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Determination of the Electronic Band Gap of Isolated Ge Ultra-fine Particles by Scanning Tunneling Spectroscopy

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The electronic band gap of *individual* Ge ultra-fine particles isolated on a highly oriented pyrolytic graphite (HOPG) surface has been investigated by scanning tunneling spectroscopy (STS). The tunneling spectra reveal that the Ge ultra-fine particle has a band gap that varies linearly with the inverse square of the particle diameter. Our results confirm that the transition across the band gap of Ge ultra-fine particle leads to near infrared photoluminescence (PL). This band gap does not correspond to the observed PL in the visible region.

Key words : germanium, ultra-fine particle, quantum confinement, scanning tunneling microscope (STM), scanning tunneling spectroscopy (STS)

1. INTRODUCTION

Since the electronic structure of a semiconductor ultra-fine particle is considerably modified by the quantum confinement effect and surface effects, the optical properties of the ultra-fine particle strongly depends on the particle size. Because of scientific and technological interest, ultra-fine particles of indirect gap semiconductors are attracting much attention. The size dependence of the optical properties of Ge ultra-fine particles embedded in a SiO_2 matrix has been extensively investigated by photoluminescence (PL).[1, 2, 3, 4] On the ground that the effective Bohr radius of bulk Ge is large compared with that of bulk Si,[5] Ge ultra-fine particles have been expected to clearly reveal the blue shift of the emission energy due to the quantum confinement effect. However, after the first observation of visible light emission from a SiO_2 matrix that contained Ge ultra-fine particles, there has been no agreement on the size dependence of the observed emission energy, and the origin of this emission is still unclear. To determine the origin of the visible emission and the intrinsic properties of the Ge ultra-fine particle, it is essential to clarify the way in which the quantum confinement effect modifies its electronic structure.

One of the greatest difficulties in these investigations is caused by the inhomogeneous broadening of the measured spectrum due to different particle-size distributions in different samples. To avoid this difficulty it is desirable to perform spectroscopic measurements of individual particles of a definite size. The scanning tunneling microscope (STM) makes it possible to measure directly the electronic properties of individual nanostructures formed on solid surfaces. The information on the local electronic density of states (DOS) can be obtained by scanning tunneling spectroscopy (STS). In this method the STM tip-sample gap is kept constant, and the tunneling current I is measured as a function of the sample bias voltage V. Then the I-V curve is numerically differentiated to obtain the normalized conductance $(dI/dV)/(I/V)$. It represents the local DOS below the STM tip.[6] In this work we report on a STS study of Ge ultra-fine particles isolated on a highly oriented pyrolytic graphite (HOPG) surface. We found that the tunneling spectra measured over individual particles with different diameters show the quantum confinement effect on the band gap energy.

2. EXPERIMENTS

We used a homemade STM operating in a high vacuum of 2×10^{-8} Torr. Silver tips used in this work were electrochemically etched and then cleaned by heating in vacuum. The sample was prepared in situ by evaporation of Ge powder charged in a tungsten boat by heating in an argon gas atmosphere at a pressure of 20 Torr. The base pressure of the evaporation chamber was 2×10^{-8} Torr. The ultra-fine particles condensed in the argon atmosphere were collected on a freshly cleaved HOPG surface placed at 75 mm above the tungsten boat. The boat temperature measured by a radiation thermometer was about 1050 °C. The evaporation rate was controlled so that individual particles were isolated on the HOPG surface. After evaporation the sample was transferred to a STM chamber. The STM was operated

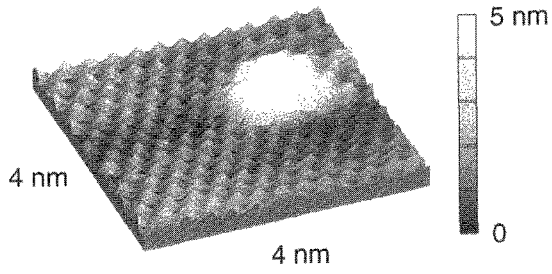

Fig.1 STM image of a Ge ultra-fine particles on the HOPG surface. A Ge ultra-fine particle isolated on the lattice of HOPG atoms is imaged as protrusion.

in a constant-tunneling-current mode. All experiments were performed at room temperature.

2. RESULTS AND DISCUSSION

A STM image of a Ge ultra-fine particle on the HOPG surface obtained at a tunneling current of 1.0 nA and a sample bias voltage of + 0.1 V is shown in Fig. 1. The image shows an atomically flat surface on which the lattice of HOPG atoms is clearly resolved. The isolated Ge ultra-fine particle is imaged as a protrusion. Although the actual shape of the particle produced by our method is expected to be spherical, the apparent shape observed from above is elliptical. The particle seen in Fig. 1 appears elongated by about 0.2 nm along the scanning direction compared with its length of 0.8 nm perpendicular to the scanning direction. Also the apparent height varied depending on the response of the STM electronic circuit. The fact that the particles appear elongated along the scanning direction suggests that the STM image is distorted by the inability of the STM electronic circuit to follow a sudden change in elevation. In our sample the Ge ultra-fine particles with the diameter on the order of a nm are isolated on an atomically flat HOPG surface. This structure is seen as a very sharp protrusion by the STM. Thus it is reasonable to suppose that the particle has a shape close to a sphere, and the diameter is equal to the minor axis of the apparent ellipse in the image.

When one considers the electronic structure of a particle deposited on a solid surface, in general one must take into account the interaction between the particle and the substrate surface. Since HOPG has a layered structure and strong covalent sp^2 bonding exists within each layer, the deposited particle only weakly interacts with the HOPG surface in the absence of defects.[7,8] We examined the bare HOPG surface before deposition of the Ge particles, and neither defects nor steps were observed in the relevant area. Thus we can assume that the contact with the HOPG surface does not significantly affect the electronic structure of the Ge particle in our sample.

To identify the electronic structure of the individual particles, we performed spectroscopic measurements by positioning the STM tip over each particle. The spectra of the normalized conductance versus sample bias voltage are plotted in Fig. 2. Spectrum (a) was measured directly on the HOPG surface and spectrum (b), (c), and (d) were measured over the Ge ultra-fine particles with diameters of 1.6 nm, 1.2 nm, and 0.80 nm, respectively. While the spectrum of the HOPG surface has no band gap as expected from the DOS of HOPG,[9] the spectra measured over the Ge particles show the band gap of 0.80 eV for the particle of 1.6nm diameter, 0.94 eV for 1.2 nm, and 1.22 eV for 0.80 nm, respectively. The band edges marked by solid lines in the spectra were determined as the energy at which the absolute value of the first order differential coefficient of the normalized conductance sharply increases. The tunneling spectra clearly indicate that the band gap energy increases as the particle diameter decreases.

Fig. 3 shows a plot of the band gap energy (solid

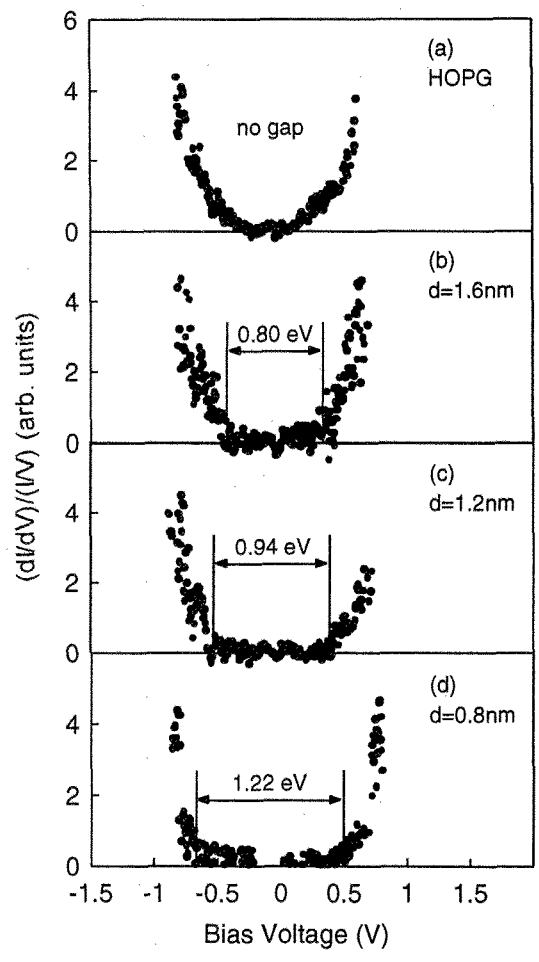

Fig.2 Tunneling spectra measured (a) on the HOPG surface and (b)-(d) over the Ge ultra-fine particle with diameter *d*. The band edges are indicated by solid line.

squares) measured by STS as a function of the inverse square of the diameter d of the ultra-fine particle. The straight line is obtained by fitting the measured band gap energy. It is clear that the band gap energy follows a d^{-2} law. In the limit of an infinite diameter, the band gap energy extrapolates to 0.66 eV, which is the value of the indirect gap (Γ_8-L_6) of crystalline Ge at room temperature.[10] We therefore conclude that the measured band gap widening results from the quantum confinement effect on the Ge ultra-fine particle. The exponent value of -2 is in good agreement with the value predicted by the effective mass approximation. However, it should be noted that the slope of the straight line in Fig. 3 is very small compared with that predicted by a theoretical calculation based on the effective mass approximation.[11]

Here we wish to note the difference in the behavior of the confined electronic structures of Ge ultra-fine particles and protrusions of porous Si that is also made of a group IV element. In case of porous Si the band gap energy of individual protrusions follows a d^{-1} law.[12] We believe that this difference most likely arises from their different three-dimensional structures. The protrusions of porous Si have a complex shape instead of being spherical. How the confined electronic states are affected by the structural shape is an interesting question that we plan to investigate.

In Fig. 3 we compare the measured band gap energy with the PL peak energy reported by Takeoka et al. in the near infrared region as a function of the *average* diameter d_0 (solid circles).[4] They concluded that the measured PL arises from the transition between the widened band gap of Ge ultra-fine particles. However, as shown in Fig. 3, the PL peak energy appears on the high-energy side of the straight line obtained by our STS measurements.

The most significant difference between these two plots is that the PL peak energies are plotted against the *average* particle diameter d_0 instead of the *individual* particle diameter d_0. The PL samples contain particles with a certain size distribution that can be approximated by the logarithmic normal function.[2] Then the PL intensity contributed by a particle with a diameter d can be represented by multiplying the size distribution function with the emission efficiency. As Takeoka et al. pointed out,[4] the emission efficiency drastically increases with decreasing size. This size dependence can be fitted by an exponential function. Because the emission from smaller particles is emphasized due to this size dependent efficiency, the distribution of the PL intensity has a peak at the effective diameter d_{eff} that is smaller than the *average* diameter d_0. The band gap energy increases following the linear relation shown in Fig. 3 as the particle diameter decreases. Thus the PL peak energy for an assembly of particles plotted against the *average* diameter d_0 appears on the high-energy side relative to

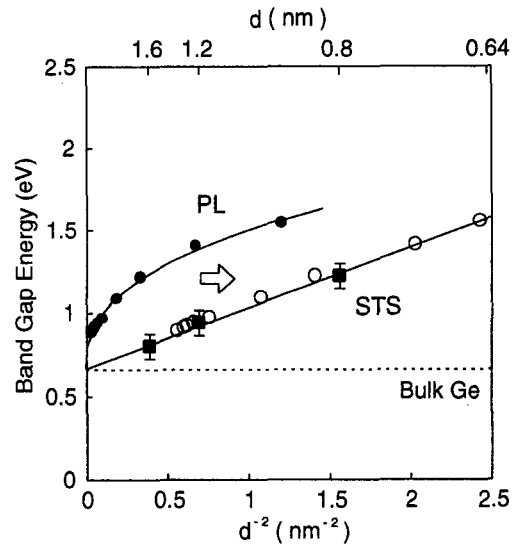

Fig.3 Band gap energy versus the inverse square of the diameter d of Ge ultra-fine particles. Solid squares are the band gap energies for individual particle determined in the present work. Solid circles are the PL peak energies taken from Ref. 4 plotted against the average diameter d_0. Open circles are replots of the PL peak energies against the effective diameter d_{eff}.

the band gap energy of *individual* ultra-fine particles. The observed PL peak energy should be correlated with the band gap energy of the particle with the effective diameter d_{eff} instead of the *average* diameter d_0. Since we can assume the particle size distribution to be represented by the logarithmic normal function, we can determine d_{eff} that corresponds to each observed PL peak position.[13] In Fig. 3 we replotted the observed PL peak energy against d_{eff} (open circles). Then the PL data points fall on the straight line obtained by our STS measurements. We can conclude that the band gap energy measured by STS corresponds to the observed PL in the near infrared region.

As seen in Fig. 3 the band gap energy of the Ge ultra-fine particle with the diameter of up to sub nm continuously increase with the inverse square of the particle diameter. In contrast, it was found that the HOMO-LUMO gap of the Ge atomic cluster consisting of up to 32 atoms reveals a discontinuous character with the number of atoms.[14] There seems to be two different size regimes. According to Hunter et al., when the particle consists of around 70 atoms the structural transition of particle geometry occurs at which the particle reconstructs to a spherical geometry.[15] They pointed out that this structural transition appears to reflect a change from atomic cluster to a more bulk like bonding arrangement. We believe that this structural transition of the particle geometry corresponds to the two different electronic behaviors.

4. CONCLUSION

In conclusion we have presented STS measurements in which the band gaps of *individual* Ge ultra-fine particles isolated on the HOPG surface are clearly resolved. We have found that the Ge ultra-fine particle has a band gap that varies linearly with the inverse square of the particle diameter. The measured band gap can be interpreted in terms of band gap widening of bulk Ge due to the quantum confinement effect. This band gap does not correspond to the observed photoluminescence in the visible range.

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