# UHV-HRTEM of Reconstructed Nano-Structure Surface

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**Abstract**

Recent studies on nano-structures by a new ultra-high vacuum high-resolution electron microscope are reviewed briefly. The microscope is equipped with a field emission gun and achieves $10^{-9}$ Pa at the specimen chamber. High brightness and fine probe of the imaging electrons are used not only for observations of multi-shell carbon fullerenes and an exotic fullerene with three horned structure, but also for nano-fablication of point contact and gold nano-wire with surface reconstruction.

## 1. Introduction

Surface reconstruction of the clean surfaces is known to effect the electronic states of the surfaces, and thus determines the physical and chemical properties of the surfaces which are different from the bulk materials. When some reconstructions occur on the surfaces of low dimensional materials, such as nano-particles and nano-wires, the surface effects become large enough to determine their physical/chemical properties , because the surface atoms occupy larger volume than its core region. The reconstructions stabilized on flat surfaces have large unit cells and they can never be stabilized on nano-sized material. Here the question coming out is "how the reconstruction on such nano-dimensional surface is possible".

To clarify not only the geometrical structures but also the electronic structures of such nano-structures in relation with their physical and/or chemical properties, it is useful to investigate the same structures by scanning tunneling microscopy and spectroscopy. Scanning tunneling microscopy has been revealed many of the surface structures and of electronic states confined at the surfaces, but its information is quite sensitive to the tip geometry. Here the second question coming out is "how the tip geometry is well-defined at the atomic dimensions to obtain reliable information of the sample surfaces." This question would be solved best by observing tip and sample surface at the same time by electron microscope. There have been several reports on the efforts of combining transmission electron microscope and scanning tunneling microscope, and some progresses are made to reveal tip-surface interaction at nanometer scale[1,2]. There has been no fruitful results which clarified the relationship between the tip and the sample structure.

In this paper we report briefly the design of a new ultra-high vacuum high-resolution electron microscope for in-situ studies of nano-structures, particularly of their surfaces, by scanning tunneling microscopy. The field emission gun of the microscope is used for fablication of nano-structures such as multi-shell carbon fullerenres and/or nano-wires. Interesting feature of some nano-structures obtained at the "particle surface" project of ERATO are shown.

## 2. Design of the UHV HR Electron Microscope with a Field Emission Gun

UHV electron microscopes and UHV HR electron microscopes have been developed by several groups in the world. The UHV-HRTEM that we have developed at ERATO has the design as shown in fig.1. The microscope (JEOL2000FV) has basically has the same design as its prototype UHV electron microscope[3], but has a field emission gun instead of LaB6 gun. In addition, the microscope is designed so as to make STM observation of the specimen surfaces. The STM allows us to study the electronic properties of the nano-structures, of which structure is well defined through high resolution electron microscopy. Another function of the microscope attached is the bi-prism, which enables us to make interferometric measurement of the phase shift of the incident electron wave on the specimens. We expect to detect a phase shift corresponding to a one carbon layer (about 50 V.A) with a high spatial resolution of 0.2nm.

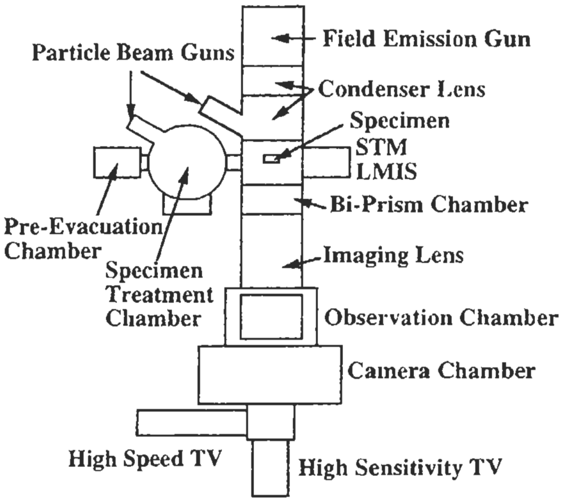

**Fig.1** Design and constructions of a ultra-high vacuum high-resolution transmission electron microscope. Field emission electron beam is used to fabricate nano-structures. High resolution interference microscopy is available by a bi-prism, and electronic states are detected by a miniaturized scanning tunneling microscope placed at the specimen position. The accelerating voltage is 200kV.

## 3. Exotic Nano-structures

Bucky onion[4] is known to have a multi-shell structure of carbon fullerenes[5] ($C_n$; n=60, 240, 540, 960, 1500, ....) as schematically shown in fig.2. The model structure in fig.2, which was obtained by molecular-dynamics method, is a view along the five-fold symmetry axis and has a concentric icosahedral structure[6]. Three characteristic feature of the model, decagonal contour, ten radial Moire fringes extending from the center towards each apex of the decagonal contour, and clustering of carbon atoms in projection to give an pseudo atom image separated 0.2nm with each other, are all reproduced in a transmission electron microscope image shown in fig.3. A new interesting behavior of the bucky onions is the trapping; the center of a bucky onion is overlapping with a corner or an edge of other bucky onions, as seen in fig.3[6]. And another interesting behavior is that the five-fold symmetry axis has a tendency to align parallel to the imaging electron beam; the five-membered rings of the carbon atoms located at each of the carbon fullerenes are lined up along the direction parallel to the imaging electron beams. This overlapping and lined-up tendency of the bucky onions may attribute to some magnetic properties of the five-membered ring, although some future experiments may be required to confirm this.

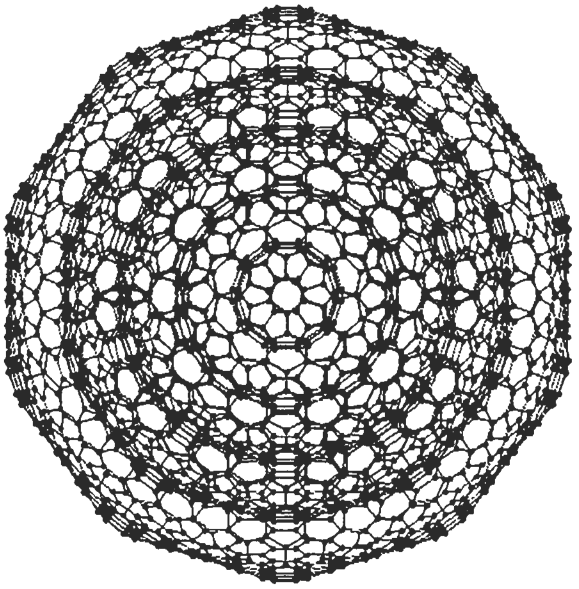

**Fig.2** Structural model of multi shell structure of carbon fullerenes (carbon onion) obtained by molecular dynamics simulation.

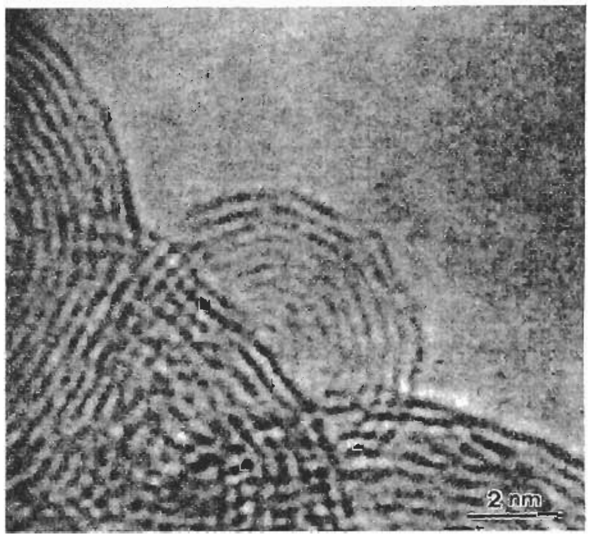

**Fig.3** High-resolution electron microscope image of carbon onions. Note that the five-membered carbon ring of the carbon onion at the center is kissed to the outer fringe of the other carbon onion.

Multi-shell fullerene with negative curvature which has been recently observed has a three-horned structure as shown in fig.4[7]. This particle has negative curvature. It has a seven-membered carbon ring at each of the three concave corners, and five five-membered rings at each convex corners, apices of the three horn, as schematically shown in fig.5. Stability and generation mechanism of such exotic structure are interesting issue to be clarified, although the three-horned structure is rarely

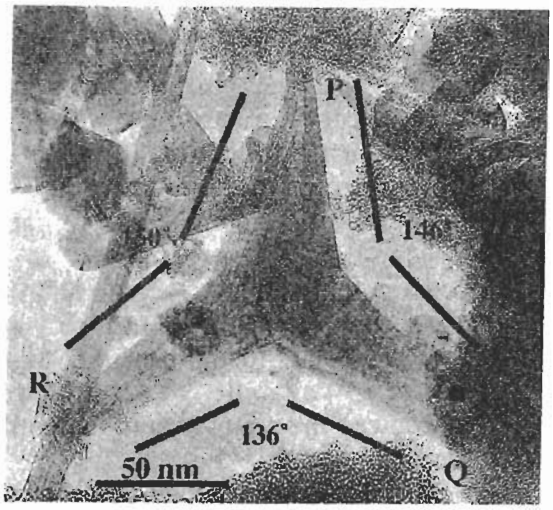

**Fig.4** High-resolution electron microscope image of a three-horned fullerene, having three negative curvatures formed by a seven-membered carbon rings for the each concave curvature.

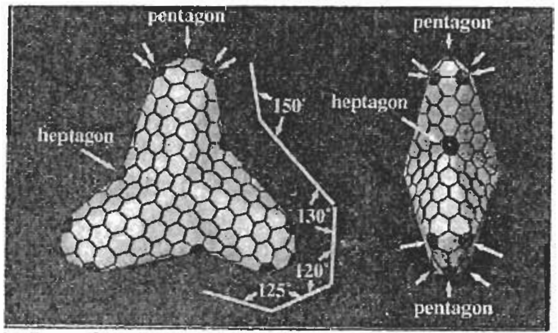

**Fig.5** Structure model of the smallest fullerene of the three-horned structure in fig.6. Note a seven-membered ring at each concave curvature, and three five-membered carbon rings at each convex curvature which form a horn.

generated by carbon discharge process.

Carbon fullerene ($C_{60}$) is a building unit of cluster crystals. Similarly to $C_{60}$, an icosahedral $B_{12}$ cluster is a building unit of boron cluster crystals. Recently, a fascinating $B_{12}$ cluster model was proposed[8] for explaining quite low sheet resistance of a high-dose boron as-implanted system in silicon crystal. Although they assumed an icosahedral $B_{12}$ clusters substituting the $Si_5$ cluster in silicon matrix, recent cluster calculation based on the first principles local density functional approach has shown a new cluster model[9]. The derived model, shown in fig.6, has a cubo-octahedral $B_{12}$ cluster. Compared with the icosahedral cluster model, the cubo-octahedral cluster model has lower total energy as large as 4.6eV. The analysis of local wave-functions (fig.7) and the partial density of states shows that the cubo-octahedral $B_{12}$ cluster is stabilized because of rather strong boron-silicon bonding at the boundary, and act as a double acceptor. To clarify the stable structure and electronic conductivity of $B_{12}$ cluster in silicon matrix, future investigation using present STM-TEM system would be quite useful.

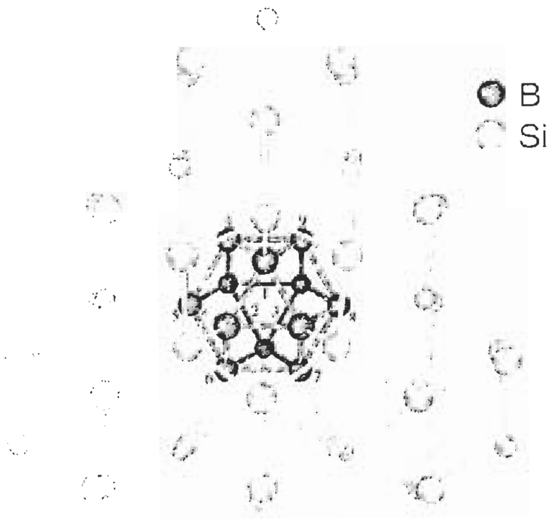

**Fig.6** Model structure of the cubo-octahedral $B_{12}$ cluster replaced the $Si_5$ cluster in the Si matrix.

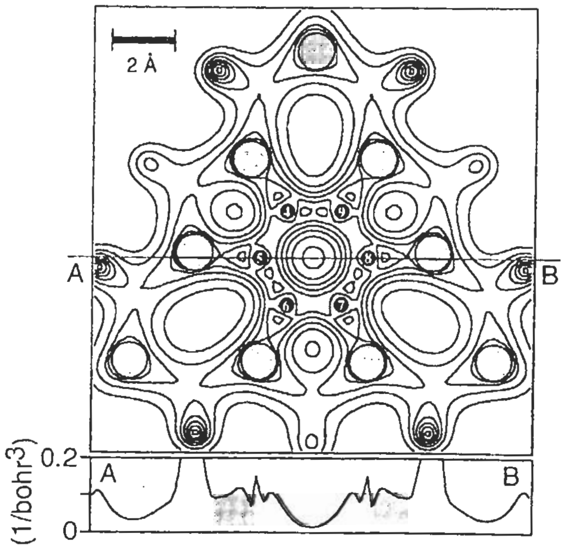

**Fig.7** Section image of the electron density map of the cubo-octahedral $B_{12}$ cluster. Note high density of electrons between the B and Si atoms which form bonding.

## 4. Surface Reconstruction of Nano-wire and Nano-particles

Nano-sized low dimensional materials also have interesting electronic properties. Quantized conductance has been generally observed for wires and for atomic contact[10]. The conductance of the point-contact is simulated by Landauer formula[11] as due to the quatization of the transverse electron motion in the contact. A new question would arise when the dimensions are further reduced down to atomic scale: how surface reconstructions do affect the electron transport properties? To answer this question we first have to develop a technique for devising such atomically well-defined nano-structures.

Nano-electron beam technique has been devised to make nano-structures in-situ in the UHV HR electron microscope. With this technique nano-wires which have several atomic rows in their cross-section and elongate as long as 10nm[12] are formed. A series of electron microscope images in fig.8 is an example of atomic point contact made by our nano-beam technique in-situ in the UHV-HRTEM[13], where we clearly see a single gold atom at the center of the two electrodes. The nano-beam technique can control atomic scale structures to much higher extent than electron beam lithography[14]. The nano-beam technique thus allow us to fabricate nano-structures well-defined at atomic scale, and would be able to clear up new aspects of quantum phenomena.

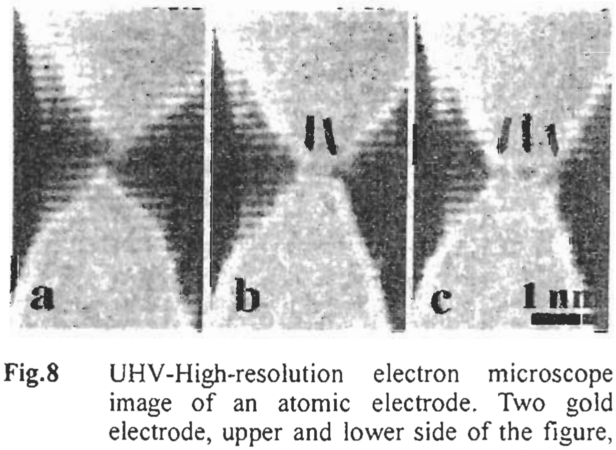

**Fig.8** UHV-High-resolution electron microscope image of an atomic electrode. Two gold electrode, upper and lower side of the figure, have a contact in (a). The contact becomes thin enough to detach the two electrode in figs. (b) and (c). Atomic contact has been realized: the dark dot in (c) which can be seen between the two electrodes is a single gold atom suspended between the electrodes.

## 5. Summary

The design of a new ultra-high vacuum high-resolution electron microscope which allows us to fabricate nano-structures at atomic scale by nano-beam technique utilizing field emission electron probe is shown. The bi-prism of the microscope allows us further to analyze projected potential and external electronic field of our specimens with an accuracy of 50VA which corresponds to the potential of a carbon single layer. Availability of scanning tunneling microscopy of the nano-structures in-situ in the microscope would be useful to derive physical/chemical properties of nano-structures which are well-defined at atomic scale.

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