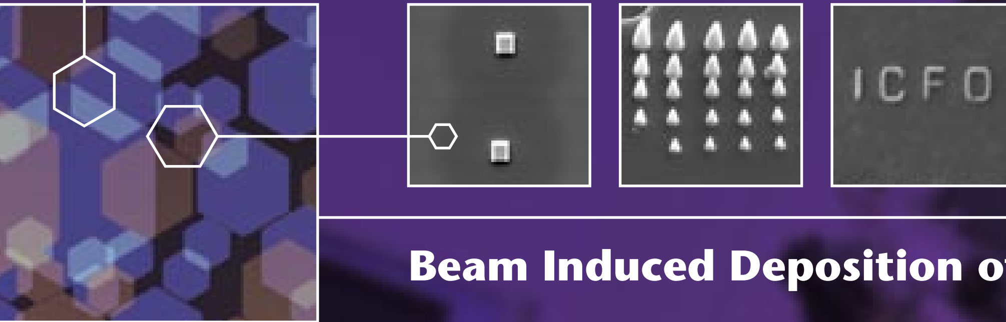
APPLICATION NOTE

FEI COMPANY™



Beam Induced Deposition of Gold

Create nanosized gold structures

Key benefits:

- direct, serial deposition of small gold deposits for application in nanotechnology
- compatible and embedded FEI™ solution, using the GIS
- creation of any structure by patterning
- complementary to e-beam litho / CVD

Introduction

The interest in local deposition of gold structures is increasing. Gold is an attractive element for its optical (near field) characteristics, for its ability to allow binding to thiol groups that in turn are coupled to biological materials such as proteins, for its electrical conductivity and for its low chemical reactivity with other elements. As gold is very heavy it is also a good material for simply depositing mass. So far, many gold structures have been created by optical or e-beam lithography, followed by for example sputtering and resist lift-off. Possible disadvantages of this technique are: it is only suited for flat samples, there are multiple process steps and all structures have the same height.

One of the precursors that can be used for this deposition is the one used in the FEI GIS system: dimethyl Au(III) acetyl acetonate. This chemical allows depositions to be created with both the electron beam and the ion beam, but it is relatively expensive and not very stable. Once the system is set up properly, it can be used routinely and a further characterization of its properties is described in this application note.

Deposition characteristics: yield, size, resistance and decay

- Electron beam yield: One of the deposition characteristics is the deposition rate or the yield. This is calculated from an area deposit, using an 18 kV beam, a beam current of 1.8 nA and a volume of 2 x 2 x 0.950 µm, resulting from a 40 minute exposure: the yield is 9. 0^{-4} µm³/nC.
- Ion beam yield: To determine the ion beam deposition yield, an area deposit has been created with a relative low beam current of 100 pA. Note that a check with beam currents of 1 and 7 nA did not reveal any deposition i.e. for these high currents, the milling component is larger than the deposition component. This indicates that for high ion beam currents, the flow of precursor molecules is too low to compensate for the milling. Using a 100 pA ion beam a 10 x 10 µm deposition with a height of 435 nm was created in a period of 7 minutes. This implies a yield of around 1 µm³/nC. The deposition rate is (as expected) noticeably higher than the corresponding electron beam deposition rate.
- Small structures: Creation of very small nanoscale structures with gold is very well possible, using the patterning capability of a DualBeam™. Note that any deposition has a starting process where the deposition grows both laterally and vertically and a saturation phase where the growth is only vertical. A real minimum lateral feature is terefore not very high. As an example a frame was created with a width of 15 nm and a height of 14 nm (determined by tilting the sample). For the creation of very small structures, a high kV electron beam at optimum focus and with

the system in immersion mode, gives the best result (see figure 1).

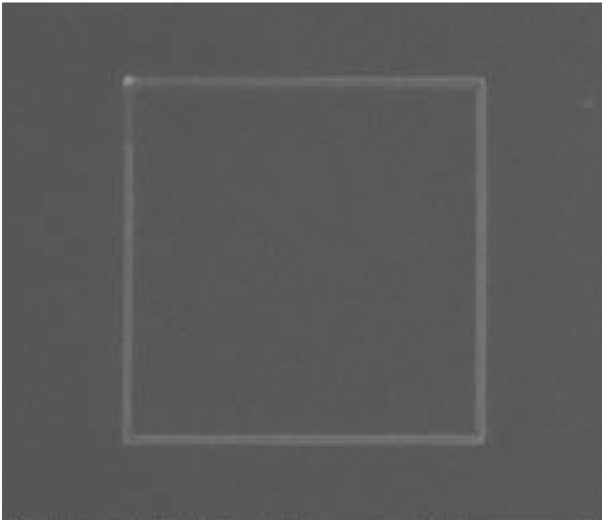


Figure 1: Au deposit on Si of a 500 nm frame, with a linewidth of 15 nm. Conditions: Nova™ 600 NanoLab using 18 kV, spot 2, Mode II and a total writing time of 2 minutes. The height of 14 nm was estimated from imaging the structure at a 45 degree tilt.

- Resistance: A dedicated patterned wafer allows to characterize the specific resistance of the material using a four point probe method. For this reason a deposit was created (figure 2) with the ion beam over a length of 100 µm, making contact with all four pads to allow a balanced measurement. In addition the deposition volume (the area cross-section) is determined.

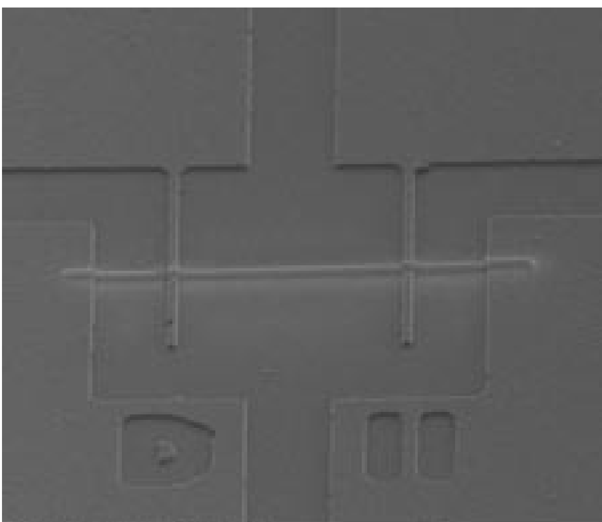


Figure 2: Au deposit on a wafer with predefined bond pads to allow electrical characterization of the Au deposit.

The procedure was repeated twice and the average specific resistivity is around 400 µOhm.cm, which is a factor of 150 higher than the pure metal. This is in-line with general values reported in literature and is due to the high organic content of the deposit.

- Decay times for precursor release: During deposition, the surface of the sample retains a layer of precursor molecules that stick to the surface. As a result of the vapor pressure curve of the applied chemical compound, the layer will be pumped away over time, once the in-flow is interrupted i.e. by closing the GIS valve. However, this will take time and one has to take this into account when switching from SEM-deposition mode to SEM-imaging mode. The decay of the precursor layer is best visualized by making successive point deposits after closing the valve. Some results are shown in figure 3 and 4.

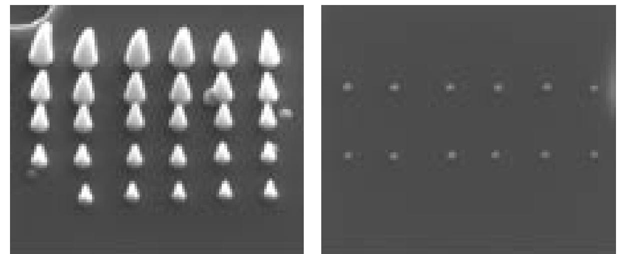


Figure 3 and 4: Point deposits of Au after closing the valve, using 30 kV spot 2. The time interval is from 0 – 15 minutes with 30 sec deposits (left) followed by a time interval 30 – 42 minutes and one minute deposits (substrate is Si).

As can be derived from figure 3 and 4, the deposition is still strong in the first 10 minutes and it is strongly recommended to allow this period for pump- out of the precursor from the surface prior to starting with imaging. Even after a longer period of pump down, still some point deposits can be made, but for actual imaging the rate is so low that it does not obstruct standard imaging. As the decay is exponential, it will disappear completely overnight.

Note: When depositions have been made with an ion beam, this effect is also present but will not likely be observed, because the ion beam is rapidly milling away any precursor residues.

Patterned deposition

Using the patterning capability of the DualBeam or the capability of an add-on generator such as the Raith Elphy or the NPGS system it is possible to create arbitrary structures. A few examples are given in the figures 5 - 8.

Figure 5 and 6: A "golden nano-scale key" deposited with the Nova™ 600 NanoLab using the direct bit-map writing facility (left) and the continuous writing of the ICFO name (Institute of Photonic sciences, Barcelona, Spain) using a Quanta™ 200 with Elphy *Plus* from Raith GmbH (right). The start of the (repeated) writing pattern (Fig 6) results in a slightly lower local deposition, which is probably due to the start-up of the surface diffusion process.

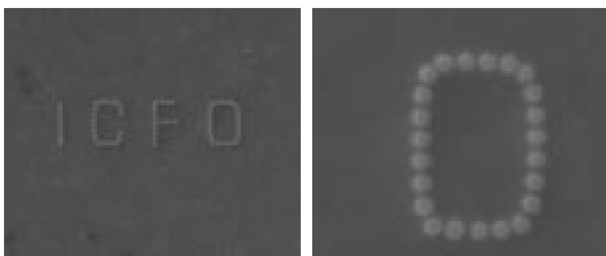


Figure 7 and 8: Patterning using separated point doses with Quanta 200. The magnified image (at the right) shows individual dots of 50 – 60 nm having a spacing of around 20 nm only. Note that a Quanta 200 is an instrument with a standard W emitter that has been set-up for long lifetime with increased Wehnelt – filament distance.

The basic elemental composition using the electron beam

- The composition of the deposition can be measured at the center of an area deposit that is thick and large enough to allow sensible low kV EDX analysis. The low kV produces an X-ray signal that is almost completely generated by the deposit and hardly by the Silicon substrate. An estimate of the required thickness was made with Monte-Carlo simulations, assuming the base formula of the precursor as the input for the sample composition. With this chemical formula as the basic molecule content and re-normalizing to C, O and Au only (as H cannot be measured with EDX), the atomic percentage of Au would be 9.9. Using an optimum spectral fit and back-ground subtraction, the composition of the deposit can be determined from the measurement: C 79.5 %, O 11 % and Au 9.5 % - so the Au content matches nicely with the atomic composition of the molecule. The composition is reported here in atomic percent (%AT) and not in the usual weight %, commonly used in EDX (%WT). In literature a Au concentration of 65 WT% can be found for $Me_2Au(tfac)$, deposited with an electron beam of 1 nA. The measured value of 9.5 AT% corresponds to a %WT of 62.6, so this value is similar to other reported values.

Influence of annealing on EBID composition for Au

In cooperation with ICFO in Barcelona the influence of annealing on a Au deposit was studied. Three deposits of Au areas were made on a piece of wafer. The square deposits had a width of 1,2 x 1,2 um and a deposition height of about 500 nm.

Following deposition two samples were annealed in a nitrogen ambient at temperatures of 250 °C and 400 °C respectively. The result of this annealing is an expected change of the composition of the elemental deposit, due to the escape of less stable chemical (organic) components of the original deposit.

The annealing did not change the shape of the deposit, meaning that the actual melting point of the deposit has not been reached. However, the actual thickness of the deposit is reduced by the anneal step, by approximately 20 % - the result is an increase of the Si peak from the wafer substrate.

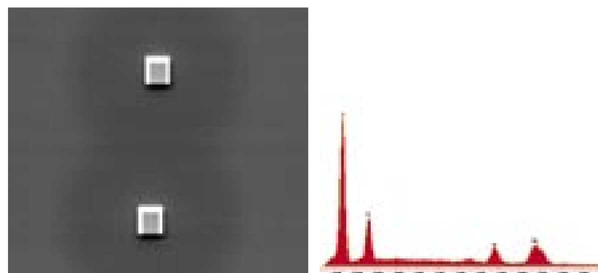


Figure 9: Image of the two depositions, 10 um apart, size 1.2 x 1.2 μm, sample 1, room temperature.

Critical in the EDX analysis is the choice of the kV as the kV must be high enough to excite the elements of interest and low enough to reduce penetration by the primary beam as much as possible. For this analysis, 4kV was aplied and a spectrum recorded with this kV is given

in figure 9. Of course for this low energy, use is made of the AuM lines (only qualitative check on AuL lines at higher kV).

The spectrum shows the presence of the background peak of Si. Clearly this element is not in the deposit and hence it is not taken into account in the quantification.

As the deposits were created on a blank, unpatterned piece of wafer, it was not easy to re-locate them, even though the rough position was known. The field of view cannot be too small, otherwise the deposits are not visible : a FOV of around 50 µm seems practical. The quickest solution was to scan the stage field by field at this magnification and use the BS detector with maximum contrast. The deposits show up as white pixels whereas most other features as dust are relatively dark.

Sample 2 did not show a different spectrum than sample 1, clearly indicating nothing had changed the deposition.
The sample (see figure 10) emits a different spectrum with a much higher Au peak and a lower C and O peak.

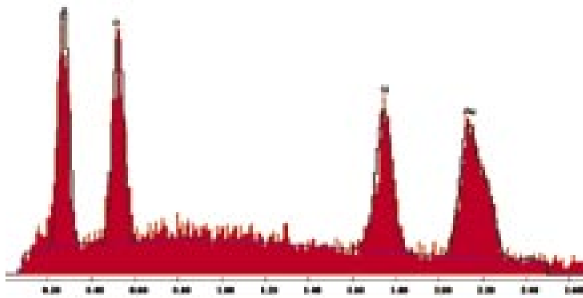


Figure 10: EDX Spectrum Analysis of AU sample 3

Note that from the spectrum the net intensities of C, O and Au are about equal. However, the x-ray absorption of C and O due to Au is higher than reverse, so the C and O intensities will be corrected upwards.
The quantified result in atomic percent is given in the table (figure 11).

Element	Sample 1	Sample 2	Sample 3
	no anneal	250°C -3 hr	400°C -3 hr
C	79.1	78.9	54
O	11.4	11.6	20.4
Au	9.5	9.5	25.6*
	100	100	100

Figure 11: Elemental Composition (% of total)

In short: Annealing at 250 °C does not change the composition. Annealing at 400 °C improves the Au content with a factor of 2.7. The lateral shape of the deposit did not change yet at this temperature.

Conclusions:

- Au deposition can be realized using the GIS and the dimethyl Au(III) acetyl acetonate: both for ion beam and electron beam
- The purity of the deposit is in the range of the molecular composition of the precursor but still not high at a level of ~ 9 % (63 %Wt)
- The behavior of the Au deposition is quite similar to the way Pt is deposited using the Pt GIS.
- Nano scale Au deposits can easily be made, both with a W based electron column and with a FEG based electron column. Minimum size for FEG is around 15 nm and for W columns 50-60 nm.
- The decay time of the precursor after closing the valve has to be taken into account when switching from deposition to imaging. Depending on the application it is recommended to wait around 10 - 15 minutes.
- The stability of the precursor over a longer period of time is not yet clear.
- Annealing of the deposition up to a temperature of 400 °C improves the Au content with a factor of 2.7.

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