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Fabrication of pure gold nanostructures by electron beam induced deposition with Au(CO)Cl precursor: deposition characteristics and primary beam scattering effects

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Abstract

In the search for a direct write, high-purity electron beam induced deposition (EBID) process, a new gold precursor that is commonly available is investigated. This precursor, Au(CO)Cl, can indeed be used to produce a high-purity golden nanostructure (>95 at% Au), at a wide variety of electron beam parameters. The use of a mass spectrometer to determine the components of the actual precursor vapour showed that the Au(CO)Cl density in the vapour is very low (estimated at <0.1%), while the main component is CO. This indicates that the electron decomposition cross-section of the actual precursor is roughly two orders of magnitude higher than for common EBID precursors. A remarkable observation is a skirt deposition at positions between 5 and 200 μm away from the beam impact point. This skirt cannot be attributed to secondary electrons of type II (SE₂), but results from local scattering of the primary beam on its way through the precursor gas. The skirt deposition is quantified experimentally and by modelling and must be present in all EBID processes with any precursor, delivered through a local supply system with fluxes in the range \(10^{16}–10^{19}\) molecules cm\(^{-2}\) s\(^{-1}\). It is shown that the skirt effect can be minimized by increasing the applied beam energy and by reducing the gas path length.

(Some figures may appear in colour only in the online journal)

1. Introduction

Electron beam induced deposition (EBID) [1–3] is a direct write technique based on the local decomposition of precursor molecules adsorbed on a substrate. The molecules are delivered to the surface through a gas injection system (GIS), as a local flow of vapour molecules originating from a liquid or solid precursor in a reservoir. The decomposition, induced by the electron beam, produces volatile components that are pumped out by the vacuum system and non-volatile components that form a local deposition on the surface. As a result of the small diameter of the electron beam and the excellent capability for patterning, the technique can be used for the direct creation of micro- and nano-scale three-dimensional structures [4, 5].

Applications in nano-research and nano-technology prototyping [6] require precise control of local material properties such as conductivity (for contacting nanowires), ferromagnetism (for domain wall pinning) or optical properties (for plasmonic structures such as bowtie antennae). However, the purity of EBID structures is typically low and the resulting nano-scale structures do not exhibit the required property. Impurities are mostly caused by incomplete decomposition of the metal-organic precursor, or from a possible residual gas
in the vacuum, resulting in high amounts of carbon [7] and sometimes oxygen in the deposition. This strongly reduces the applicability of the EBID process. Post-processing, such as anneal steps, improves the purity, but induces loss of shape [8] and hence has only a limited application. As an example, the resistivity of directly deposited Pt from MeCpPtMe₃ at 5 keV and 1 nA is around 10⁶ μΩ cm, whereas the related annealed structure can be as low as 1500 μΩ cm. Although this is an improvement, the volume loss due to the “burn-off” of carbon is substantial and the resistivity is still two orders of magnitude higher than 10.6 μΩ cm for bulk platinum. Whereas in many applications the bulk value is not always required, deviations of one or two orders of magnitude nevertheless severely limit the application range of the EBID process.

Depositions with high purity have been reported using UHV equipment instead of HV instruments such as a scanning electron microscope (SEM) using, e.g., Fe(CO)₅ for the deposition of pure Fe [9, 10]. Improvements in purity have also been achieved by the use of non-organic precursors such as Pt(PF₃)₄ [11]. Although these precursors yield higher purity compared with standard organo-metallic precursors, the release of halogenide atoms may induce etching effects and enhanced oxidation through a reaction with the residual water vapour adhered to the sample surface.

Here we investigate the non-organic precursor Au(CO)Cl (CAS 50960-82-2) for the deposition of pure gold and first show in section 2 that it yields high-purity gold. Etching by release of chlorine is discussed in section 3, followed by observations about the change in gas composition over time in section 4. In section 5 we evaluate the effect of scattering of the primary beam on the gas flow from the GIS.

2. Deposition of pure gold with Au(CO)Cl

In nano-technology research there is interest in a direct write technique for the deposition of nano-scale structures of pure gold. Applications are plasmonic structures, local contact strips for electrical measurements and local binding sites, which have a (bio)chemical binding capability for thiol-ending organic molecules. In the case of gold deposition, the precursor Me₂Auacac (CAS 14951-50-9) can be used to produce a gold deposition at a yield of 4 × 10⁻⁴ μm³ nC⁻¹. The energy dispersive x-ray (EDX) spectrum of such a deposition is shown in figure 1 (black line). By annealing of the deposition this Au content can be improved [8] from 10 to 60 at% Au.

We investigated a new EBID precursor for the production of gold depositions, which is the non-organic Au(CO)Cl. The EDX spectrum of a deposition made with this precursor is also shown in figure 1 (red). For this precursor, the Au peak is clearly much higher compared with the deposition made with Me₂Auacac and the carbon content is close to zero. Quantitatively, the composition results are listed in table 1.

As can be seen, the decomposition of Au(CO)Cl produces a pure gold deposition, without oxygen (at 0.5 keV in the EDX spectrum) and chlorine (at 2.61 keV). The yield is 6.5 × 10⁻⁴ μm³ nC⁻¹ for 5 keV and 0.1 nA. The carbon content is so low that it is very difficult to measure with EDX, due to the overlap of C K α and Au N x-ray lines. The C K α is at 0.280 keV and the Au N line has two components: the N4 → N6 and the N5 → N6,7 transition at 0.265 keV and 0.244 keV, respectively. A spectral calibration against a true gold standard and a manual correction for the overlap have shown that the C content is 5 at% maximum. It should be noted that high-purity Au depositions have also been reported by the use of Au(PF₃)₄ [12] but this material is not commercially available and produces a higher amount of halogenide atoms per dissociated precursor molecule than Au(CO)Cl.

For other precursors, it has been reported that the composition of the deposition is dependent on the actual choice of the beam parameters, generally with a higher purity for high beam currents and low landing energies [13]. For the Au(CO)Cl precursor this effect has not been observed. The purity of the depositions is always above 95 at% Au. This indicates that the decomposition process only produces volatile (CO and Cl, Cl₂) and non-volatile parts (Au) of the precursor molecule.

3. Etching by release of chlorine

One of the expected side effects is the release of Cl atoms possibly inducing additional etching of the substrate. Furthermore, water molecules adhered to the surface
complicate the etching process even further due to a possible reaction between Cl, H2O and the substrate. Therefore, the shape of the deposition depends on both the etching and deposition processes, which are both driven by the applied beam current and dwell time. Figure 2 shows five examples of depositions made on a SiO2 (30 nm)/Si substrate, using a 5 keV beam and a constant dose of 32 nC and constant dwell time of 10 μs, but different beam currents of 60, 126, 241, 515 and 939 pA. The depositions show a halo around the irradiated area. This halo is attributed to the SE2 generated by back scattered electrons and is common to all EBID precursors. For Au(CO)Cl however, there is a remarkable sharp ring in the halo for low beam currents. EDX measurements only show substrate elements and gold, while Cl is not detected anywhere. The bright ring for the low beam currents is identified as a slightly higher rim of pure gold. As it depends on the beam current, it is conjectured that the balance between local precursor depletion and etching is the cause of this phenomenon. With other deposition processes, such as for Pt deposition with MeCpPtMe3 or W deposition from W(CO)6 the halo is also present but the shape is independent of the current and smoothly becomes thinner away from the deposition.

The release of chlorine induces an etching effect of the substrate itself. In particular, Si substrates will be easily etched, but the simultaneous presence of the electron beam and possible water molecules will also enhance the etching effects on substrates such as SiO2 and Si3N4. The etching effect not only changes the surface, but also has an effect on the shape of the actual deposition, as it can even induce delamination of the deposited layer due to the formation of larger pores at the edge of the deposition. An example of these pores is shown in figure 3 in a TEM cross-section of a FIB prepared lamella in the central region of the deposition.

The best deposition results, with low etching effects and good shape control, were obtained on samples with a SiO2 top surface and finished with a mono-layer of HMDS (hexamethyldisilazane). This HMDS finish reduces the adherence of water vapour to the surface. The lower amounts of water adhered to the surface indeed improve the depositions, and especially the halo is now smoother, has no strong edge and is more in line with depositions of other non-etching precursors (see figure 4).

4. Changes in the precursor gas components

Another effect observed for the Au(CO)Cl precursor is related to the actual transition of the solid Au(CO)Cl material into the vapour phase. Most stable precursors have a single balance between solid and vapour phases, whereas this precursor has several vapour phases. For Au(CO)Cl, opening of the valve results in a short pressure burst and then, after typically 5–8 s, the pressure stabilizes at a level of 3 × 10⁻⁶ mbar above the base level. It is assumed that this burst is caused by release of the CO pressure that has been building up in the reservoir during the period when the valve is closed. The pressure level immediately after opening of the GIS reflects the equilibrium pressure of CO, which balances the CO release and uptake by the precursor material. It is also observed that, with increased reservoir temperature, the pressure burst is much higher and for a reservoir temperature of only 28 °C it already exceeds the trip level of the vacuum chamber. To reduce the pressure burst to a level well below this trip level, all depositions reported here were made with the Au(CO)Cl reservoir at a reduced temperature of 9 °C. The steady-state flux of particles out of the supply system is then around 3 × 10¹⁷ molecules cm⁻² s⁻¹. This is calculated from the nozzle conductance, the pump speed and the measured pressure increase in the vacuum chamber upon opening of the GIS.

In order to understand the actual supply of the molecules to the sample, the gas components released by 0.5 g Au(CO)Cl are monitored over a period of 28 h using a mass spectrometer or residual gas analyser (RGA). The applied RGA system can detect atoms with a maximum mass/charge number (M/Q) of 200 and this implies that the detection of Au atoms (atomic mass 197) is at the limit and close to the noise level, while the Au(CO)Cl precursor molecule cannot be observed because its molecular mass is larger than 200. However, it is possible to measure CO at M/Q = 28, Cl at 35 and at 37 (two isotopes) and these components are directly related to the precursor molecule.

The overall decrease in the chamber pressure in the first 2 h is related to the pump out of residual water vapour. M/Q = 28 is attributed for at least 90% to CO although its M/Q also corresponds to N2. The contribution of N2 is estimated using the ratio with M/Q = 14 (not shown in the graph), which can only be N. M/Q = 35 and 37 are shown in the same graph at very low levels and hence it can be concluded that the major component of the gas is CO. A very rough estimate, using a direct translation from the Cl ion current to the partial pressure of the components, would imply a precursor pressure of around 0.05% of the total pressure. As the deposition yield of the process of 6.5 × 10⁻⁴ μm² nC⁻¹ is in the usual range for most common EBID precursors, we conclude that the Au(CO)Cl molecules have a very high decomposition cross-section for electrons.
5. Scattering of the primary beam

The decomposition of Au(CO)Cl by electrons has a very high yield and results in >95% pure gold depositions that can be observed with good contrast and low S/N ratio. On a bulk sample it was observed that gold deposition occurred in the irradiated area, but in a wide area around it some nano-scale dot depositions appeared as well. Partially, this can be explained by the SE2 that are induced by back scattered electrons in the substrate and hence to the applied beam energy and the average Z of the substrate material. From simulations it is known that this is confined to a halo diameter around the deposition of around 1–2 µm, depending on the substrate type and conditions. The small gold grains appearing, for example, at a distance of 70 µm from the deposition area, as shown in figure 6, cannot be explained this way.

A possible explanation for the phenomenon shown in figure 6 is scattering of the primary electron beam while passing through the gas flow close to the nozzle of the supply system. Under the conditions of the experiment in figure 6 the average pressure across the nozzle diameter is 10−3 mbar. The electron beam has a probability of scattering at a low angle, but due to the large distance above the sample, the resulting impact point can be far away from the original beam focus point. This kind of beam scattering through a gas is described well for environmental scanning electron microscope (ESEM) conditions, where the whole chamber is filled with a gas and the beam scattering is defined by the beam gas path length (product of pressure and the distance the electron travels in this high-pressure regime).

5.1. Experimental quantification of the scattering process

In order to compute the effect of scattering in the gas, the beam gas path length and the gas density gradients for the supply of gas through a nozzle were computed for the geometry...
as sketched to scale in figure 7. A gas flux model for the exhaust of the flux into the vacuum is applied [14]. In the graph the iso-density areas are indicated with a colour referring to the fraction (see the legend) of the average density at the exit of the nozzle. In absolute scale this refers to a flux of $3 \times 10^{17}$ molecules cm$^{-2}$ s$^{-1}$. With the given nozzle geometry and flux distribution the gas path length can be calculated as $4 \times 10^{-5}$ mbar cm. With this value and data reported elsewhere on electron scattering in ESEM [15, 16], it can be concluded that the experiments were carried out in a single scattering regime [17].

As most practical applications require the use of a bulk sample, a scattering experiment was conducted on a bulk Si sample with native oxide only (to avoid any influence of possible charging). On this sample, scattering events will similarly induce the production of small amounts of Au due to scattering. The small gold grains produce good contrast in the image, as a result of the high SE yield of pure gold and hence it is possible to determine the area coverage quantitatively by image analysis. The area coverage is then proportional to the amount of scattering by the primary beam, as long as the distance to the impact point is larger than the escape area of SE$_2$ (in this case using 5 keV in Si roughly 1 $\mu$m). An example of such an image series showing higher particle densities closer to the beam impact point is given in figures 8(a)–(d). Image analysis was applied on the individual images and included shading correction, noise filtering and manual threshold setting using optical feedback. The quantitative outcome is the % area coverage of Au nanodots.

Figure 8 shows a conspicuous decrease in the density of gold particles on the surface with increasing distance to the beam impact point. To study the influence of the primary beam energy, the gold coverage area distribution was measured for energy settings of 2, 5, 10 and 20 keV. The corresponding quantitative results are given in figure 9 and it shows that scattering is consistently higher for lower energy, independent of the distance from the deposition centre. The gas scattering effect is substantial and cannot be ignored when evaluating the material properties of the deposition, especially at a low beam energy.

The measurement error in the graph is mainly related to the statistical error (when there are only a few gold grains visible in the image), as well as to setting of the white level threshold for selection of the Au nanodots.

It is possible to reduce the gas path length by reducing the nozzle diameter. The local output flux remains the same, but the effective gas path length is shorter. Figure 10 shows the results of depositions at 2 and 5 keV using a nozzle with an internal diameter of 350 $\mu$m. In this case, the scattering effect is reduced compared with the large nozzle experiment of figure 9. For example for 2 keV at a distance of 15 $\mu$m the large nozzle would result in an area fraction of 6%, whereas the smaller nozzle gives only 0.4%. So to reduce scattering by the precursor flux, the smaller nozzle is much more favourable and, as long as small structures are made with EBID technology, the possible precursor flux gradient on the sample is not relevant. An additional experimental test using a very small diameter nozzle (80 $\mu$m) showed that the influence of scattering can be
Figure 8. Images recorded (a) 15, (b) 30, (c) 45 and (d) 60 µm away from the beam impact point using 2 keV primary beam energy and the nozzle geometry shown in figure 7.

Figure 9. Area coverage (%) by induced gold particles as a function of the distance from the deposition area, for four different primary beam energies. The nozzle diameter is 500 µm.

Figure 10. Area coverage (%) by induced gold particles as a function of the distance from the deposition area, for two different primary beam energies, 2 and 5 keV, and nozzle diameter 350 µm.

5.2. Numerical simulations of the scattering process

In addition to the experiments, some scattering simulations were made with Geant4 electron scattering simulation software using Mott cross-sections [18]. For the experimental conditions of 2, 5, 10 and 20 keV beam energy, the calculated average gas density for CO and the applied nozzle/sample geometry, as given in figure 7, the scattering process was simulated. The dose was set to $10^9$ electrons, which is a good compromise between statistical accuracy and run time of the simulation. The result is shown in figure 11.

Comparing the simulations with experiments it is obvious that the trends are very much the same. For example, using 2 keV both the curves of figures 9 and 11 show a decrease in the scattering with a factor of 10 between 5 and 50 µm distance. Also, at 50 µm we can compare the scattering at 2 and 20 keV and both curves show that at 20 keV the scattering is around a factor of 18 lower than the scattering at 2 keV.

In the 2 keV experiment at 45 µm distance from the beam, the simulations show that the field of 0.512 × 0.48 µm will be hit by $10^4$ electrons (the dose at the experiment was constant at $2 \times 10^{12}$ electrons as opposed to the dose of $10^9$ electrons used for the simulations). So the $10^4$ electrons result in a gold grain distribution, as shown in figure 8(c), which represents around 800 measured particles with a diameter larger than 0.6 nm. This again demonstrates the high efficiency of the decomposition process.

6. Conclusion and discussion

Au(CO)Cl is a precursor that produces high-purity gold structures by direct deposition under a wide variety of beam
conditions. The release of Cl during the decomposition results in a delicate balance between deposition and residual etching of the substrate, which results in poor shape control. The etching effect, due to the release of small amounts of Cl, needs to be taken care of, for example by using an etch-resistant substrate and/or by adjusting the deposition timing parameters. The actual amount of precursor molecules delivered from the supply system is low and the major component is CO; the composition of the flux changes over time and the lifetime of the precursor is limited. Assuming that the amount of precursor molecules is only a fraction of the total molecule supply (as derived from the low Cl signal in the mass spectrometer) it is concluded that the precursor molecule has a high decomposition cross-section for electrons compared with commonly used EBID precursors.

This high sensitivity for decomposition by electrons has enabled the quantitative analysis of a phenomenon that has received minimal attention so far: scattering of the primary electron beam due to the presence of a higher pressure gas regime. This scattering is quantified using commonly used beam conditions and reveals that deposition occurs as far as 50–100 µm away from the beam impact point. The scattering can be minimized by application of a reduced gas path length, obtainable by application of a smaller nozzle diameter. Results from simulations using Geant4-based simulation software show a trend, which is in line with the experimental data.

The scattering effect, as shown for example in figure 9, is a general effect that will occur for all precursors used during a standard EBID process and will lead to a thin film/small grain deposition at large distance from the beam impact point. This side effect may, for example, contribute to a slight error in the measurement of conductivity of a material, even when using a four-point probe structure. In particular, for depositions over a long time, a wide-area thin film may become substantial.

Finally, it was observed that the small Au particles induced by the scattering beam are not equal in size. This could imply that the reaction of a single electron with the precursor adhered to the surface can lead to the decomposition of multiple precursor molecules at the surface reaction point, and that very close Au nanoparticles coagulate into larger grains [19].

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