cannot be interpreted by the quantum confinement.

Small particles in a dielectric matrix have attracted much attention due to their fundamental interest and promising applications [1]. As the nanoparticle size is decreased, a blueshift in the volume plasmon energy with decreasing size has been reported in Si, Ge, CdS and Bi nanoparticles [2–8] and nanowires [9,10]. It was initially considered that the blueshift of the energy is associated with the dispersion relation of the volume plasmon, since the volume plasmon energy has to be integrated over certain scattering angles, $\boldsymbol{q}$, due to the limitations of the instrumentation [2]. The dispersion relation for plasmon energy can be approximately written as $E_p(q) = E_p + \alpha \cdot q^2$, where α is the dispersion coefficient [11]. The minimum value of $\boldsymbol{q}$ is dependent on particle size R, i.e. $q_{\min} \sim \pi/R$. Later, it was reported that the plasmon energy increases in proportion to the inverse square of the nanoparticle size, and thus was interpreted as a quantum confinement effect [3]. The energy shift is given by $\Delta E = A/R^2$, in which the constant A is determined by the volume plasmon and the band gap energy of the materials [3]. The broadening of the plasmon peak and the shift in the position of the maximum were also observed in a thin layer of Si (∼1 nm) in a Co–Si multilayer structure [12]. The phenomenon was, however, interpreted as a result of the interaction between incident electrons with multilayer dielectric media rather than the quantum size effects on the plasmon modes in a thin layer [12].

In most systems, such as Si, Ge and CdS, the energy shifts only occur at very small sizes: <10 nm, and the energy shifts are usually less than 1–2 eV [3,6]. On the contrary, the energy shift occurs in bismuth at a quite large size, $R \sim 50$ nm [5,9]. To obey the R^{-2} rule, it was reported that the energy shift was as much as 10 eV (or even 20 eV) when the particle size is reduced to 5 nm (or 3.5 nm) [8]. However, such a large shift in volume plasmon energy is a very unusual experimental observation. From an experimental point of view, it is very difficult to unambiguously identify plasmon energy if the particles are very small due to the broadening of the plasmon peak and the suppression of volume plasmon by the surface excitations. The situation becomes worse if the nanoparticles are embedded in or supported by the dielectric thin films. In this letter, we present our experimental measurements of the volume plasmon in Bi nanoparticles embedded in SiO_2, using electron energy loss spectroscopy (EELS). The results contradict Wang et al's claim [8] and cannot be interpreted as a quantum confinement effect [3].

The specimen used in this study was prepared by impregnating $Bi(NO_3)_3$ into porous SiO_2. The impregnated samples were dried at 150 °C for 2 days and then heat-treated at 1000 °C for 1 h in hydrogen. The detailed preparation process is given elsewhere [13]. Thin specimens for transmission electron microscopy (TEM) were prepared by crushing the samples into powders in acetone, and picking them up using a Cu grid covered with lacy carbon thin films. The specimens were then immediately transferred into and observed in

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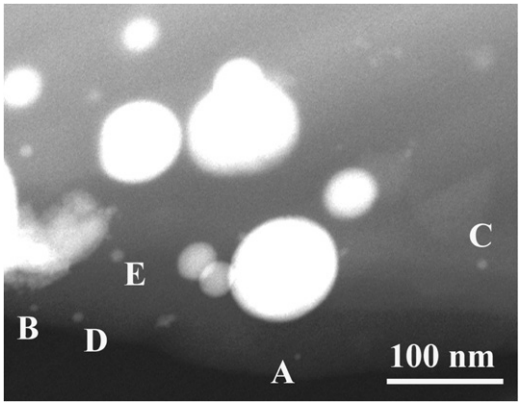

Fig. 1. Annular dark-filed image showing Bi nanoparticles in the Bi impregnated SiO_2.

a JEOL-2010 STEM with a field-emission gun operating at 200 keV. The EELS spectra were acquired using a parallel electron energy-loss spectrometer (Gatan Enfina). The full width at half maximum (FWHM) of the zero-loss peak was about 1.0 eV. The dispersion of the spectrometer was 0.1 eV/channel. The STEM probe was about 0.5 nm in diameter, the semiangle of the collection aperture was 22 mrad, and the convergence semiangle was 21 mrad. All spectra were acquired and processed using Digital Micrograph.

In the specimen, the size of the Bi nanoparticles varied from several nanometers to nearly half a micron. As shown in Fig. 1, the sizes of the Bi nanoparticles marked by upper case letters are 5.5, 6.0, 8.5, 9.0 and 11.0 nm in alphabet sequence, respectively. Particles smaller than 5 nm were also observed. However these particles were unstable under the electron beam: they can be eliminated during the acquisition of the EELS spectrum. This is probably due to the low melting temperature of bulk Bi (271.5 °C), which can be further reduced by reduction of particle size [14]. Therefore, all EELS data were collected from particles larger than 5 nm. To avoid possible beam damage, the data were acquired as a STEM probe is moved across the particle, step-by-step, with steps of 0.5∼1.0 nm, starting from the SiO_2 matrix. The dwell time for each spectrum was 10^{-3} or 10^{-2} s, depending on specimen thickness.

In large particles (>90 nm), the EELS spectrum of Bi (without noticeable contribution from the SiO_2 matrix) can be obtained from some particles extending over the edge of the specimen, so these will be used as a reference spectrum to evaluate the volume plasmon shift in small particles. In small particles (<10 nm), however, it is difficult to eliminate the contribution from the SiO_2 matrix. Fig. 2 gives an example of EELS data acquired form a 7.5 nm Bi nanoparticle. A total of 28 spectra were acquired by running the STEM probe across the nanoparticle. The total length of the run was about 16 nm, and each spectrum was recorded about 0.6 nm apart. The integrated intensities of the Si L_{23} edge are plotted against their acquired positions in Fig. 2(a), along with the ADF (annular dark-field) image of the particle. Since the SiO_2 matrix is not very thick [15], the Si L_{23} intensity is approximately proportional to the thickness of SiO_2. The decrease of Si L_{23} edge intensity in the particle region indicates that the particle is embedded or partially embedded in the SiO_2 matrix.

Five selected spectra from Fig. 2(a) across the particles are shown in Fig. 2(b). For a comparison, the spectrum of Bi from the large particle (∼90 nm in diameter), whose position of the maximum is at 14.7 eV, and the spectrum of the SiO_2 matrix, whose position of the maximum is at 23.8 eV, are also plotted in Fig. 2(b). Due to the small volume of Bi nanoparticle, the differences between spectra recorded on, and off, the Bi particle are not significant. The changes only involve intensity increases

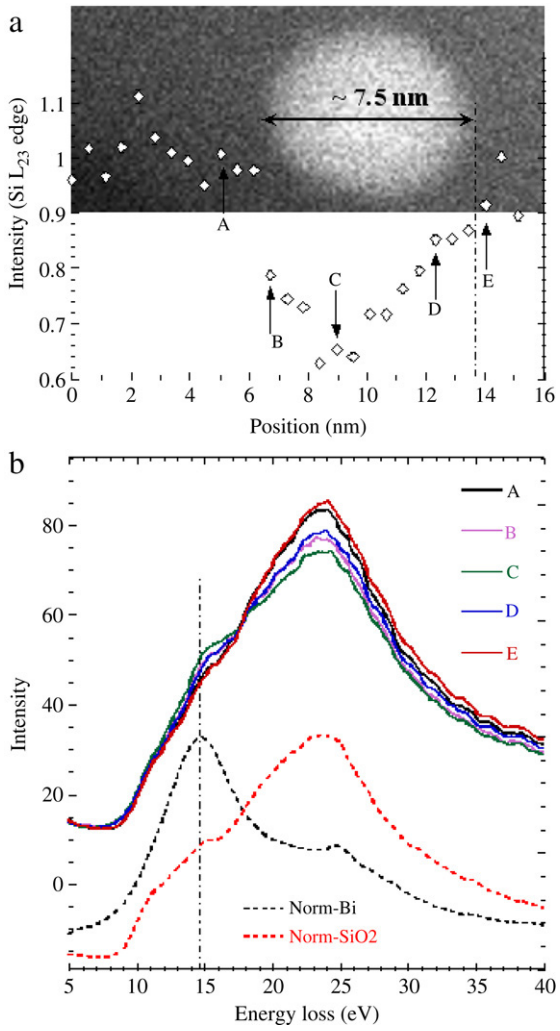

Fig. 2. (a) Si L_{23} edge intensity versus positions, along with the ADF image of the particle where spectra were acquired; (b) EELS spectra across the particle. The letters indicate the positions where the spectra were acquired. The vertical chained lines are guided for eyes.

at around 15 eV, and decreases around 25 eV when the probe is on the particle. The former is due to the increasing excitation of the volume plasmon of Bi, while the latter is due to the decrease of SiO_2 thickness in the Bi particle region. Although it cannot be explicitly obtained from Fig. 2(b), one can still readily see that the plasmon energy of the Bi nanoparticle should be also around 15 eV in this 7.5 nm-particle, rather than at 20–25 eV as predicted by quantum size effects in [8]. This is simply because the intensities in this energy range are decreasing relative to those around 15 eV as the probe is moved into the nanoparticle.

According to the dielectric excitation theory [16], the EELS of nanoparticle embedded structure can be calculated using the effective medium response function ε_{eff}:

$$\text{Im}\left(\frac{-1}{\varepsilon_{\text{eff}}}\right) = A\cdot\text{Im}\left(\frac{-1}{\varepsilon_{\text{Bi}}}\right) + B\cdot\text{Im}\left(\frac{-1}{\varepsilon_{\text{SiO}_2}}\right) + C\cdot\text{Im}\left(\frac{-3}{\varepsilon_{\text{Bi}}+2\varepsilon_{\text{SiO}_2}}\right).$$

The first two terms in the right-hand side are energy loss functions of the Bi nanoparticle and SiO_2 matrix respectively. The third term represents the excitations due to the Bi/SiO_2 interfaces. The constants A, B and C are weight factors, and $A+B+C=1$. If the interface contribution is small, i.e. $C \ll A, B$, it might be reasonable

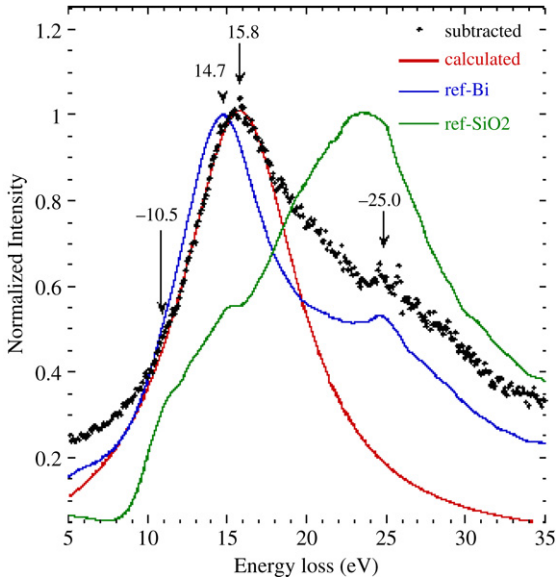

Fig. 3. Comparison of subtracted spectrum in the 7.5 nm Bi nanoparticle with calculated volume plasmon loss using Drude approximation, reference spectra of Bi and SiO_2.

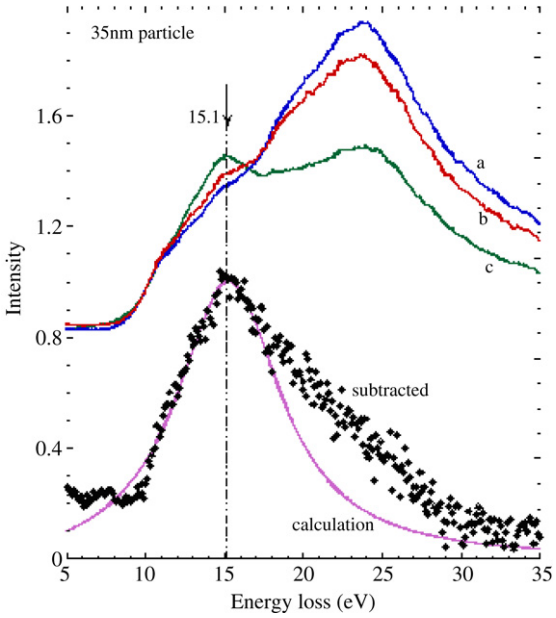

Fig. 4. Spectra acquired across a 35 nm bi nanoparticle. The subtracted spectrum is compared with the calculated volume plasmon loss using Drude approximation.

to interpret the loss spectrum by the volume fractions of Bi particle and SiO_2 matrix, i.e. $A + B = 1$. In other words, the spectrum in the particle region is the sum of the contributions from Bi and SiO_2 respectively.

To extract the volume plasmon loss of the Bi nanoparticle from Fig. 2(b), we can take advantage of the thin specimen approximation, in which the probabilities of plural scattering events are negligible. Compared with the SiO_2 region outside the particle, the reduction of the Si L_{23} intensity in the particle region is not great, and reaches only 1/3 around the particle center (Fig. 2(a)). Since the particle size is quite small, its dimension along the beam direction must also be small. In addition, the estimated thickness of the SiO_2 matrix adjacent to the particle is only around 55 nm. We then normalize all spectra to the intensity of the Si L_{23} edge, and subtract the reference SiO_2 spectrum from those in the particle region. The average of the subtracted spectra is given in Fig. 3. As compared with the references of the Bi (90 nm) and SiO_2 matrix, the subtracted spectrum is dominated by the contribution of the Bi nanoparticle, justifying our kinematical assumption. We note that there is a small shoulder around 10.5 eV in the subtracted spectrum. This feature can be tentatively interpreted as the surface plasmon of the Bi particle [17]. A small peak around 25.0 eV is also seen in the big Bi particles, which is due to excitation of the Bi O_{45} edge [18].

In Fig. 3, the position of the maximum loss is at 15.8 eV in the 7.5 nm Bi nanoparticle, which is only 1.1 eV higher than that in the 90 nm one. If the quantum confinement effect starts to occur in the Bi nanoparticle at around 40 nm in diameter, this value is much smaller than that predicted by the R^{-2} rule [3], and the result clearly contradicts the observations in [8].

It should be pointed out that the kinematical approximation used in this work does not guarantee an error-free determination of volume plasmon energy in the embedded or partially embedded nanoparticles, but the error should not be large as long as the specimen is not too thick. In this case significant error may be introduced in the integrated Si L_{23} intensity due to plural scattering. To confirm the validity of our method, we also carried out measurements in a 35 nm Bi nanoparticle. Fig. 4 shows three representative spectra acquired from areas adjacent to the particle (spectrum a), near the edge (spectrum b) and in the center region (spectrum c) of the particle, respectively. In the central region, Bi dominates along the path of the electron beam, and thus the peak at 15.1 eV due to volume plasmon excitation can be separated from other features without the need of any data processing. In the area near the edge of the particle, on the other hand, only a shoulder can be seen at around 15 eV in the spectrum, which resembles the spectrum in the 7.5 nm Bi nanoparticle in Fig. 2(b). We normalize spectra a and b to their integrated Si L_{23} edge intensities, and then subtract spectrum a from b. As shown in Fig. 4, the position of the maximum of subtracted spectrum is also at 15.1 eV, which is consistent with the direct measurement from spectrum c.

This work confirms that the plasmon shift in Bi does occur at very large sizes. However, the shift energy is very small, only about 0.4 eV and 1.1 eV although R decreases from 90 nm to 35 nm and 7.5 nm, respectively. This indicates that the quantum confinement effect on bulk plasmon in the Bi nanoparticle may not be the reason if it obeys rule of R^{-2}. The origin of the blueshift of volume plasmon in Bi nanoparticles in EELS measurements can, however, be complicated due to the poor q-resolution of EELS in TEM/STEM. The integration effect suggested by [2] is definitely an important source. The lattice distortion due to large surface area in small particles can be also a determining factor, although the accurate measurement of lattice distortion in such a small single nanoparticle is not feasible.

In conclusion, we have carefully measured the energy at the maximum energy loss indifferent sized Bi nanoparticles. These values contradict previously reported results for Bi nanoparticles [8]. It is more reasonable to interpret the blueshift as induced by the plasmon dispersion effect [2], rather than the quantum confinement mechanism [3].

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