

# Electron beam induced oxidation of direct–write deposits: a simulation

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Electron beam direct–write has recently taken a large step forward with the discovery of techniques to purify deposits *in-situ*. This development has opened the door for future direct–write device prototyping and editing. *In-situ* electron beam curing/etching using H<sub>2</sub>O and O<sub>2</sub> has been shown to remove most residual carbon (>95%)<sup>1-3</sup> from Pt deposits which are highly contaminated following deposition (~PtC<sub>4-8</sub>) providing a powerful, minimally invasive method to purify deposits at room temperature. However, the exact reaction mechanism and the distribution of the reactant gas inside the deposit during purification are not yet fully understood.

A simulation will be presented consisting of an electron scattering (Monte Carlo) component that predicts the deposited energy profile from the primary electron beam in the deposit during curing coupled with numerical approaches used to solve differential equations related to O<sub>2</sub> transport by diffusion as well as the chemisorption of O<sub>2</sub> on *embedded* Pt nanoparticles within the deposit. The construction of the purification model was based on experimental observations for the purification of nominal PtC<sub>5</sub> deposits derived from the precursor molecule MeCpPt<sup>IV</sup>Me<sub>3</sub><sup>2</sup> – an internal morphology consisting of Pt nanoparticles embedded in an amorphous carbon matrix (*aC*) served as the initial condition. The simulation was specifically tailored to account for deposit shape changes that occur in concert with the liberation of carbon as carbon oxide gas (CO<sub>x</sub>) at a fixed metal content effectively increasing the deposit density in time. Including this phenomenon required consideration in the simulation of the feedback with repeated looping of the (1) Monte Carlo step and (2) transport simulations to account for the transient deposit densification which couples into transport calculations (figure 1). Simulation results revealed that the solubility of O<sub>2</sub> in the *aC* matrix as well as the chemisorption of the atomic oxygen on embedded Pt nanoparticle surfaces were key aspects of the simulation required to capture features consistent with real experiments.

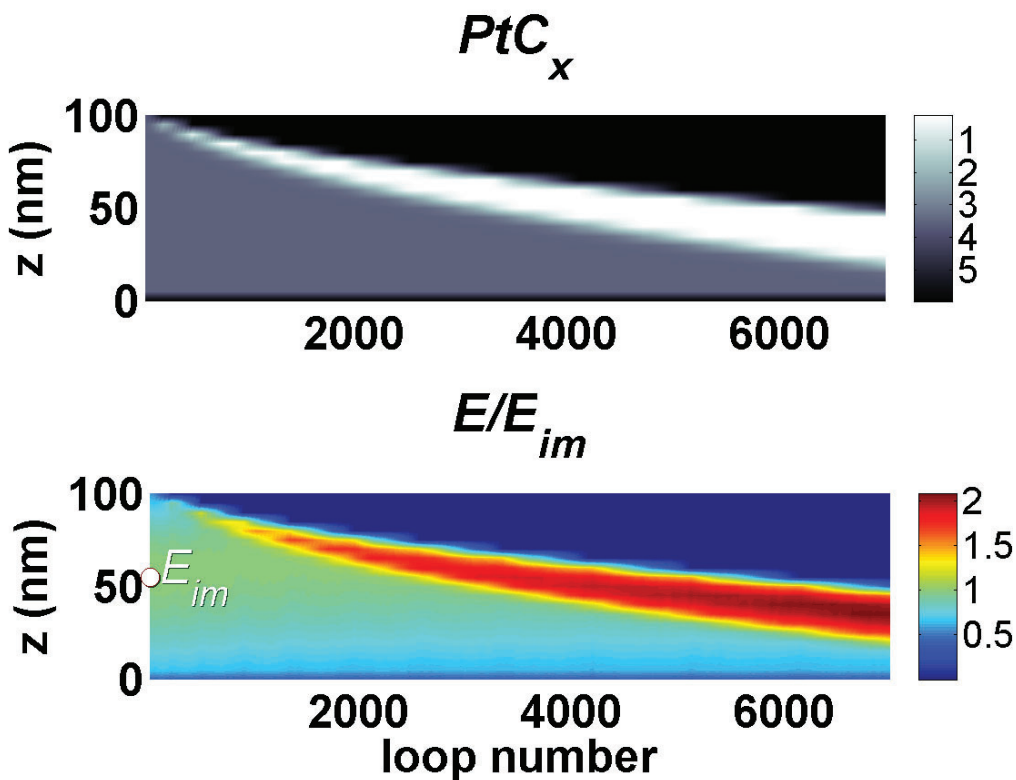


Figure 1. A simulation of the electron beam induced purification of a  $PtC_5$  deposit that was initially 100nm thick ( $z$ -dimension). The deposit was square shaped in the  $x$ - $y$  plane with an edge dimension of 620nm. A primary beam energy of 5keV and a beam current of 1800pA was used to purify the deposit in the presence of a constant surface pressure of 2mTorr  $O_2$  using a raster scan pattern with a beam dwell time per pixel of 100nm and pixel spacing of 0.65nm. Results are shown after 7000 loops. The top image shows the change in the composition of the deposit as a function of time while the bottom image shows the relative change in electron energy loss as purification ensues as a function of loop time over the deposit surface. The indicated energy ( $E_{im}$ ) shows the depth coordinate of the maximum in electron energy loss during the first loop in order to highlight the relative change in the deposited energy depth profile as purification ensues. The underlying model assumes that penetrating electrons react with chemisorbed atomic oxygen on the surface of embedded Pt nanoparticle surfaces. The electron stimulated reaction drives the formation of carbon oxide ( $CO_x$ ) effectively liberating the amorphous carbon matrix as a dissolved gas which ultimately escapes the deposit.

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