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POSITION AND SIZE CONTROLLED FABRICATION OF NANO-METALS AND -SEMICONDUCTORS WITH FINE FOCUSED ELECTRON BEAM

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Abstract. Nanofabrication with fine focused electron beam was reviewed, and position and size controlled fabrication of nano-metals and -semiconductors are demonstrated. The nanowire of GaAs was shown to have an about 3 nm in diameter. We have discovered that Si nanocrystals with 2 to 3 nm can be formed in a SiO_2 thin film under irradiation of an electron beam $4 \cdot 10^8$ C/m^2 at 850K. An array of the Si nanocrystal dots was also fabricated using this method. Similarly, when decomposable gases such as $W(CO)_6$ were introduced at the beam irradiated areas, nano-metal islands are formed depending upon the beam diameter and the exposure time. The diameter of the dots was reduced to about 3.5 nm with the FE-STEM, while those were limited to about 15 nm in diameter with the FE-SEM. Self-standing structures were successfully fabricated.

1. INTRODUCTION

The production of nanodevices including single electron devices, electron wave interference devices and single molecular devices [1-4] requires well-defined fabrication techniques in nanometer scale. As compared with the conventional process of photolithographic patterning and etching, electron beam-induced (EBI) fabrication is one of the promising techniques, because of short wavelength which results in much smaller resolution limit than several 10 nm [5-8]. Most of the EBI fabrication studies were performed using conventional scanning electron microscopes (SEMs) with tungsten or LaB_6 filaments. Typical sizes of the structures produced in these studies were in the range between 20 to 500 nm by using probe sizes of several 10 nm. The limitation of the size is not due to the wavelength, but because of the electron gun and lens system in SEM. The probe size of electron beams can be reduced to sub-nanometers in field emission (scanning) transmission electron microscopes (FE-TEMs and FE-STEMs). This would lead to the reduction in size of the fabricated structures in the range of 1.0 nm.

Moreover, the use of electron beam provides several variations in the nanofabrication method itself. Firstly, in addition to drilling samples by very fine probe less than 1.0 nm, the EBI reaction with specimens, typically electron stimulated decomposition (ESD) can result in embedded metal or semiconductor nanostructures in insulator substrates. Fabrication using ESD has, so far, been applied to various materials such as Al_2O_3 [9], MgO [10] and Si [11]. We have applied ESD to form single-crystalline Si nanocrystals using an ultra-high vacuum (UHV) FETEM at high temperature [12-14].

Secondly, the EBI chemical vapor deposition (EBI-CVD) can be carried out when organic or metal-organic gases are introduced in the electron irradiated area. Focused ion beam (FIB) has been usedfor the fabrication of small structures such as dots, rods, coils and a miniature wine glass [15-16]. Because of the probe sizes of FIB, the sizes of the deposits were in a range from several 100 nm. However, once SEMs with W or LaB_6 guns were employed, then the sizes of the deposits were approximately 100 nm for W, Pt, Au and Cu [5-8, 17]. Furthermore,

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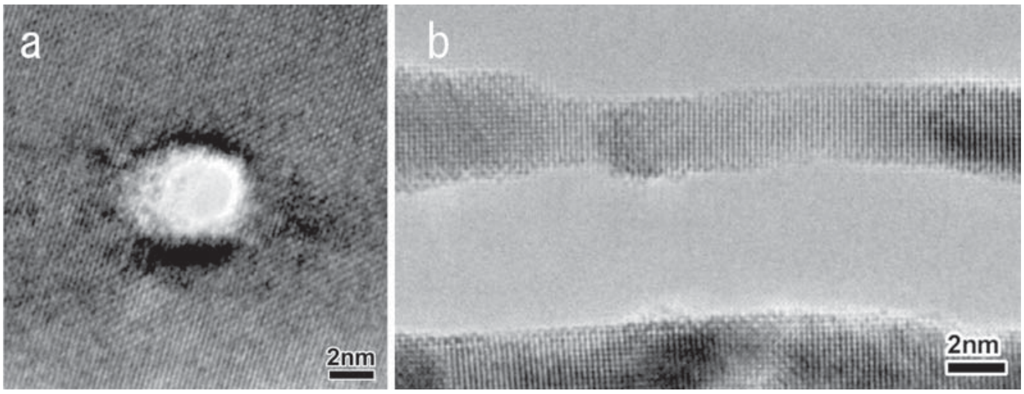

Fig. 1. (a) a nanohole and (b) a nanowire fabricated by 200 kV focused electron beam with UHV-FE-TEM. The diameter of the hole and the wire is about 3 nm which is as same as the beam diameter.

Matsui [18] and Kislov [19] used 100 and 120 kV TEMs for the deposition, respectively, but the minimum size was still 15 nm in diameter. Smaller probe sizes are achieved by using field emission guns and EBI-CVD using a FE-SEM, FE-TEM and FE-STEM was, however, reported in our very recent study [20-22]. In this paper, FE-SEM and FE-TEM were used for simple nanofabrication (drilling), ESD and EBI-CVD, and the results were discussed in terms of the advantages of electron-beam induced process.

2. EXPERIMENTAL

The electron microscopes used in this study were FE-SEM (JEOL JSM-6700F, 30 kV), FE-STEM (JEOL JSM-2500SE, 200 kV) and UHV-FE-TEM (JSM-2000VF, 200 kV). All of them equipped field emission guns with the probe size of less than 2 nm and the probe current of more than 0.5 nA at the specimen position. The UHV-FE-TEM was developed at National Institute for Materials Science (NIMS) with a high-vacuum specimen chamber of less than $2 \cdot 10^{-8}$ Pa, which prevents a specimen from chemical reaction with hydrocarbon and other residual gases. For other microscopes, the vacuum level at the specimen area was maintained less than $2 \cdot 10^{-5}$ Pa. Most of the experiments were done at room temperature, except for the ESD experiments using SiO_2. For the simple nanofabrication (drilling), GaAs thin films were employed in the UHV-FE-TEM and fabricated by the focused electron beam to create nanowires. Amorphized SiO_2 thin films were used for the ESD experiments in the UHV-FE-TEM. The acceleration voltage of an electron beam was tuned to 100 kV in order to reduce sputtering for Si atoms. The temperature was kept at 850K. The electron beam was focused to 2-3 nm in diameter with a current of about 3 nA, of which the scanning was controlled by PC. For the EBICVD studies, a gas introduction system with a nozzle and a reservoir of the gas source of tungsten hexacarbonyl, $W(CO)_6$ was installed on FE-SEM and FE-STEM. The inner diameter of the nozzle was about 0.1 mm. The gas sublimates slightly and the vapor pressure is approximately 20 Pa at room temperature. The flux of the gas was estimated to be approximately $2 \cdot 10^{-4}$ $Pa \cdot l \cdot s^{-1}$ for both the FE-SEM and FE-STEM, assuming the Knudsen condition. The measured value of the background pressure of the chambers did not change at this gas flux. The specimens of EBI-CVD experiments were done with Si thin films and carbon grids at room temperature.

3. RESULTS AND DISCUSSION

3.1. Simple nanofabrication (drilling) of GaAs with the UHV-FE-TEM

It was previously reported by Oshima *et al*. [23] and Kondo *et al*. [24-25] that the surface reconstructed nanowires of gold were fabricated by the focused strong electron beam of 3.0 nm and 2.0 nA under the UHV conditions. The diameter of the wires was quite uniform because of the anormalous bonding of surface Au atoms. Fig. 1 shows nanostructures of GaAs with 200 kV electron beams of about 2 nm in diameter and about 2 nA in current. Once the spot beam set on the specimen at room temperature, a nanohole was easily drilled within several seconds as shown in Fig. 1a). The size of the hole was increased at first and came unchanged due to the profile of the electron beam. A nanowire of about 3 nm in diameter and more than 20 nm in length was easily fabricated as shown in Fig. 1b) when the beam

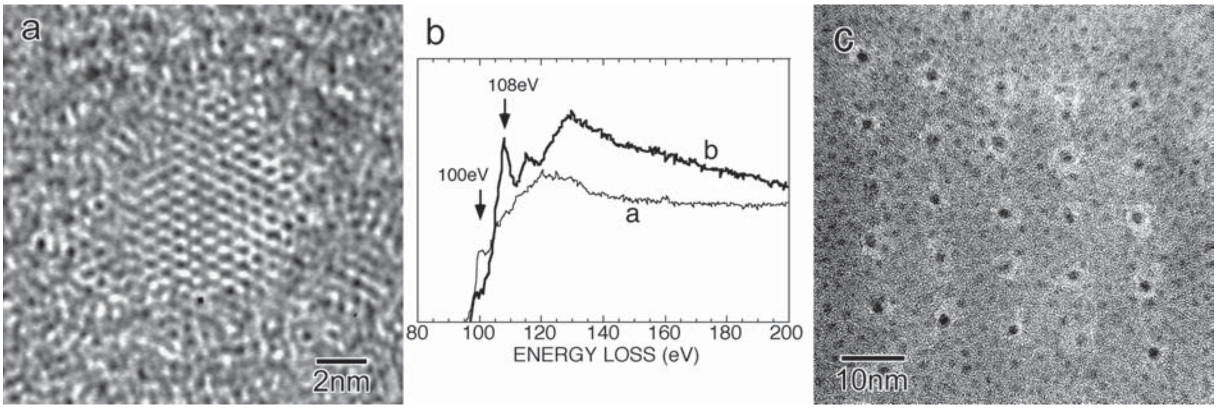

Fig. 2. (a) HRTEM image of Si nanocrystal formed in amorphous SiO_2 thin film using the 100 kV focused electron beam, (b) EELS spectra of Si-L_{23} edge taken from a nanocrystal (curve-a) and amorphous region (curve-b) showing typical spectra of pure Si and SiO_2, (c) TEM image of an array of 5x5 Si nanocrystal dots fabricated in amorphous SiO_2 thin film.

was scanned along the edge of the specimen. The speed was about 1.0 nm/s. The GaAs {100} pattern was clearly seen in the figure. There is any evidence of neither the surface reconstruction nor the anormalous structures. This may be due to the difference in the chemical bond between semiconductor-GaAs and metal-gold. The local chemical composition changes due to the difference in the sputtering rate between Ga and As may be another factor.

3.2. The fabrication of Si nanodot structures by electron stimulated decomposition (ESD) with the UHV-FE-TEM

The nanodot structure of Si was firstly reported by Chen *et al.* [11] that amorphous Si nanoparticles with the size of about 2 nm in diameter were fabricated by ESD in the microscope at room temperature. We have tuned the experimental condition not for amorphous but for nanocrystals [12-14]. Fig. 2a shows a clearer example of Si nanocrystal formed by a dose of $2 \cdot 10^9$ C/m^2 and embedded into amorphous SiO_2 matrix. In this case, the diameter of the convergent beam was about 3 nm. An electron dose of $1\text{-}2 \cdot 10^9$ C/m^2 or more at high temperature formed such nanocrystals with a good reproducibility in the present experiments. Fig. 2b shows EELS spectra of the Si-L_{23} edge taken from the nanocrystal (curve-a) and its neighbor amorphous region (curve-b). A peak at near 100 eV with an onset at 99 eV in the curve-a proves that the chemical composition of the nanocrystal is pure Si, while the peak of the edge in the curve-b chemically shifted to near 108 eV indicates amorphous SiO_2. Fig. 2c shows a TEM image of an array of Si nanocrystal dots in the amorphous SiO_2 thin film, fabricated by scanning the electron beam intermittently which was controlled by the PC. Dwell time was 5 seconds; 5x5 dots can be seen as dark contrast. The interval between the dots is about 10 nm. The diameter of the dots is about 2 nm, which is much the same as that of the beam. These results clearly indicate the possibility of the position and size controlled nanostructures of Si.

3.3. Electron beam induced chemical vapor deposition (EBI-CVD) using FE-SEM and FE-STEM for 2 to 3 dimensional tungsten nanostructures

A gas introduction system including a nozzle for EBI-CVD is illustrated in Fig. 3a. Tungsten hexa carbonyl gas, $W(CO)_6$, was supplied through the nozzle of about 0.1 mm in diameter placed near the substrate. The bulk substrate of Ge was used for the deposition in the FE-SEM and The energy dispersive spectroscopy (EDS) was applied for the chemical analysis of the deposits. An array of dots deposited on a Ge substrate using the FE-SEM with 20 keV electron beam is shown in Fig. 3b. Each dot was formed during an electron beam irradiation for 5 s. The diameter of each dot was approximately

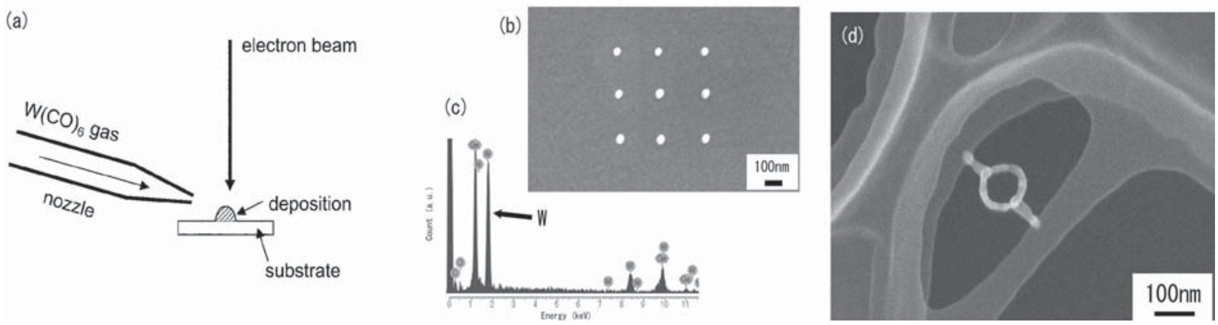

Fig. 3. Schematic illustration of electron beam induced chemical vapor deposition. FE-SEM image (a) and a result of EDS analysis (b) of an array of dots deposited on a Ge substrate using a FE-SEM at 20 kV. (c) SEM image of a self-standing ring grown from edges of a carbon grid into space using a FE-SEM.

15 nm. This size is comparable to the minimum size of such deposits previously obtained [18] and is much smaller than those produced by conventional SEMs [5-7]. Fig. 3c shows a result of EDS analysis from a dot. The peaks of W and C are seen in the figure, as well as the peak from the Ge substrate. This indicates that the dots mainly consist of W and small amounts of C, which is consistent with the results by Kislov [19] that tungsten carbide and tungsten oxide were found in addition to pure tungsten in a rod produced by EBI-CVD. Fig. 3d shows a self-standing tungsten ring, about 100 nm in diameter, formed inside a hole of a carbon grid with the same gas introduction system. The deposition started on a certain edge of the grid, and subsequently, the beam position was slowly moved into the space to form a ring pattern drawn with a single stroke of the electron beam. The speed of this patterning is about 5.0 m/s. The minimum line width of the structure grown in a space was about 20 nm. Although the impurities of C and others in the structure were not eliminated so far, it is definitely possible to fabricate nano-sized three dimensional structures by EBI-CVD using the FE-SEM. It is also necessary to optimize the experimental condition in detail to achieve high quality in the deposits.

Si (110) thin films were used as a substrate for deposition with the FE-STEM. The gas introduction system is the same as that of FE-SEM. The experiments were carried out under the accelerating voltage of the microscope of 200 kV at room temperature. The electron beam was focused similar to the normal operation, then the size of the probe is about 0.8 nm with the current of 0.5 nA. Fig. 4a shows a bright field image of a dot array formed on a Si substrate. The dots were arranged at a constant interval by moving the beam position. Most dots were formed for a deposition time of about 0.3 s. Some dots were deposited for 0.5 s and then became slightly larger. This indicates that the size of dots can be controlled by changing deposition

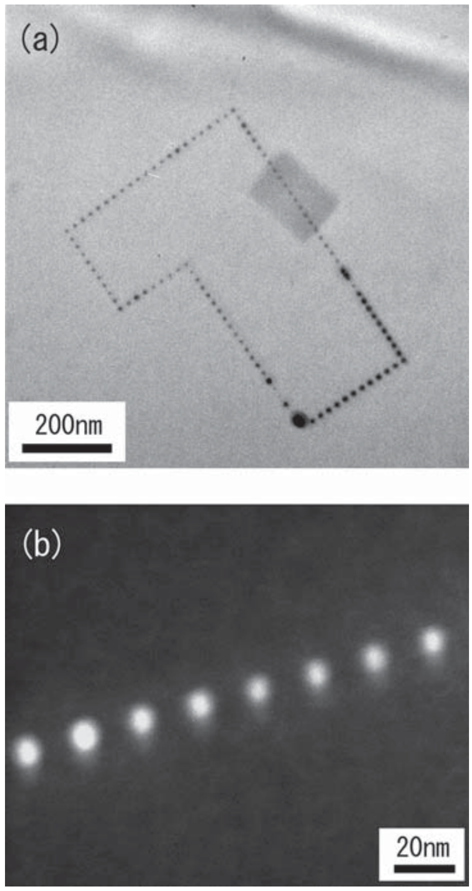

Fig. 4. Bright field (a) and annular dark field (b) images of a dot array deposited using a FE-STEM at 200 kV. The annular dark field image clearly shows the high-Z contrast of W dots.

time. A high-angle annular dark field STEM (HAADF-STEM) image of a part of Fig. 4a is shown in Fig. 4b. HAADF-STEM produces Z-contrast images so that the bright dots in Fig. 4b are considered to consist of W, because a W atom is heavier than a Si atom. The minimum size of the W dots is turned out to be about 3.5 nm in diameter. Based on the fact that the size of fabricated structures is smaller in FE-STEM than in FE-SEM at the same gas flux and temperature, the reduction in probe size and the increase in the accelerating voltage are considered to be very effective to create smaller size nanostructures with EBI-CVD. It was previously reported [26] that the saturated diameter of vertically grown rods would be about 20 nm according to the prediction of secondary electron generation by Monte Carlo simulation. However, the present results indicate that the fabrication of nanostructure less than several nm is possible when the proper experimental conditions was achieved such like this study.

4. SUMMARY

Nanofabrication with fine focused electron beam was reviewed, and position and size controlled fabrication of nano-metals and -semiconductors are demonstrated.

1) The nanowire of GaAs with about 3 nm in diameter was shown without any evidence of surface reconstruction as contrast to Au case.
2) We have discovered that Si nanocrystals with 2 to 3 nm can be formed in a SiO_2 thin film under irradiation of an electron beam at 850K. The typical electron beam current density was $4 \cdot 10^8$ C/m^2. The exposure time is around 5 s. An array of the Si nanocrystal dots was also fabricated using this method.
3) When decomposable gases with electron beams, such as $W(CO)_6$ were introduced at the beam irradiated areas, nano-metal islands can be formed depending upon the beam diameter. The diameter of the dots was reduced to about 3.5 nm with the FE-STEM, while those were limited to about 15 nm in diameter with the FE-SEM. Self-standing structures were successfully fabricated. The combination of these methods indicates the possibility of position and size controlled fabrication of nanomaterials.

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