Electron beam induced deposition of gold using the Au(CO)Cl precursor

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Electron beam induced deposition (EBID) is a technique for the local direct deposition of material by decomposition of a precursor gas, adsorbed at the sample surface and induced by the patterning electron beam. This maskless technique is useful for rapid prototyping thanks to its pattern flexibility and lack of resist processing / lift-off. In addition, it allows 3Dimensional growth as the height is determined by the local dose. A possible problem in applicability however, is due to the general impurity of the deposit[1)]. Most EBID structures contain a high amount of carbon as the decomposition is not complete and hence, the property may deviate strongly from the bulk/thin film property.

One of the materials of interest is gold, which is used for a variety of applications: for contacting nano tubes (conductivity), for plasmonic structures (optical property) and for binding sites of bio-molecules (bio-activity). Gold can be deposited using the precursor Me2Auacac and this produces around 10 %AT gold and additional anneal steps can enhance this to 60 %AT[2)]. The latter technique strongly affects the shape of the structure and hence is less useful. Another precursor is AuCl(PF_3) reported to produce a high content of gold but this material is not commercially available and is also very sensitive to spontaneous decay and therefore has a short life-time and low practical use[3)].

The search for another, more stable and readily available precursor has resulted in tests on Au(CO)Cl. This precursor has been investigated to show the usefulness as a precursor for Au deposition with a high Au content without necessity for annealing and a suitable, practical life-time. The precursor has enough vapor pressure for a sufficient flux onto the sample and its yield at 5 kV beam energy has been determined to be 6.5 10^{-4} ∝m^3/nC at 100 pA and 1.3 10^{-4} ∝m^3/nC at 400 pA, showing a lower yield at higher current and thus indicating a gas flux limited process. The yield is similar as for most other EBID precursors. The composition shows a purity > 92 % at as derived from EDX spectra at low kV and manually compensating the presence of the x-ray N line[4)]. The spectrum in overlay with a gold standard from a gold plated contact, is shown in figure 1. Depositions on a 1 x 1 ∝m pad made at 5 kV and 0.1 nA, have also been analyzed using EBSD. Only a few percent of the area shows a pattern (that can be indexed see figure 2). This indicates that the sample is non-crystalline, or the grain sizes are below the EBSD lateral resolution limit of around 20 nm. For conductivity measurement a 10 ∝m line was made at 5 kV and 0.4 nA). The cross-section was 0.62 ∝m^2, as determined from a FIB milled section, see figure 3) and a 6 points measurement of the structure indicates a specific resistivity of 8.5 ∝Ohm.cm, and a contact resistance of 4.7 Ohm (on an overlap area of 1.2 ∝m^2). This compares very favorably with the bulk resistance of 2.44 ∝Ohm.cm and is to our knowledge the lowest reported EBID resistivity so far. All depositions were made at room temperature and with active cryo pumping to reduce the water vapor content. Special instrumental provisions allow the extended use of this precursor without spontaneous decomposition. The life-time so far is at least better then 1 month.

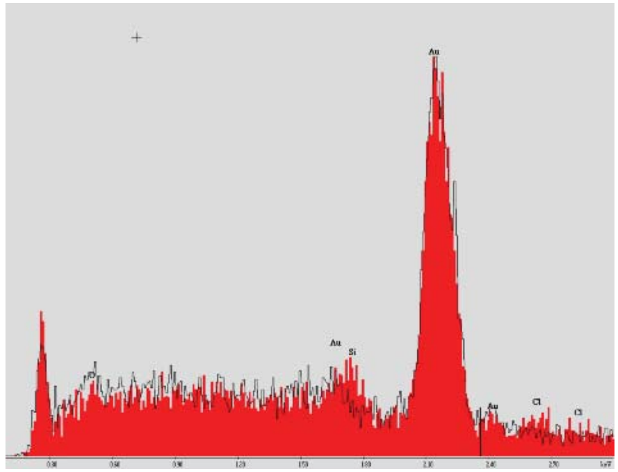

Figure 1: A 5 kV EDX spectrum of a deposition made with Au(CO)Cl (red) and comparison with a gold plated sample (black line) – the differences are marginal. The deposition shows a small Si contribution form the sample and negligible amounts of Cl and O. The quantitative determination of possible, low amounts of C in Au require manual data correction, due to the overlap of CKα and AuN in the region 0.26 - 0.28 keV. As the sensitivity for C is extremely high in presence of a heavy element, this analysis is at the limits of its sensitivity. The amount of Au can be stated as > 92 %AT.

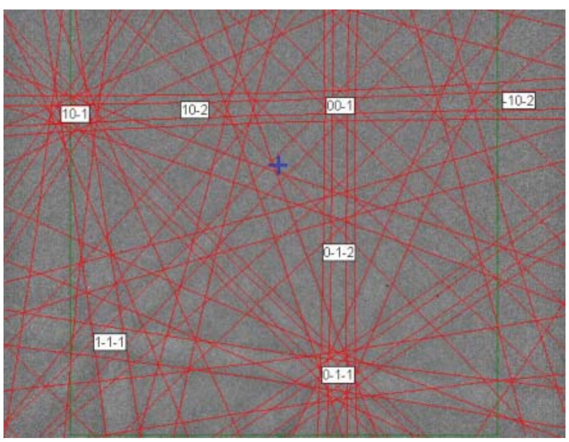

Figure 2: Example of a spurious (indexed) EBSD pattern from an Au(CO)Cl EBID pad created at 5 kV and 0.1 nA. Most of the pad shows no EBSD at all.

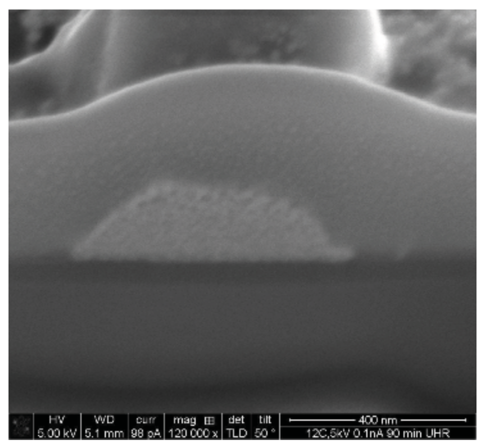

Figure 3: FIB cross-section showing the 0.62 ∝m^2 area used for calculation of the specific resistivity. The interface to the 60 nm SiO_2 (dark layer) is smooth. The top thick layer is a FIB protective layer made with Pt EBID

References:
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3) I. Utke, P. Hoffmann et al., J.Vac.Sci Technol. B 18 (6), 3168-3171 (2000)
4) J.J.L. Mulders, A. Botman, Proc. Microscopy and Microanalysis,1126, Richmond (2009)