Selective In-Situ Atomic Layer Deposition on Structures Created with EBID


INTRODUCTION
Recent developments in nanotechnology have an inherent need for the creation of very small, nanoscale structures. The most commonly applied techniques for this are often based on lithography methods. Although these can be very successful, they require multiple process steps, and in the case of optical lithography, a relatively expensive mask set. While optical lithography is well suited for mass production, the flexibility in the test phase of a process is low. Electron beam lithography does not require a mask set, but it is still mask based and only suited for two dimensional (2D) structures that all have the same height. Nano imprint lithography (NIL) has a direct three dimensional (3D) capability but also relies on the application of a mask (stamp) and the requirement for a dedicated alignment strategy.

In the case of rapid prototyping, as applied in nanotechnology, other direct techniques, such as focused ion beam (FIB), for the local removal of material can be quite beneficial. Similarly an ion beam or an electron beam, as available in a dual-beam FIB-SEM, can be used to deposit structures locally with excellent control of position and height. The technique for deposition is referred to as IBID (ion beam-induced deposition) or EBID (electron beam-induced deposition) [2]. Although it is a serial technique (and thus relatively slow) it can accommodate the growth of 3D structures by direct deposition. Because the beam is driven by a computer-controlled patterning engine, the flexibility towards modifications is very high, while the lateral dimensions can be below 10 nm. This makes the technique well suited for rapid prototyping.

In this paper an extension of this EBID technique is presented, using a seeded growth by EBID, followed by an additional, selective growth by atomic layer deposition (ALD).

ELECTRON BEAM INDUCED DEPOSITION (EBID)
The principle of EBID is quite simple (see Figure 1a): within a SEM chamber a precursor gas is released in the vacuum that subsequently adsors on the surface of a substrate. When the electron beam hits the surface, the (secondary) electrons induce the decomposition of the precursor molecules into volatile and non-volatile parts. The volatile part is pumped away while the non-volatile part resides as deposited material on the substrate, at those

Figure 1:
Schematic overview of the EBID process (a), the ALD process (b) and the combined processes (c), including the most relevant features of each process.
locations where the beam has irradiated the substrate.

Often, precursor molecules applied for EBID are the same as those used in chemical vapour deposition (CVD)-based processes and therefore a wide variety of materials is commercially available. Ideally a precursor molecule is split completely into the base atom and its ligands such as CO. For example, W(CO)₆ would ideally be decomposed following the reaction:

\[ \text{W(CO)}₆ + \text{electrons} \rightarrow \text{W} + 6\text{CO}^+ + \text{electrons} \]

In practice however, the decomposition is not 100 percent complete, and hence, the deposited material contains other atoms from the precursor. For most precursors, this refers to carbon that is present in the precursor molecule. In the case of W(CO)₆ for example, one would roughly get 37 atomic percent (at%) W, 35 at% C, and 28 at% O. For this reason the small deposited structure does not have the same properties as bulk W material would have. Another example is the use of methyl cyclopentadienyl platinum trimethyl (MeCpPtMe₃) for Pt-EBID, which leads to around 16 at% Pt and 84 at% C [3]. Due to the high content of carbon, the resistivity of the material is not even close to the value for bulk material (~10⁴ µΩcm versus 11 µΩcm). In short: the lower purity of the EBID technique puts a limit to its applicability.

When comparing EBID to IBID the characteristics slightly change. For IBID the process is roughly a factor of 100 faster, the resolution a factor 2-5 times worse while the substrate is slightly damaged at the onset of the process due to the milling by the energetic Ga⁺ ions, and the deposition always contains implanted Ga. Although Ga would help to increase the conductivity, its presence in magnetic, isolating, optical or bio-active structures is not favoured. Hence it is useful to concentrate on EBID as a nanotechnology prototyping technique, with the aim to improve the purity and bring the local nanoscale property in line with expectations derived from the bulk material.

Recently various methods have been developed to improve the purity of the material: optimization of the deposition parameters, improvements in the control of the vacuum conditions of the system and post-processing steps such as annealing in an oxygen or hydrogen atmosphere [4]. For oxygen, the carbon can be combusted, if the material of interest is a noble metal, unlikely to oxidize. In addition, the use of other precursors may help to improve the purity of the deposition such as the use of the Pt(PF₃)₄ precursor: a carbon-free precursor for the deposition of Pt [5]. The disadvantage of this precursor however, is the release of fluorine during the deposition process, which may simultaneously etch the substrate. It has also been shown that the precursor CO₂(CO)₆ can be used to produce local depositions of Co at a purity >92 at% [6]. So depending on process and chemistry, the purity can be good enough for a nanotechnology application.

Although post-annealling is also a nice way to (further) improve the purity, the release of material from the deposition certainly also changes its shape and hence shape control is lost to some extent. In addition not all substrates are suited for annealling temperatures, typically up to 400-500°C. However, despite the aforementioned challenges, today EBID technology is ready to serve the first applications such as contacting nanotubes and nanowires for sensor and transistor applications. A general example of an EBID structure is shown in Figure 2, using the Pt deposition process.

**ATOMIC LAYER DEPOSITION (ALD)**

ALD has recently become a very popular technique as it is well suited for the production of high purity and high quality thin films with excellent thickness control [7]. Compared to CVD it is relatively slow, but the overall step coverage is very good while the process generally occurs at much lower substrate temperatures. The technique is based on the alternate and cycle-wise exposure of a substrate to precursor molecules and an activator gas. Reactions are self limiting at sub-monolayer level (see Figure 1b) and the amount of molecules applied in the reaction is not critical, once a certain threshold is exceeded. The cyclic process creates roughly one atomic layer per full cycle (hence the name atomic layer deposition) and by repeating the process the thin film is grown. Not only thin films can be made this way, but also stacks of nm-thick layers (nanolaminates) because the precursor and activator can (in principle) be changed per full cycle. Generally the growth process is based on surface chemistry of adsorbed species in combination with exposure to an activator (molecules, radicals and/or ions) and many processes are being developed for a variety of materials ranging from a single element metal to (doped) oxides, nitrides, carbides and salts [8].

As an example, metal deposition can be realized for Ru using a ruthenocene precursor (RuCp₂), Pd using Pd(hfac)₂ and Pt using MeCpPtMe₃. ALD is applied industrially to create very thin films as buffer layers or dielectrics in semiconductor applications. The search for new chemistry and the actual implementation in a commercial tool can be a tedious and long process. Especially the excellent step coverage and the relative low temperature can be a critical factor to apply ALD instead of CVD. Of course ALD is a thin film technique and the actual patterning to obtain lateral resolution must be arranged by other techniques such as lithography.

Recently a thermal Pt ALD process using...
MeCpPtMe₃ with oxygen gas has been developed [9] and studied in more detail using a cold-wall ALD reactor [10]. From the latter study it is possible to compare the most relevant characteristics of the ALD process and the previously discussed EBID process, both for the deposition of Pt (Table 1).

Note that under certain process conditions, thermal ALD can be realized on a substrate that already has a Pt surface finish, acting as a seed layer. This first coating can be made by regular sputtering but also by plasma-assisted ALD (with more energetic particles), after which the thermal ALD process can be applied for further growth [10]. Under these same conditions, the thermal ALD process does not start on a base SiO₂ substrate as shown in Figure 3. This opens the way to selective growth: the thermal ALD process is selective towards the substrate and enables growth on Pt but not on SiO₂.

It should also be noted that the pressure regime plays a critical role here and only a certain oxygen pressure window will show this behaviour. If the pressure is too low, the thermal ALD will not start at all; if the pressure is too high the thermal ALD will also grow on the bare SiO₂ and hence the selectivity is lost.

As shown in Table 1, the base vacuum conditions in an ALD reactor and in the SEM/Dual-Beam chamber can be very similar. Therefore it is relatively straightforward to embed ALD processes in a SEM dual beam.

**COMBINATION OF THE TWO TECHNIQUES**

The most important characteristics for both processes, as shown in Table 1, are quite complementary: the material purity of ALD is very high while for EBID it is low. ALD has no lateral resolution as it is a thin film technique, while EBID resolution is very high. Both processes use the same precursor. The interesting question is whether or not the combination of the two techniques can benefit from ‘the best of both worlds’.

To provide an answer to this question, a new process has been developed where EBID is used to create a thin seed layer, which is then exposed to the ALD process to selectively grow Pt on top of the seed layer (see Figure 1c). This process was first tested in two separate instruments and has shown to work well even for very small seed layers with an estimated thickness of ~1 nm only [11]. The EBID seeded ALD structures have a purity of >95 at% and a microtexture similar to thermal ALD-grown thin films. The process remains selective up to a thickness of at least 100 nm when using SiO₂ as a substrate. The total process speed for EBID and ALD can also exceed the process speed of EBID alone. Assuming an ALD growth of 0.045 nm/cycle and a cycle time of 5 seconds in combination with a EBID seed layer of 2 nm and an EBID yield of 10⁻³ μm²/cm² at a 1 nA beam current, the combined process is faster than EBID alone for coverage of areas larger than 400 μm².

It is interesting to study the possibility to create patterned ALD structures in situ, i.e. the growth of the ALD film is realized in an SEM or dual beam, directly following the local EBID depositions. Because the applied pressures during ALD are critical it is important to have them well defined. The oxygen pressure applied during the activation cycle is quite high (typically 10⁻² mbar or more). The in-situ ALD can basically be realized using two different strategies:

1. Use of the system’s specimen chamber as a reactor at equal pressure. This method operates with the column valves closed, but does require a system modification because the level of 10⁻² mbar is not a standard pressure of the system, and hence interlocks will interrupt the system. So the main system has to be modified to accommodate the temporary higher pressure during the ALD oxygen cycle. It should be noted that the supply of the Pt precursor is through a standard gas injections system and not through a large valve to the chamber. Hence the precursor supply is local anyway. It should also be noted that for the safety of the total system, ALD growth has to be induced at the sample only and not on other (delicate) parts of the system, as they may lead to malfunctioning, for example of the optical encoders of the stage.

2. Use of a localized oxygen flux on the sample by an additional local supply system. This method has the advantage that both the oxygen and the Pt precursor are supplied locally through a needle (typical internal diameter 250 μm) so the total system pressure in the chamber remains low. The disadvantage is that the actual pressure on the sample is not known very well and that the sensitivity for the needle/sample geometry is quite high. It also sets a bit of a limit to the lateral field size that can be applied because there is a pressure gradient over the sample surface. However, in practice this is no problem as the interest is in the creation of small structures anyway, and the variations over a width of 100 μm are around 10% only.

As a first test for the second strategy mentioned above, a setup with two opposite nee-
dles was used and by a full, automated control the valves were opened and closed at pre-defined moments. This needle-based ALD set up used typical exposure periods of 10 seconds on/off. By tuning the process selective in-situ growth has been achieved (Figure 4b). The thickness of the local ALD structure has been determined in situ by EDX (see Appendix).

CONCLUSIONS AND OUTLOOK

It has been shown that Pt can grow selectively by thermal ALD on seed structures made with EBID, using the same precursor MeCpPtMe₃ for both processes. The purity and lateral definition of the structures are both very good and reflect the strengths of both techniques, leading to high purity, high resolution Pt structures. The implementation of ALD in a dual-beam SEM/FIB needs careful consideration and the strategy with local supply only, has been shown to be effective. This strategy is favourable because the process is localized and is safe for some of the delicate instrument parts such as stage encoders and detector. The observed gradient in the structures can be optimized if necessary, by change of the needle design. The total process can be executed without chamber vent and the ALD process can easily be run several hours – over night – without operator presence. The additional diagnostic energy-dispersive X-ray (EDX) method for determination of the thickness is very fast and convenient at the development phase of the ALD process and the confirmation of selectivity. The total process has the potential for full automation and unattended operation. The result shown in Figure 4b is a first result obtained and needs further optimization. The process time, for the creation of the EBID seeds is very short, as a seed layer of only 1 nm is enough to start the successive thermal ALD process. A typical patterned seed layer with a total area of around 400 µm² can easily be made in less then a few minutes. Because the pattern capability and resolution of the EBID process can now be combined with high quality, selectively grown Pt, the application for nanotechnology is within reach.

Future developments may result in further optimization of the current process as well as in exploration of other material combinations for both the seed layer and the ALD process. In addition, application to nanotechnology related issues, such as the contacting of sensor wires, can be tested in view of the compatibility with the new process.

APPENDIX

For the development of an ALD deposition method for (metal) films, an in-situ thickness measurement is very useful. Optically, a very high sensitivity can be obtained by spectroscopic ellipsometry through measurement of the polarization changes of circularly polarized light reflecting from a surface during growth: individual layers can be measured so that each ALD growth step can be confirmed. The sensitivity of this method is very good (< 0.5 nm) and useful to study the growth process. The optical signal could also be used in a control feed back loop. For metal layers the thickness can be measured as long as the substrate is optically still transparent: once the film thickness is >30 nm the method gradually looses its accuracy.

Although spectroscopic ellipsometry is quite frequently applied in ALD studies, for very small structures this method is inadequate as the spot diameter is (much) larger than the structure size, while for larger structures extensive in-situ alignment is required. To study the ALD direct growth in a dual beam SEM/FIB it is very valuable to have an in-situ measurement of the film thickness similar to the optical measurement method in a dedicated ALD reactor. For this reason an EDX-based method has been developed that allows the local measurement of the film thickness. At a given primary energy of the electron beam the EDX signal is a mix between Si and Pt. So by normalizing the Pt net peak intensity to the sum of both peak intensities (SiKα and PtM) a parameter can be defined that represents the local Pt thickness. By calibrating this parameter to the optically measured large area thin film, the graph in Figure A1 was made.

As can be seen from Figure A1, the sensitivity of the method is quite good and the linear part of the curve (<40 nm) indicates that thickness variations of around 2 nm can be monitored. The lateral resolution of this method is estimated to be around 0.5 µm, as determined from Monte Carlo scattering calculations. It should be noted that it is possible to tune the curve shown in Figure A1, by using different beam energy in the range 3.5 < E < 30 kV. The minimum level is dictated by the requirement of PtM excitation while the upper limit is given by the instrument. For an energy lower than 5 kV the curves will be compressed to the left, showing an increased sensitivity towards lower thickness. For high energy the curve will be amplified to the right, enabling the measurement of much thicker films up to >2 µm. In that case the calibration method has to be adapted for example to the use of a FIB-based cross-section measurement of a series of ALD grown pads. The method has shown to be very convenient, in situ, fast and accurate, though not to the level of one single ALD cycle.

As an example the method has been applied to confirm local uniform growth of a 7 µm x 7 µm ALD grown pad by a line scan analysis using the EDX thickness parameter (Figure A2). The error indicated in the graphs is the statistical error in the EDX counts.

REFERENCES