Gas-mediated electron beam induced deposition using ammonia as a purification medium

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Electron beam induced deposition (EBID) has been used to fabricate nanostructures such as gold and platinum-containing nanowires, nanotips for field emission and atomic and magnetic force microscopy, and metallic contacts to carbon nanotubes. However, the technique suffers two major drawbacks with respect to other growth methods such as chemical vapor deposition (CVD), namely a lower growth rate and lower material purity. EBID deposits typically contain a high proportion of impurities such as carbon (typically > 50 at. %) due to incorporation of species originating from precursor ligands and background hydrocarbon contaminants. As there are relatively few carbon-free precursors with suitable properties to enable use in EBID, several other methods have been used in an attempt to improve deposit purity, with varying degrees of success [1]. The methods include post-EBID heat treatments and growth in the presence of a purification medium, namely oxidative gases such as H_2O and O_2. However, these gases typically reduce the EBID growth rate.

Here, we report the use of ammonia (NH_3) as an alternative purification medium for EBID of gold and platinum using dimethyl gold acetylacetonate ($((CH_3)_2Au(C_5H_7O_2))$) and methylcyclopentadienyl platinum trimethyl ($MePtCpMe_3$) precursors. Room temperature EBID was performed using two methods: local injection of the precursors and NH_3 into a high vacuum scanning electron microscope through a capillary-style gas injection system [2], and by using the gases in environmental scanning electron microscopy. The use of ammonia at small overpressures (up to three times) relative to that of the deposition precursor results in a substantial decrease in the carbon content (from ~50 at. % C to 25 at. % C) and increase in the gold content (from 45 to 70 at. %) (Fig. 1). Nitrogen incorporation in the deposits has been observed, but only at high NH_3 overpressures (> 10 times that of the deposition precursor). The compositional changes are accompanied by a substantial decrease in resistivity. Unlike previously reported gas mixtures, deposition in an NH_3 environment enhances the volumetric EBID growth rate, as quantified by depositing pillars under a focused beam in the absence (Fig 2a) and presence (Fig 2b) of NH_3 at an overpressure of ~2. The pillar height increases from 2.81 to 3.09 μm, while the base width increases from 450 to 480 nm. The growth rate enhancement is modest (a factor of approximately1.3 under these conditions), but significant because other reported purification media such as H_2O reduce the already low EBID growth rate.

The observed purification is ascribed to electron beam induced dissociation of NH_3 to form H* which can react with C to form volatile CH_x species, preferentially etching carbon during EBID. The change in growth rate may be the result of a NH_3-mediated increase in the diffusivity of deposition precursor adsorbates at the sample surface. These and other potential mechanisms will be discussed on the basis of dependencies on EBID growth parameters and models of EBID growth kinetics.

References.

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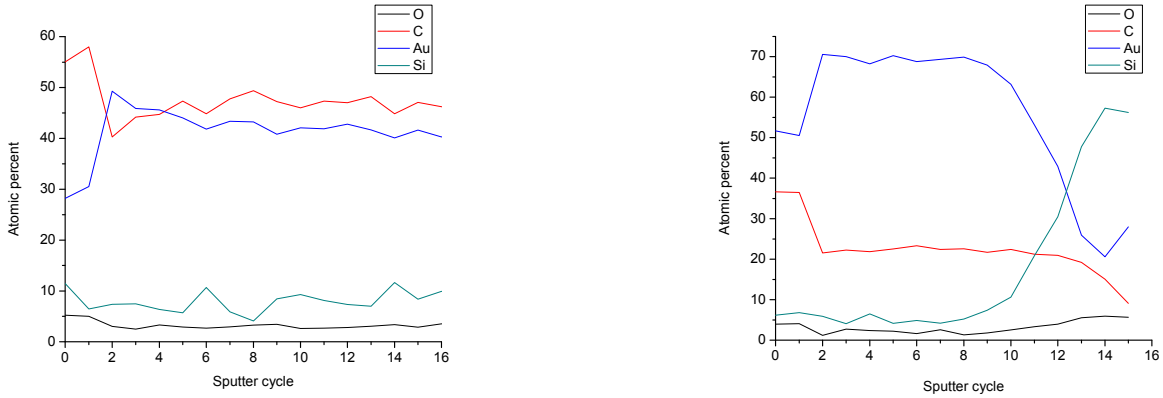

Fig 1. Auger electron depth profiles of EBID deposits formed from dimethyl gold acetylacetonate precursor. The typical bulk gold content (neglecting the first few analysis point and the contribution of the substrate) rises from ~45 at. % in a standard high vacuum environment (a) to ~70% at. % in the presence of NH_3 at an overpressure of ~ 3 times that of the deposition precursor (b).

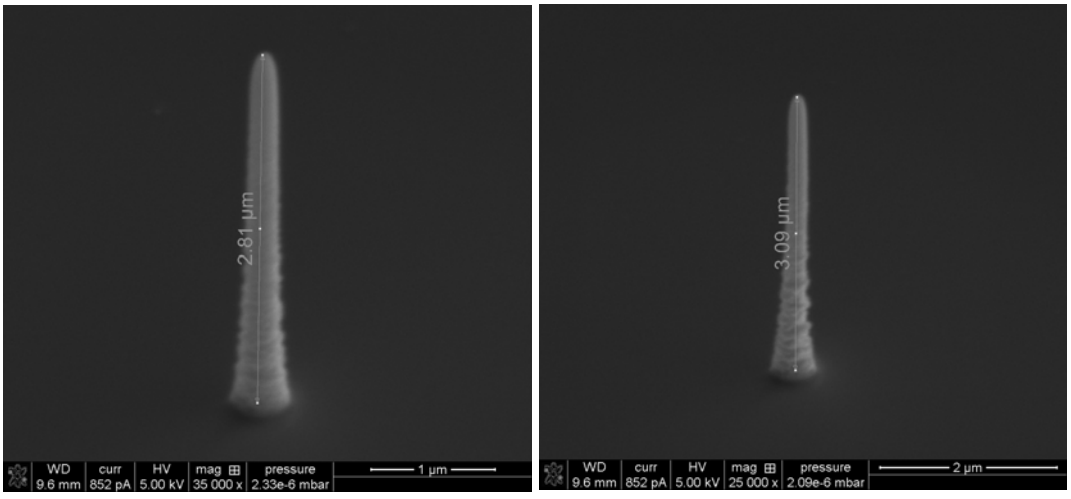

Fig 2. EBID deposits formed under a focused electron beam from $MePtCpMe_3$ precursor in the absence and presence of NH_3 (10 min deposition time, I_b=0.84 nA). (a) without NH_3, P=5.1x10^{-6} mbar (b) with NH_3, P=1.3x10^{-5} mbar.