In-situ Deposition of Metal Nanoparticles on Si(110) Thin Film Surfaces in UHV-FE-TEM

Miyoko TANAKA+, Masaki TAKEGUCHI and Kazuo FURUYA
National Research Institute for Metals, Sakura, Tsukuba 305-0003, JAPAN

(Received October 2 1998; accepted November 27 1998)

Fabrication and structural observation of In and Pd nanoparticles deposited on Si (110) substrate were performed in an ultrahigh vacuum field emission transmission electron microscope (UHV-FE-TEM). High-resolution electron microscopy (HRTEM) of both nanoparticles shows structural fluctuation. Smaller In nanoparticles frequently change their shapes under the electron beam, sometimes showing coexistence of amorphous/liquid and solid. Larger In nanoparticles show coalescence. Pd nanoparticles keep their configuration under electron beam for a while and then begin to show slower structural fluctuation.

1. Introduction

The structure of small particles attracts great interest for their distinctiveness. A lot of studies have been performed to clarify their structures and properties that are different from bulk ones [1-3]. When the particles are small enough to be called as "nanoparticles", they sometimes show configurational and structural fluctuations of which mechanism is still under investigation0 [4,5]. Recent development of ultrahigh vacuum transmission electron microscopes (UHV-TEM) has provided a powerful way to solve the precise structure of small particles [6], their growth process [7], as well as surface structure of them [8].

In this study, indium and palladium nanoparticles were deposited on Si (110) TEM samples and have been investigated with an ultrahigh vacuum field emission transmission electron microscope (UHV-FE-TEM) [9]. High resolution transmission electron microscopy (HRTEM) was performed and dynamic observation of In and Pd nanoparticles during and after the deposition was carried out. Structural fluctuation was observed for both nanoparticles.

2. Experimental

The microscope used in this study is UHV-FE-TEM (JEOL-2000VF) with an accelerating voltage of 200 kV. Its point resolution at Scherzer defocus is 0.21 nm and lattice resolution at information limit is 0.1 nm. It is equipped with a ZrO/W Schottky-type thermal FEG with energy spread of 0.7 eV at the electron source. The base pressure of the column is less than 2.0×10^{-8} Pa. Mass spectroscopy inside column indicates that the main residual gas is hydrogen [9]. EDS and EELS apparatus are attached for chemical analysis.

Two evaporators are attached to the column in order to perform in situ evaporation of metals. One is an electron beam (EB) evaporator and another is a thermal heating evaporator with tungsten wire. The thermal type evaporator is used for deposition of Indium nanoparticles and the EB evaporator is for palladium.

Samples were cut from B doped p-Si (110) wafers and were prepared to TEM specimens by chemical etching, with etchant H_3PO_4: HNO_3: HF: CH_3COOH = 4:3:2:1. Deposition of In and Pd was carried out in the TEM column during observation at room temperature. The amount of deposited metals could not be measured during the deposition process in the present experimental configuration, but the thickness of In estimated from HRTEM images is about 1-2 nm and that of Pd is about 2-4 nm. Thus the deposition rate is calculated to be about $1\text{-}3 \times 10^{-3}$ and $3\text{-}6 \times 10^{-3}$ nm/s for In and Pd, respectively. A TV-rate video camera provides dynamic observation of deposition process.

3. Results and Discussion

Nanoparticles with various sizes were formed during in-situ deposition of In. The particles with size of less than 10 nm are found to be unstable in their shapes under the electron beam. Fig. 1 shows a series of micrographs of a deposited In nanoparticle that stays at the edge of Si thin substrate and constantly changes its shape. These micrographs are still images grabbed from videotape and the time difference between each image is 2-5 seconds. In each micrograph, the image of a nanoparticle with size of 7 nm is clearly captured. The electron beam intensity was about 10 A/cm^2. The particle shows lattices fringes of body centered tetragonal (bct) structure in the left part of it in Fig. 1a, in

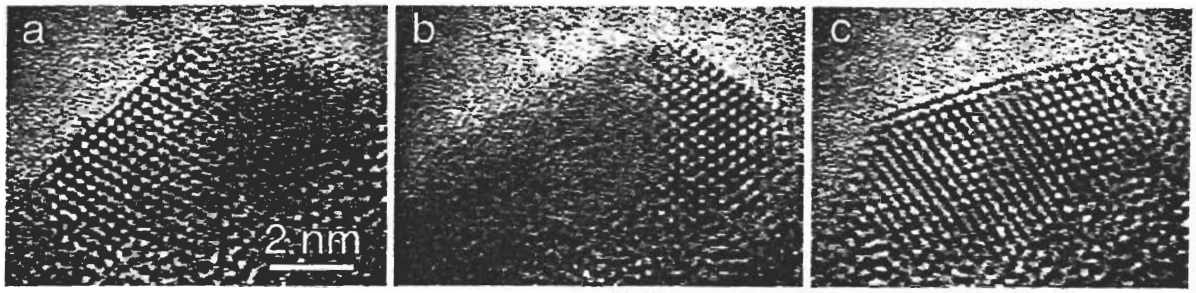

Fig. 1. TEM micrographs showing structural fluctuation of In nanoparticle deposited on Si (110) sample about 7 nm in diameter. a, b) Half-melted or amorphous state. The solid-liquid boundary is seen. c) Full crystal state.

the right part of it in Fig. 1b and in Fig. 1c. In each case, the particle is located along <111> direction, with {101} facets that have minimum surface energy for tetragonal structure. The right part of the particle in Fig. 1a and the left part in Fig. 1b, which do not show clear crystal image, are considered to be changing its shape in amorphous or melting phase.

These structural fluctuations are considered to be induced by electron beam irradiation. Although no model can explain this type of configurational transition completely [2,4,5,8], it is generally recognized that these particles are above the temperature at which the thermal fluctuation is large enough to overcome the potential energy barriers for shape change and the particles are able to constantly change their shapes in quasi-molten phase [10]. Obviously, the present In particle system was energetically raised to this phase by electron beam irradiation. The exact measurement of the local temperature raise by electron beam irradiation has not been done in the present study, but it should be within 50 K in the present beam condition [8]. Thus the temperature required for quasi-molten phase should be quite low for In nanoparticles about 7 nm in size

The influence of electron beam was more apparent on bigger nanoparticles. When the observation position of the sample is changed and the electron beam was irradiated to the new place of the sample, the coalescence of nanoparticles was occurred. Fig. 2 shows a series of micrographs taken during the coalescence process. Fig. 2a is a still image taken just after the focusing of the electron beam and Fig. 2b-2d are taken after 0.10, 0.13 and 0.17 seconds, respectively. The electron beam density was about 2 A/cm^2 this time. In Fig. 2b, faint contrast that looks like a bridge across the central two particles begins to be observed. At this stage, it is considered that the atom diffusion from each particle to the other started. After less than 0.10 seconds, the particles seem to merge into one particle. After this, no more coalescence procedure was observed.

These phenomena occurred only when the distance between two nanoparticles was smaller than 2-3 nm and the particle size is less than 15 nm. Since the coalescence begins to occur just after the electron irradiation, it can be concluded that electron beam activates this process but only for small nanoparticles less than 15 nm in size. As the electron beam density is lower and the particle size is larger than in the case of Fig. 1, the influence of electron beam irradiation on particles becomes smaller so that the structural fluctuation was not observed.

Nanoparticles with size of 3-5 nm were formed after the in-situ deposition of Pd. Typical images of the Pd nanoparticles with two different orientations are shown in Fig. 3. The particles stay at the edge of the Si substrate as same as the In case. While the

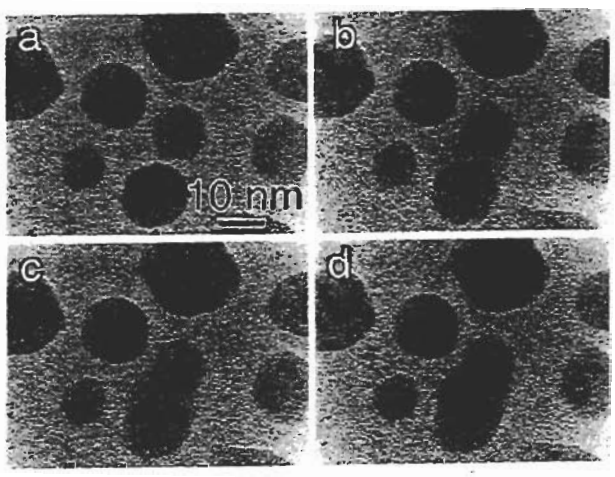

Fig. 2. Sequential images of In particles undergoing coalescence. a)Just after the focusing, b) 0.10sec., c) 0.13 sec. and d) 0.17sec. later.

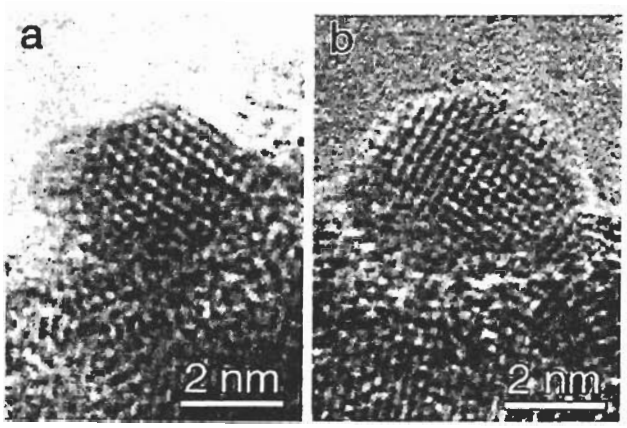

Fig. 3. TEM micrographs of Pd nanoparticles just after focusing. a) With <110> beam incidence and b) <100> beam incidence.

particle in Fig. 3a shows <110> plane and have {111} and {100} facets of its fcc structure, the one in Fig. 3b is aligned along <111> and seems to have {110} and {100} facets. Although the clear images were obtained just after the changing of the observation place as shown here, the structural fluctuation similar to In nanoparticles began to occur after ten to several tens seconds of continuous electron beam irradiation.

Fig. 4 shows the fluctuation of Pd nanoparticles. The time difference between each image is about 10 seconds. The electron beam intensity was also about 10 A/cm^2. At the beginning, the particle showed lattice fringes as in Fig. 4a for about ten seconds, but after that it began to fluctuate its structure and changed to/from a state where all part of the particle does not show any lattice fringes but a hemispherical configuration which is considered to be in amorphous phase (Fig. 4b,e) to/from solid states with fringes but with different orientations (Fig. 4c,d). In Fig. 4f, the particles shows lattice fringes and amorphous like image (lower left) at the same time. The fluctuation continues as the observation goes on. The fluctuation rate is much slower than in the case of In although the particle size is smaller.

The fluctuation difference between In and Pd represents the difference in their melting temperature. The melting point of bulk In and Pd are 430 K and 1825K, respectively. The melting point of small particle becomes lower as the particle size becomes smaller [11,12], and the quasi-molten temperature, which is far below the melting temperature, becomes lower in turn. Although the size of In nanoparticles is larger than that of Pd nanoparticles, quasi-molten temperature of Pd nanoparticles are much higher than that of In. Thus In nanoparticles showed instant fluctuation as the observation started while Pd

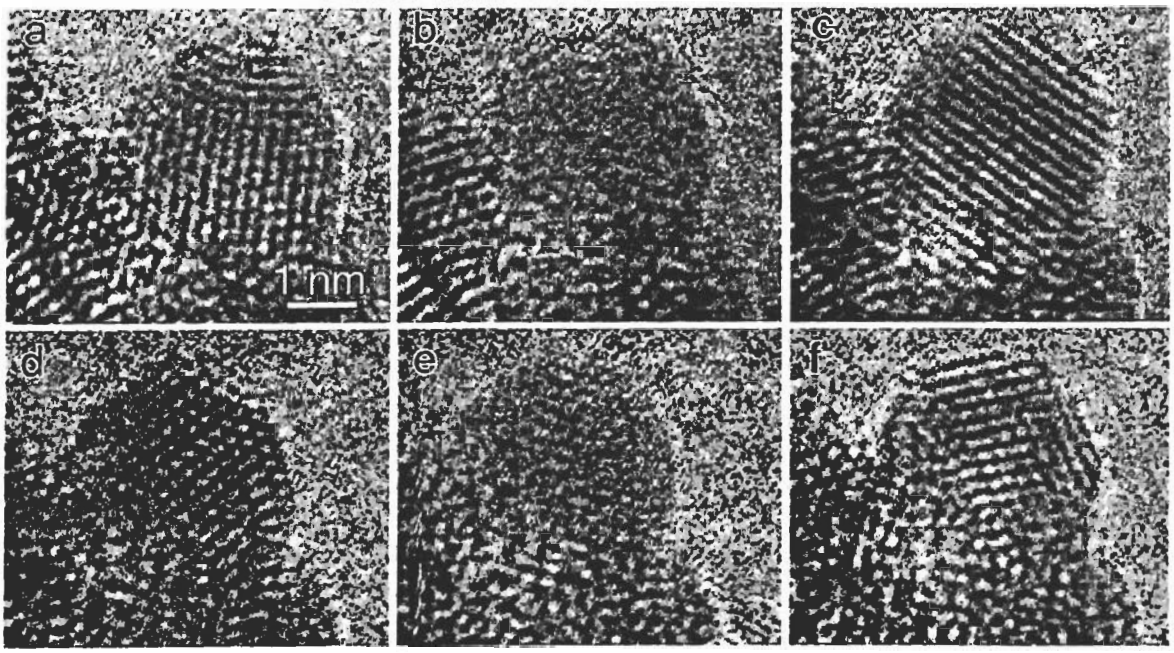

Fig. 4. Sequential images of Pd nanoparticle under electron beam irradiation. They change from single crystal (a, c and d) to amorphous or liquid state (b, e) and half-crystal state (f).

nanoparticles do not.

4. Summary

Fabrication and structural observation of In and Pd nanoparticles deposited on Si (110) substrate were performed with UHV-FE-TEM. Dynamic observation of In deposition shows the formation of nanoparticles with various sizes. Nanoparticles less than 10 nm in size showed structural fluctuation in a very short time scale, sometimes showing coexistence of amorphous/liquid and solid. Nanoparticles about 15 nm in size showed coalescence when two of them are nearer than 2-3 nm. Pd nanoparticles also showed configurational fluctuation but only after electron beam irradiation for about or more than 10 seconds. These results may be due to the electron beam irradiation which affect the system to a certain state here the particles prefer to change their structure.

5. References

1. M. J. Yacaman, S. Fuentes and J. M. Dominguez, Surf. Sci. 106, 472 (1981)
2. S. Iijima and T. Ichihashi, Phys. Rev. Lett. 56, 616 (1986)
3. S. Iijima, Jpn. J. Appl. Phys. 26, 357(1987)
4. A. Howie, Nature 320, 684(1986)
5. P. Williams, Appl. Phys. Lett. 50, 1761(1987)
6. L. D. Marks and P. M. Ajayan, J. Matter. Res. 5, 1496 (1990)
7. M. Mitome and K. Takayanagi, Surf. Sci. 242, 69 (1991)
8. M. Mitome, Y. Tanishiro and K. Takayanagi, Z. Phys. D 12, 45(1989)
9. M. Tanaka, K. Furuya, M. Takeguchi and T. Honda, Thin Solid Films 319, 110(1998)
10. P. M. Ajayan and L. D. Marks, Phase Transitions 24, 229(1990)
11. R. Kofman, P. Cheyssac and R. Garrigos, Phase Transitions 24, 283 (1990)
12. T. Castro, R. Reifenberger, E. Choi and R. P. Andres, Phys. Rev. B42, 8548(1990)