Electron Beam Induced Fabrication and Characterization of Nanostructures

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Abstract. Two examples of electron beam induced deposition (EBID) are described in terms of the fabrication of metal nanostructures with transmission and scanning electron microscopy (TEM and SEM). Both need the reaction of gas molecules, W(CO)$_6$ and Fe(CO)$_5$, near substrate surfaces, which is introduced by a nozzle from outside. For the first example, electric conductive substrates were used to deposit metal nanostructures right on the beam irradiated area, and self-standing 2D and 3D structures were grown in the range of diameters of 3 to 100 nm. In case of iron deposit, magnetic properties were analyzed with electron holography. For the second example, insulator substrates were used to cause the electron charge-up on the surface. Due to the fractal distribution of electrons, metal deposits grew dendrite-like nano-trees with many branches of 2 to 3 nm width to 10 to 100 nm in length.

1. Introduction
The reaction of gas molecules with electrons near material surfaces sometimes causes solid deposits, which have a variety in size and shape depending on the substrate materials and the profile of electrons [1-2]. Once gases containing tungsten (W) and iron (Fe) are introduced in the electron microscopes, noble metal nanostructures can be fabricated in-situ. Electron beams control both the nucleation and growth processes [3].

Due to the controllability of the electron beam and products, electron beam induced deposition (EBID) has mainly been performed on electrically conductive substrates with scanning electron microscopes (SEMs). Typical sizes of the structures were in the range between 20 to 500 nm [4-5]. In this paper, using field emission transmission electron microscopes (FE-TEMs) and scanning TEMs (FE-STEMs), we describe the examples of the self-standing 2D and 3D nanostructures, which can be achieved by fully taking its advantages of fine probe and high accelerating voltage of 1 to 10 nm in diameter and up to 200 kV, respectively. Particularly, the fabrication of magnetic nanostructures with the partial pressure of iron containing precursor gas is discussed with electron holography [6-8].

Another example is the formation of dendrite-like or filament-like structures on insulator substrates with EBID [9-11]. The charge-up electrons on the surface of substrates due to electron beam irradiation and the supply of precursor gas in this region are considered to be the main reason. We fabricated and characterized the first time position-controllable tungsten-contained self-standing nanodendrites and fractal nano-trees on Al$_2$O$_3$ substrates with EBID.

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2. Experimental

A gas introduction system consists of an external variable leak valve, a gas nozzle which is about 0.2 mm in diameter, and a heating system was developed to attach to the specimen chamber of several JEOL electron microscopes, such as JSM-7800FV (FE-UHV-SEM), JEM-2500SE (FE-STEM) and JEM-2010F (FE-TEM). The distance between the nozzle and the electron beam position is about 1 mm. Typical substrates were Si (110) and carbon grids for conductive materials, while those were Al2O3 for insulators. The EBID was done at room temperature with the precursor gases of W(CO)6 and Fe(CO)5 below the base pressure of the TEMs [12]. Thus, the flux of the gas was not measured but estimated to be approximately 2x10⁻⁴ PaL/s, assuming the Knudsen condition. For FE-UHV-SEM, the partial pressure of the gas was controlled to be about 7x10⁻⁵ Pa. Schematic drawings of experiments are illustrated in Figure 1. For conductive substrates, the electron beams were focused to about 1 to 2 nm in diameter for TEMs and to 2 to 5 nm for SEM with the current of about 5x10⁻³ - 5x10⁴ A/cm². The position and motion of the electron beam were controlled by a PC-computer to fabricate 2D and 3D patterns. For insulator substrates, the beam was defocused to 200 to 2000 nm in diameter to change the current density of 0.75 to 33.0 A/cm² under the steady state irradiation at the edge of specimens.

3. Results and Discussion

3.1. Fabrication of 2D and 3D nanostructures with EBID

A typical example of 2D array of nanodots of W on Si (110) by the EBID using FE-STEM is shown in Figure 2(a) as the effect of the deposition period. The voltage of the microscope was 200 kV. 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. It is obvious that shorter the time results in smaller the size. Figure 2(b) consists of a HRTEM image of a nanodot deposited for 275 ms. The deposition less than this did not form clear image of a dot. The size of this dot can be calibrated accurately to be 3.5 nm in diameter from the lattice spacings of Si (200) and (111), which are known to be 0.27 and 0.31 nm. Furthermore, the lack of moiré like contrast in the HRTEM image indicated that the nanodots are amorphous [13].

An annular dark field (ADF) STEM image of a 2D demonstration example of nanometer-sized letters written on a Si substrate is shown in Figure 2(c). The density of the dots was 0.75 dots/nm². 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. This technique may be used for high density nanopatterning. Figure 2(d) shows an ADF-STEM image of an example of a freestanding ring produced at the edge of a carbon grid using the FE-STEM. The beam position was moved at a speed of 5 nm/s. Thus, the ring was formed in less than 100 s. The width of the line was about 8 nm. The width of a freestanding rod changes with beam-scan-speed. The width decreases with increasing scan...
speed and a width of 8 nm was the minimum for this gas flux and the beam intensity. A beam scan with a speed of more than 5 nm/s resulted in an interruption of deposit growth [12].

When the precursors gas source was changed to iron carbonyl, Fe(CO)₅, iron nanostructures can be made in a similar manner. EBID was carried out using the FE-UHV-SEM at 30 kV at room temperature. Figure 3 shows scanning electron micrographs of a tungsten (W) tip with a nanometer-sized iron base deposit. The insert shows an enlargement of the rod-like deposit. Its width and length were 120 nm and 600 nm, respectively.

The magnetic performance of this rod-like deposit was characterized by electron holography. The electron wave passing through the sample and vacuum regions is deflected by the electrostatic potential around a biprism so that an interference pattern is formed in the image plane of TEM. This interference pattern is called “electron hologram”, in which phase information of the object passing through the sample can be recorded. By reconstructing the hologram, the phase shift due to electric and/or magnetic fields is extracted quantitatively. The objective lens of TEM has to be turned off during the electron holography experiment [14].

Figure 2. (a) W nanodots array on Si, in which the size of a dot increased with increasing time, (b) a HRTEM image of a nanodot, (c) and (d) examples of ADF-STEM images of 2D and 3D patterns created with EBID.

Figure 3. SEM images of iron rod-like deposit on a W tip apex, fabricated by EBID with Fe(CO)₅ at room temperature. The length of the deposit is about 600 nm.
After transferring the rod-like deposit on a W tip the TEM with a biprism (JEOL JEM-3000F), the magnetization of the iron deposit was firstly made to introduce the W tip into a magnetic field of an objective lens of the TEM. After that, the objective lens was turned off, and the residual magnetic field is estimated to be less than 100 mT. The magnetic field from the iron deposit, therefore, produced an electron hologram for the nanostructures as shown in Figure 4(a). Reconstructing it digitally by a computer, a phase image was extracted in Figure 4(b) as an “interference micrograph”. A TEM image was superimposed in this figure. It is found that magnetic fields were leaked from the nanostructure body and the whole was likely to be one “nano-magnet”. In the phase image, dark fringes are equivalent to equi-potential contour lines. The spacing of the dark fringes corresponds to a phase shift of \( \frac{\pi}{2} \) rad. A line profile of the phase across the line is shown in Figure 4(c). It is possible to measure the phase jump across the nano-magnet to be 13.0 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 described as

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

where \( S \) is a cross section area of the nano-magnet. Using an amplitude image from Figure 4(a), the \( S \)-value was estimated to be \( 3.0\times10^{-14} \) m\(^2\), and therefore the \( B \)-value was calculated to be about 0.5 T, which is sufficient to interact with the magnetic nanostructures [14-15].

### 3.2. Growth of nano-dendritic structures on insulators with EBID

For EBID with insulator substrates, the thin films of Al\(_2\)O\(_3\) were irradiated by the electron beam with the precursor gas of W(CO)\(_6\) at room temperature in FE-TEM [16]. The growth of nano-dendrites were observed in-situ and recorded by a video. Figure 5(a) shows a grabbed micrograph of the initial stage of the growth under the current density of about 0.75 A/cm\(^2\). The electron beam irradiated the sample from a direction perpendicular to the plane of the micrograph. After 50 s irradiation, nanowires are observed to nucleate at the edge of the substrate. The deposits grew self-standing at positions separated each other in several nanometers in parallel and nearly perpendicular to surface of the substrate, as indicated by arrows A to F. The thickness of these wires is about 3 nm with the length of about 10 nm. As shown in Figure 5(b), the growth speed is not so high as to observe clear differences in morphology after 120 s irradiation. By increasing the current density to about 12.9 A/cm\(^2\) the growth speed was increased to more than 5 times. Figure 5(c) shows a micrograph recorded at 216 seconds. The nanowires grew longer and also denser with an almost even thickness. Branching is observed to take place at tips of the nanowires, and the morphology becomes like “nano-dendrites”. The further increase in the current density to 33.0 A/cm\(^2\) resulted in the extensive branching and the formation of complicated nano-tree structures. It may be concluded that the growth of nanowires, to
nano-dendrites and then nano-trees can be controlled by the intensity of electron beams.

Figure 6(a) presents nano-dendrites grown for 30 s at a current density of about 3.2 A/cm$^2$, which corresponds to an intermediate intensity in Figure 5. The nano-dendrites only grew at edge of the substrate with the convex surface in the electron beam irradiated area. The length reached to about 100 nm and the branches are observed at the tip, which diameter is about 3 nm. The thickness of the dendrites becomes thicker with the trunks near the substrate.

Since the precursor gas contained carbon and oxygen as well as tungsten, the chemical composition of nano-dendrites were characterized with energy dispersive X-ray spectroscopy (EDS). Figure 6(b) demonstrates an EDS spectrum obtained at the middle of the nano-dendrites in Figure 6(a). The size of the probe for the EDS analysis is about 15 nm, where several branches are included. It is

Figure 6. (a) Nano-dendrites grown on Al$_2$O$_3$ substrate. The irradiation time is about 30 s at a current density of about 3.2 A/cm$^2$ and (b) an X-ray energy-dispersive spectrum (EDS) obtained from nano-dendrites.
confirmed that W, the aimed element, has been effectively deposited in and composes this deposit, although small amount of O and Al are considered to be come from the substrate. It should be noted that very few amount of carbon was detected in the spectrum. This may be due to the charge-up electrons which produced non-equilibrium chemical decomposition of the precursor gas as compared with the case of electron conductive materials.

4. Summary
Using electron beam induced deposition (EBID), we have succeeded to fabricate 2D and 3D structures in nanometer size with transmission and scanning electron microscopy (TEM and SEM). With conductive substrates, such as silicon, 3D nanostructures of W or Fe compounds can be made by the beam scanning technique. This is quite effective by fully taking its advantage of fine probe of 1 to 10 nm in diameter. Free-standing nano-antennas were fabricated with the presence of Fe(CO)₅ gas, and the structures and properties were examined with electron holography. The line-width and length of the iron rod-like deposit are 100 and about 600 nm, respectively. The magnetic field which was leaked from the nanostructure body produced an electron hologram around the nanostructures and it is found that the whole was likely to be one “nano-magnet”. When insulator materials were used as a substrate, inhomogeneous deposition occurs due to the fractal distribution of charge-up electrons and forms nano-dendritic tree-structures. At about 0.75 A/cm² of electron current density with the flow of W(CO)₆ precursor gas, the deposits grew self-standing each other and perpendicular to surface. The length is several ten nanometers. The thickness of the dendrites becomes thicker near the substrate, but is about 3 nm at tips. Branches are observed at the tip. It becomes a fractal-like tree structure grown to 100 nm and more in length at a current density of about 33.0 A/cm².

References
[1] Koops H W P, Kretz J, Rudolph M and Weber M 1993 J. Vac. Sci. Technol. B. 11 2386
[2] Folch A, Tejada J, Peters C H and Wrighton M S 1995 Appl. Phys. Lett. 66 2080
[3] Kohlmann-von Platen K T, Buchmann L M, Petzold H C and Bruner W H 1992 J. Vac. Sci. Technol. B. 10 2690
[4] Utke I, Luisier A, Hoffmann P, Laub D and Buffat P A 2002 Appl. Phys. Lett. 81 3245
[5] Kohlmann-von Platen K T, Chlebek J, Weiss M, Reimer K and Oertel H 1993 J. Vac. Sci. Technol. B. 11 2219
[6] Takeguchi M, Shimojo M and Furuya K 2005 Nanotechnology 16 1321
[7] Takeguchi M, Shimojo M, Mitsuishi K, Tanaka M, Che R C and Furuya K 2006 J. Mater. Sci. 41 4532
[8] Che R C, Takeguchi M, Shimojo M, Zhang W and Furuya K 2005 Appl. Phys. Lett. 87 223109
[9] Banhart F 1995 Physical Rev. E 52 5156.
[10] Zhang J Z, Ye X Y, Yang X J and Liu D 1997 Phys. Rev. E 55 5796.
[11] Song M, Mitsuishi K, Takeguchi M and Furuya K 20005 Appl. Surf. Sci. 241 107
[12] Shimojo M, Mitsuishi K, Tanaka M, Han H and Furuya K 2004 J. Microsoc. 214 76
[13] Mitsuishi K., Shimojo M, Han M, Furuya K 2003 Appl. Phys. Lett. 83 2064
[14] Takeguchi M, Shimojo M, Che R C and Furuya K 2006 J. Mater. Sci. 41 2627
[15] Furuya K, Takeguchi M and Mitsuishi K 2007 Solid State Pheno. 124-126 139
[16] Song M, Mitsuishi K, Tanaka M, Takeguchi M, Shimojo M and Furuya K 2005 Appl. Phys. A 80 1431

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