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Local deposition of high-purity Pt nanostructures by combining electron beam induced deposition and atomic layer deposition

A. J. M. Mackus,^{1,a)} J. J. L. Mulders,² M. C. M. van de Sanden,¹ and W. M. M. Kessels¹

¹Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

²FEI Electron Optics, Achtseweg Noord 5, 5651 GG Eindhoven, The Netherlands

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An approach for direct-write fabrication of high-purity platinum nanostructures has been developed by combining nanoscale lateral patterning by electron beam induced deposition (EBID) with area-selective deposition of high quality material by atomic layer deposition (ALD). Because virtually pure, polycrystalline Pt nanostructures are obtained, the method extends the application possibilities of EBID, whereas compared to other area-selective ALD approaches, a much higher resolution is attainable; potentially down to sub-10 nm lateral dimensions. © 2010 American Institute of Physics. [doi:10.1063/1.3431351]

For the fabrication of future nanodevices, nanomanufacturing approaches are required that are able to create nanostructures by bottom-up processing. Challenges for these approaches lie in the control of dimensions and material properties as well as in the processing compatibility with device components. A direct-write technique that has recently attracted much attention due to its ability to directly deposit nanostructures with sub-10 nm lateral dimensions is electron beam induced deposition (EBID).^{1,2} It has been demonstrated that nanoscale dots as small as 3 nm in diameter can be fabricated in a scanning electron microscope (SEM) by EBID, while it is expected that even higher resolutions are attainable.³ A significant drawback of the technique, which currently limits its application possibilities, is the low material purity that is typically obtained.² When a metal-organic precursor is used, a relatively large amount of carbon is deposited along with the desired element, and consequently, the material can generally be described as a polycrystalline material consisting of small metal grains embedded in a matrix of amorphous carbon.⁴ For Pt nanostructures, which are considered to provide electrical contacts in future nanoelectronics,^{5–7} a Pt purity of only ~15 at. % is typically achieved by EBID and resistivity values in the order of 10^6 – 10^7 $\mu\Omega$ cm have been reported.⁸ Several methods to improve the purity of the EBID deposits have been proposed as recently reviewed by Botman *et al.*,⁸ but these are almost all accompanied by processes that may jeopardize the functionality of the material or they are not compatible with other processing steps. For Pt and many other metals practically none of these methods have enabled the deposition of low-resistivity material required for the envisioned applications. Atomic layer deposition (ALD) on the other hand allows for the deposition of high-purity (~100%) and low resistivity (13 ± 1 $\mu\Omega$ cm) Pt films^{9,10} with a submonolayer accuracy of the film thickness. However, ALD provides no intrinsic control of the film growth in lateral dimensions. A possibility to achieve area-selective deposition by ALD is by tailoring the surface properties prior to growth as ALD processes rely

critically on surface reactions. Previously, several area-selective ALD approaches based on masking designated areas by resist films¹¹ or self-assembled monolayers¹² using top-down patterning techniques have been investigated, but to date only the fabrication of structures with micrometer dimensions have been demonstrated by these approaches.

In this Communication, an approach for the fabrication of high-purity Pt nanostructures is proposed which combines the patterning capability of EBID with the ability to deposit high quality materials with good thickness control of ALD. The concept allows direct local deposition of high purity material with an ultimate control of lateral and thickness dimensions. Proof of concept is demonstrated in this work, the underlying mechanisms are discussed, and the material properties relevant for Pt nanowiring applications are addressed.

The *combinatorial EBID-ALD* approach is illustrated in Fig. 1. It consists of two steps, first a seed layer is deposited in a predefined pattern by EBID and subsequently this pattern is built bottom-up in thickness by ALD. Since the bulk

FIG. 1. (Color online) Schematic representation of the combinatorial EBID-ALD approach to deposit nanopatterns. The two-step method comprises seed layer deposition in a predefined pattern by EBID followed by bottom-up building of the pattern by area-selective ALD. The ALD process consists in turn of two alternating half-reactions A and B. For Pt the same metal precursor (MeCpPtMe_3) is used for EBID and ALD whereas the second reactant for ALD is O_2 .

^{a)}Electronic mail: a.j.m.mackus@tue.nl.

FIG. 2. SEM images of (a) an array showing nine $5 \times 5 \mu\text{m}^2$ seed layers (A–I) of various thicknesses as deposited by EBID, and (b) an identical EBID seed layer pattern on which 400 ALD cycles were performed. (c) Figure legend listing the thickness values of the seed layers shown in (a) and of the deposits depicted in (b) (top and bottom number, respectively). The seed layer thicknesses were estimated based on the deposition dose and a value of the EBID yield determined prior to the deposition. The accuracy of this procedure was independently verified by AFM. EDX was employed to determine the total thicknesses of the deposits after ALD. The substrate was Si(100) covered by 50 nm ALD-synthesized Al_2O_3 .

of the material in the nanopattern is deposited by ALD, the material quality is similar to that of ALD films which means that the material properties are considerably improved over those obtained by EBID only. In addition, the combinatorial EBID-ALD approach has the potential to alleviate another drawback of EBID, namely its low throughput. A higher overall throughput is attainable when the deposition of a thin seed layer pattern is combined with the parallel ALD building of (a number of) samples with an extensively patterned surface. Furthermore it is important to note that, in contrast to most other area-selective ALD methods, the combinatorial EBID-ALD approach relies on locally stimulating ALD growth instead of deactivating specific areas by masking. As starting surface for the ALD step the EBID seed layer is required to stimulate ALD growth either by enhancing the precursor adsorption and/or by catalyzing one of the surface reactions. On the substrate material no growth should take place, in other words, the ALD surface reactions should occur selectively on the EBID seed layer.

For combinatorial EBID-ALD of Pt nanostructures, the thermal ALD process of Pt from (methylcyclopentadienyl)-trimethylplatinum (MeCpPtMe_3) and O_2 dosing as studied by Aaltonen *et al.*¹³ and Kessels *et al.*¹⁴ was adopted. In this process, oxygen atoms are created at Pt surfaces by dissociative chemisorption reactions of O_2 and these oxygen atoms oxidatively decompose MeCpPtMe_3 molecules when these are exposed to the surface.^{13,14} The dissociative chemisorption of O_2 is strongly surface dependent as well as sensitive to the operating conditions (i.e., temperature and pressure), and this property can be exploited to obtain area-selective deposition. In case O_2 pressures below 0.1 Torr are employed, an extremely long nucleation delay takes places on an oxide substrate, while growth quickly initiates on a Pt covered surface.¹⁰ Hence, area-selective ALD can be achieved on the EBID defined seed layer by carefully choosing the O_2 pressure.

Figure 2(a) shows a SEM image of a matrix of nine EBID seed layers prepared in a FEI Nova 600 DualBeam system using the same MeCpPtMe_3 precursor as employed for ALD. After EBID seed layer deposition, the samples were taken out of the dualbeam system and transferred to the

ALD reactor. ALD was carried out at a substrate temperature of 300 °C and at an O_2 pressure of 0.02 Torr. A SEM image of an identical sample but on which 400 ALD cycles were carried out is shown in Fig. 2(b). From the difference in contrast for the deposits it is concluded that ALD growth can successfully be initiated on an EBID seed layer. SEM and energy-dispersive x-ray spectroscopy (EDX) inspection of the substrate surface in between the deposits shows no evidence of Pt growth indicating that the ALD process occurs selectively. Furthermore the images reveal that an EBID seed layer of only 0.5 nm is already sufficiently thick to initiate ALD growth. Taking the relatively low material purity of the EBID seed layer (~ 15 at. %) into account, this means that a layer equivalent to less than a monolayer Pt atoms is sufficient for dissociative chemisorption of O_2 and hence, to start the area-selective ALD process. After an initial nucleation period, the thickness increase per cycle is expected to be equal to the steady-state growth per cycle of the ALD process (i.e., 0.045 ± 0.002 nm/cycle or $(3.0 \pm 0.2) \times 10^{14}$ cm^{-2} Pt atoms/cycle)¹⁰. The 16 nm thickness of the deposit labeled “C” deviates from the growth expected for 400 ALD cycles, which suggests that there is a nucleation delay on extremely thin seed layers.

The composition of the material was analyzed by EDX. All peaks present in the EDX spectrum could be assigned to Pt, and from this it is concluded that the Pt purity is virtually 100%, with the carbon detection limit estimated at 5 at. % (acknowledging the limitations of EDX for detecting light-element impurities). This high purity is line with the high material quality obtained for ALD synthesized Pt films for which the impurity levels are determined to be below the detection limits of Rutherford backscattering spectroscopy (< 5 at. %)¹⁰ and x-ray photoelectron spectroscopy (< 1 at. %).¹⁵ Apparently the carbon in the EBID seed layer does not notably contribute to the impurity level of the material. These analyses demonstrate that unparalleled high purities can be achieved for Pt nanostructures by the combinatorial EBID-ALD approach when compared to EBID and other related methods.

FIG. 3. SEM image of an 6×6 array prepared by EBID of laterally small Pt seed layers followed by 200 cycles ALD. The small seed layers were deposited by operating the SEM in spot mode. The elongated shapes of the deposits reveal that the focused electron beam suffered slightly from astigmatism.

Atomic force microscopy of a 25 nm thick deposit initiated on a 2 nm thick EBID seed layer revealed that the method results in smooth deposits with a root-mean-square roughness of 0.5 ± 0.3 nm comparable to the roughness of a film deposited by thermal ALD on a plasma-assisted ALD grown seed layer (0.7 ± 0.3 nm).¹⁰ The roughness is lower than literature values of films deposited by thermal ALD without a seed layer,^{9,10} which can likely be attributed to the fact that ALD growth quickly initiates on the EBID seed layer as layer-by-layer growth instead of island growth. Examination of the microstructure of a 40 nm thick deposit with electron backscatter diffraction (EBSD) showed that the material is polycrystalline Pt and that the grains have a preferred orientation with their (111) lattice planes parallel to the deposit surface, which is also the texture found for Pt ALD films.¹⁰ Based on the abovementioned observations it is concluded that the Pt nanostructures fabricated by combinatorial EBID-ALD have comparable good material properties as Pt films deposited by ALD. It can therefore be expected that the resistivity of the Pt nanostructures is also low and comparable to the resistivity of ALD films ($13 \pm 1 \mu\Omega$ cm), which makes Pt nanostructures synthesized by combinatorial EBID-ALD suited for nanowiring applications.

Laterally smaller features were fabricated by depositing an array of nanoscale seed layers and thickening the structures by 200 cycles ALD. A SEM image of the resulting array is depicted in Fig. 3. The features were only detectable by SEM after the ALD building step and not after the seed layer deposition step which indicates that the structures are predominantly built by ALD. The deposits have a size in the order of 80 nm and consist of several small dots of approximately 20 nm diameter. It appears that the deposits are formed by ALD initiated at small Pt nucleation sites which may be the individual metal grains (present in the EBID seed layer material) or conglomerates of such grains. Note, that the lateral size of the dots is roughly equal to the Pt thickness

expected for 200 cycles ALD. This implies that if the growth starts immediately the nucleation sites have to be only a few nanometers in size. Because the deposits also laterally broaden during the ALD building step, combinatorial EBID-ALD is limited to the fabrication of low aspect ratio structures. The experiment clearly illustrates that ALD can be initiated on EBID seed layers with very small lateral dimensions. Since, it has been demonstrated that deposits of a few nanometers in size can be created by EBID,³ it can be stated that combinatorial EBID-ALD approach allows the fabrication of structures down to sub-10 nm resolution. This is a much higher resolution than what is currently accessible using other area-selective ALD approaches.

In conclusion, we have introduced an approach for the fabrication of Pt nanostructures consisting of seed layer deposition by EBID followed by selective, bottom-up building of the structure by ALD. Especially the high material quality in terms of Pt purity that can be achieved with this approach is a major improvement compared to the synthesis of such nanostructures by exclusively EBID. The resolution of the method is higher than that of other area-selective ALD methods, and a higher throughput than for EBID is achievable when processing large footprints of Pt nanostructures. We expect that the approach is extendable to more material systems, particularly including (but not necessarily limited to) transition metals for which the ALD process shows similar properties with respect to film nucleation as the Pt ALD process. Because it combines direct-write processing, dimension control, and high material quality, we believe that the combinatorial EBID-ALD approach, which can also be classified as *direct-write ALD*, has a wide application range and can become an enabling technology for future nanoelectronics.

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