TOPICAL REVIEW

Nanofabrication by advanced electron microscopy using intense and focused beam*

Kazuo Furuya

High Voltage Electron Microscopy Station, National Institute for Materials Science, 3-13 Sakura, Tsukuba 305-0003, Japan
E-mail: FURUYA.Kazuo1@nims.go.jp

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Abstract
The nanogrowth and nanofabrication of solid substances using an intense and focused electron beam are reviewed in terms of the application of scanning and transmission electron microscopy (SEM, TEM and STEM) to control the size, position and structure of nanomaterials. The first example discussed is the growth of freestanding nanotrees on insulator substrates by TEM. The growth process of the nanotrees was observed in situ and analyzed by high-resolution TEM (HRTEM) and was mainly controlled by the intensity of the electron beam. The second example is position- and size-controlled nanofabrication by STEM using a focused electron beam. The diameters of the nanostructures grown ranged from 4 to 20 nm depending on the size of the electron beam. Magnetic nanostructures were also obtained using an iron-containing precursor gas, Fe(CO)₅. The freestanding iron nanoantennas were examined by electron holography. The magnetic field was observed to leak from the nanostructure body which appeared to act as a ‘nanomagnet’. The third example described is the effect of a vacuum on the size and growth process of fabricated nanodots containing W in an ultrahigh-vacuum field-emission TEM (UHV-FE-TEM). The size of the dots can be controlled by changing the dose of electrons and the partial pressure of the precursor. The smallest particle size obtained was about 1.5 nm in diameter, which is the smallest size reported using this method. Finally, the importance of a smaller probe and a higher electron-beam current with atomic resolution is emphasized and an attempt to develop an ultrahigh-vacuum spherical aberration corrected STEM (Cs-corrected STEM) at NIMS is reported.

Keywords: electron-beam-induced deposition, iron carbonyl, nanorod, electron holography, ultrahigh vacuum, Cs corrector, scanning transmission electron microscopy

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

The fabrication of ordered nanoscale structures has attracted considerable scientific and commercial attention because of their potential utilization in electronic, optical and micromechanical devices [1, 2]. One approach to the fabrication of nanometer-sized structures has been to use a naturally occurring structure as a host for the fabrication. This ‘bottom-up’ approach is promising, particularly for the preparation of large-area, nanometer-sized structures with desired aspect ratios. Self-organization during deposition and the growth process of nanoparticles create characteristic features in terms of size, shape and arrangement

* Invited paper.
Electron-beam-induced deposition (EBID) for maskless nanofabrication is a promising technique that has been studied by many researchers because of its higher resolution due to the smaller beam spot, and because of the possible combination of top-down and bottom-up approaches. Organic or metalorganic gases are decomposed by the electron beam, and carbon or metal atoms are deposited on substrates without resists. EBID has mainly been performed in scanning electron microscopes (SEMs) [8–10]. However, the smallest structures fabricated in SEMs have a typical width of 15–20 nm, no matter how small the primary-electron beam is [11]. This is usually attributed to the fact that the distribution of secondary electrons, rather than primary electrons, determines the size of the deposits. The profile of the secondary electrons exhibits some spread, particularly for the energy range of SEMs. Even for primary electrons of zero diameter, the profile of secondary electrons has a range of more than 15 nm [12]. Hence, it was believed that the resolution limit of EBID was at most 15 nm. However, we have attempted to minimize the secondary-electron effect by using a field-emission scanning transmission electron microscope (FE-STEM) [13–16]. Mitsuishi et al [13] successfully fabricated nanodots of 3.5 nm diameter using a 200 keV FE-STEM. They found that the dot size does not depend on the substrate thickness; rather, the deposition period and speed are strongly dependent on the intensity of the electron beam. Tanaka et al [14] have also successfully fabricated nanodots containing W by EBID in an ultrahigh-vacuum FE-TEM (UHV-FE-TEM). The size of the dots can be controlled by changing the pressure in the chamber. The smallest particle size was less than 2 nm in diameter, which is the smallest reported size so far.

Here, it should be pointed out that two factors, i.e. electron-beam intensity and a vacuum in the chamber, are very important and have not been optimized yet to increase the speed and quality of maskless nanofabrication by EBID. In the present review, we first describe the experimental data obtained from EBID experiments to demonstrate the use of this method, and then report the present status of the new development of UHV Cs-corrected STEM at NIMS and its future prospects.

2. Experiment on electron-beam-induced deposition

EBID is a versatile nanofabrication technique in which a precursor gas is introduced into a chamber. The precursor gas is adsorbed on the substrate and is decomposed by an intense and focused electron beam. As the electron beam can be focused onto a region of one nanometer to several hundred nanometers using a modern electron microscope, a solid deposit is formed in the irradiated regions on the surface of the substrate. Schematic illustrations of the experimental setup for EBID are shown in figure 1 and the details of the experiments are given elsewhere [14–19]. For example, when the vapor of tungsten hexacarbonyl (W(CO)$_6$) is used as a precursor gas, the electron irradiation decomposes the gas into W, CO, C, O and various molecular species. W atoms are deposited on the substrate, while the volatile materials are pumped out. Details of the deposited materials are given elsewhere [20]. When insulator materials are used for a substrate, inhomogeneous deposition occurs due to the charged-up electrons, as shown in figure 1(a), and nanodendritic tree structures are formed. The fractal-like growth may be controlled by the amount of charged-up electrons depending on the topography of the surface as well as by the electron-beam intensity. When using conductive substrates, such as silicon, the deposited area can be limited to a nanometer scale when the electron beam is finely focused. The deposit grows upwards from the surface when the beam is stationed at one point, and a line is produced by moving the beam position. Accordingly, more complicated shapes can be formed if the position of the beam is controlled by electrical deflection using a computer. A schematic illustration of an arbitrary structure nanofabricated using by EBID is shown in figure 1(b). The electron beam was positioned on the edge of the substrate and was then moved away from the substrate, which resulted in the formation of a freestanding rod. The growth of the nanorod follows the position of the electron beam; thus, the shape of the freestanding rod can be controlled arbitrarily.
Figure 2. Nanostructures grown on Al2O3 substrate by EBID at room temperature: (a) and (b) at a current density of about 0.75 A cm\(^{-2}\), (c) at a current density of 12.9 A cm\(^{-2}\) and (d) at a current density of 33.0 A cm\(^{-2}\) nanodendrites (reproduced with permission from J. Phys. Conf. Ser. © 2008, IOP Publishing, Ltd).

3. Nanogrowth using intense electron beam

3.1. Growth of nanostructures on insulators by EBID

Although the growth of carbon fractal-like structures has already been observed on insulator substrates under electron-beam irradiation due to the existence of pump oil remaining in the atmosphere of the vacuum chamber [21–23], EBID using insulator substrates was first reported by Song et al [17]. Thin films of Al2O3 [17–19, 24–26] and SiO2 [27–30] were irradiated by an electron beam in TEMs with organometallic precursor gases at room temperature. Figure 2(a) shows a micrograph of the initial stage of the growth of nanostructures under a current density of about 0.75 A cm\(^{-2}\). After 50 s irradiation, nanorods are observed to nucleate at the edge of the substrate, as indicated by arrows A to F. The thickness of these wires is about 3 nm with a length of about 10 nm. As shown in figure 2(b), the growth speed kept low so that clear differences in morphology can be observed after 120 s irradiation. By increasing the current density to about 12.9 A cm\(^{-2}\), the growth speed was increased by a factor of more than 5. Figure 2(c) shows a micrograph recorded after 216 s. The nanorods were longer and also denser than those grown at the lower current density with an almost even thickness. Branching is observed to take place at the tips of the nanorods, and the morphology becomes dendritic. A further increase in the current density to 33.0 A cm\(^{-2}\) resulted in extensive branching and the formation of complicated nanotree structures. It is concluded that the growth from nanorods to nanodendrites and then nanotrees can be controlled by the intensity of the electron beam [17, 25].

Figure 3(a) shows nanodendrites grown on a SiO2 substrate with an electron-beam accelerating voltage of 400 kV and a fluence of 6.0 × 10\(^{21}\)e cm\(^{-2}\) [30]. The nanodendrites show a tendency to grow at the edge of the substrate. Since the precursor gas contained carbon and oxygen as well as tungsten, the chemical composition of the nanodendrites was characterized by energy-dispersive x-ray spectroscopy (EDS). Figure 3(c) shows an EDS spectrum obtained from the middle of the nanodendrites shown in figure 3(b). The size of the probe used for the EDS analysis is about 15 nm, and several branches are included in the analysis. It is confirmed that W, the target element, effectively comprises the deposit, although very small amounts of O and C were detected in the
spectrum. This may be due to the charged-up electrons, which induced the nonequilibrium chemical decomposition of the precursor gas. It was confirmed that body-centered cubic (bcc) tungsten nanocrystals with an amorphous structure comprised the nanostructures and that the fraction of the crystalline structure increased with increasing energy of the electron beam \([17, 27, 30, 31]\).

It is possible to fabricate novel composite structures using the nanostructures grown on insulator substrates by EBID. Au or Pt nanoparticles were deposited by an ion-sputtering method on W nanodendrites to form Au- or Pt-nanoparticle-decorated structures \([32]\). Figure 4 shows the composite structure of a Au nanoparticle/W nanodendrite fabricated on a SiO\(_2\) substrate. It was confirmed that the Au nanoparticles were nearly uniformly distributed on the W nanodendrites. The particle size can be easily controlled by varying the ion-sputtering time. In a similar process, a Pt nanoparticle/W nanodendrite composite structure was also fabricated \([32]\). These composite nanostructures may have potential applications for catalysts and sensors, and in gas storage.

3.2. Selective deposition into ordered nanohole arrays by EBID

Instead of using thin films of insulator materials, the selective deposition of a metal into ordered nanohole arrays was performed by EBID, as illustrated in figure 5. A porous alumina membrane on an aluminum substrate was prepared by a two-step anodization process \([33]\) and the substrate was removed by etching. The diameter of the holes is about 40 nm, and the interval between the centers of the holes is about 100 nm. The total thickness of the membrane is about 1000 nm, but there are electron transparent regions at the bottoms of the holes. Me\(_2\)Au(acac) was used as the precursor gas source. The gas was supplied through a nozzle placed near the membrane on the side of the pores. The electron beam simultaneously irradiated the membrane from its reverse side. The deposition was carried out at room temperature.

Figure 6 shows a TEM image of the anodic porous alumina membrane after Au deposition \([34]\). The diameter of the electron beam during irradiation was about 1900 nm. The irradiation time was 1 min. The black dots in the image indicate the deposits. The size of the formed pattern is almost the same as that of the electron-beam-irradiated area. Also the deposition only occurs in the holes of the electron-beam-irradiated area. All the holes in the electron-beam-irradiated area are filled with the deposit, while no deposit was found outside the region. The EDS spectra in figure 7 clearly show that the Au peak only appears inside the holes \([34]\).

Figures 8(a) and (b) show a microdiffraction pattern and a high-resolution TEM (HRTEM) micrograph taken from the electron-beam-irradiated area, respectively \([34]\). These diffraction rings can be indexed to metal Au, as indicated in the figure. The center part in the image of the HRTEM is the as-deposited nanoparticle in a hole, and the surrounding part is the alumina membrane. It is clear that there are many nanocrystallites in each as-deposited nanoparticle, which is consistent with the result obtained from electron microdiffraction pattern analysis. Judging from the lattice fringes of the grains, it is estimated that the diameter of these nanocrystallites is smaller than 5 nm. A grain indicated by A in the image is Au crystal with a face-centered cubic (fcc) structure in the \(\langle 110 \rangle\) direction. It is demonstrated that the as-deposited nanoparticles in the holes fabricated by EBID consist of many nanocrystallites of Au metal. Tungsten nanoparticle arrays were also fabricated by a similar method \([35, 36]\).

4. Nanofabrication using focused electron beam

4.1. Fabrication of tungsten nanostructures by EBID using STEM

One of major interests in the EBID of electrically conductive materials is the fabrication of metallic nanostructures with
desired shapes at desired local regions of semiconductors such as Si and Ge. In particular, downsizing the deposits obtained using a field-emission-TEM and -STEM (FE-TEM and FE-STEM), which generate a relatively high energy electron beam of more than 200 keV and a small probe of less than 1 nm, will make it possible to fabricate much smaller and denser devices.

Figure 9(a) shows a bright-field image of a dot array formed on a Si substrate using an FE-TEM at room temperature [15]. The precursor gas was W(CO)$_6$. The dots were arranged at a constant interval by moving the beam position. The beam current was about 1.0 nA. Most dots were formed with a deposition time of about 0.3 s. Some dots were deposited for 0.5 s, which were slightly larger. This indicates that the size of dots can be controlled by changing the deposition time. The high-angle annular dark-field STEM (HAADF-STEM) image in figure 9(b) indicates that the bright dots consist of W, which was confirmed by Z-contrast imaging.

The effect of the deposition time, experimentally examined by depositing an array of dots with various times, is shown in figure 10(a) [13]. The nominal deposition time was increased in 25 ms steps from 1 ms at the upper left to 2.5 s at the lower right. Figure 10(b) shows an HRTEM image of a nanodot deposited for 275 ms. Deposits formed with a time shorter than this did not have a clearly defined shape at the irradiated position. In the figure, the (200) and (111) lattice fringes of Si are 0.27 and 0.31 nm, respectively. Therefore, the size of the dot can be calibrated accurately and is found to be 3.5 nm, i.e. a very small dot was deposited by EBID with position control. The HRTEM image exhibits no Moiré-like contrasts due to the interference between Si and W lattice fringes. This means that, under these deposition conditions, the nanodots are amorphous.

The relation between deposition time and dot size is plotted in figure 11 for a number of dots fabricated with a much wider range of deposition times [13]. The dot size was measured using at the full width at half maximum (FWHM) of the intensities of the dot images to exclude the effect of image contrast. The relation is almost linear, and the extrapolation to 0 s gives a size of about 3.6 nm, which coincides with the size of the smallest well-defined deposit obtained. The slope of the plot is less steep than that obtained in a previous analysis of SEM images [37] because of the difference in the probe size between the smaller TEM probe, only 0.8 nm, and the larger SEM probe, 3.1 nm.

It has been argued previously [38] that the EBID process is mainly caused by secondary electrons generated by primary electrons. The curves of the dissociation cross section as a function of electron energy are known for simple gases [39], but such curves for gases used in EBID are limited [40–42]. Curves for EBID gases generally have
Figure 5. Schematic diagram of the fabrication process involving selective deposition into ordered nanohole arrays of an anodic porous alumina membrane by EBID: (a) porous alumina after second anodization; (b) removal of Al layer; (c) the selective deposition by EBID and (d) ordered nanoparticle array in the holes of anodic porous alumina membrane.

Figure 6. TEM micrograph of anodic porous alumina membrane after EBID for 1 min (reproduced with permission from Appl. Surf. Sci. 241 (2005) 91, © 2005, Elsevier, Ltd).

Figure 7. EDS spectra taken from the deposition area: (a) from a hole and (b) from the matrix between the holes (reproduced with permission from Appl. Surf. Sci. 241 (2005) 91, © 2005, Elsevier, Ltd).

a peak at a low energy of approximately 100 eV and the secondary-electron distribution has been studied using a Monte Carlo method proposed by Silvis-Cividjian and coworkers \[43, 44\]. Figure 12 shows a schematic illustration of the display window of our Monte Carlo simulation \[45\] during calculation. It was recognized that the distribution of primary electrons determined the shape of the deposit. Since low-energy electrons do not travel a long distance due to their short mean free paths, although they have a high dissociation cross section, the overall distribution, which is generated by low-energy secondary electrons, almost overlaps the distribution of primary electron trajectories. This means that the shape of the deposit can be roughly estimated from the trajectories of the high-energy primary electrons.

The effects of primary-electron energy on the EBID process have been studied by Liu et al \[46–51\] by comparisons between simulation and experimental data. Figure 13 shows the morphology of tungsten tips fabricated using 20, 200 and 400 keV electrons on silicon film. Using 20 keV electrons, a tip grew on the top surface of the substrate but no tip was grown on the bottom surface. Even using 200 keV electrons, the bottom tip was still short compared with the top one. When 400 keV electrons were used, the size of the bottom tip (over 1 µm) was comparable to that of the top one. If the substrate thickness was smaller than the penetration depth of the electron beam, a bottom tip would be deposited.
Figure 8. (a) Microdiffraction pattern taken from as-deposited nanoparticle in a hole. The electron-beam size in bright-field mode was about 30 nm in diameter, (b) corresponding HRTEM micrograph of a nanoparticle in the hole (reproduced with permission from Appl. Surf. Sci. 241 (2005) 91, © 2005, Elsevier, Ltd).

on the bottom surface, which should be considered when thin film is used as a substrate for EBID.

The Monte Carlo simulation method was used to investigate the growth of the bottom tip by changing the electron energy and substrate thickness, the principle of which has been described in a separate paper [49]. Figure 14 shows the simulated growth process of tungsten tips on a tungsten point substrate (0.3 × 0.3 × 0.3 nm$^3$) using 20, 200 and 400 keV electrons with an idealized 0 nm electron probe. The horizontal coordinate is the number of incident primary electrons. Linear growth of the top tip occurred at rates of 0.1360, 0.0015 and 0.0003 nm e$^{-1}$ for 20, 200 and 400 keV electrons, respectively. Low-energy electrons result in a higher growth rate of the deposit. The growth of the bottom tip becomes saturated independent of the energy. The simulations were also carried out for a tungsten film substrate with different thicknesses. It was found that the height of the bottom deposit increases with increasing electron energy and also with decreasing substrate thickness. This highlights the importance of the primary energy of electrons in EBID experiments.

From the application point of view, it is important to demonstrate the flexible fabrication of two- and three-dimensional (2D and 3D) nanostructures. An HAADF-STEM image of a demonstration in which the 2D nanometer-sized characters ‘NIMS’ were written on a Si substrate using an FE-STEM by the deposition of dots with 3.5 nm diameter with a W(CO)$_6$ precursor is shown in figure 15(a) [52]. The density of the dots was 0.75 dots nm$^{-2}$. The letter ‘N’ consists of 384 dots. Each dot was formed in 0.1 s. Thus, each letter was written in a few tens of seconds. The width of each letter was about 40 nm. Figure 15(b) shows an image of a freestanding ring produced on a carbon grid using an FE-STEM. The beam position was moved at a speed of 5 nm s$^{-1}$. Thus, the ring was formed in less than...
Figure 10. (a) Array of dots fabricated with different deposition times increasing from 1 ms at the upper left to 2.5 s at the lower right. (b) HRTEM image of a nanodot in (a). In the figure, the lattice fringes of Si are also seen. The diameter of the dot is 3.5 nm (reproduced with permission from Appl. Phys. Lett. 83 (2003) 2064, © 2003, American Institute of Physics).

100 s. The width of the line was about 8 nm. The width of the freestanding rod decreases with increasing scanning speed of the beam and a minimum width of 8 nm was obtained for this gas flux and beam intensity. A beam scan with a speed of more than 5 nm s\(^{-1}\) resulted in the interruption of deposit growth.

In this technique, the reproducibility in terms of size and location is very high. That of the location depends mainly on the stability of the specimen stage, which is on the order of 0.1 nm over a few seconds, and that of the size depends only on the deposition time, which is accurately controlled by a computer. Some studies have been carried out to realize quantum devices and other types of devices by EBID [5, 53, 54]. EBID deposits can also be used as masks for ion milling to fabricate fine structures [55–57]. EBID is thus one of the most promising techniques for the fabrication of nanostructures such as quantum devices.

Figure 11. Relation between deposition time and nanodot size. The dot size was measured using the FWHM to exclude the effect of image contrast; (circles) observed by HAADF-STEM and (squares) and (diamonds) deposited at thin and thick regions and observed by SEM, respectively (reproduced with permission from Appl. Phys. Lett. 83 (2003) 2064, © 2003, American Institute of Physics).

4.2. Fabrication and characterization of magnetic nanostructures

One of the most serious drawbacks of EBID is carbon contamination of the deposit. When iron-containing organic
precursors such as biscyclopentadienyl iron (ferrocene) \[58\] or iron pentacarbonyl, Fe(CO)\(_5\) \[59–62\] are used to fabricate magnetic nanostructures, carbon atoms, which originate from the dissociated ligands of organic molecules, may affect the properties. Some attempts have been made to prevent carbon contamination of the deposit, including the modification of precursors \[63–66\] and postdeposition heat treatments \[67–69\].

Nanodots, nanorods and freestanding square frames have been fabricated by EBID in an UHV-FE-SEM using the precursor gas of Fe(CO)\(_5\). Figure 16(a) shows a TEM image of nanostructures formed on a carbon grid film at room temperature \[68\]. The nanorods were fabricated at a speed of 2 nm s\(^{-1}\). Subsequently, square frames were also fabricated on the top of the nanorods. Figure 16(b) shows a TEM image of a typical square frame structure with a width of 30–50 nm. The diffraction pattern (figure 16(c)) and the result of electron energy loss spectroscopy (EELS) (figure 16(d)) from the circular area in figure 16(b) indicate that the freestanding rods and frames were composed of iron, carbon and oxygen, and that the diffraction indices and corresponding ring positions are in agreement with those of \(\alpha\)-iron and possible iron oxides \[70\]. Hence, it is deduced that the faint polycrystalline rings were from iron oxide nanocrystals existing near the surface and that the broad rings were from the amorphous phases inside the structures.
After heat treatment at about 873 K for 1 h, the surface oxide layers disappeared and the freestanding nanorods and frames transformed into single-crystal or polycrystalline phases. Figure 17(a) shows an HAADF-STEM image of the square frame after heating [68]. The diffraction pattern is shown in figure 17(b) and is identical to that of \( \alpha \)-iron, taken near the (111) zone axis. The dark field TEM image in figure 17(c) clearly exhibits the grain structure in the square frame. The grains labeled A and B in the figure had an \( \alpha \)-iron phase with different crystallographic orientations. Oxygen and carbon were hardly detected in the EELS taken from grains A and B, as shown in figure 17(d). \( \alpha \)-iron grains were only formed in the freestanding nanorods and frames.

Figures 18(a) and (b) show SEM images of variously shaped iron 3D nanostructures formed on a Si edge at room temperature. After transferring the specimen to an FE-TEM, electron holography was employed to characterize its magnetic properties. The structures were magnetized by introducing the specimen into a magnetic field of about 1 T under the objective lens of the TEM. After that, the objective lens was turned off, and the residual magnetic field was estimated to be less than 100 mT. This magnetic field produced an electron hologram for the nanostructures shown in figure 18(c). By reconstructing the hologram digitally using a computer, a phase image was obtained, which is shown in figure 18(d) as an interference micrograph [71]. It was found that the magnetic field leaked from the nanostructure body, which appeared to act as a ‘nanomagnet’ because of the square and ring shapes.

To quantitatively analyze the magnetic properties of EBID iron nanostructures, a simple nanorod was fabricated on a tungsten (W) tip, as shown in figure 19 [72]. The insert shows an enlargement of the rodlike deposit. Its width and length were 120 and 600 nm, respectively. Figures 19(a) and (b) show the electron hologram and reconstructed phase image of the rodlike deposit on a W tip [72]. In the phase image, dark fringes are equivalent to equipotential contour lines. The spacing of the dark fringes corresponds to a phase shift of \( \pi/2 \) rad. A line profile of the phase across the line is shown in figure 19(c). The phase jump across the nanomagnet was measured to be 12.2 rad, which is caused by internal magnetic flux. The phase jump across the nanorod \( \Delta \phi \) caused by the internal magnetic flux density \( B \) is given by

\[
\Delta \phi = 2\pi \left( e / h \right) BS,
\]

where S is the cross-section area of the nanomagnet. Using the amplitude image from figure 20(a), the S-value was estimated to be \( 2.07 \times 10^{-14} \) m², and therefore the B-value was calculated to be about 0.48 T, which is sufficient to interact with the magnetic nanostructures [72–74].

5. Effects of ultrahigh vacuum on nanofabrication

5.1. Resolution limit in ultrahigh vacuum

The effect of the partial pressure (namely, the flow rate) of the precursor gas was precisely examined using a UHV-FE-TEM (less than \( 1 \times 10^{-7} \) Pa in the column) with the precursor gas of
Figure 18. (a) SEM image of freestanding nanostructures with a desired shape on a thin silicon substrate obtained by EBID using Fe(CO)$_5$ at room temperature, (b) enlarged image of frame in (a), (c) electron hologram and (d) reconstructed phase (interference) image in (b). The phase was amplified by a factor of 4.

Figure 19. SEM images of iron rodlike deposit on a W tip apex, fabricated by EBID using Fe(CO)$_5$, at room temperature. The length of the deposit is about 600 nm (reproduced with permission from J. Mater. Sci. 41 (2006) 2627, © 2006, Springer-Verlag).

Figure 20. (a) Electron hologram of iron rodlike deposit on a W tip, (b) reconstructed phase image with an amplification factor of 4 and (c) the line profile of the phase distribution across the line in (b) (reproduced with permission from J. Mater. Sci. 41 (2006) 2627, © 2006, Springer-Verlag).

W(CO)$_6$ [14]. The details of the UHV-FE-TEM are described elsewhere [75]. Figure 21 shows typical TEM photographs of arrays of nanodots formed using a 2 nm probe while changing the pressure of the precursor [14]. The size of the dots decreases as the partial pressure decreases; the dots of about 5, 4 and 3 nm diameter were grown at partial pressures of $1 \times 10^{-5}$, $5 \times 10^{-6}$ and $2 \times 10^{-6}$ Pa and a deposition time of about 10 s, respectively. The enlarged image of the dots in figure 21(d) shows the lattice fringes of the Si substrate used to calibrate the actual sizes of dots of about 2.4 nm. Interestingly, we could seldom observe dot formation at a partial pressure of less than $1 \times 10^{-6}$ Pa, regardless of the beam intensity. We infer that there is a critical partial pressure for the dot fabrication, although it is possible that the nanodots were too small to be distinguished.

Figure 22(a) shows an array of dots formed using a 1 nm probe and a deposition period of 5 s [16]. The dots are located at the intersections of the white lines, but it is difficult to distinguish them from the amorphous substrate. One of the dots is enlarged in figure 22(b). The size of the dots is thought to be about 1.5 nm, which we believe to be the smallest nanodot ever fabricated by EBID. To prove their existence, HAADF-STEM images were taken and are shown in figure 22(c). By the Z-contrast imaging of the HAADF-STEM, W atoms can be easily distinguished from Si atoms. The distance between the dots and their size almost match our estimated values. Hence, it is clear the images are of nanodots.
The dependence of the dot size on the partial pressure and deposition time is summarized in figure 23 [14]. The tendency is clear: the better the vacuum, or the shorter the time, the smaller the dot. For a current density of $5 \times 10^3$ A cm$^{-2}$, the partial pressure dependence is more apparent. For a gas pressure of $2 \times 10^{-6}$ Pa, the current density dependence is also shown. The smallest dot size is about 1.5 nm, which was obtained by 5 s deposition at $1.5 \times 10^{-6}$ Pa using a 1 nm probe. To our knowledge, this is the smallest reported nanodot ever fabricated by EBID.

5.2. Selective deposition and growth of iron silicides in ultrahigh vacuum

One of the characteristic features of UHV deposition is the clean surface of samples, and therefore one can observe the reaction between deposits and the surface without any effect from contamination if the sample is clean. In particular, the reactions between semiconductor surfaces and EBID deposits are important for applications to the fabrication of advanced devices.

Using a 1.5 nm probe, arrays of dots have been successfully fabricated on cleaned Si (111) substrates from Fe(CO)$_5$ [76]. The substrates after cleaning (before deposition) showed a 7 × 7 superstructure, and EELS measurement did not show any carbon-related peaks. Figure 24(a) shows a TEM micrograph of one of the as-deposited arrays. The dots were fabricated with an irradiation time of 5 s at $2 \times 10^{-6}$ Pa. The reduced size of the dots can be intuitively understood to result from the smaller probe size of the TEM [77]. The subsequently measured EELS spectrum is shown in figure 24(b). In addition to the major iron L$_{2,3}$ edges (not shown), some carbon K edges are obtained. No oxygen edge was detected. Because no hydrocarbons are expected to be formed in the environment, the only source of carbon is the ligand of the precursor (CO). This result is in agreement with the results of previous studies.
on the C concentration in electron-beam-deposited Fe films on clean Si surfaces [78, 79]. It can be concluded that the deposited dots are composed of a large quantity of iron and a small amount of carbon.

After annealing at 700 K, the dots on the clean specimen did not change their location on the substrate, but their structure changed. Figure 25(a) shows an array of dots after annealing. Close observation of each dot revealed that the dots have a crystal structure with an epitaxial relationship with the substrate. The lattice fringes of the dots are clearly superimposed on the Si (220) fringes in figure 25(b). They sometimes exhibit Moiré fringes in the same direction, as can be seen in the figure. A fast Fourier transformation (FFT) of the images, as shown in figure 25(c), revealed the resulting crystal structure. There are many binary and ternary compounds in the Fe-Si-C system [80]. Among the many stable and metastable phases, the compounds that are responsible for the dot structure according to the present FFT result are either Fe silicide or $\alpha$-Fe (ferrite). Fe carbide does not match the FFT result. After excluding Fe silicides because of the epitaxial relationship between the Si substrate and the deposit, the only candidate left is $\alpha$-Fe with a bcc structure. This might contradict the results expected from conventional Fe evaporation followed by silicidation [81]. The reason for this may be that the carbon concentration at the interface prevented silicidation and assisted the formation of pure iron crystals.

High-temperature EBID at 850–900 K in ultrahigh vacuum exhibits completely different deposition behavior [82]. The formation of nanorod arrays was observed, as shown in figure 26. The irradiation time for each rod was 5 s. From EELS analysis, only Si and Fe peaks were detected from the area. It is seen that four rods, all aligned in one direction (Si(110)), form an array. This means that the fabrication of Fe-containing nanorods at controlled locations can be achieved.

The nanorod length, on the other hand, depends on the irradiation time. Figure 27 shows typical images of the nanorods obtained for different deposition times. Nanorods formed after deposition times of 5, 10 and 15 s are shown in figures 27(a), 27(b) and 27(c), respectively. It is clear that the longer the deposition time, the longer the nanorod becomes. In contrast, their width did not change markedly with time. It is expected that thermally stable Fe(CO)$_5$ molecules are not adsorbed on the surface. The Fe(CO)$_4$ compound is only formed when a ligand is lost from the molecule by electron impact, and is thermally disproportionate at temperatures above 423 K. Thus, Fe atoms are deposited close to the molecular decay sites initiated by electron-beam irradiation. The continuous supply of Fe atoms then promoted further nuclei growth in the long-axis direction. In conventional iron deposition on Si (111) substrates at 850–900 K, we observed the formation of iron silicide nanorods and nanotriangles [83]. The silicide phase was a metastable cubic phase (either CsCl-type FeSi$_{1+x}$ or $\gamma$-FeSi$_2$), which is a precursor phase of the semiconducting $\beta$-FeSi$_2$ phase. The nanorods are aligned along one of the Si (110) directions, and are perpendicular to the vicinal inclination direction of the substrates. Their length can be controlled.
by changing the irradiation time. The maximum length of the nanorods reaches almost 100 nm. This technique will be useful in the formation of nanorods, particularly when the beam is scanned along the preferential growth direction.

Figure 27. Deposition time dependence of the rod length. Deposition times: (a) 5 s, (b) 10 s and (c) 15 s (reproduced with permission from Appl. Phys. Lett. 86 (2005) 183104, © 2005, American Institute of Physics).

6. Ultrahigh-vacuum Cs-corrected scanning transmission electron microscope at NIMS

The further development of EBID requires the application of state-of-the-art electron microscopy technology, such as precise positioning of a nanometer-scale electron beam, of which the accuracy should be about 1 Å, and a high current, enabling the achievement of small structures with a much higher fabrication speed. Furthermore, as mentioned above, a UHV environment in the specimen chamber is desirable to prevent the deposits from contamination. Cutting-edge electron microscopy technology fortunately provides one solution to this problem, namely, aberration correction.

Aberration correction of the probe-forming lens used for STEM has been recently established at several laboratories, and exciting results are being produced [84–89]. An aberration corrector provides a smaller probe size, which enables atomic column-by-column analysis. The smaller probe diameter with a higher current is also effective for various nanofabrication techniques [13, 90]. However, a corrector that is compatible with a UHV environment has not been developed yet. The National Institute for Materials Science (NIMS) at Tsukuba, Japan has launched a project to install a UHV-compatible third-order spherical aberration (Cs) corrector [91]. We now describe the current status and some results from the project.

The basic instrument is a 200 keV field-emission TEM/STEM (JEM-2500SE), of which the point resolution at the Scherzer defocus is 0.21 nm and lattice resolution at the information limit is 0.1 nm. It has a ZrO/W Schottky-type thermal field-emission gun, which provides a large probe current density of $10^5$ A cm$^{-2}$ and small energy spread of 0.7 eV at the electron source. It also has a double-stage condenser lens (CL) and an objective minilens (CM) in the illumination system and a standard goniometer and sample...
Figure 28. Schematic drawing of a UHV Cs-corrected STEM being developed at the National Institute for Materials Science (NIMS), Japan.

Figure 29. Photograph of the UHV Cs-corrected STEM at NIMS.

The illumination system was modified by installing a UHV-compatible Cs corrector between the CL and the CM, and the objective lens (OL) including the goniometer and specimen chamber was replaced with a UHV-compatible lens. Furthermore, the treatment chamber was attached to the column to allow sample cleaning, gas treatment and metal deposition. Details of a similar UHV system were described for the previous UHV-FE-TEM by Tanaka et al [92]. A schematic drawing and a photograph of the microscope are shown in figures 28 and 29, respectively. Figure 30 illustrates the vacuum of the microscope. The column is evacuated by four ion pumps and one titanium sublimation pump. All lens systems above the OL are sealed by a metal o-ring and can be heated to 423 K. The combination of heating and pumping results in a pressure of less than $1.0 \times 10^{-7}$ Pa in the column.

Figure 30. Diagram of vacuum of UHV Cs-corrected STEM, showing four ion pumps, one titanium sublimation pump and the treatment chamber used for sample loading.

The Cs-corrector is of the dual-hexapole type, often called the Rose/Haider type [93], and is already commercially available (CEOS, GmbH). It was developed for a 200 keV UHV JEOL column by JEOL, Ltd. A schematic drawing of the corrector is shown in figure 31. It consists of two 12-poles with different dimensions, two transfer lenses, and two sets of deflectors. One rotational lens was added for comparison with the CEOS corrector, so that the adjustment of the two hexapole fields can be simplified without changing the current of the 12-pole. Each 12-pole acts mainly as a double hexapole and can also be operated as two dipoles and two quadrupoles for the compensation of beam shifts and astigmatisms. The preliminary results of probe-shape simulation are given in figure 32 as a function of Cs. Even though higher-order spherical aberrations were not taken into account, the FWHM of the electron intensities shows that the radius of the probe decreases with decreasing Cs and reaches less than 0.05 nm at Cs = 0.01 mm. As an experimental result, figure 33(a) shows an HAADF-SEM image obtained from Si (110) using the corrected microscope and figure 33(b) shows the FFT results. The image clearly shows the boundary between the silicon atoms, and the power spectrum demonstrates that the transfer distance is as low as 1.0 Å.
The electron-beam intensity of the STEM is defined by the sweet spot area in the Ronchigram. In the Cs-corrected STEM, the sweet spot area increases with the usable area of the OL, and subsequently the maximum semi-angle ($\alpha$) available for focusing the primary-electron beam ($\alpha$), which is determined by the radius of the condenser aperture, is increased significantly. Table 1 gives a comparison between the calculated probe diameter and the intensity of the electron beam for the 200 keV STEM with and without the Cs-corrector. The defocus value was adjusted and the optimum value was chosen for use with the corrector. It is clear that the beam intensity increases by a factor of about 10 at a given probe diameter with the introduction of the Cs-corrector. Furthermore, this increase is almost linear with the probe diameter at a given $\alpha$. Figure 34 shows the Ronchigram obtained from a carbon grid using the Cs-corrected STEM. The outer circle is located at the 45 mrad position. The extended sweet spot area of this Ronchigram indicates that the corrector on this machine is operating properly.

One of the features of the Cs-corrected STEM is the UHV environment in the sample chamber, which reduces contamination during operation. After confirming that a vacuum of $1 \times 10^{-7}$ Pa could be achieved, beam contamination was observed for a SrTiO$_3$ TEM sample.
Table 1. Estimated probe diameters and probe currents for the Cs-corrected STEM compared with the uncorrected microscope.

|                         | Cs corrected probe | Uncorrected probe |
|-------------------------|--------------------|-------------------|
| Probe diameter (nm)     | 0.2 0.5 1.0        | 0.2 0.5 1.0       |
| Spherical aberration    | 0.001 0.5          | 0.5               |
| (Cs, mm)                |                    |                   |
| Semi-angle (α, mrad)    | 40.0 12.0          |                   |
| Defocus (nm)            | −1.9 −42.5         |                   |
| FWHM of probe (nm)      | 0.22 0.52 1.026    | 0.56 1.0          |
| Probe Current (nA)      | 1.6 9.9 39.8 0.143 | 0.895 3.85        |

*The chromatic aberration (Cc) and the beam energy spread (ΔE) are assumed to be 1.1 mm and 0.7 eV.

Figure 34. Ronchigram obtained using the Cs corrector. The circle is at the 45 mrad position. The extended sweet spot area of this Ronchigram indicates that the corrector is working properly. The estimated probe size under this condition is about 0.2 nm (reproduced with permission from Microsc. Microanal. 12 (2006) 456, © 2006, Microscopy Society of America).

Figure 35 shows HAADF-STEM images of the same as-thinned SrTiO$_3$ TEM sample taken using (a) standard STEM (JEM-2100F) with a regular vacuum and using the Cs-corrected STEM with the UHV environment. Because of the contamination in the standard STEM, its magnification was lower. It is clearly observed that the contamination of the sample was greatly reduced in the UHV environment. Also, the contamination originates from the vacuum environment instead of the surface of the sample.

A preliminary result using the Cs-corrected STEM was obtained for a GaAs quantum ring in AlGaAs [94]. No strain contrast can be expected for this sample because the difference in the lattice parameter between AlGaAs and GaAs is less than 0.1%. Furthermore, the compositional difference is too small to produce clear Z-contrast images using standard STEMs. Figure 36(a) shows a cross-sectional HAADF-STEM image of an as-grown GaAs quantum ring. A GaAs nanostructure was formed on top of a 0.6-nm-thick 2D layer. A clear dent is visible at the top of the nanostructure, indicating that the ring structure varied in the AlGaAs matrix while keeping its original shape. The magnified image in figure 36(b) indicates the deposition of one or two GaAs layers on the AlGaAs substrate, which extend from the edge of a GaAs dot. This result demonstrates the high signal-to-noise ratio of imaging for the present Cs-corrected STEM.

7. Summary

High-quality, intense and focused electron beams have been used for the fabrication of nanomaterials with controlled size and position as well as for the characterization at atomic scale by electron microscopy. EBID was used as an advanced method to fabricate nanostructures ‘in situ’ by a maskless process. The reaction of gas molecules with electrons near the material surface causes the formation of a solid deposit whose size and shape depend on the substrate materials and the profile of the electrons. When gases containing tungsten (W), iron (Fe) and other metals are introduced into the
microscope, noble-metal nanostructures can be fabricated in situ. The electron beam controls both the nucleation and growth processes.

When insulator materials were used as a substrate, inhomogeneous deposition occurred due to the charged-up electrons and nanodendritic tree structures were formed. At an electron current density of about 0.75 A cm$^{-2}$ with flow of W(CO)$_6$ precursor gas, freestanding deposits grew at positions separated from each other and perpendicular to the surface. Their length was several tens of nanometers and the thickness was about 3 nm at the tips. Branches were observed at the tip. Upon further deposition a fractal-like tree structure of 100–300 nm length was formed. These W nanodendrites can be used for catalysis studies in combination with the ion-sputtering method to form a compound metal nanoparticle/W nanodendrite structure.

Using conductive substrates, such as silicon, 3D nanostructures of W or Fe compounds can be fabricated by the beam-scanning technique. This is effective for the direct fabrication of nanosized structures by taking advantage of its fine probe of 1–10 nm diameter. Freestanding nanoantennas were fabricated in the presence of Fe(CO)$_5$ gas. The typical line width and length of the iron nanoantennas were 30–50 and about 300 nm, respectively. The application of a magnetic field produced an electron hologram from the nanostructures. It was found that the magnetic field leaked from the nanostructure body which appeared to act as a ‘nanomagnet’. The effect of a vacuum on the size and growth process of fabricated nanodots containing W was investigated using a UHV-FE-TEM. The size of the dots can be controlled by changing the dose of electrons and the partial pressure of the precursor. The smallest particle size obtained was about 1.5 nm in diameter, which is the smallest size reported using this method.

The further development of EBID requires the application of state-of-the-art electron microscopy technology such as precise positioning of a nanometer-scale electron beam, a high current for the achievement of small structures with a much higher fabrication speed, and a UHV environment for eliminating contamination of the deposits. An attempt to develop UHV Cs-corrected STEM at NIMS was described in detail. Even though nanofabrication using a UHV Cs-corrected STEM is still to be investigated in experiments in the near future, the satisfactory performance of the newly developed microscope has been demonstrated.

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