AIP Applied Physics Letters

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Citation: Applied Physics Letters **85**, 49 (2004); doi: 10.1063/1.1765736
View online: http://dx.doi.org/10.1063/1.1765736
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/85/1?ver=pdfcov
Published by the AIP Publishing

# Metal delocalization and surface decoration in direct-write nanolithography by electron beam induced deposition

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(Received 10 December 2003; accepted 30 April 2004)

The ability to interconnect different nanostructures is crucial to nanocircuit fabrication efforts. A simple and versatile direct-write nanolithography technique for the fabrication of interconnects is presented. Decomposition of a metalorganic precursor gas by a focused electron beam resulted in the deposition of conductive platinum nanowires. The combination of *in situ* secondary electron imaging with deposition allows for the simultaneous identification and interconnection of nanoscale components. However, the deposition was not entirely localized to the electron beam raster area, as shown by secondary ion mass spectrometry measurements. The electrical impact of the metallic spread was quantified by measuring the leakage current between closely spaced wires. The origins of the spread and strategies for minimizing it are discussed. These results indicate that, while this direct-write methodology is a convenient one for rapid prototyping of nanocircuits, caution must be used to avoid unwanted decoration of nanostructures by metallic species. *© 2004 American Institute of Physics*. [DOI: 10.1063/1.1765736]

Planar semiconductor fabrication technology is approaching its limits even as the aggressive scaling of transistor dimensions continues. One-dimensional (1D) nanostructures, such as semiconductor nanowires and carbon nanotubes, are currently subjects of intense research as building blocks for future nanoelectronics. Significant progress has been made in the bottom-up synthesis and characterization of these building blocks.[1] Less attention has been paid to the techniques of interconnecting them for the fabrication of functional nanocircuits. Traditionally, 1D nanostructures are connected to larger electrodes by a multistep electron beam lithography process. This is a complex and time-consuming process, often resulting in poor yield due to misalignment and incomplete metal lift-off. Nanocircuit interconnect fabrication can be greatly simplified by combining patterning and metal deposition into a single step. One such technique, direct-write nano-patterning by electron beam induced deposition (EBID), has recently received a lot of attention.[2–8] In EBID, a metalorganic precursor is vaporized and injected into the path of an electron beam. Precursor molecules adsorbed on the substrate are decomposed by beam induced surface reactions, resulting in localized deposition of a metal-rich conductive material. It is generally accepted that low energy secondary electrons emitted from the substrate are responsible for deposition.[2,3,6,9] This limits the minimum feature size to be larger than the beam diameter. Monte Carlo simulations have been employed to show that secondary electrons are excited from an area far exceeding the primary beam size.[9,10] A thrust of recent research has been to reduce the minimum feature size. Mitsuishi *et al.*[2] and Silvis-Cividjian *et al.*[3] have performed EBID on ultra-thin electron transparent substrates in scanning transmission electron microscopes, depositing sub-10 nm features by limiting the secondary electron emission volume.

A systematic evaluation is necessary in order to use EBID for nanocircuit interconnect applications. In this study, we present detailed electrical and microstructural characterization of EBID, providing an important benchmark for these direct-write nanoscale interconnects. A solid metalorganic precursor, trimethylcyclopentadienyl-platinum $[(CH_3)_3CH_3C_5H_4Pt]$, was vaporized by heating to 50 °C. The gas was injected, by means of a 0.5-mm-diam needle, into the path of a scanning electron beam in a FEI Strata 235 M dual (focused ion and electron) beam (FIB/SEM) system. The electron beam spot size ranged from 8 nm at an accelerating voltage of 5 kV to 5 nm at 20 kV. The probe current ranged from 1.6 nA at 5 kV to 2.4 nA at 20 kV. The chamber pressure was $\sim 10^{-5}$ Torr during deposition, which was performed at room temperature. The wires were deposited on oxidized silicon substrates with photolithographically pre-patterned gold electrodes in order to facilitate electrical measurements. Figure 1(a) is a SEM image of a typical Pt wire deposited to connect two adjacent Au electrodes. The raster dimensions were 40 $\mu$m in length and 250 nm in width. Several wires were deposited by varying the energy of the electron beam while keeping all other parameters constant. The wires had a Gaussian-type cross section as shown in Fig. 1(b), which is an image of a section through a wire created by FIB milling. The dimensions of the wire cross section were obtained by such FIB sectioning, after resistance measurements had been performed. The microstructure consisted of nanocrystallites of Pt embedded in an amorphous carbon-containing matrix, as seen in Fig. 1(c), which is a cross-section TEM image. The resistivity of the wires as a function of beam energy is shown in Fig. 1(d). Linear current–voltage characteristics were obtained in each case. It is noteworthy that the resistivity was relatively insensitive to the electron beam energy (resistivity decreased only

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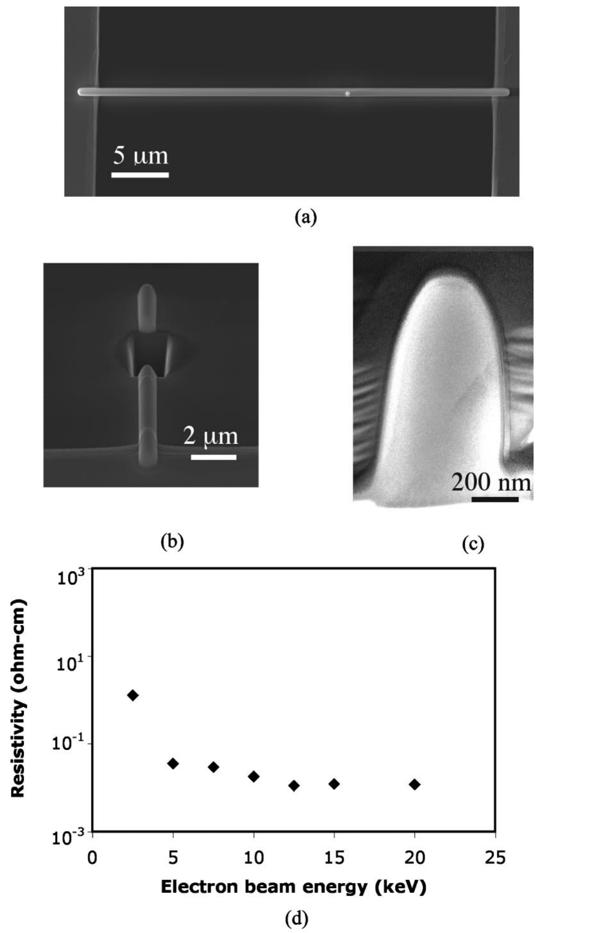


FIG. 1. (a) SEM image of Pt wire deposited by EBID. (b) SEM image of the cross section of a Pt wire created by FIB milling. The cross-sectional area necessary for obtaining resistivity was measured from such images. (c) Cross-sectional TEM image of an EBID Pt wire. (d) Resistivity of Pt wires as a function of electron beam energy.

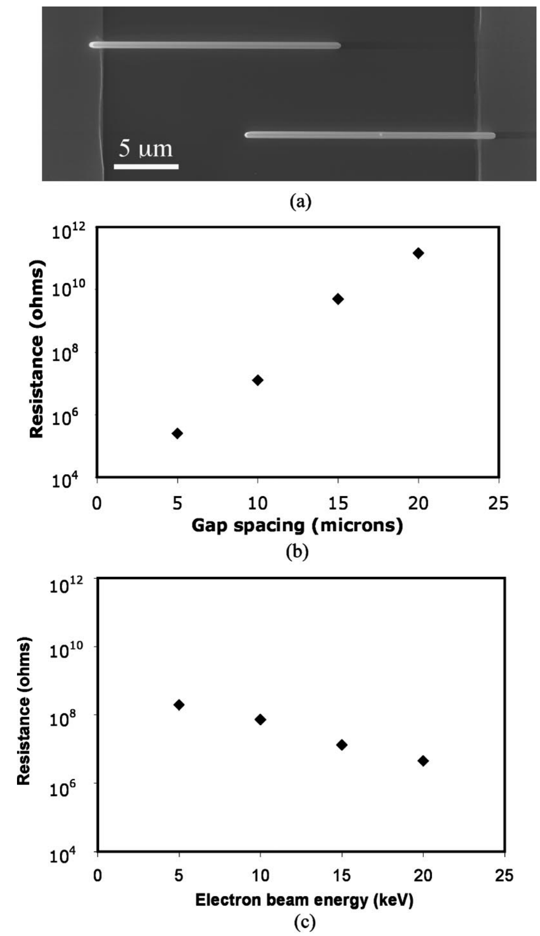


FIG. 2. (a) Two Pt lines spaced 10 $\mu$m apart for leakage current measurements. (b) Leakage resistance as a function of electron beam energy for pairs of Pt wires spaced 10 $\mu$m apart. (c) Leakage resistance as a function of gap spacing. The deposition was carried out at 20 keV beam energy.

by a factor of 3 with increase in deposition energy from 5 to 20 keV).

An important requirement for nanoscale interconnects is that there be little or no crosstalk between closely spaced metal lines. Any leakage pathway between two metal lines interconnecting a nanostructure can easily lead to erroneous interpretation of its transport properties. We investigated this by patterning pairs of closely separated wires [Fig. 2(a)] and measuring the leakage current between them. Leakage current increased exponentially with beam energy, as plotted in Fig. 2(b). Similarly, the leakage current was found to decrease exponentially with increased gap spacing, as shown in Fig. 2(c). Several workers have reported broadening of EBID metal deposits exceeding the dimensions described by the beam raster.[3,4,7] This is consistent with the mechanism of secondary electron mediated decomposition. However, the measurement of electrical leakage between lines spaced several micrometers apart implies a widespread metal decoration that cannot be explained by secondary electron induced broadening.

The deposit was chemically analyzed by energy dispersive spectroscopy (EDS). The intensity of the Pt–M line was tracked as a semiquantitative measure of the Pt content in the deposited material. Figure 3(a) is a comparison of the Pt–M intensity for wires deposited at 5 and 20 kV. The spectra were collected as line scans across the long axis of the wires. The Gaussian-type profile is a reflection of the deposition cross section [refer to Fig. 1(b)]. The 20 kV wire has a larger full width at half maximum than the 5 kV deposited wire, consistent with a larger secondary electron excitation volume. However, the EDS data do not shed light on the electrical leakage between lines spaced several micrometers apart. This was investigated by time-of-flight secondary ion mass spectrometry (TOF-SIMS), which is far more surface sensitive than EDS, as well as having lower detection limits. Figure 3(b) is a composite positive ion map showing surface decoration around a pair of wires spaced 10 $\mu$m apart. Figure 3(c) shows the corresponding Pt ion map. That the wires cannot be distinguished clearly in this map indicates the extent of metallic spread. Figure 3(d) is a carbon ion map from the same region. Carbon appears to be more localized than Pt to the beam raster area.

Our results suggest that the delocalization of metal outside the electron beam exposed area occurs through two distinct mechanisms. The first is the broadening due to secondary electron assisted decomposition, which can be easily seen in a SEM image of the deposit. The second is a widespread delocalization that can only be detected by surface sensitive techniques such as TOF-SIMS. To illustrate this, a substrate was exposed to a 10 keV electron beam in spot mode (diameter ~ 7 nm) while the metalorganic gas flowed for 60 s. A SEM image of the resultant deposit and the corresponding TOF-SIMS Pt ion map are shown in Figs. 4(a)

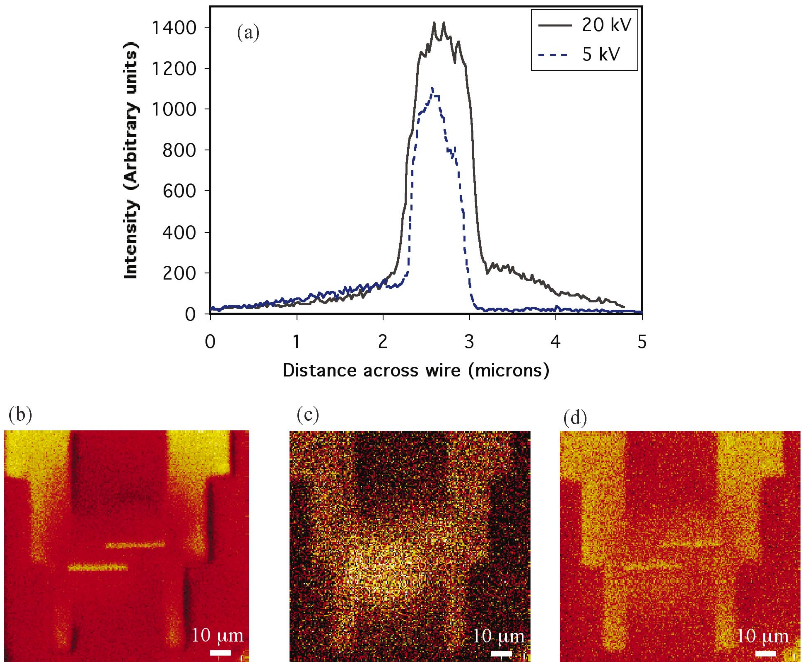


FIG. 3. (Color) (a) EDS spectra of Pt wires deposited at beam energies of 5 and 20 keV. TOF-SIMS ion maps depicting the extent of spread: (b) total positive ion map, (c) Pt ion map, and (d) C ion map.

and 4(b), respectively. The TOF-SIMS map shows a Pt spread exceeding 10 $\mu$m in diameter, clearly larger than the secondary electron excitation area. We believe that the large spread results from thermally assisted diffusion of the deposited Pt, with the primary beam locally heating the substrate during exposure. This would explain the exponential increase in leakage current with increased energy of the primary beam, as well as the exponential dependence of leakage with gap spacing. We attempted to deposit Pt on a sample mounted on a cold stage to verify this hypothesis. However, the precursor gas condensed on the substrate and electron beam induced deposition did not occur.

In summary, direct-write nanolithography by EBID is simple, versatile, and hence very attractive for prototyping nanocircuit contacts and interconnects. However, as the leakage current and TOF-SIMS data show, there is considerable metallic spread. This can decorate nanostructures of interest and contribute to misleading electrical results. Care must be exercised in interconnecting very closely spaced nanostructures. The spread is a strong function of the electron beam energy, but the resistivity of the deposit is rather insensitive to this parameter. Hence, it is desirable to deposit material at low primary beam energy (5–10 keV). In its present form, the technique is best suited for interconnecting widely spaced nanoscale components. The most practical means of extending the utility of EBID is to improve the conductivity of the as-deposited metal. This will minimize deposition time, and prevent the formation of a leakage pathway between adjacent lines. Recent reports of improved crystal quality by water vapor incorporation during deposition[5] are very promising in this regard.

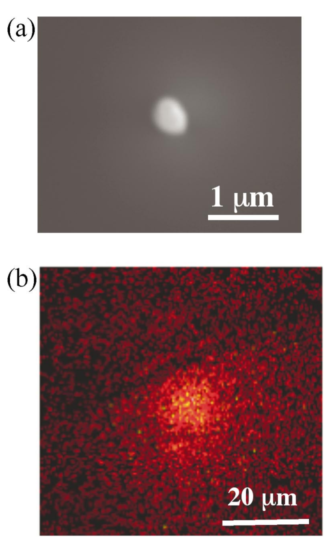


FIG. 4. (a) (Color) Secondary electron image of Pt deposited in spot mode for 60 s. The primary beam voltage was 10 kV, the beam diameter was ~7 nm. (b) TOF-SIMS Pt ion map from the same region illustrates widespread surface decoration.

This work was supported by the Office of Science, Basic Energy Sciences, Division of Materials Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The authors thank Professor Peidong Yang, University of California at Berkeley for the use of the probe station for electrical measurements. Dr. Warren Moberly-Chan of Harvard University is acknowledged for performing cold stage depositions.

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