Application of a UHV-MBE-TEM system on the deposition and HRTEM study of indium nanoparticles

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A UHV-system that consists of a 200 keV TEM, a MBE deposition apparatus and specimens transfer mechanisms was newly developed to investigate as-fabricated nanostructures. The base pressure inside all of the chambers including the TEM is less than 3x10-8 Pa. This system allows us to deposit materials under the control in nanometer scale and to characterize the structure without any contamination. Indium nanoparticles were firstly deposited on silicon surface and studied with HRTEM after the transportation of specimens in vacuum to the TEM, while the oxidation of indium was dominated when specimens were once exposed in air. Nanocrystals of indium with a single crystal, a simple twin and multiple twins were observed and analyzed in terms of the transition of its crystal structure between bct and fcc. The structural fluctuation was also observed using video in the TEM.

1. INTRODUCTION

Nanostructures and nanoparticles have been attracting many research interests in recent decade because of their unique properties associated with their structures that would not represent bulk materials, and that are affected by the ratio of atoms on the surface to those inside particles. Many methods can be used to study those structures such as scanning tunneling microscopy, X-ray diffraction and photoelectron emission spectroscopy. Among them, transmission electron microscopy (TEM) is one of the most powerful methods due to the capability of the characterization inside a particle as well as surfaces. By using high resolution transmission electron microscopy (HRTEM), the observation of lattice images or even of isolated atoms images can be achieved in profile- and plain-views imaging techniques. Also the chemical composition of nanostructures can be characterized by energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Furthermore, the energy states of localized electron in nanostructures can also be achieved with EELS.

One of the major problems is the specimen preparation of nanostructured materials. The specimens are usually loaded to TEMs from air environment. Then, the specimens that contain nanostructures have to be exposed to air after the deposition and fabrication in controlled environments such as in high vacuum and in gases. This exposure is a big problem for some materials, which are easily oxidized or contaminated. To prevent the structural changes due to the reaction with environments, samples have to be covered by other materials. However, the covering sometimes can also dramatically change the nature of the nanostructures. Another choice is to make samples inside TEM, which also enables in situ examination [1]. But the combinations between materials and methods for in situ fabrication of nanostructures are limited. For example, Fe and other magnetic materials can not be deposited inside TEM because they may damage the magnetic lenses. The deposition methods that will not influence the vacuum inside the TEM can be only applicable. Furthermore, a general problem for in situ experiments is the uncertainty of deposition rate, which can not be easily measured in the narrow space inside the TEM. These facts strongly stimulate the development of a UHV-system in which a TEM is connected with a MBE through specimen transfer mechanisms. This paper demonstrates the usefulness of a UHV-system which we have newly developed and which that consists of a 200 keV TEM and a MBE deposition apparatus in a vacuum of $3x10^{-8}$ Pa.

2. EXPERIMENTAL

A new UHV-MBE-TEM system was developed at National Research Institute for Metals (NRIM) by combining a 200 keV UHV-FE-TEM (JEOL-2000VF), a UHV-MBE and specimen transfer mechanisms. A

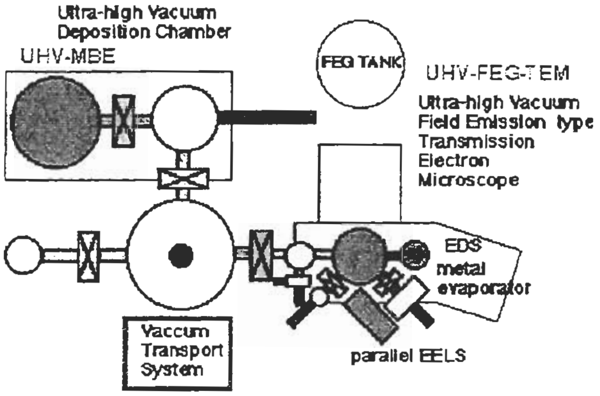

Fig. 1 A schematic diagram of the UHV-MBE-TEM system.

schematic drawing is shown in Fig. 1. The UHV-FE-TEM has a ZrO/W Schottky type thermal field emission gun which provides large probe current density of 10^5 A/cm^2 and small energy spread of 0.7 eV at the electron source. Its point resolution at Scherzer defocus is 0.21 nm and lattice resolution at information limit is 0.1 nm. The TEM column is evacuated by eight sputter ion pumps, three titanium sublimation pumps and a cryo pump. All lens system are sealed by metal O-ring to be baked up to 150 °C. The combination of baking and multi-pumping leads the vacuum level of the column to about 2.0 x 10^{-8} Pa. Mass spectroscopy of residual gases reveals that main residual gas is hydrogen. This TEM is connected to a standard MBE deposition apparatus through the specimen transfer mechanism in which a cartridge specimen holder can be transported by a rack-and-pinion and rotation movements. This system is evacuated by ion pumps to maintain a vacuum in 10^{-8} Pa range. The MBE is evacuated by a magnetically suspended turbo-molecular pump to a vacuum of 10^{-8} Pa. Two Knudsen cells and one electron beam deposition source equipped in MBE chamber enable preparation of various materials. A quartz crystal thickness monitor is used for measuring deposition rate and film thickness. A detailed description of this system can be found in elsewhere [2].

By using this system, 0.5nm thick indium has been deposited onto Si (110) TEM specimens at room temperature by a Knudsen cell equipped in the MBE chamber. The base pressure in the chamber is below 3x10^{-8} Pa. The pressure during deposition is around 3x10^{-7} Pa. The deposition rate is controlled at a constant speed of 0.2 nm/min. After deposition, the samples were transferred directly into the UHV-FE-TEM for HRTEM examination through the transport mechanism. The influence of air exposure on the structure of deposited indium was investigated with specimens which were prepared by a separated UHV-MBE system and were taken out in air at room temperature.

3. RESULTS AND DISCUSSION

Fig. 2a shows a HRTEM picture of indium nanoparticles deposited in a MBE chamber on amorphous C film. After deposition, the sample were taken out into the air and then moved into a microscope. Several sizes of nanoparticles with lattice fringes were observed in the figure. It is important to note that the electron diffraction pattern in Fig. 2c shows the co-existence of indium and In_2O_3. The surface of large particles and the whole body of small particles have already changed into In_2O_3. Fig. 2b shows a small particle of In_2O_3 in a diameter of about 3nm. The formation of facetted indium multiply-twinned

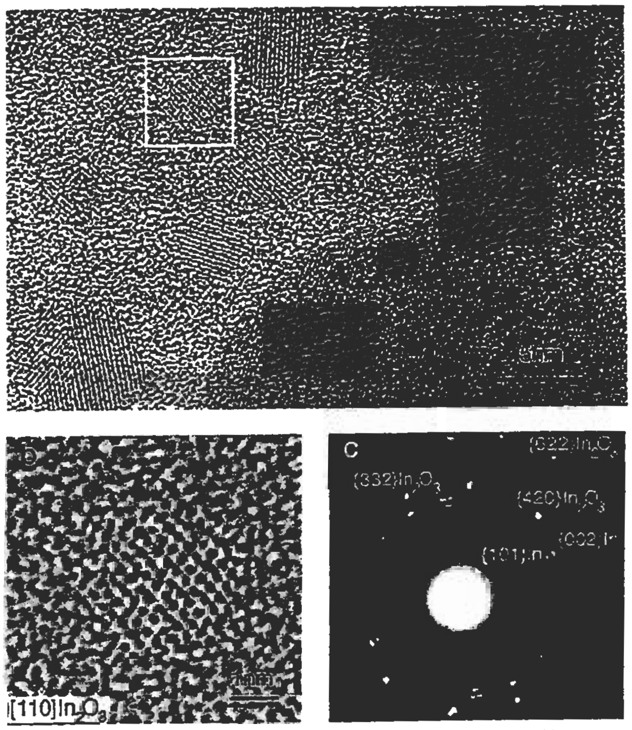

Fig. 2 The structure of indium nanoparticles deposited in MBE on amorphous C film and exposed to air at room temperature. a) a low magnification HRTEM micrograph, b) an enlarged HRTEM image of an In_2O_3 particle and c) diffraction pattern taken from area shown in 2a.

particles (MTPs) as well as their structure fluctuation were observed with in situ deposition [3]. These phenomena are not found in the present sample. The reason is that chemisorption and contamination of the surface have very dramatic effect upon surface energies, and will, therefore, alter the equilibrium shape or even the nature of small particles [4,5].

First results of as-deposited indium microstructure which was obtained from the sample deposited in the UHV-MBE chamber and directly transferred to UHV-FE-TEM are shown in Fig. 3. Instead of forming a thin film, indium nanoparticles are observed to form by self-organization. The fact that only indium and Si substrate can be found in the diffraction pattern from this sample indicates that there is not oxygen contamination on the surface of indium nanoparticles. EDS and EELS examinations of this sample do not show oxygen contamination, either. Freshly made indium nanoparticles have a round shape in plain-view images. This is on the contrary to the facetted shape observed with in situ deposition, where the effect of the electron beam can not be ignored [3]. Most of the nanoparticles at the present study are in the size range of 8-15 nm in diameter. There are also some larger particles obviously formed by the coalescence of two particles.

Not like the sample made outside UHV system, single crystal, twinned crystal (some times even pseudo twin with $[111]_A//[100]_B$ and $(10\text{-}1)_A//(0\text{-}1\text{-}1)_B$) or decahedral MTP were observed for the structure of indium particles. The structure of single crystal and twinned particles is confirmed to be body-center-tetragonal (bct) structure, which is the same as that of bulk indium. An early work [6] on X-ray study has already shown that small indium particles less than about 5 nm in diameter have a face-center-cubic (fcc) structure. The fcc structure was found in neither single crystal nor twinned particles of indium in the present work because the size of the particles are larger than about 8 nm. The structure of indium MTPs is complicated. Fig. 4 shows an enlarged HRTEM experimental image of an indium MTP patched with HRTEM simulation images for bct and fcc structures. The truncated five-fold decahedral structure is very similar to that of the MTPs in fcc materials such as Au, Ag and Pb. Good agreement with HRTEM image simulation, however, indicates that the crystal structures of

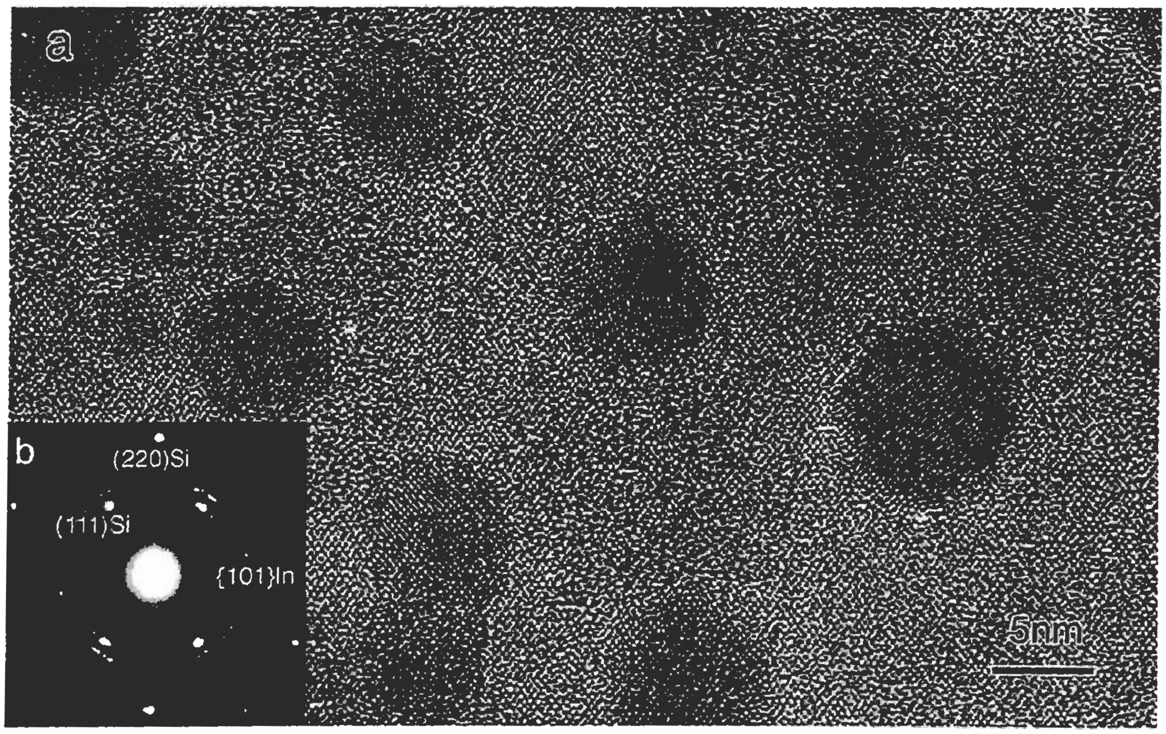

Fig. 3 A HRTEM image of indium nanoparticles deposited in the UHV-MBE-TEM system on Si surface. a) round shape crystals with single crystal or MTP structure and b) diffraction pattern, showing {101} of In with body centered tetragonal (bct) structure without any spot from In_2O_3

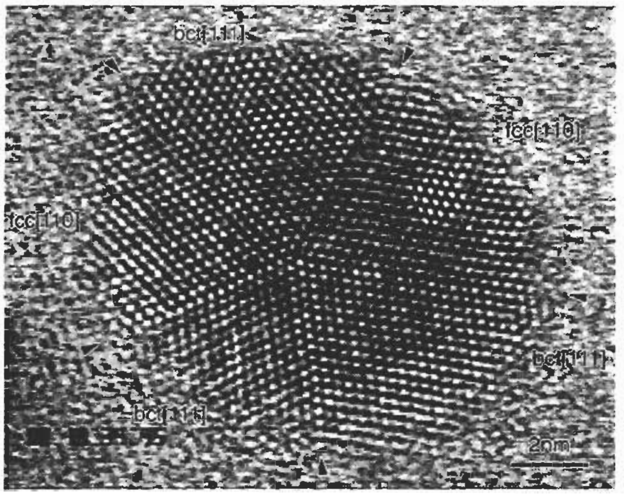

Fig. 4 An enlarged HRTEM experimental image of a multiply twinned particle (MTP) of indium, patched with simulated HRTEM images for bct and fcc structures.

the present MTPs are the mixture of both bct and fcc structures in one particle. Although MTPs are popular in small particles having fcc structure, they have not been found having non-cubic structure before, neither been found having different structures in one particles.
Furthermore, structural fluctuation was also observed during TEM observation, similar to in situ experiments. The changing process of shape and structure is in a random way. The shape and orientation of a single crystal change suddenly. The transition among a single crystal, twinned particle and MTP also occur. The fluctuation frequency for smaller particles is higher than that for larger particles, because larger particles are more stable than smaller particles. A detailed discussion on the structure and the structural fluctuation of indium nanoparticles can be found in elsewhere [7]. Several indium nanoparticles as small as 2.5 nm in diameter on the surface of Si substrate are also observed to show structure fluctuation, which means their surface have not been contaminated. Fig. 5 shows one of them in decahedral MTP shape with possibly fcc structure. Comparing with the small In_2O_3 particle shown in Fig. 2b indicates clearly the importance of clean surface on the study of nanoparticles and the application of the UHV-MBE-TEM system.

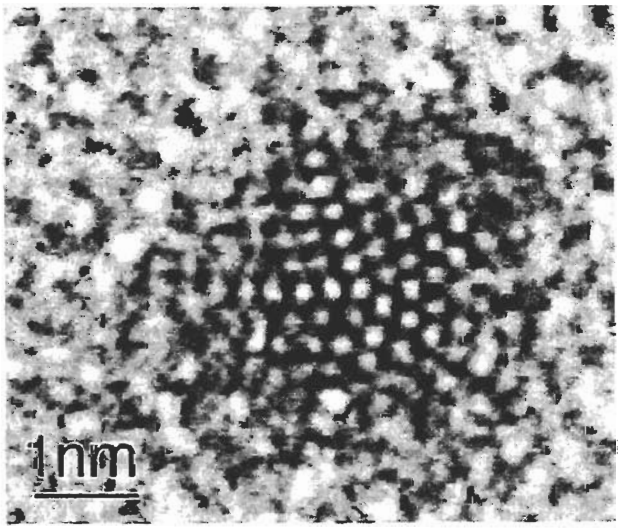

Fig. 5 Small indium MTP particle on surface of Si substrate containing less than 200 atoms in each unit.

4. Conclusions

A UHV system that consists of a 200keV TEM, a MBE deposition apparatus and specimens transfer mechanisms was newly developed to investigate as-fabricated nanostructures. This system allows us to deposit materials under the control in nanometer scale and to characterize the structure without any contamination. Indium nanoparticles were firstly deposited and studied with HRTEM after the transportation of specimens in vacuum to the TEM. Unusual structure has been observed for the indium nanoparticles with clean surface. The structure fluctuation has also been observed.

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