Electron Beam Chemical Vapor Deposition

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Introduction and Objectives

Nanoscale materials and devices offer great promise for many applications, but their fabrication often proves problematic. Similarly, integrating nanostructures with microsystems or other nanostructures is one of the main roadblocks to transitioning from single structure fabrication to true nanomanufacturing. This research focuses on Electron Beam Chemical Vapor Deposition (EB-CVD) which has an excellent potential for solving these problems.

An electron beam has been shown to interact with reagent chemicals that are adsorbed onto the surface of a solid substrate causing a chemical reaction(s) that lead to the deposition of a solid metal or ceramic. Importantly, the deposition occurs with minimal heating and thus sensitive substrates or deposits are not thermally damaged. The work of several research groups, including ours [1,2], has established feasibility for nanoscale deposition of several metals and ceramics. Since an electron beam can be focused to spot sizes on the order of 1 nm, it is possible to fabricate truly nanoscale devices.

The goals of the research are to develop focused and broad beam EB-CVD systems, fundamentally understand and model relevant physico-chemical processes, and perform thorough characterization of the structure and properties of deposits. This complimentary approach will permit establishment of the process-nanostructure-property relationships for deposited materials – the key step towards a predictable nanomanufacturing process.

Research Accomplishments

Progress has been made in the following three interdisciplinary areas: 1) experimental deposition of platinum using a highly focused electron beam and detailed characterization of the deposits, 2) low energy electron interactions and stimulated dissociation and patterning of $SiCl_4$ multilayers, and 3) modeling of key transport processes controlling EB-CVD.

Platinum Deposition: **Q**uantitative process-structure relationships for the EB-CVD of platinum fibers and lines using an environmental SEM as the electron gun were established. Extensive statistically designed and analyzed experiments defined the influence of beam voltage and current, deposition time, dwell time, and line time on deposition rate, and geometric features such as fiber diameter, line width, and aspect ratio. Beam voltage, current, and precursor replenishment time have been shown to be the key process variables. The statistical regression model permitted prediction of processing conditions that should optimize, i.e., maximize, deposition rate and aspect ratio of nanostructures and have been confirmed through subsequent experimentation. Growth rates up to 0.9 _m/min have been successfully demonstrated.

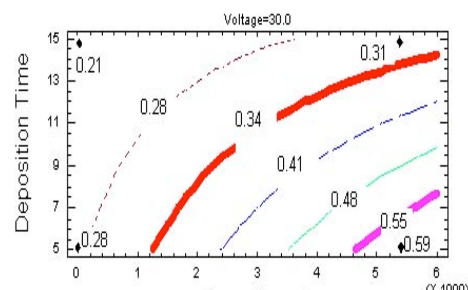

Fig. 1. Contours of constant Pt fiber growth rate (_m/min) as function of deposition time and beam current.

Figure 1 shows response contours for the vertical growth rate of platinum fibers. The statistical model we developed [1,2] accurately correlates the growth rate with the process variables as reflected by a correlation coefficient of 97.3% and confirmed by comparison with experimental results shown in the corners of the graph. The deposits were shown to have

an exceptionally high platinum content, i.e., no carbon was detected. This offers promise that the deposits will be very conductive.

These results are significant in that they accurately correlate EB-CVD process variables and geometric attributes of the resulting deposit. Such a correlation is invaluable for the manufacture of nanoscale platinum components. Expected applications include repairs of masks and prototype microelectronic devices, selective coatings for biomedical and chemical sensing devices, nanolaminates, and integrating nanomaterials with microsystems.

Low Energy Electron Interactions: Previously we demonstrated an enhancement in the deposition of silicon from $SiCl_4$(g) onto a Si(111) substrate due to the presence of 100 eV electron interactions with the adsorbate-substrate system. Electron assisted deposition of metals or semiconductor material has been performed with high energy electron beams. However, inelastic scattering of the primary electron and multiple secondary electron production can amplify the contributions from low energy processes (5 – 100 eV). To fully understand low energy electron interactions in CVD processing, we performed electron stimulated desorption (ESD) experiments on multilayers of $SiCl_4$ condensed on a Si(111) surface. Multilayer experiments allow us to obtain a fundamental understanding of desorption mechanisms from only $SiCl_4$ interactions via eliminating substrate effects. This must be done before moving to the complex $SiCl_4$-Si(111) interface.

Figure 2 depicts desorption products (cations) as a function of the incident electron energy. It can be seen that there is structure in the Cl^+ data which is not present or apparent in any of the other channels. Over this incident electron energy range, $SiCl^+$ and $SiCl_3^+$ have comparable yields whereas the $SiCl_2^+$ and Si^+ yields are smaller relative to the other ions. In addition, there appears to be distinct threshold for these sets of products. At ~ 17eV, Cl^+ and $SiCl_3^+$ are the only observable ions. This is true until 24-25 eV where Si^+, $SiCl^+$, and $SiCl_2^+$ begin to desorb thus the ions are segregated into two distinct thresholds. The mechanisms assigned to these thresholds and the structure in the Cl^+ yield have been assigned to direct ionization, 2-hole states, and 2-hole, 1-electron states. A more detailed discussion can be found in our publication[3].

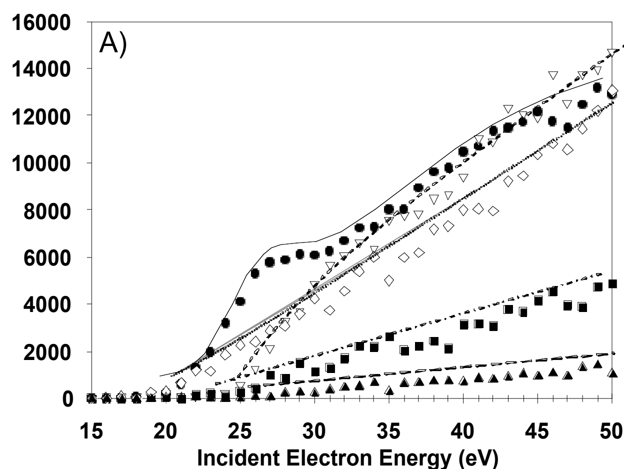

Fig. 2. Cation yields as a function of incident electron energy. Si^+ (_), Cl^+ (●), $SiCl^+$ (▽), $SiCl_2^+$ (■), $SiCl_3^+$ (◇). The Cl^+ ion yield was divided by a factor of six.

Besides cation desorption, we have looked at the ESD of neutral atomic chlorine. The ground state chlorine yield is 5.8 times larger than the excited state chlorine yield [4].

Transport Process Modeling: Both precursor molecules and the primary/secondary electrons facilitating nanostructure deposition. Depending on the operating pressure (determines the mean free path of molecules), either continuous advection-diffusion equation or kinetic Boltzmann Transport Equation (BTE) describes the transport of precursor molecules from the bulk to the substrate surface. At the surface, some of them are adsorbed, and a fraction of the adsorbed molecules become converted into a solid deposit upon interaction with the secondary electrons.

The pertinent question becomes what controls the rate of the deposition process, i.e., both the magnitude and the trend of the time dependent growth of the nanostructure?

We have obtained a preliminary answer to this question via simple scaling arguments and analytical predictions. Clearly, the transient evolution (trend) of the deposit growth is defined by the slowest process in the transport-conversion sequence of the precursor molecules. Since adsorption and adsorbate-to-deposit conversion are much faster than bulk-to-surface mass transport, the latter is expected to define the deposit transient evolution behavior. However, it is the efficacy of adsorption (given by the sticking coefficient s_i) and adsorbate-to-deposit conversion aided by secondary electrons (given by the conversion factor X) that appear to be the rate limiting processes defining the amount of deposited material and its characteristic size at any time instant.

Figure 3a shows the time evolution trend in the dimensionless deposit size, which clearly contrasts the difference in the growth behavior (square-root vs. linear) that one would expect to see during the transition from the high pressure (continuous transport) to low pressure (kinetic transport) reactor operation. Figure 3b shows the predicted deposit size (on a logarithmic scale) as a function of the product of the sticking coefficient and the conversion efficiency for the system parameters typical of methane deposition. The deposit size and evolution trend predictions with a sticking coefficient times conversion efficiency factor equal to $\sim 10^{-3}$ correspond well to experimental results obtain in our group [1,2] and by others. These results are preliminary and require careful, fully-coupled reaction-transport calculations to reach a definitive conclusion on what controls the size and transient evolution of the deposit in EB-CVD.

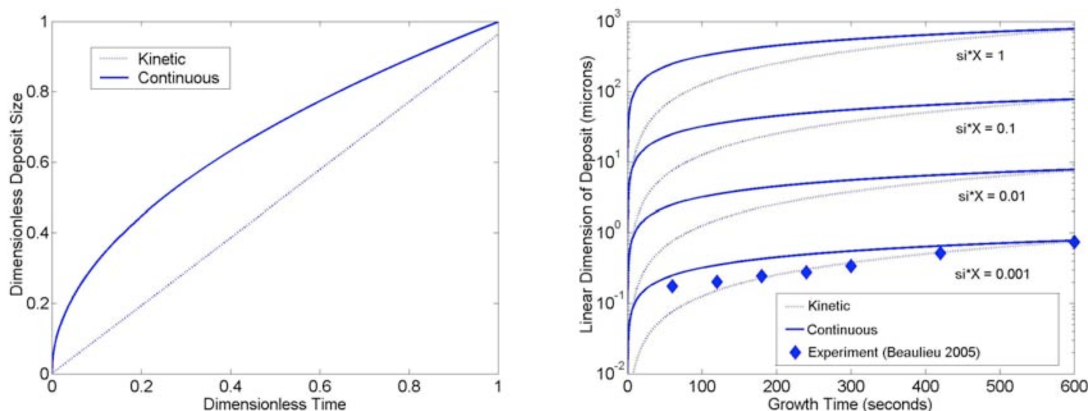

Fig. 3. (a) Deposit size evolution as function of transport mode (continuous vs. kinetic); (b) prediction of carbon deposition from methane as a function of the product of the sticking coefficient and adsorbate-to-deposit conversion factor (s_iX).

References

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[4] C. D. Lane and T. M. Orlando,"State-resolved detection of neutral products produced during low-energy electron interactions with $SiCl_4$ multilayers", *J. Chem. Phys.* (in press).