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Nanostructures and electronic properties of carbon and boron nitride nanocapsules

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Carbon (C) nanocapsules with gold nanoparticles and boron nitride (BN) nanocapsules with cobalt nanoparticles were fabricated, and their electronic properties were investigated by scanning tunneling microscopy at room temperature. The current-voltage characteristics of the BN nanocapsules showed Coulomb staircase-like behavior, and the photoluminescence spectrum of BN nanocapsules showed a peak at 3.8 eV. It is believed that the BN layers would act as tunnel barriers and that double-barrier tunnel junctions would be formed.

Key words: boron nitride, carbon, cluster, TEM, STM, nanoparticle.

Introduction

In recent years, downsizing of electric devices has become difficult, and consumption of the electric power has become high. Single-electron charging effects in small tunnel junctions were observed in 1987 [1], which means a single electron device is feasible [2-8]. Single electron devices have received considerable attention because they are operated at low electric power. The single electron transistors consist of electrodes and quantum dots of extremely small size. The smaller the size of the quantum dot, the higher the operating temperature of the single electron device. For operation of the devices at room temperature, the size of the quantum dots should be below dozens of nanometers. Nanocapsule structures are one of the candidates that is applicable for quantum dots of single electron transistors.

Various carbon (C) nanocapsules encaging nanoparticles have been produced [9-12] after the discovery of C_{60} [13]. C has heat and chemical resistance, and C nanocapsules have various properties such as cluster-protection, lubricity, amongst others. Boron nitride (BN) nanocapsules were also produced recently [11, 14-18]. BN has excellent properties of high temperature stability and chemical stability. Although C shows metallic behavior, BN has insulation properties.

The purpose of the present work is to investigate the electronic properties of C and BN nanocapsules, and to discuss the possibility of their application for single electron transistors. Gold (Au) nanoparticles were selected for C nanocapsule formation in the present work because of easy control of cluster size [19], and gold colloids have been used for the formation of single electron transistors [4]. Cobalt (Co) nanoparticles were also selected for BN nanocapsule formation in the present work because they worked as catalytic metal for production of carbon nanocapsules and single wall carbon nanotubes [20, 21]. To investigate the microstructure, high-resolution transmission electron microscopy (HREM) was carried out [22-24]. Scanning tunneling microscopy (STM) was used to investigate the electronic properties of the C and BN nanocapsules. The electronic states of a single nanocapsule can be measured from the current-voltage (I-V) behavior by using STM. Photoluminescence (PL) measurements of the BN nanocapsules were also carried out by fluorescence spectrophotometer to investigate the energy gap [25]. These studies will give us a guideline for designing C and BN nanocapsules, which are postulated for future nanoscale devices.

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Experimental procedures

Au nanoparticles (ULVAC Ltd.) with a size of *ca*. 5 nm were used in the present work for the synthesis of carbon nanocapsules. The surface of these nanoparticles was stabilized by α-terpineol ($C_{10}H_{18}O$) in toluene solution. The solution of Au nanoparticles was dispersed on holey carbon grids with a thickness *ca*. 15 nm (Oken Syoji. Co. Ltd.). After drying the specimens, they were loaded into a vacuum chamber and annealed at 200°C for 30 minutes in vacuum of *ca*. 7×10^{-4} Pa.

For the synthesis of BN nanocapsules, boron particles (99%, 40 μm, 1 g, Niraco) were mixed with Co nanoparticles (<100 nm, ULVAC Co. Ltd.). The mixed powder was set on an alumina boat and heated up to a temperature of 800°C in a NH_3 (30%) and H_2 (70%) flow for three hours in a furnace. The atomic ratio of B : Co was 1 : 1.

HREM observations were performed with a 300 kV transmission electron microscope (JEM-3000F), which has a point-to-point resolution of 0.17 nm. STM observations were performed with an STM system (easyScan, Nanosurf AG) in air at room temperature. Pt/Ir wires with a diameter of 0.25 mm were used for STM tips. The STM tips were checked by imaging atoms on highly-oriented, pyrolytic graphite (HOPG). PL measurements were carried out at room temperature (fluorescence spectrophotometer, Hitachi, F-4500), and the excitation wave length of the Xe lamp was 215 nm.

Results and Discussion

Figure 1(a) shows an HREM image of Au nanoparticles annealed at 200^{o}C on an amorphous carbon (a-C) thin film. Au nanoparticles grow by coalescence during the annealing, and the particle size is in the range of 10~30 nm. An enlarged image of the interface between a Au nanoparticle and carbon layers is shown in Fig. 1(b). The carbon layers indicated by arrows in Fig. 1(b) have a disordered structure, and the thickness is ~1 nm. Figure 2(a) shows an STM image of carbon nanocapsules with gold nanoparticles on a-C thin films. The measurement conditions were constant current mode with a current of 1 nA, a sample bias of +0.5 V and a scanning area of 60×60 nm. The carbon nanocapsules show white contrast, and the diameter is in the range of 10~30 nm, which agrees well with the HREM results. Figure 2(b) shows I-V curves of background (a-C) and a single C nanocapsule (with a diameter and height of 15 nm) indicated by an arrow in Fig. 2(a). The I-V curve of the single C nanocapsule, which was calculated by subtracting background data from the whole data in Fig. 2(b), is shown in Fig. 2(c). These data were obtained from four I-V measurements. The first data was taken on the carbon nanocapsule, and the other data were taken on the background of the a-C thin film. Figure 2(d) is the conductivity (dI/dV) curve of the carbon nanocapsule calculated from the I-V curve in Fig. 2(c), which shows the V shape behavior.

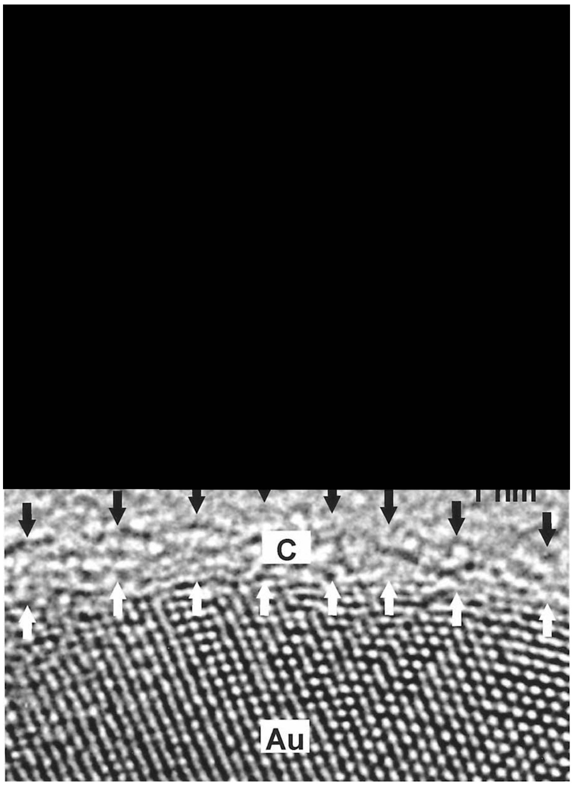

Fig. 1. (a) HREM image of annealed Au nanoparticles on a-C thin film. (b) Enlarged image of the interface between the Au nanoparticle and carbon layers.

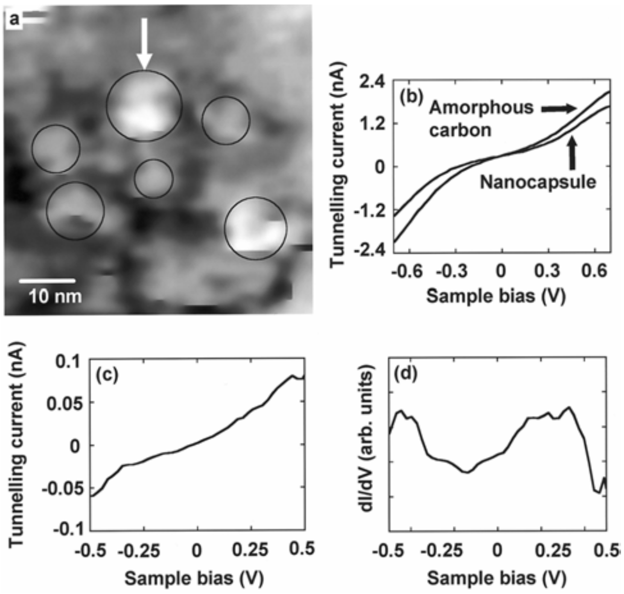

Fig. 2. (a) STM image of carbon nanocapsules with gold nanoparticles on the a-C thin film. (b) I-V curves of background and the single C nanocapsule indicated by an arrow in Fig. 2(a). (c) I-V curve of the single C nanocapsule, calculated by subtracting background data from whole data in Fig. 2(b). (d) Conductivity curve of the carbon nanocapsule calculated from the I-V curve in Fig. 2(c).

Figure 3(a) shows an HREM image of BN nanocapsules with cobalt nanoparticles. The size of the BN nanocapsules is in the range of 20~60 nm, and the thickness of boron nitride layers is in the range of 3~5 nm. An enlarged image of a BN nanocapsule with a Co nanoparticle is shown in Fig. 3(b). Lattice fringes of 0.34 nm, plane spacings of {002} planes of hexagonal BN, are observed on the outside of the Co nanoparticles. Lattice fringes with plane spacings of {111} and {200} planes of Co were also observed in the nanoparticle.

Figure 4(a) shows an STM image of a BN nanocapsule with a Co nanoparticle on the HOPG. The measurement conditions were the same as for the C nanocapsules and the scanned area was 74×74 nm. The BN nanocapsules show white contrast, and the diameter is in the range of 10~15 nm. The I-V characteristic of the single BN nanocapsule (with a diameter

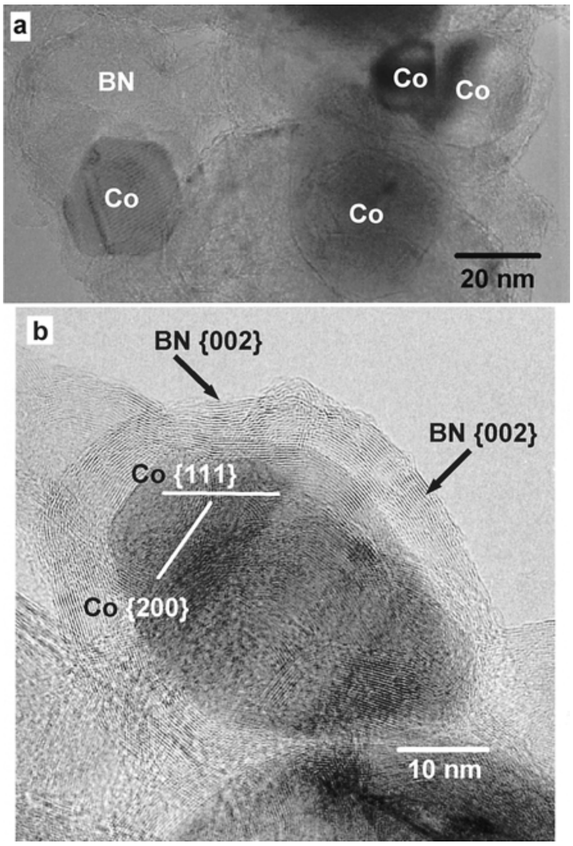

Fig. 3. (a) HREM image of BN nanocapsules with cobalt nanoparticles. (b) Enlarged image of a BN nanocapsule with a Co nanoparticle.

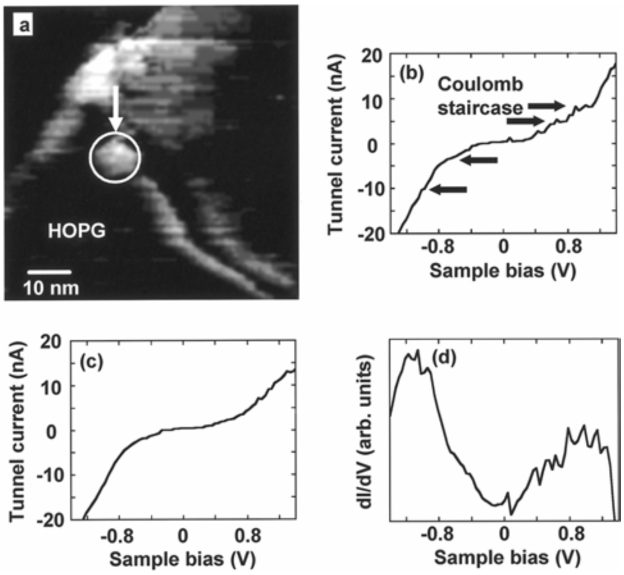

Fig. 4. (a) STM image of the BN nanocapsule with the Co nanoparticle on HOPG. (b) I-V characteristic of the single BN nanocapsule, indicated by an arrow in Fig. 4(a). (c) I-V characteristic of HOPG. (d) Conductivity curve of the BN nanocapsule calculated from the I-V curve in Fig. 4 (b).

of 12 nm), which is indicated by an arrow in Fig. 4(a), is shown in Fig. 4(b). The I-V data in Fig. 4(b) shows Coulomb staircase-like behavior. Figure 4(c) shows the

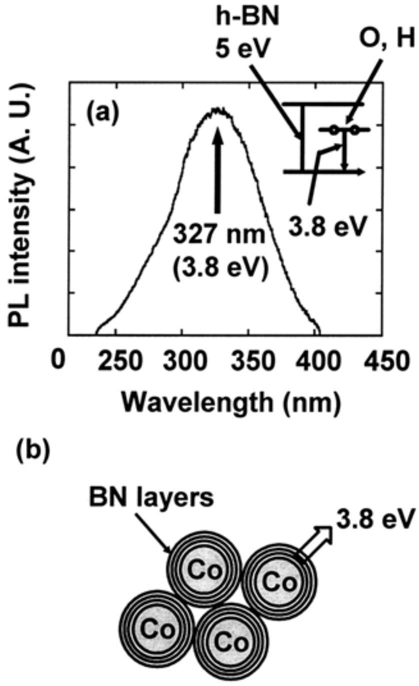

Fig. 5. (a) PL spectrum of BN nanocapsules with Co nanoparticles. (b) Schematic illustration of PL of BN nanocapsules.

I-V characteristic of the HOPG (background). Figure 4(d) is the conductivity (dI/dV) curve of the BN nanocapsule calculated from the I-V curve in Fig. 4(b), which shows the conductivity is close to 0 at a sample bias of 0 V.

The PL spectrum of Co nanoparticles in BN nanocapsules is shown in Fig. 5(a). The background data of the PL spectrum was deducted from the spectrum data. Figure 5(b) shows a schematic illustration of the PL of the BN nanocapsules. The PL measurements of BN nanocapsules shows a peak at 3.8 eV (327 nm), which is considered to be impurity level (oxygen or hydrogen) of the BN layers (5 eV). A schematic illustration of the impurity level is shown in Fig. 5(a) as an inset.

The atomic scale observations by HREM indicated that the carbon nanocapsules with gold nanoparticles have diameters in the range of 10~30 nm, and that the nanocapsules are covered with disordered carbon layers with *ca*. 1 nm thickness. The disordered carbon layers would be formed from amorphous carbon which was graphitized by the catalytic effect of the active Au surface at the lower temperature of 200°C compared to that of the ordinary chemical formation of carbon nanocapsules [11]. All nanoparticles are surrounded and isolated by double or triple carbon sheets, which would prevent the nanoparticles from growing and act as a protection against clustering. The HREM observations of the BN nanocapsules with Co nanoparticles show the diameters to be in the range of 20~60 nm, and the nanocapsules are covered with BN layers with *ca*. 5 nm thickness. The Co nanoparticles would play the role of a catalyst because the BN did not form

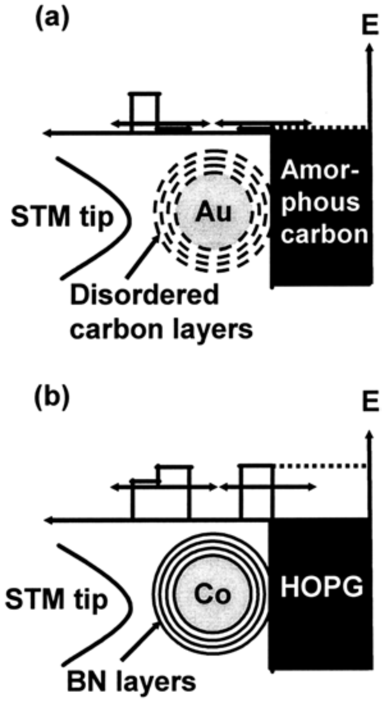

Fig. 6. Schematic illustration of the I-V measurements for (a) C nanocapsule and (b) BN nanocapsule.

without the Co nanoparticles in the present method. The chemical reaction of BN nanocapsules is calculated as follows: $2B + 2NH_3(g) \rightarrow 2BN + 3H_2(g) + 93$ kcal/mol (800°C), which indicates the reaction is exothermic.

The dI/dV of the C nanocapsule, which is proportional to the local density of states, showed V shape characteristics, but it did not approach to 0 at the sample bias of 0 V. This result indicates that the carbon nanocapsules would not have semiconductor-like behavior but metallic behavior. Coulomb staircase-like behavior is observed in the I-V measurements of BN nanocapsules at room temperature in Fig. 4(b). A schematic illustration of the I-V measurements of a C nanocapsule and a BN nanocapsule are shown in Fig. 6(a) and (b), respectively. Although the C layers have no tunnel barrier, the BN layers would produce a double tunnel junction. One tunnel junction is provided by the BN layers and the gap between the STM tip and BN nanocapsule. The other is provided only by BN layers. It is believed that the present Coulomb staircase-like behavior would be due to the BN layers around the Co nanoparticles. The BN layers would be the barrier, which have suitable tunnel height and thickness. First, an electron transports through the BN layers when the sample bias goes beyond the Coulomb gap. Second, the electron is blocked in the Co nanoparticle with BN layers. At last, it also transports through the BN layers when the sample bias goes beyond the next Coulomb gap. Since the impurities such as oxygen or hydrogen would be doped in BN, the luminescence would be due to the impurity level of 3.8 eV in the energy gap of BN. BN nanocapsules would be suitable for quantum dots of single electron transistors.

Conclusion

C and BN nanocapsules with metal (Au and Co) nanoparticles were produced, and the nanostructures were investigated by HREM. STM was used for I-V measurements of these nanocapsules, and the I-V characteristic of the C nanocapsule showed metallic behavior for the disordered carbon layers around Au nanoparticles. The I-V characteristic of the BN nanocapsule showed Coulomb staircase-like behavior, and the energy gap of BN nanocapsules was measured to be 3.8 eV from the PL spectrum. The present work indicates that BN nanocapsules could be applied to quantum dots for single electron transistors.

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