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INVESTIGATION ON THE STRUCTURE AND ELECTRIC PROPERTIES OF BUCKY ONIONS*

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Bucky onions were fabricated by the DC discharge method and their behaviors and electric properties on Highly Oriented Pyrolytic Graphite (HOPG) were studied by using an atomic force microscope (AFM), a scanning tunneling microscope (STM) and a transmission electron microscope (TEM). Small-sized Bucky onions demonstrated the properties of semiconductors and as the size increased their metallicity became stronger. AFM and STM images revealed the tendency of Bucky onions to form dimers.

Keywords: electrical conductivity, electron states
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I. INTRODUCTION

Very Large Integrated Circuits (VLICs), which are mainly made from silicon materials, have entered almost every field of the modern society. The electronic industry based on VLICs actually constitutes the economic pillar for the developed countries. In this sense, we are now in the "silicon time". Meanwhile, nanometer electronic device, which will work with a different mechanism, is expected to be the future successor of current microelectronic device. The question is now being hotly probed into whether the principal material of nanometer device will still be silicon.

Carbon, which is in the same family as silicon in the periodic table, is more plentiful than the latter in the Earth and even in the universe. Moreover, carbon is the fundamental element for building up organic materials and lives. Human being's future will probably be "carbon time". The discovery of C_{60},[1] which bears a nanometer-scale hollow spherical structure, revealed a new form of existence of carbon element besides the already well-known graphite, diamond and amorphous carbon. C_{36} and C_{70} also have similar stable nanometer-scale structures as C_{60}, and collectively they are named "Fullerenes". As a further development of the study on the carbon, in the year 1991, Iijima discovered carbon nanotube in carbon soot,[2] which can be modeled by a seamless tube formed by the curling of hexagonal graphite sheets. Carbon nanotubes can be classed as single-wall nanotubes and multi-wall nanotubes, with the former further grouped into armchair, zigzag and chiral structures, depending on the angle and the length of the chiral vector. The diversity of their structure leads to the diversity of their electric property, which is deemed to be very helpful in fabricating complex nanometer electronic devices. With Transmission Electron Microscope (TEM) Iijima also observed C_{60} and multi-layer graphitic particles as by-products of carbon nanotubes.[3] In the year 1992, Ugarte observed the process of graphitic sheets curling into multi-layer carbon particles under the irradiation of TEM electron beams.[4] This kind of carbon particles contain as many as 70 concentric spherical graphitic cages, with the interlayer distance matching that of bulk graphite (0.35nm). Since then, it has been established that the fabrication of the nanotubes are usually accompanied by the generation of nanomet-

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ric graphitic particles, which are named "onions" or "Bucky onions". So far, their fabrication, structures and transition to diamond have been studied.[5−7] The authors of this article have also studied their fabrication, structures and electric properties, as is described in the following sections.

II. EXPERIMENTAL RESULTS

The DC discharge method was used in the fabrication of Bucky onions in much the same way as in the fabrication of carbon nanotubes.[8,9] The anode was a highly pure graphite rod of 6mm diameter and 30mm length, into which a hole of 3mm in diameter and 70mm in depth was drilled and filled with graphite and YNi_2 powder with a molar ratio of 1:1. The cathode, which was a graphite rod of diameter 10mm, was processed into a conical tip pointing to the anode, so that the deposition of the discharge products on the cathode could be minimized. The arc was generated by a current of 40–100A in a helium environment of pressure 93.1kPa. During the discharge, the anode-cathode separation was held at constant 5mm by continuously driving the anode. After the conclusion of the discharge, the obtained cloth-like soot, which contained carbon nanotubes, Bucky onions and amorphous carbon, was collected from the inner wall of the chamber.

Then the sample was purified. 200mg raw-soot was heated at 350°C for 2 hours in an air current with a flow rate 70 sccm. The remaining soot, which was believed to be free from amorphous carbon, was soaked in 36% (v/v) hydrochloric acid for one day and than centrifuged for the purpose of removing the metal YNi_2 catalyst clusters. The obtained sediment was washed using de-ionized water three times, ultrasonically dispersed in 200ml 0.2% benzalkonium chloride solution and filtered with a $\phi 1\mu$m porous polytetra fluoroethylene (PTFE) membrane disc filters in vacuum. The dispersion and filtration were performed twice with the view of ensuring the removal of carbon nanotubes. Then the filtrate was further filtered with a $\phi 0.2\mu$m Supor Membrane Disc filter in vacuum and pure carbon onions were obtained on the filter. Finally, the carbon onions were ultrasonically dispersed in ethanol and stored in the form of colloidal solution.

The colloidal solution of carbon onions in ethanol was applied onto newly cleaved highly oriented pyrolytic graphite (HOPG) substrates and observed with an atomic force microscope (AFM) purchased from NT-MDT Company. The AFM was operated in an ambient environment in tapping mode with a resonant frequency of 460.8kHz. The result of the observation is given in Figure 1, showing that the main component of the sample were balls of diameters smaller than 100nm.

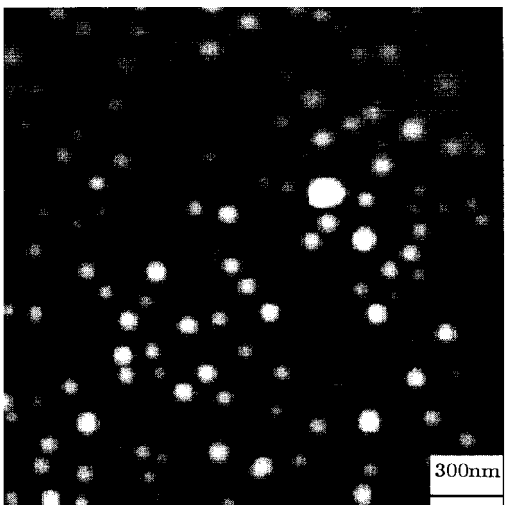


Fig.1. AFM images of Bucky onions (topographic).

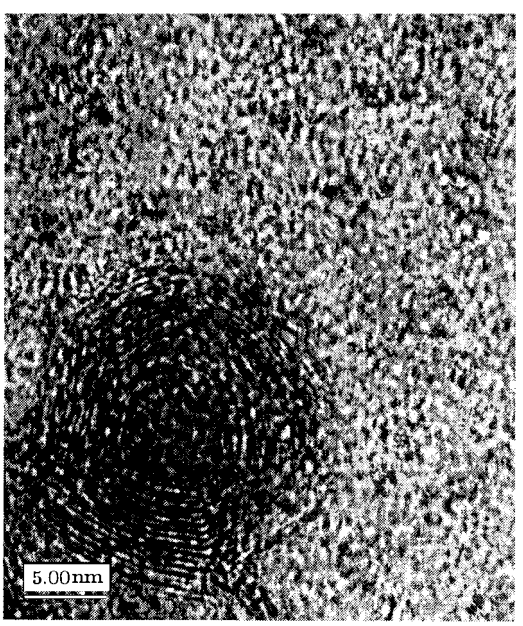


Fig.2. TEM image of Bucky onions.

The structural properties of Bucky onions were also analyzed. Drops of the Bucky onion colloidal solution were dropped onto the porous carbon microgrid. After thorough evaporation of the solvent, the sample was introduced into a High Resolution Transmission Electron Microscope (HRTEM)(JEOL-2010), with a working voltage of 200kV. The result of the

observation is presented in Figure 2, from which can be found that, instead of being a perfect sphere, the Bucky onion has some edges and corners. And it was also discovered that under the bombardment of electron beams the edges could be somehow smeared and the sphericity of the Bucky onions could be improved.

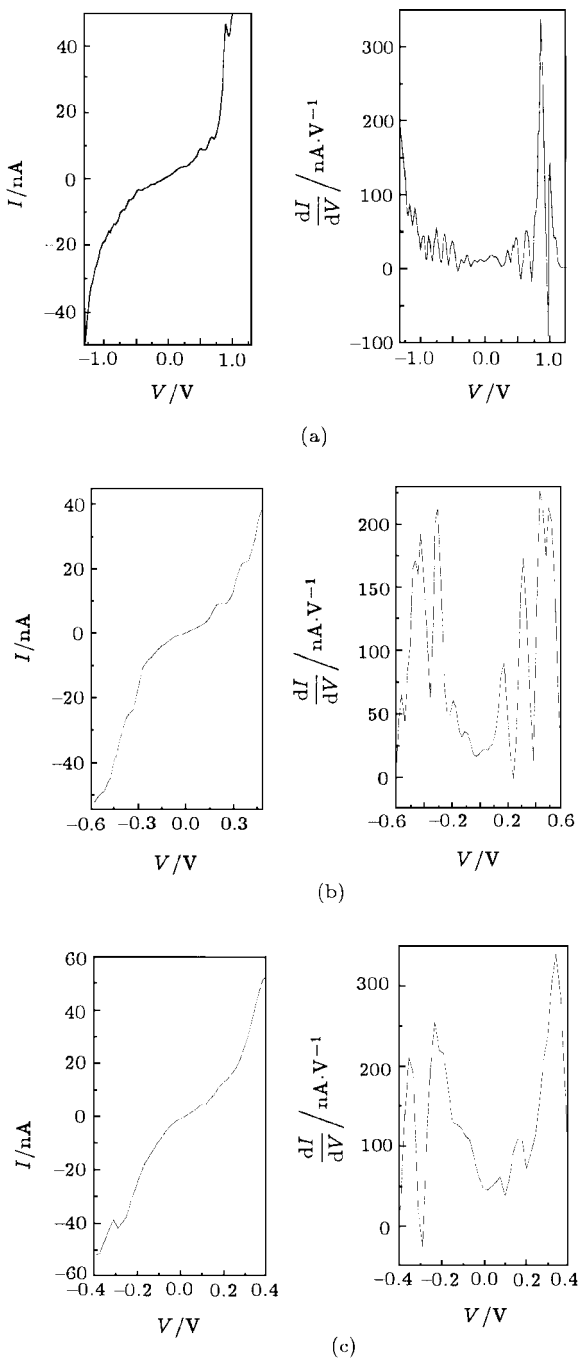


Fig.3. I-V and dI/dV-V curves corresponding to Bucky onions with various size. (a)15nm; (b)36nm; (c)50nm.

The scanning tunneling microscopy (STM) observation of the Bucky onions was also carried out. The colloidal solution of the Bucky onions in ethanol was dropped onto a gold substrate and after the evaporation of the ethanol the sample was studied with an STM working in air (NT-MDT). The STM tip was moved to the position right above the center of the Bucky onion and then lowered down to contact directly with it, so that the I-V curve and the dI/dV-V curve could be measured. As shown in figure 3, the behaviors of I-V and dI/dV-V curves differ depending on the size of the Bucky onions.

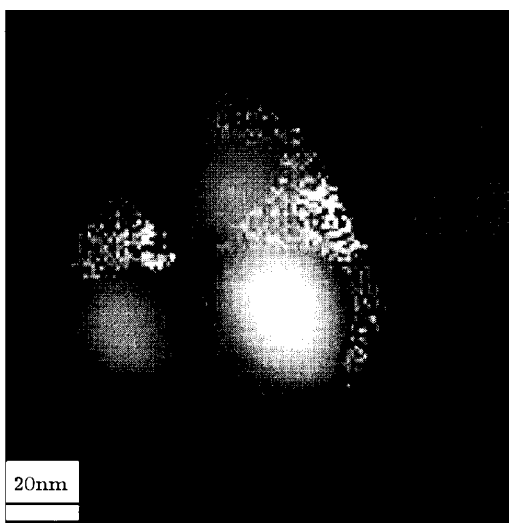


Fig.4. AFM image of a Bucky onion dimer.

Besides the individual Bucky onions, their aggregations were also observed, as shown in figure 4, which is AFM image obtained in tapping mode with a resonant frequency of 484.2kHz.

Ⅲ. DISCUSSION

Among all the allotropes of carbon, graphite is macroscopically the most stable one. Under external action, small hexagonal graphitic sheets can curl into single-wall carbon nanotubes (SWCNTs) or multi-wall carbon nanotubes (MWCNTs), or into single wall hollow balls, such as C_{60} and C_{70}, and multi-wall hollow balls, namely Bucky onions. In both multi-wall carbon nanotubes or Bucky onions, the inter-layer separations are 0.35nm, which is identical to that of graphite. As a kind of stable structure, Bucky onion is a member of the Fullerene family. According to the data in hand, the Bucky onions with a diameter smaller than 15nm show electric properties of semiconductors and have a band gap of approximately 1.0eV. While the Bucky onions with diameter larger than 36nm show electric properties of metals. This characteristic is tentatively attributed to the assumption that the outmost layer

is not the sole layer that functions in the conduction process. Further investigation is now under way.

In the experiment it was also found that STM images usually had a much poorer quality than AFM ones. (Therefore no STM images are presented in this paper.) It is very possible that the conductivity of Bucky onions is undermined by the amorphous carbon and impurity adsorbed on their surface. For a better understanding of the structure and the electric properties of Bucky onions, an ultrahigh vacuum STM might be indispensable, where the absorbates can be removed.

Just like other kinds of nanometer balls, Bucky onions also have the tendency of aggregating. Stable dimers were found in the observation. The dimerization observed in Fig.4 is thought to arise from the bonding between the atoms in the outmost layers of the Bucky onions. That is, the bonds of the atoms in the outmost layers might break, so that the neighboring Bucky onions could be connected to construct a stable dimer.

IV. CONCLUSION

Multi-layer concentric carbon nanoballs, nicknamed as Bucky onions, were fabricated using the DC arc discharge method, similar to that for the fabrication of carbon nanotubes. It was verified experimentally that Bucky onions are electrically conductive. Small-sized Bucky onions (diameter $<$15nm) exhibited electric properties of semiconductors. While relatively large Bucky onions showed electric properties of metals, probably resulting from the participation of all carbon layers in the process of electric conduction. Bucky onions exhibited the tendency to aggregate and dimers have been observed experimentally. As nanometer-scaled reservoirs of electric charges, Bucky onions will hopefully find their applications in future single electron devices.

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