

Focused Electron-Beam-Induced Deposition of 3 nm Dots in a Scanning Electron Microscope

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ABSTRACT

Electron-beam-induced deposition allows the creation of three-dimensional nanodevices within a scanning electron microscope. Typically the dimensions of the fabricated structure are from 20 nm to several micrometers. Until now the record for the smallest deposited feature in an SEM was 3.5 nm, measured by an indirect method. We have achieved a nanodot having a full width half-maximum of 2.8 ± 0.3 nm, measured directly in the same microscope after deposition.

Electron-beam-induced deposition¹ (EBID) allows the rapid creation of three-dimensional nanodevices directly within a scanning electron microscope (SEM). The deposited material depends on the precursor chosen, for instance, tungsten material can be deposited from the precursor tungsten hexacarbonyl. The decomposition of the gaseous precursor is caused by the interaction of an electron beam with a solid substrate. Typically the dimensions of the fabricated structure are in the range 20 nm to several micrometers; with further work nanowires and nanodots with single-digit nanometers lateral size can be made.^{2–7} A comprehensive review of EBID can be found in the reviews of Randolph et al.,¹ van Dorp et al.,⁸ and Utke et al.⁹

We present our efforts in performing high-resolution EBID in an SEM. Previous work in our group^{3,10} resulted in 0.7 nm nanodots being created by EBID using a scanning transmission electron microscopy (STEM).⁴ However it is also desirable to demonstrate high resolution EBID in an SEM since the instrument is more widespread and easier to use. In principle, in a modern SEM with a probe size below 1 nm, sub-2 nm small nanodots can be similarly achieved.^{11–13} Until now the record was 3.5 nm, measured indirectly by an AFM and correcting for the tip shape.¹⁴ A direct measurement of the deposited nanodots would be preferable since this decreases complexity and time-to-results.

We used an FEI Quanta field-emission gun (FEG) SEM operated at 30 kV and smallest spot size for which a resolution of 1.2 nm is specified and about 5 pA of current in the spot. A STEM detector was used to collect the image in dark field mode. The substrate material the nanodots were

deposited onto was a thin carbon film from Agar Scientific, S160-4H. In principle equally small nanodots can be produced on bulk substrates;¹¹ however, it is much harder to detect them afterward given the small deposited volume compared to the background signal from the substrate. The SEM is equipped with a fast electrostatic beam blander and the scanning during deposition is driven by external (custom) software.

To provide good contrast in the image of the deposited nanodots the precursor chosen was methylcyclopentadienyl platinum trimethyl (MeCpPtMe_3 , CAS: 94442-22-5), resulting in a material nominally containing 10 to 15 at % platinum with the remainder being carbon.¹⁵ Recently, from XPS studies on adsorbed layers of MeCpPtMe_3 , irradiated by electrons, the composition of the deposit was determined as PtC_8 .¹⁶ The heavy mass of the platinum should ensure a good signal in the dark field (DF) STEM detector despite the small volume of the deposit.

From previous work, we know^{4,13} that the key to success in nanodot deposition is low material growth rate and small deposition times. With that in mind the deposition parameters were as follows: 30 kV, spot 1, array $150 \times 150 \mu\text{m}$, dwell time 100 ms, 1 loop, spot mode for each dot, 15 nm separation distance between dots. The base pressure in the SEM chamber was 10^{-6} millibar before deposition and 10^{-5} millibar during deposition. No gas injection system (nozzle-based EBID) was used; instead the entire chamber was filled with the precursor. This reduced the precursor pressure (such that the growth rate would be lower) and ensured a more uniform gas flux across the sample. Depositions were performed outside normal working hours to minimize mechanical vibration contributions from the building and human

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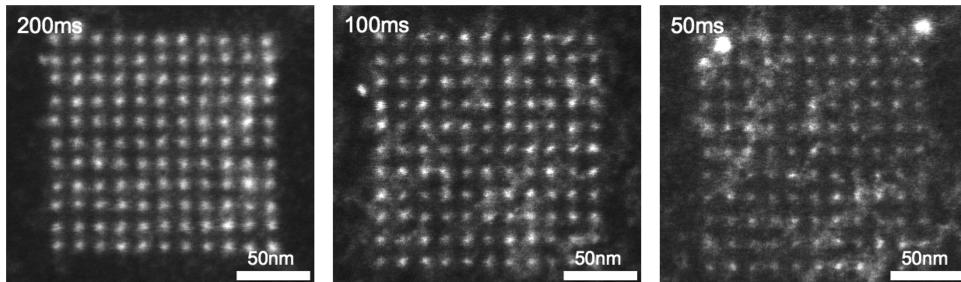


Figure 1. Dark field transmission image of three nanodot arrays deposited with the platinum precursor MeCpPtMe₃ on a thin carbon membrane with dwell times of 200, 100, and 50 ms.

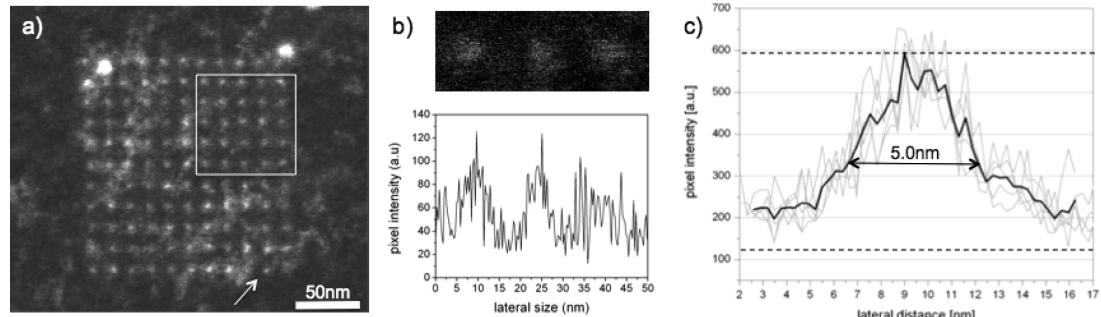


Figure 2. (a) Dot array with 50 ms exposure time and spacing of 15 nm. The arrow indicates the smallest dot of the array. (b) Some dots and their line scan, the half-maximum lies lower than the noise peaks. (c) The line scans of all the 25 dots in the square are added up resulting in a fwhm of 5.0 nm.

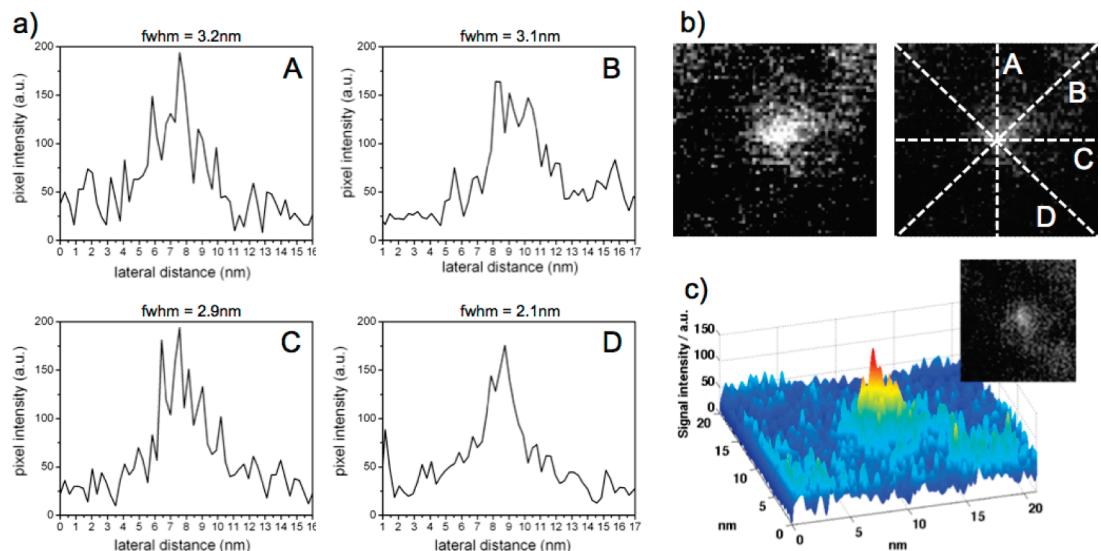


Figure 3. Nanodot with fwhm 2.8 ± 0.3 nm. (a) Line scans in four directions of the nanodot. (b) Postenhanced image of the dot on the left and on the right the line scan directions used to determine the fwhm. (c) A surface plot of the pixel intensity.

activity. Plasma cleaning of the chamber and substrate was performed before each experiment to minimize hydrocarbon contamination. After deposition the platinum gas is allowed to pump out for a few minutes, then one single high-resolution scan is made to image the deposited dots. This is therefore a direct and immediate *in situ* measurement of the dot properties, as opposed to reports in the literature where the dots were analyzed in a different setup (for instance AFM¹⁴).

Three typical arrays are shown in Figure 1. One may observe relatively good control over the deposit size at the higher exposure time, but at lower exposure time (from 100

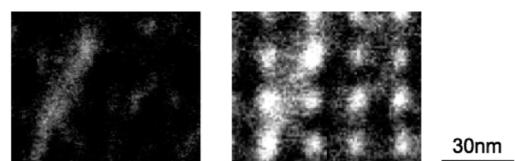


Figure 4. Image of the same area on the substrate before deposition and after. Nanodots deposited in the vicinity of substrate inhomogeneities appear significantly broader and presumably contain more mass, due to the extra electron scattering from the additional substrate material.

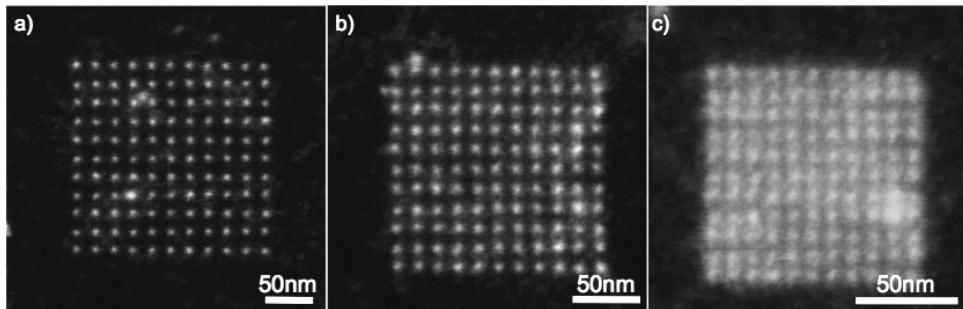


Figure 5. Decreasing the nanodot separation (20, 15, and 10 nm from left to right) but keeping the dwell time identical (200 ms) results in broader deposits. This additional growth due to secondary electrons re-emitted from neighboring deposits is known as the proximity effect.

ms and below) variations in intensity within the same array can be seen.

The full width half-maximum (fwhm) was measured using image analysis techniques both for the entire array (averaged) and for each dot in every array. The procedure to obtain the average fwhm is shown in Figure 2; however because of the variation in size and also position³ this value is less relevant than the measurement of individual fwhm's. In Figure 3, we show the smallest nanodot we found in one of the deposited arrays (indicated by an arrow in Figure 2a) as well as how the fwhm value was obtained. It has a fwhm of 2.8 ± 0.3 nm. The aspect ratio of these small deposits will be at most equal to one, analogous to results we obtained for a different precursor, using AFM to measure the height of the deposits.³ We believe this is a new world record for the smallest structure deposited by EBID in an SEM and also directly observed therein after deposition.

We noted there was a distribution of fwhm's within each array. This may be attributed to various reasons, such as mechanical vibrations or variations in the local precursor gas supply. The previously reported statistical nature of the deposition process³ might also contribute to the observed variations. Furthermore local substrate inhomogeneities may play an important role; an image of the substrate taken before deposition showed contrast features. These were attributed to local thickness and density variations of the carbon film. These denser or thicker areas emit a larger amount of secondary electrons compared to the other areas. EBID material growth is significantly affected by the amount of secondary electrons¹³ hence it is not unreasonable to expect that nanodots created at those areas will have a larger fwhm than those at other areas in the same array. Indeed this is what can be observed, as demonstrated in Figure 4, where an image of the same area on the substrate was taken before and after deposition: the nanodots deposited in the vicinity of substrate inhomogeneities appear significantly broader and presumably contain more mass due to the extra electron scattering from the additional substrate material.

In the course of depositing the nanodot arrays, another effect was noticed that directly impacts the minimum size of the nanodots: decreasing the nanodot separation but keeping the dwell time identical results in broader deposits. This additional growth, shown in Figure 5 (arrays with a pitch of 20, 15, and 10 nm but constant exposure time of

200 ms), is due to secondary electrons scattered and re-emitted from neighboring deposits and is widely known as the proximity effect.^{17,18} Therefore to obtain the smallest possible nanodot, only a single dot, rather than an entire array, should be deposited. However this leads to difficulties in locating the nanodot after deposition. Furthermore, the final goal is to make nanostructures embedded within and around other structures, so in principle efforts should be made in creating closely spaced dots and other such structures, and dealing with the proximity effect by applying corrections to the patterning (for instance by adjusting the beam dwell times), along similar lines as already demonstrated by van Dorp.¹⁰

The main reason we have not made even smaller nanodots yet is the difficulty in imaging them after deposition. The deposited volume becomes so small that the signal from the nanodot is buried in the noise of the signal from the substrate. Though difficult to quantify numerically, we have seen qualitatively that with even smaller dwell times, smaller nanodots can be created. The measurement problem is one of obtaining adequate signal-to-noise and may be solved in the future by using thinner films or by using a STEM detector with more segments and better sensitivity.

In summary, we have created a nanodot with a fwhm of 2.8 ± 0.3 nm, measured directly with the dark field transmission signal in the same SEM soon after deposition (Figure 3). We discussed the current limitations of the experiments: the detectability of the just-performed deposit, proximity effects during growth, and local inhomogeneities in substrate secondary electron yield. We are confident that even smaller nanodots can be deposited in the SEM provided these issues can be addressed.

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