

Electron beam deposition of gold nanostructures in a reactive environment

Albert Folch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 and
Facultat de Física, Universitat de Barcelona, 08027 Barcelona, Spain

Javier Tejada

Facultat de Física, Universitat de Barcelona, 08027 Barcelona, Spain

Christopher H. Peters and Mark S. Wrighton

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 28 October 1994; accepted for publication 27 January 1995)

Electron beam deposition (EBD) is a maskless technique suitable for the fabrication of nanometer scale structures. Metals can be deposited from an organometallic gas, but simultaneous carbon deposition typically yields grossly impure ($\sim 25\%$ metal) deposits. We have found that the metal content of the deposited solid is dramatically improved by performing the whole EBD process in a reactive gaseous environment containing a source of oxygen (O_2 or H_2O) in addition to the organometallic gas. With simple procedures we prepared Au deposits showing significantly diminished C content (up to 50% metal) as the partial pressure of O_2 (or H_2O) is increased in the gas. © 1995 American Institute of Physics.

Electron beam deposition (EBD)^{1,2} provides an inexpensive way to create features of different sizes, shapes, and materials in the submicron or nanometer scale. The focused e^- -beam of a scanning electron microscope (SEM) has been shown to cause the growth of dots, columns (typically less than 100 nm diam), lines or thin films, if an appropriate gas is present in the vicinity of the substrate. Some or all of the gas molecules that adsorb on the area that is irradiated by the electrons are dissociated, and a deposit is formed consisting of the nonvolatile remains from that dissociation. Metallic nanostructures can be created by using an organometallic precursor gas.³⁻⁷ In previous EBD work, through, the metallic purity of the deposits has been limited by a substantial amount of simultaneously deposited carbon, coming both from the residual hydrocarbon contamination gases inside the SEM chamber and from the organometallic precursor compound itself.

Here we present a method that significantly reduces carbon incorporation in EBD. Our method is based on the simultaneous presence of two gases during the deposition process: the organometallic precursor gas and an "environmental gas." Since, in our case, the partial pressure of organometallic gas is constant and around two orders of magnitude smaller than that of environmental gas, we denote the measured total pressure as environmental pressure P_{env} . In our experiments the environmental gas is either H_2O vapor, Ar, or a mixture of 80% Ar and 20% O_2 (Ar/ O_2). We found that the presence of Ar/ O_2 or H_2O reduces the C content of the deposits whereas Ar does not. Although no precautions were taken to reduce the residual contamination in the SEM chamber, nor to carefully handle or clean the sample, we obtained Au contents as high as 50%.

Instead of a conventional SEM we used an environmental SEM (ESEM) for the EBD process.⁸ The ESEM allows imaging in the presence of up to 20 Torr of certain gases. Ionization of gas molecules above the surface allows the detection of secondary electrons for imaging. Here we show that this highly ionized gas, which constitutes our environmental gas, can also create a reactive environment which

reduces the C content of Au deposited by EBD. In addition, we simplified the usual subchamber setup for EBD. Generally, the sample is placed inside a subchamber within the SEM chamber to allow the presence of a gas around the sample without breaking the SEM vacuum. Instead of feeding the precursor gas into the subchamber from an external source, we put a small quantity of the organometallic compound in a built-in reservoir inside the subchamber (see Fig. 1). The reservoir communicates with the subchamber through a fixed $50\text{-}\mu\text{m}$ aperture and the sample is accessed by the e^- -beam through a fixed 1-mm aperture. We could not, therefore, vary the partial pressure of the organometallic gas, estimated to be ~ 130 mTorr above the substrate by comparing our growth rates with those reported in Ref. 6. Its exact value does not affect our findings, since it is constant while we vary P_{env} . Accurate control of the growth rate would require variable apertures, pressure gauges, and an electron dose gauge, as reported by others.^{5,6} Our efforts were directed toward improving the composition of the Au deposits by judicious choice of the environmental gas (Ar, Ar/ O_2 , or H_2O) and its partial pressure ($\sim 0\text{--}10$ Torr). The substrate was mounted close to the top aperture of the sub-

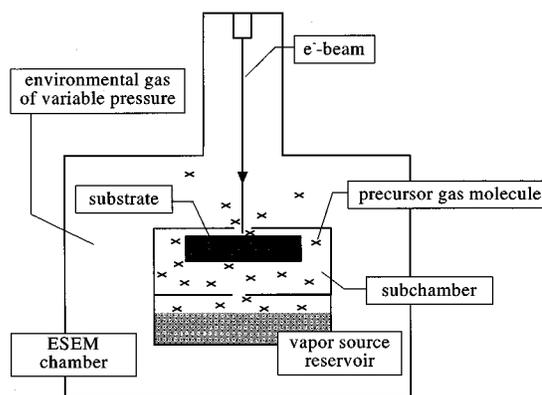


FIG. 1. Schematic of our simplified subchamber setup (the environmental gas, filling up the whole ESEM chamber, is not depicted for clarity).

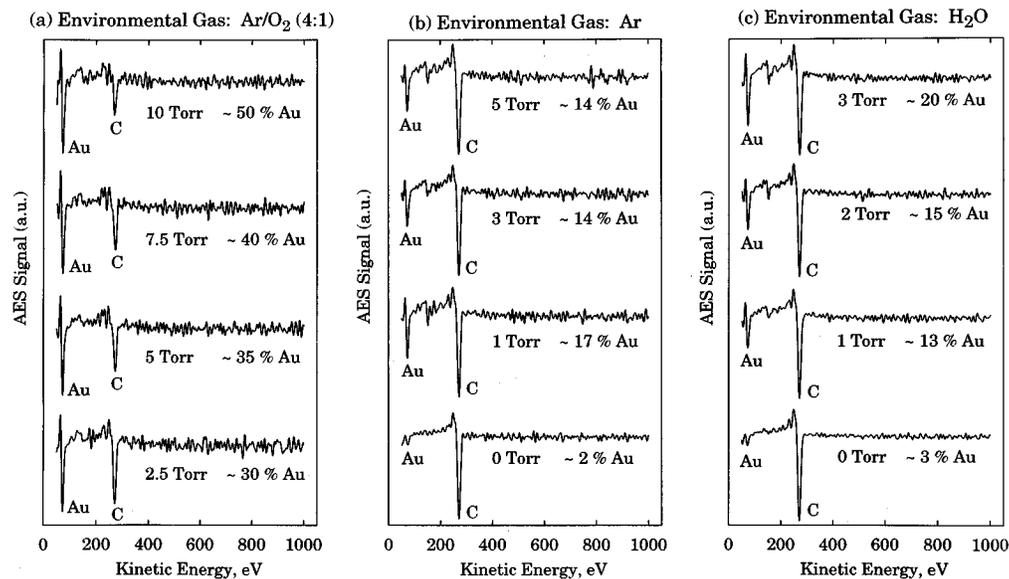


FIG. 2. Auger electron spectroscopy (AES) of Au deposits. Each spectrum was taken at the center of a $10\ \mu\text{m} \times 5\ \mu\text{m}$ thick film deposit created at the indicated environmental pressure P_{env} of (a) Ar/O₂ (4:1 ratio) mixture, (b) Ar, or (c) H₂O vapor. One Au:69 eV peak and one C:272 eV peak are visible in each spectrum. All plots are normalized to their highest peak, and only the ratio of the Au peak height to the C peak height is relevant and used to determine the indicated atomic percentages of Au and C. The corresponding Au composition ($\pm 5\%$) is shown above each spectrum. When P_{env} is dropped to 0 Torr [as in (b) or (c), bottom curves], hydrocarbon contamination deposition dominates and the Au content is very low.

chamber, and the whole subchamber-reservoir assembly⁹ was placed on the ESEM sample stage for each experiment. We emphasize that the precursor gas emanated from the reservoir and that the environmental gas was directly introduced into the ESEM chamber, both being present during deposition. We deposited Au from Au(CH₃)₂(hexafluoroacetylacetonate), a liquid with a vapor pressure of 700 mTorr at 20 °C, on an indium–tin oxide (ITO) substrate at room temperature. We did not observe a dependence of the composition on the beam current, magnification or energy (10–30 keV) settings. This is explained by the lack of selectivity in the chemical bonds ruptured by high-energy electrons. Hence we used the typical settings in ESEM imaging.

In each experiment, four rectangular ($10\ \mu\text{m} \times 5\ \mu\text{m}$)¹⁰ thin film (~ 20 – 40 nm thick) deposits were created under different values of P_{env} (± 50 mTorr) by rastering the e⁻-beam across those areas. The sample was then transferred in air to a scanning Auger microanalysis (SAM) system. Exposure to air caused the adsorption of a hydrocarbon layer on the deposits, which was removed by Ar sputtering the sample for a few seconds until the Auger C signal was minimized. Figure 2 shows the three representative experiments, corresponding to different types of environmental gases: (a) Ar/O₂, (b) Ar, and (c) H₂O vapor. The four Auger spectra in each experiment correspond to four rectangles deposited under decreasing values of P_{env} . Each spectrum was taken at the center of one of the rectangles, and did not show any In, Sn, or O peaks from the underlying ITO substrate or F or O peaks from the organometallic molecule. In Fig. 2(a) one observes that the C peak decreases, i.e., the Au content increases with increasing Ar/O₂ pressure. Note that 10 Torr of Ar/O₂ are equivalent to 2 Torr of pure O₂ and resulted in 50% ($\pm 5\%$) Au content. When Ar alone is used

instead as the environmental gas the Au content of the deposit is not significantly affected by changes in Ar pressure above 0 Torr and is low (around 15%), as shown in Fig. 2(b). A behavior similar to that of Ar/O₂ is observed when H₂O vapor is used instead [see Fig. 2(c)], but with an overall smaller Au content (up to 20% under 3 Torr). The bottom curves of Figs. 2(b) and 2(c) show the Auger analysis corresponding to deposition in the absence of environmental gas. Au contents lower than 12.5% (i.e., Au:C ratios lower than 1:7 as present in the organometallic molecule) were systematically observed when P_{env} was dropped below 0.1 Torr. This is a clear indication that hydrocarbon contamination in the ESEM chamber is being deposited at the same time as the organometallic compound. We note that, since contamination deposition is present in every experiment, our result of 50% Au composition represents a significant improvement. Although the absolute Au (or C) percentages varied ($\sim 10\%$) from experiment to experiment due to variations in the background carbon deposition, the three distinct behaviors shown in Fig. 2 were consistently observed throughout all our experiments. The qualitative dependence of composition on P_{env} is more clearly seen by examining an Auger map of the deposits. In the example shown in Fig. 3 we imaged the presence of Au in another group of four $10\ \mu\text{m} \times 5\ \mu\text{m}$ rectangles, each deposited under different pressures of H₂O as labeled. The brighter areas signal higher Au content and correspond to higher values of P_{env} .

The Ar/O₂ or H₂O gases, therefore, create a reactive environment that enhances the Au content of the deposit. We believe that the C in the deposits is being desorbed in the form of CO or CO₂ molecules at the same time as deposition occurs. The oxygen-containing species necessary for that reaction to occur are supplied by the environmental gas. Both the dissociation of precursor gas molecules adsorbed on the

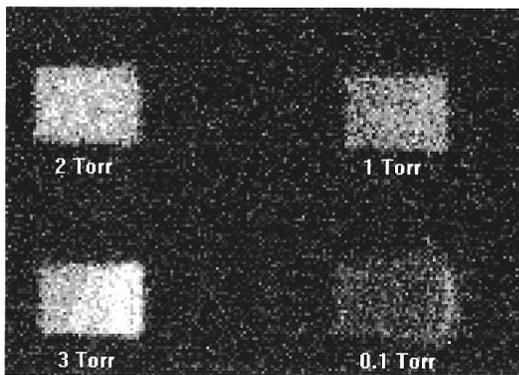


FIG. 3. An Auger map of Au deposits vs H_2O pressure in the environmental gas. Each pixel is assigned a gray level that corresponds to the intensity of an Auger peak of Au, depicting the relative abundance of Au. The rectangles were deposited under different H_2O pressures, as labeled, showing greater Au content with increasing pressures of H_2O in the environment.

sample surface and the ionization of environmental gas molecules above the surface generate highly reactive species, the recombination of which leaves the observable deposit. We explain the superior results with Ar/O_2 as compared to H_2O by its richer presence of O at the compared pressures. Using pure O_2 should yield better results.¹¹ The fact that Ar does not create a reactive environment is consistent with the inert nature of Ar.

We stress that the high P_{env} values used in our study, or the ESEM itself, are not essential to prove the idea that the presence of a second, reactive gas can reduce the carbon incorporation during EBD. It is probably the ratio of the partial pressures of the two gases that determines the composition of the deposits. One would expect, though, that high gas pressures result in a broadening of the EBD features due to scattering of the beam electrons. Surprisingly, we did not observe any dependence of the feature width on P_{env} below 5 Torr. Despite electron scattering, the linewidth of our EBD features was routinely 100 nm or less, as demonstrated in the structures shown in Fig. 4. It is possible that a concentric plasma sheath, and its associated electrostatic field, builds up around the beam and causes self-focusing of the beam.¹² In any case, since the growth rate increases with increasing partial pressure of precursor gas, lower total pressures of a similar mixture of gases could be used in high vacuum for higher-resolution deposition at a slower rate. Our simple sub-chamber did not allow us to perform EBD in the ESEM high-vacuum mode. With the ESEM we avoid the natural incompatibility between precursor gas pressure/growth rate maximization and the high vacuum requirements of a conventional SEM chamber. We achieved growth rates of 40 nm/s in fixed e^- -beam spot exposure (see Fig. 4).

We conclude that by performing EBD in the presence of an oxygen-rich reactive gas we are able to reduce the carbon content of the deposits. With little effort and a simple experimental setup based on an ESEM we achieved 50%-Au/100 nm-wide deposits. Using pure O_2 as the environmental gas and cleaner, more sophisticated setups should result in higher purities and smaller features.

The authors thank the Advanced Research Projects Agency, National Science Foundation and Ministerio de

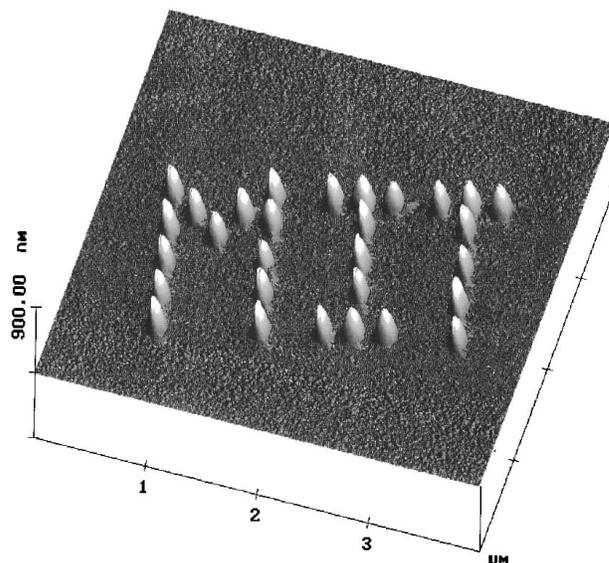


FIG. 4. The height or thickness of the deposits was measured with an atomic force microscope (AFM) (Ref. 13). Shown here is a tapping-mode AFM image of a pattern reading "MIT" that was written by sequentially depositing Au columns under 2 Torr of Ar/O_2 . Each column was deposited by stopping the e^- -beam in a given spot for 5 s and is around 100 nm wide and 200 nm high, yielding an average growth rate of 40 nm/s. Note that the columns appear wider than they really are due to convolution with the AFM tip. The e^- -beam was positioned by moving a mouse-driven cursor on the ESEM screen.

Educación y Ciencia (Spain) for partial support of this research. They used a commercial ESEM and SAM acquired by the C. M. S. E. (M. I. T.) under NSF Grant No. DMR90-22933 and were assisted by M. Frongillo, A. J. Garratt-Reed (ESEM) and E. L. Shaw (SAM). The AFM image was taken by J. Servat and A. F. With a Nanoscope III (Digital Instruments, Inc.) loaned to the U. B. by Instrumat, S.A. A.F. is grateful to J. R. Martin, J. del Alamo (M. I. T.), E. Lora-Tamayo (C. N. M.), R. Fontarnau (S. C. T.), M. Seco, F. Sanz, and J. Esteve for stimulating discussions. They are indebted to J. Melngailis for providing us with the gold compound.

- ¹A. N. Broers, W. W. Molzen, J. J. Cuomo, and N. D. Wittels, *Appl. Phys. Lett.* **29**, 596 (1976).
- ²S. Matsui and K. Mori, *Jpn. J. Appl. Phys.* **23**, L706 (1984).
- ³R. B. Jackman and J. S. Foord, *Appl. Phys. Lett.* **49**, 196 (1986).
- ⁴S. Matsui and T. Ichihashi, *Appl. Phys. Lett.* **53**, 842 (1988).
- ⁵H. W. P. Koops, R. Weiel, D. P. Kern, and T. H. Baum, *J. Vac. Sci. Technol. B* **6**, 477 (1988).
- ⁶K. L. Lee and M. Hatzakis, *J. Vac. Sci. Technol. B* **7**, 1941 (1989).
- ⁷K. T. Kohlman-von Platten, J. Chlebek, M. Weiss, K. Reimer, H. Oertel, and W. H. Brüngrer, *J. Vac. Sci. Technol. B* **11**, 2219 (1993).
- ⁸G. D. Danilatos, *Micron Microsc. Acta* **14**, 307 (1983).
- ⁹Our device will be described in detail in a forthcoming paper and was machined by J. Santana and D. Binagui (U.B.).
- ¹⁰The large size of the deposits and the conductive ITO substrate were chosen only to facilitate the Auger analysis. A microelectrode pattern on the ITO fabricated by T. Gardner served as a landmark to easily locate the deposits.
- ¹¹Pure O_2 could react with the oil of the ESEM mechanical pump.
- ¹²G. D. Danilatos, *Adv. Electron. Electron Phys.* **71**, 109 (1988).
- ¹³G. Binnig, C. F. Quate, and Ch. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).