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## ADVERTISEMENT



## Fabrication by electron beam induced deposition and transmission electron microscopic characterization of sub-10-nm freestanding Pt nanowires

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We present a method to reduce the size and improve the crystal quality of freestanding nanowires grown by electron beam induced deposition from a platinum metal organic precursor in a dual beam system. By freestanding horizontal growth and subsequent electron irradiation in a transmission electron microscope, sub-10-nm polycrystalline platinum nanowires have been obtained. A combined transmission electron microscopy–electron energy loss analysis has shown that the amorphous carbon, mixed to nanocrystalline platinum in the as-deposited material, is removed from the wires during irradiation. The same treatment progressively transforms nanocrystals dispersed in the amorphous matrix in a continuous polycrystalline platinum wire. © 2006 American Institute of Physics. [DOI: 10.1063/1.2206996]

One motivation for fabricating freestanding nanowires is their potential use as both interconnects and functional components in future nanoelectronics.<sup>1</sup> In addition, nanowires present innovative fundamental aspects in electron transport,<sup>2</sup> phonon transport,<sup>3</sup> and structural properties<sup>4,5</sup> when grown without physical influence of the substrate.

At present, there are few methods for preparing freestanding metal nanowires uniform in diameter, sufficiently long, and placed and aligned to desired configurations or patterns. The most widely used top-down fabrication method is a multistep electron beam lithography process.<sup>6</sup> This is a complex and time-consuming process, often resulting in poor yield due to misalignment and incomplete metal lift-off. Very short ( $\sim 6$  nm) Au nanowires of excellent purity and ultimate width of 0.6 nm have been fabricated in ultrahigh vacuum (UHV) transmission electron microscope (TEM).<sup>4</sup> Different successful approaches have been exploited to fabricate very long and uniformly thick nanowires like step-edge decoration<sup>7</sup> and nanoimprint lithography.<sup>8</sup> The main drawback of these methods is the difficult site control of freestanding growth which is mandatory for studying fundamental properties and fabricating interconnects.

Nanowire fabrication could be greatly simplified by combining patterning and metal deposition into a single step. One such technique, direct-write nanopatterning by electron beam induced deposition<sup>9</sup> (EBID) uses a metal organic precursor which is vaporized and injected into the path of the beam. Precursor molecules adsorbed on the substrate are decomposed by beam induced surface reactions, resulting in localized deposition of material. Many studies have been carried out using scanning electron microscopes (SEMs) for various depositions showing excellent growth control in both vertical [W,<sup>9</sup> Pt,<sup>10</sup> Au, Cu, Ru, and tetraethyl orthosilicate<sup>11</sup> (TEOS)] and lateral geometries.<sup>12</sup> Using this method and a Pt precursor, interesting transport properties have been demonstrated<sup>13,14</sup> and tilted pillars separated by a 5 nm gap have been fabricated under direct visual control.<sup>15</sup> Despite these improvements, the minimum size of EBID objects (wires and dots) fabricated on bulk substrate is limited to a few tens of nanometers. It was argued that the size of the deposited objects was constrained by the distribution of secondary electrons generated by primary beam interaction with the substrate.<sup>16</sup> This fact limits the minimum feature size to be larger than the beam diameter and increases the leakage current due to metallic deposition spread.<sup>17</sup>

Strong efforts have been done to reduce the minimum feature size performing EBID in scanning TEM on ultrathin electron transparent substrates to limit the secondary electron emission volume, thus obtaining sub-10-nm wide features.<sup>18,19</sup> An additional step to extend the usefulness of EBID in nanowire fabrication is to improve the crystal quality (which in turn affects the electrical conductivity) of the deposited metal. For example, the conventional Pt metal organic precursor, used for metallic interconnect and in the present work, results in a highly resistive deposit, composed of a carbon-rich mixture of amorphous C (*a*-C) and nanocrystalline Pt.<sup>10,13-15</sup>

In this letter, we present a different approach to reduce the minimum size and improve the crystal quality of EBID freestanding wires, grown from a Pt metal organic precursor in a dual beam focused ion beam (FIB)-SEM system. Improvement of the minimum size has been achieved by setting up a method to laterally grow suspended nanowires, about 10 nm wide and hundreds of nanometers long, with selectivity of the growth site linked to SEM resolution. To test the spatial resolution of the overall process, freestanding nanowires were grown in between two pillars with ending tip less than 50 nm wide. Irradiation by the electron beam of a conventional 200 keV TEM has been used to improve the crystal quality of the deposit and to decrease wire width. As shown by detailed TEM analysis of both as-deposited and irradiated samples, freestanding polycrystalline Pt nanowires, about 5 nm wide, were formed by simultaneous Pt grain growth and a-C removal.

Nanowire growth was performed using a solid metal organic precursor, (trimethyl)methylcyclopentadienylplatinum (IV),  $(CH_3)_3CH_3C_5H_4Pt$  vaporized by heating to 44 °C. The

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FIG. 1. SEM top view (a) and side view (b) of a typical nanowire. From these images width, thickness, and length can be directly determined with good accuracy.

gas was injected into the path of the electron beam in a FEI Strata 235 M dual beam system. The nominal electron beam spot size was 5 nm, probe current was 90 pA, and accelerating voltage was 15 kV. The chamber pressure was 6  $\times 10^{-6}$  mbar during deposition, which was performed at room temperature. Before metal deposition, the Si substrate was prepared with FIB patterned slits in order to enable TEM measurements during irradiation. The wires were deposited on the tip of tilted pillars grown from the same metal organic precursor on silicon substrate, using a procedure similar to the one reported in literature for nanogap fabrication,<sup>15</sup> where, in order to increase the control of the growth rate and to avoid anisotropic growth effects,<sup>20</sup> we introduce the gas precursor without needle insertion. Freestanding horizontal wires were obtained by setting up a computer controlled procedure that, starting from a pillar, laterally shifts the electron beam in spot mode by a fixed step of 5 nm. The dwell time of the electron beam was varied in the range of 60-200 ms in order to obtain thickness and width uniformity and desired wire length. With this method only a few seconds are needed to grow 200-300 nm long wires with a very high spatial resolution.

TEM analysis and irradiation experiments were performed with a JEOL 2010 (point resolution of 0.19 nm, LaB<sub>6</sub> emitter) high resolution electron microscope (HREM) equipped with a Gatan imaging filter (GIF200) corrected for image distortion (maximum distortion better than 1%) for image recording, energy filtering, and electron energy loss spectroscopy (EELS) analysis. All the EELS spectra were acquired with the TEM operating at 200 keV in diffraction mode, focusing the beam on the wire. The spectrometer dispersion was 0.3 eV/pixel, the acceptance angle was 10 mrad, and the beam convergence angle was 6 mrad. Energy dispersive x-ray spectroscopy (EDS) was performed using a Link Inca 100 system attached to the same microscope.

Figure 1 shows two SEM images of a typical nanowire, as viewed from the top (a) and side (b). The wire is about 250 nm long, 20 nm wide, and 30 nm thick. Since the wires were directly grown on a perforated, prethinned silicon sample, TEM analysis [bright field (BF), EDS, selected area electron diffraction (SAED), HREM, and EELS] could be performed directly on the wires, without additional TEM specimen preparation. EDS allows a semiquantitative estimation of the mean composition (C70% and Pt30%) which roughly agrees with previously reported analysis on thicker and longer wires deposited on the substrate.<sup>10</sup>

In Fig. 2(a) a low magnification BF TEM image of the wire is reported; a magnified image of the central part of the wire and the relative SAED pattern are shown in Figs. 2(b) and 2(c), respectively. The BF images show the morphology and the structure of the nanowires: they are formed by a low electro-optical density amorphous matrix (bright contrast) and nanoareas ( $\sim 2$  nm wide) having high electro-optical



FIG. 2. As-deposited nanowire: (a) Morphology from the BF TEM image. (b) Structural details from higher magnification BF TEM image. (c) SAED pattern typical of amorphous/nanocrystalline material. (d) RDF extracted from the SAED shown in (c). The reported atomic distances corresponding to the G(r) peaks are in agreement with Pt fcc structure ones.

density (dark contrast). The SAED pattern reveals the presence of broad diffraction rings typical of amorphous/ nanocrystalline materials. Similar morphology and structure have been already observed in thicker and wider films pre-pared with substrate-mediated EBID.<sup>10,13–15</sup> In order to obtain quantitative data on the structure of the wires we have performed analysis of the SAED pattern of Fig. 2(c) in terms of radial density function (RDF) G(r), which is reported in Fig. 2(d). As it is well known, the RDF can be derived by Fourier sine transform of diffracted intensities and describes the fluctuation of the local density with respect to its average value.<sup>21</sup> Therefore, RDF peaks reveal the most probable atomic distances. We measure a first neighbor distance of  $0.28 \pm 0.01$  nm, a second neighbor distance of  $0.39 \pm 0.01$  nm, and a third neighbor distance of  $0.49 \pm 0.01$  nm. Since all these distances reproduce well first, second, and third neighbor distances of Pt fcc cubic unit cell (a=0.3919 nm), we can deduce the nanocrystalline arrangement of Pt atoms inside dark contrast details dispersed in the a-C matrix. In addition, we observe that the intensity of the SAED pattern is completely dominated by Pt atoms so we cannot obtain any information on the C atoms forming the amorphous matrix from diffraction data (as expected by a simple comparison on total elastic scattering cross section of Pt and C). On the contrary, EELS is the elective tool for this kind of elemental/ structural analysis.<sup>22</sup> In Fig. 3 is reported the typical C Kedge of an as-deposited wire. A sharp preedge peak (285 eV)



FIG. 3. C K edge extracted from EELS spectra taken in as-deposited nanowires and after electron irradiation steps shown in the legend. The intensity of the edge relative to the as-deposited wire has been reduced by a factor of 5 for the sake of clarity. The vanishing of the carbon signal after 180 s irradiation time is evident.



FIG. 4. Structural evolution during irradiation. (a) BF TEM image taken after 60 s irradiation at the wire center (arrowed). (b) BF TEM image taken after a sequence of five 180 s irradiations performed on different areas of the wire, in order to remove *a*-C over the total wire length. (c) HREM image and corresponding fast Fourier transform of a grain junction showing the  $\{111\}$  Pt lattice fringes.

followed by a broader one (290–302 eV) is clearly visible in the spectrum. The preedge peak is ascribed to the  $1s \rightarrow \pi^*$ transitions typical of  $sp^2$  hybridized C, whereas the broad peak is ascribed to  $1s \rightarrow \sigma^*$  transitions.<sup>22</sup> The edge shape looks very similar to those observed in evaporated amorphous carbon films characterized by large  $sp^2/sp^3$  ratio (>80%).<sup>23</sup> It is worth noting that the freestanding growth of the wires reduces their lateral dimension with respect to the substrate-mediated case, without affecting their morphology and chemical composition.

A sequence of spectra taken at the center of a wire similar to the one shown in Fig. 2(a), after 60 s electron irradiation steps, using a current density of 50 A/cm<sup>2</sup> in a spot size of about 50 nm, is also reported in Fig. 3. A C K signal loss without appreciable edge modification is clearly detected after each irradiation step. After 180 s of total irradiation time the vanishing of C K edge is observed.

Energy filtered images (taken with the zero loss peak) showing the structural modification of the wire during irradiation are reported in Fig. 4. In particular, Fig. 4(a) has been recorded after 60 s irradiation of the central part of the wire. It shows the growth of Pt grains at the wire center and the loss of a-C at the lateral edge (arrowed). The image recorded after five irradiations of 180 s, performed on different areas of the wire in order to remove *a*-C over the total wire length, is reported in Fig. 4(b). The formation of a polycrystalline Pt structure is clearly observed by diffraction contrast details. In addition the HREM image of Fig. 4(c) shows lattice fringes spaced by 0.231±0.006 nm, a mean value obtained from different grains visible in the image that agrees quite well with {111} Pt crystallographic plane spacing (0.226 nm). The experimental evidence of a-C removal and Pt grain growth could be explained invoking different mechanisms, based on the energy transfer between the high energy electron beam and the wires. Heating, knock-on effects on the organic matrix,<sup>24</sup> and the formation of C–O compounds in the presence of residual oxygen gas and/or water vapor<sup>25</sup> are possible candidates, probably acting at the same time during electron irradiation; discriminating among them is an important issue and work is in progress in this field.

In conclusion, we have reported a controlled method to fabricate sub-10-nm freestanding Pt wires exploiting horizontal suspended growth by EBID and TEM irradiation. A detailed TEM-HREM-EELS analysis has shown that *a*-C matrix can be removed from the wire during high energy electron irradiation. This process produces pure metallic wires. We have shown that this combined approach features site selectivity of the growth and improves minimum size and crystal quality of the deposit, thus it seems promising for both nanoelectronic applications and fundamental studies.

- <sup>1</sup>Z. L. Wang, *Nanowires and Nanobelts*, 1st ed. (Kluwer Academic, Boston, 2003).
- <sup>2</sup>H. Ohnishi, Y. Kondo, and K. Takayanagi, Nature (London) **395**, 780 (1998).
- <sup>3</sup>M. D. LaHaye, O. Buu, B. Camarota, and K. C. Schwab, Science **304**, 74 (2004).
- <sup>4</sup>Y. Kondo and K. Takayanagy, Science **289**, 606 (2000).
- <sup>5</sup>O. Gülseren, F. Ercolessi, and E. Tosatti, Phys. Rev. Lett. **80**, 3775 (1998).
- <sup>6</sup>G. S. Paraoanu and A. M. Halvari, Appl. Phys. Lett. **86**, 093101 (2005).
- <sup>7</sup>M. P. Zach, K. H. Ng, and R. M. Penner, Science **290**, 2120 (2000).
- <sup>8</sup>X. M. Yan, S. Kwon, A. M. Contreras, J. Bokor, and G. A. Somorajai, Nano Lett. **5**, 745 (2005).
- <sup>9</sup>H. W. P. Koops, R. Weiel, D. P. Kern, and T. H. Baum, J. Vac. Sci. Technol. B **6**, 477 (1988).
- <sup>10</sup>H. W. P. Koops, A. Kaya, and M. Weber, J. Vac. Sci. Technol. B **13**, 2400 (1995).
- <sup>11</sup>T. Bret, I. Utke, A. Bachmann, and P. Hoffmann, Appl. Phys. Lett. **83**, 4005 (2003).
- <sup>12</sup>T. Bret, I. Utke, C. Gaillard, and P. Hoffmann, J. Vac. Sci. Technol. B 22, 2504 (2004).
- <sup>13</sup>L. Rotkina, J. F. Lin, and J. P. Bird, Appl. Phys. Lett. 83, 4426 (2003).
- <sup>14</sup>L. Rotkina, S. Oh, J. N. Eckstein, and S. V. Rotkin, Phys. Rev. B 72, 233407 (2005).
- <sup>15</sup>G. C. Gazzadi and S. Frabboni, J. Vac. Sci. Technol. B 23, L1 (2005).
- <sup>16</sup>N. Silvis-Cividjian, C. W. Hagen, L. H. A. Leunissen, and P. Kruit, Microelectron. Eng. 61–62, 293 (2002).
- <sup>17</sup>V. Gopal, E. A. Stach, V. R. Radmilovic, and I. A. Mowat, Appl. Phys. Lett. 85, 49 (2004).
- <sup>18</sup>K. Mitsuishi, M. Shimojo, M. Han, and K. Furuya, Appl. Phys. Lett. 83, 2064 (2003).
- <sup>19</sup>N. Silvis-Cividjian, C. W. Hagen, P. Kruit, M. A. J. v. d. Stam, and H. B. Groen, Appl. Phys. Lett. **82**, 3514 (2003).
- <sup>20</sup>T. Bret, I. Utke, and P. Hoffmann, Microelectron. Eng. **78–79**, 307 (2005).
- <sup>21</sup>D. J. Cockayne and D. R. McKenzie, Acta Crystallogr., Sect. A: Found. Crystallogr. 44, 870 (1988).
- <sup>22</sup>R. F. Egerton, *Electron Energy Loss Spectroscopy*, 2nd ed. (Plenum, New York, 1996).
- <sup>23</sup>A. C. Ferrari, A. Libassi, B. K. Tanner, V. Stolojan, J. Yuan, L. M. Brown, S. E. Rodil, B. Kleinsorge, and J. Robertson, Phys. Rev. B **62**, 11089 (2000).
- <sup>24</sup>L. Reimer, *Transmission Electron Microscopy*, 2nd ed. (Springer, Berlin, 1989), Chap. 10, pp. 438–457.
- <sup>25</sup>I. Utke, J. Michler, P. Gasser, C. Santschi, P. Hoffmann, D. Laub, M. Cantoni, P. A. Buffat, and C. Jiao, Adv. Eng. Mater. 7, 323 (2005).