Composition Control of Electron Beam Induced Nanodeposits by Surface Pre-treatment and Beam Focusing

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Complete List of Authors:	Sychugov, Ilya; National Institute for Material Science, Quantum Dot Research Center Nakayama, Yoshiko; National Institute for Material Science, High Voltage Electron Microscopy Station Mitsuishi, Kazutaka; National Institute for materials science, High Voltage Electron Microscopy Station

Composition control of electron beam induced nanodeposits by surface pre-treatment and beam focusing

Ilya Sychugov^{}, Yoshiko Nakayama and Kazutaka Mitsuishi*

Quantum Dot Research Center, National Institute for Materials Science, Sakura 3-13, Tsukuba, Ibaraki,
305-0003 Japan

sychugov.ilya@nims.go.jp

Cross-sectional transmission electron microscopy with elemental analysis was used to investigate shape and composition of nanostructures fabricated by electron beam induced deposition. The nanostructures were deposited on a thin edge of the silicon membrane allowing characterization without intermediate distorting preparation steps, such as focused ion beam milling. The effect of the surface carbon contaminants and the electron beam focusing on nanostructure composition was studied. It is shown how carbon content of nanostructures can be reduced by sample preheating, forming metal nanostructures with higher purity advantageous for circuitry and lithography applications.

KEYWORDS: EBID, nanostructures, composition

1. Introduction

Electron beam induced deposition (EBID) is a nanofabrication technique capable of surpassing spatial resolution of the ordinary electron beam (e-beam) lithography. Nanostructures with dimensions below ~ 20 nm can be routinely formed without additional metal deposition and lift-off processes associated with the conventional e-beam patterning. As a result, the fabrication of nanostructures by this method is considered advantageous for a number of applications, such as circuitry, lithography and stencil mask repair, among others (for recent reviews see [1, 2]).

In general, it is believed that the dissociation of precursor gas molecules adsorbed on the sample surface is responsible for the formation of nanostructures. Their shape and composition depend on many parameters, such as precursor gas content, beam current density, surface condition, etc. While the deposition takes place under vacuum, the omnipresent surface carbonaceous layer inevitably contributes to the nanostructure formation process. The contribution can be either direct, when carbon atoms become incorporated into deposits, or indirect, when the surface chemistry changes for precursor gas molecules affecting their adsorption/desorption/dissociation routine. Although a contamination build-up itself can be used, for example, for carbon nanowire fabrication [3], its incorporation into metal nanodeposits is detrimental to their electric properties.

Thus a special effort is being devoted to the fabrication of nanostructures with high metal content, desirable for circuitry and lithography applications. For example, better purity deposits can be obtained under ultra-high vacuum (UHV) conditions [4] or by employing post-deposition annealing [5]. It was also shown that metal nanowires formed on the surface pre-treated by the oxygen plasma ashing and annealing indeed possess superior conductivity properties [6]. While the important role of the carbonaceous layer is generally admitted, a dedicated observation of the actual nanodeposits composition affected by surface preparation, to our knowledge, has not been performed as of yet.

In this work the mechanism of the contamination contribution has been studied by the cross-sectional transmission electron microscopy with elemental analysis. Metal/carbon distribution inside nanodeposits was visualized through the bright field imaging and analyzed by the electron energy loss spectroscopy. It

is shown how the presence of a surface carbonaceous layer affects both size and structure of nanodeposits fabricated from an organic precursor gas. It appears that deposits with a higher metal content can be obtained by relatively simple surface preheating. The effect of the electron beam current density was also investigated by changing beam focusing during the fabrication.

2. Experimental methods

A scanning electron microscope (SEM, JEOL JSM-6700-F) with a precursor powder evaporation unit was employed for EBID. A 30 keV energy beam with 30 pA sample current were used with $\text{W}(\text{CO})_6$ precursor gas at pressure $4 \cdot 10^{-4}$ Pa for all the depositions. Nanostructures were characterized by scanning transmission electron microscope (STEM, JEOL JEM-2500SES) equipped with electron energy loss spectrometer (EELS) for elemental analysis. In order to avoid possible artifacts caused by sample preparation involving standard focused ion beam (FIB) milling the deposition was performed on a thin edge of Si membranes. The membranes were prepared by ion dimpling of Si disks with subsequent cleavage and additional low-angle sputtering (Fig. 1, top). By examining obtained membranes in optical microscope thin areas suitable for deposition (< 100 nm) could be identified by the presence of color fringes. After the deposition membranes were immediately transferred to the STEM unit for analysis.

To reduce surface contamination contribution some membranes were baked at 80°C for 5 minutes in air or at 300°C for 1 hour in vacuum (at 10^{-4} Pa). The former method is well-known in the TEM community as a practical way of contamination reduction for better quality high-resolution imaging [7]. Membranes annealed in vacuum were quickly moved in air to the deposition unit after the treatment. Quantitative analysis of the baking effect on surface chemistry was carried out by x-ray photoelectron spectroscopy (XPS, Ulvac PHI Quanter SXM).

3. Results

1 In Fig. 1 (bottom) SEM images of the dots deposited on the membranes baked at 80°C for 5 min.
2 (right) and untreated (left) are shown. It is seen that while the dots have similar lateral dimensions the
3 secondary electron signal intensity is higher for the unprocessed sample. This is a general trend and for
4 four pairs of dots measured for comparison the average intensity ratio was about two times. Such an
5 effect was reported in [6], where nanowire height was evaluated with an atomic force microscope
6 (AFM) yielding lower values for nanodeposits formed on pre-cleaned surfaces. In general, however, the
7 difference in SEM signal intensity can originate both from the size and composition differences.
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10 In Fig. 2 (top) a typical STEM bright-field image of the nanodot formed on as-prepared surface is
11 shown. Lattice fringes of the silicon substrate can be discerned with two different layers present on top
12 of it. The layers are identified by the EELS analysis (not shown) as a native silicon dioxide layer with a
13 carbon-rich film on top of it. The dot shape profile is a Gaussian, as would be expected for a typical
14 deposition shape profile from the Monte-Carlo simulations [8]. The elemental analysis of the dot itself is
15 shown below for another nanostructure, which dark-field STEM image is also presented (brighter areas
16 on a dark-field image correspond to a higher atomic number element). It is seen from the EELS data
17 how tungsten peak first grows following the increase in dot diameter and then drops practically to zero
18 for the lower part of the structure. Such a composition with a carbon-rich “basement” is found to be
19 typical for the untreated substrate and was repeatedly observed for a large number of nanodots.
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22 The quantitative effect of the sample annealing in air is shown in Fig. 3, where XPS spectra of the C
23 1s line are presented for untreated and pre-heated membranes. It is seen that the intensity of the carbon
24 peak drops about two times after the treatment, while the left shoulder of the peak, associated with a C-
25 O bond, increases in relative units.
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28 While the change in the amount of carbon seems to be only moderate as a result of the annealing, the
29 nanodot composition undergoes a remarkable transformation. In Fig. 4 STEM bright-field images of
30 nanodots are shown both for the membranes annealed in air (top) and in vacuum (bottom). The top
31 image was taken at a tilted angle, while the sample drift during the deposition is probably responsible
32 for the inclined dot geometry for the bottom image. The dots are dominantly composed of tungsten
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without significant traces of carbon visible. An EELS tungsten profile for another dot is shown in Fig. 5 confirming results of the bright-field imaging. Metal content is growing with increasing dot diameter all along the structure until its foundation. Again, a large number of dots revealing similar composition were observed.

Finally, the effect of beam current density on nanodeposit composition is shown in Fig. 6. Three nanostructures formed with beam focusing increasing from right to left are shown for the unprocessed substrate (Fig. 6, top). The tungsten content is clearly growing with a higher current density, however no dots without a carbon “basement” were ever observed for the untreated substrate. Below on the same figure a nanostructure formed with a defocused beam on the substrate annealed in vacuum is shown. The metal content is low all across the observed cross-section, unlike for the dots shown in Fig. 4.

4. Discussion

From the comparison of dot images in Fig. 2 and Fig. 4 it appears that the metal content can be significantly enhanced by the substrate preheating. Elevating baking temperature further does not seem to have a profound effect on the deposited nanodots composition (cf. Fig. 4, top and bottom). We also note that although the total amount of the surface carbon does not change drastically upon baking (cf. Fig. 3), this treatment does remarkably affect nanostructure composition. It was shown that the surface diffusion of the mobile hydrocarbons to the deposition site provides the necessary supply for polymerization and consequent contamination build-up [9]. In general, the baking process on top of reducing the amount of surface contaminations can also alter their chemical state and surface mobility [10]. The latter is probably the main reason for the observed here effect of the sample preheating. While the surface diffusion of carbon-based compounds is reduced due to possibly better chemical bonding with the surface, the precursor gas molecule behavior remains virtually unaffected. Considering that the dot formation is usually governed by the rate equation including different processes, such as diffusion, desorption, etc. [1], the higher metal concentration and the smaller height of the nanostructures formed on preheated surfaces can indeed be expected.

1 An important application of the EBID technique is the fabrication of lithographical pattern
2 subsequently transferred to the substrate by the etching [11]. In a separate study we show how small
3 metal nanodots can be used as an etching mask for the fabrication of semiconductor nanostructure
4 featuring quantum-confinement effects [12]. The presence of a carbon “basement” in that case has a
5 negative effect on surface adhesion for smaller metal dots as well as on the etched semiconductor
6 nanostructure size, effectively acting as a mask prolongation [13]. From this perspective higher purity
7 metal nanostructures achievable with good beam focusing on pre-treated surfaces also appear
8 advantageous. Another widely used application of EBID is nanowire formation for circuit fabrication
9 and repair [14]. It was shown how better conductivity wires can be produced on surfaces with reduced
10 contamination [6]. An oxygen plasma etching was mentioned as a useful tool along with the sample
11 preheating, discussed here.

12 The nanostructures formed by the deposition with a defocused beam in general contain less metal and
13 its content increases with beam focusing (Fig. 6). The observed result is in line with previous
14 observations of the beam current effect [15], where higher metal content was typically found in
15 nanostructures produced with a higher current probe. This effect can be explained by the beam induced
16 local heating, forcing carbon-based volatile compounds to detach [2]. For the deposition on the
17 preheated surface, on the other hand, the constituting carbon presumably originates from the precursor
18 gas itself rather from surface contaminations. Here an organic precursor gas was used, while inorganic
19 compounds like WF_6 are also available and known for yielding higher metal content deposits compared
20 to their organic counterparts [2].

21 The same “local heating” argument can be used to explain the higher metal content at the top of the
22 dot for as-prepared samples (cf. Fig. 2). While the dot develops both laterally and vertically with time,
23 metal content does not visibly increases at the dot foundation, where there is less dissipated energy from
24 the primary beam. We also note that adjacent mobile hydrocarbons would diffuse longer to the dot upper
25 part and are more likely to get polymerized at the dot basement, forming the structure seen in Fig. 2.

1 In Fig. 7 findings of this work are summarized in a schematic picture describing the EBID process
2 flow. The deposition proceeds on a surface having physically or chemically adsorbed species like CO,
3 CO₂, CH₄, together with precursor gas molecules W(CO)₆ adsorbed after introducing the sample into the
4 deposition chamber. For the deposition with a focused beam on as-prepared surfaces the dissociation of
5 carbon-based compounds and their surface diffusion to the deposition site form carbon-rich basement,
6 while metal atoms tend to precipitate at the top part of the nanodeposits. At the same time with reduced
7 beam current the fraction of metal decreases and the nanostructures composed largely of carbon are
8 formed. On the other hand, when the amount of surface contaminations is reduced by sample preheating
9 and, presumably, their surface mobility is suppressed, nanostructures smaller in height but with a larger
10 metal content can be fabricated. The reduction of the beam current density reduces metal content in a
11 similar way as for untreated substrates.

12 Using cross-sectional TEM imaging with elemental analysis the role of surface contaminations in the
13 nanostructure formation by EBID was investigated. It is found that nanodeposits with higher metal
14 content can be obtained by simple sample preheating accompanied with proper beam focusing. In this
15 way improved quality nanodeposits for circuitry and lithography applications can be fabricated.

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43 machine.

FIGURE CAPTIONS

Figure 1. (top) Schematic representation of the Si membrane preparation for the STEM observation. Membranes were ion-milled and cleaved to form a thin (< 100 nm) flat surface in the middle. Color fringes under white light illumination indicate the location of the thin area. (bottom) Top view SEM images of dots deposited on a Si sample with (right) and without (left) pre-baking. Dots deposited on as prepared sample yield stronger signal intensity than the ones deposited on the baked sample, suggesting difference in height.

Figure 2. (top) Bright field STEM image of a nanodot deposited on as-prepared Si membrane from $W(CO)_6$ precursor gas. EELS analysis (not shown) reveals a presence of carbonaceous layer on top of the native SiO_2 layer formed on the membrane surface. (bottom) Dark-field STEM image of another dot (right) and corresponding W line profile measured by EELS (left). While the top part of such dots consists of tungsten nanocrystals, the bottom part is formed by carbon presumably from the surface contamination layer.

Figure 3. XPS spectra of a silicon membrane baked at $80^\circ C$ for 5 min. (dark squares) in comparison with an unprocessed sample (bright circles). Carbon peak intensity drops about two times as a result of the heat treatment. Note the relative increase in the curve left shoulder, corresponding to the C-O bond.

Figure 4. Bright field STEM images of nanodots deposited on baked membranes: (top) at $80^\circ C$ for 5 minutes in air and (bottom) at $300^\circ C$ for 1 hour in vacuum. A slightly tilted view is shown for the

former and the deposition dwell time was longer in the latter case. The dots are composed of uniformly distributed metal nanocrystals without significant traces of carbon.

Figure 5. Dark field STEM image (left) and the EELS tungsten profile for the selected region of the nanodot. Tungsten content is increasing along with the dot diameter until the very foundation of the nanodeposit.

Figure 6. Bright field STEM images of nanodots deposited with slightly defocused beam: (top) for as-prepared sample and (bottom) for the sample baked at 300oC for 1 hour in vacuum. For as-prepared membrane three dots are shown with the degree of beam focusing increasing from right to left. The metal content grows following the increase of the beam current density. Nanostructures without carbon inclusions, however, have never been observed for substrates without preheating.

Figure 7. Qualitative representation of the EBID process scenario derived from the present experiment. (top) Deposition with focused and slightly defocused electron beams takes place when growth components diffuse to the deposition site both for as prepared (left) and baked (right) samples. Carbon contaminations, physically or chemically adsorbed on the surface in the form of CO, CO₂ and CH are schematically shown. Precursor gas molecules W(CO)₆ are depicted as large spheres representing W atoms with smaller carbon and oxide atoms around it. (bottom) Lower concentration of the carbon compounds on the surface and their suppressed mobility for the heat treated sample leads to higher metal content dots fabricated by the focused beam (right). The dots formed on the untreated surface, on the other hand, contain larger fraction of carbon, dominantly at the dot basement, making them generally larger in size (left).

REFERENCES

- (1) Utke, I.; Hoffmann, P.; Melngailis, J. *J. Vac. Sci. Tech. B* **2008**, 26, 1197.
- (2) van Dorp, W.F.; Hagen, C. W. *J. Appl. Phys.* **2008**, 104, 081301.
- (3) Jin, C.H.; Wang J.Y.; Chen Q.; Peng L.-M. *J. Phys. Chem B* **2006**, 110, 5423.
- (4) Lukasczyk, T.; Schirmer, M.; Steinruck, H.-P.; Marbach, H. *Small* **2008**, 4, 841.
- (5) Botman, A.; Mulders, J.J.L.; Weemaes, R.; Mentink, S. *Nanotechnology* **2006**, 17, 3779.
- (6) Hiroshima, H.; Suzuki, N.; Ogawa, N.; Komuro, M. *Jap. J. Appl. Phys.* **1999**, 38, 7135.
- (7) Williams, D.B; Carter, C.B. in “*Transmission electron microscopy. Basics*” (Plenum Press, 1996) p. 123.
- (8) Mitsuishi, K.; Liu, Z.Q.; Smimojo, M.; Han, M.; Furuya K. *Ultramicroscopy* **2005**, 103, 17.
- (9) Amman, M.; Sleight, J. W.; Lombardi, D.R; Welser, R. E.; Desphande M. R.; Reed, M. A.; Guido L. J. *J. Vac. Sci. Technol. B* **1996**, 14, 54.
- (10) Hren, J.J. *Ultramicroscopy* **1979**, 3, 375.
- (11) Guan, Y.; Fowlkes, J.D.; Retterer, S.T.; Simpson, M.L.; Rack, P.D. *Nanotechnology* **2008**, 19, 505302.
- (12) Sychugov, I.; Nakayama, Y.; Mitsuishi, K. (in preparation).
- (13) Allee, D.R.; Umbach, C.P.; Broers A.N. *J. Vac. Sci. Tech. B* **1991**, 9, 2838.
- (14) Kohlmann-von Platen, K.T.; Buchmann, L.-M.; Petzold, H.-C.; Brunger, W.H. *J. Vac. Sci. Tech. B* **1992**, 10, 2690.

(15) Weber, M.; Koops, H. W. P.; Rudolf, M. R.; Kretz, J.; Schmidt, G. *J. Vac. Sci. Tech. B* **1995**, 13, 1364.

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Fig. 1
Sychugov et al.
81x65mm (600 x 600 DPI)

Fig. 2 Sychugov et al.
82x124mm (600 x 600 DPI)

Fig. 3 Sychugov et al.
84x58mm (600 x 600 DPI)

Fig. 4 Sychugov et al.
85x140mm (600 x 600 DPI)

Fig. 5
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84x63mm (300 x 300 DPI)

Fig. 6
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Fig. 7
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