Integration of microplasma with transmission electron microscopy: Real-time observation of gold sputtering and island formation

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An in situ platform for characterizing plasma-materials interactions at the nanoscale in the transmission electron microscope (TEM) has been demonstrated. Integrating a DC microplasma device, having plane-parallel electrodes with a 25 nm thick Au film on both the cathode and anode and operating in 760 Torr of Ar, within a TEM provides real-time observation of Au sputtering and island formation with a spatial resolution of < 100 nm. Analyses of TEM and atomic force microscopy images show the growth of Au islands to proceed by a Stranski-Krastanov process at a rate that varies linearly with the discharge power and is approximately a factor of 3 larger than the predictions of a DC plasma sputtering model. The experiments reported here extend in situ TEM diagnostics to plasma-solid and plasma-liquid interactions.

Plasma-materials interactions are fundamental to the synthesis and performance of numerous materials and fabrication processes, respectively. Realizing nanoscale versions of tubes, wires, cones and belts, for example, often relies on plasma processing¹–⁴, and the contributions of nonequilibrium plasmas to lighting⁵, semiconductor device fabrication⁶, and the disinfection of biological tissue⁷ are difficult to overstate. Owing to the localized and nonlinear nature of plasma-materials interactions, however, the current understanding of the associated physical mechanisms is limited. Compounding the problem is the availability of few tools capable of directly observing such processes, particularly when probing the growth of nanomaterials of increasing technological interest. Consequently, gaining a deeper understanding of plasma-materials interactions at the nanoscale requires new approaches to surface characterization at the relevant spatial scale and in the presence of a challenging environment.

This Communication describes the implementation of an in situ platform for probing plasma-materials interactions with sub-100 nm spatial resolution by integrating a microplasma device⁸ with a transmission electron microscope (TEM). Argon plasma, generated between two Au films separated by 75 µm, in an enclosed environmental cell provides a versatile tool with which the sputtering and deposition of metal (for example) can be observed in real-time with unprecedented resolution. Data presented here demonstrate that the rate for Au deposition on the microplasma device anode varies linearly with the power deposited into the plasma and the experimental measurements correlate well with a theoretical model for sputtering in a DC plasma. In situ TEM was first demonstrated in 1942 (Ref. 9) but, in recent years, several environmental cell TEM techniques have been developed for examining fundamental physical and chemical processes in the gas and liquid phases⁹–¹¹. The sputtering/deposition microcell adopted here extends in situ TEM techniques to the investigation of plasma-solid and plasma-liquid interactions by incorporating Au-coated windows having an overall thickness of ~300 nm and separated by 75 µm. Such a cell allows for direct observations of both metal sputtering and deposition in the prototypical Ar-Au system to be made in situ to the microscope and in real time.

**Results**

Dynamics of gold film sputtering and island formation. Sputtering of a gold film by Ar ions arriving at the cathode surface is evident in the timelapse (the in-situ TEM video of the plasma-sputtering of a gold cathode film is shown in S1), bright field images of Fig. 1 (and S2). Results are presented as false-color maps acquired at $t = 0$ (panel (a)) as well as 13 min, 26 min, and 42 min after the initiation of processing. In recording these data, the
voltage imposed across the two electrodes of Fig. 6 was fixed at 400 VDC. It should be noted that the dark circles are contaminant particles having diameters \( \leq 150 \) nm. From the normalized image pixel profile of Fig. 1 and the sample thickness, the sputtering rate for the Au film is calculated to be \( 1.2 \times 10^{-2} \) nm–s\(^{-1}\) when the power deposited in the plasma is \( 700 \) VDC and \(~80\) mW, respectively. For these experiments, the discharge voltage and power delivered to the plasma were maintained at levels higher than those of Fig. 1 for the purpose of accelerating the growth process. Gold deposits initially in the uncoated (masked) circular regions of the anode as broad, thin films situated primarily near the center. This initial growth phase is attributable primarily to neutral Au atoms liberated by Ar\(^+\) bombardment of the cathode. Within seconds of the start of the deposition process, signs of island formation are observed. De-wetting of the broad thin films and the appearance of small islands (sub-20 nm) as early as \( t = 5 \) s is presumably the result of Au surface diffusion driven by interfacial energy considerations. Such kinetics closely resemble the Stranski-Krastanov growth mode in which the growth process is characterized by a transition from layer deposition to adatom clusters and islands when the layer thickness reaches a critical value. In the present experiments, formation of the critical precursor film is, indeed, observed immediately after ignition of the microplasma, and the island growth mode follows shortly thereafter.

Ex situ AFM scans of uncoated regions of the anode surface, similar to that of Fig. 2 for the cathode, corroborate the phenomena described above. Fig. 4 is a tomographic map, displayed in false color, of the morphology of a film deposited onto another circular, initially-uncoated region produced on the anode surface by a polystyrene sphere. Preferential nucleation of Au at the periphery of the 1 \( \mu \)m diameter circle is evident but film growth is also occurring at the center of the uncoated substrate region, as documented previously in Fig. 3. Based on feature height measurements from the AFM data, the Au island morphology appears to be that of truncated spheres. For
the experimental conditions of Fig. 3 (700 VDC discharge bias, \(\sim 80\) mW deposited power), an area-normalized growth rate of \(3 \times 10^{-2}\) nm-s\(^{-1}\) was extracted from both the TEM and AFM images. When the discharge voltage and power are increased to 800 VDC and \(100\) mW, respectively, the normalized growth rate rises to \(3.7 \times 10^{-2}\) nm-s\(^{-1}\).

### Discussion

To interpret the measured island growth rates, we adopt the expression proposed by Stutzin et al.\(^{13}\) for the rate of film growth due to sputtering in a parallel plate, DC discharge:

\[
R = \frac{P_d \langle x_{th} \rangle}{G \rho (1 + \gamma) E_s q}
\]

where \(P_d\) is the discharge power density, \(\langle x_{th} \rangle\) is the mean thermalization distance for an atom, \(G\) is the anode-cathode gap between the two parallel electrodes of Fig. 6, \(\rho\) is the atomic number density for the deposited film, \(\gamma\) is the secondary electron emission coefficient, \(E_s\) is the average sputtering energy for the material under study, and \(q\) is the magnitude of the charge on an electron. This expression, based upon a diode model, predicts the primary experimental trends observed in these and other experiments—namely, the linear variation of the film deposition rate with power deposited into the plasma, and the inverse dependence of \(R\) on the anode gap \(G\). Although explicit measurements of several of the variables in equation (1) are not available in the literature, all are readily estimated and, in accord with Ref. 13, we take \(\gamma\), \(E_s\), and \(\langle x_{th} \rangle\) to be 0.2, \(\sim 1\) keV, and \(60\) mTorr-cm/P (for Ar, where P is the gas pressure expressed in Torr), respectively.

Fig. 5 summarizes both theory and experimental measurements of the dependence of the Au island growth rate on the power dissipated by the microplasma. The solid line represents the prediction of equation (1) [Ref. 13], assuming the values for \(\gamma\), \(E_s\), and \(\langle x_{th} \rangle\) to be those presented earlier. Experimental data are indicated by the open circles (○) and the error bars associated with each point reflect the estimated uncertainty for that measurement. The broken line is included in Fig. 5 to indicate that theory and experiment differ by a factor of \(\sim 3\). However, considering: 1) the cumulative uncertainty introduced by several parameters in equation (1), and 2) the value for \(\langle x_{th} \rangle\) cited in Ref. 13 has been measured at Ar pressures considerably lower than those of interest here, one concludes that the factor of 3 discrepancy between theory and experiment in Fig. 5 can be viewed as reasonable agreement.

In summary, experiments have been described in which a microplasma has been generated \textit{in situ} to a TEM. The growth rate for

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**Figure 3** | False-color TEM images similar to those of Fig. 1 but recorded for a region of the anode surface (shown in red) that had been partially masked by polystyrene spheres. Data are presented for: (a) \(t = 0\); (b) \(t = 5\) s; (c) \(t = 38\) s, and (d) \(t = 2.5\) minutes following the start of the growth process. Island formation is evident at the later stages of the growth process.

**Figure 4** | AFM tomographic map, shown in false color and analogous to that of Fig. 2 except that the data were obtained in the vicinity of a circular, uncoated region on the anode. The calibration scale at right spans a range of 50 nm.
Figure 5 | Dependence of Au island growth rate on the power delivered to the microdischarge. The solid line represents the predictions of equation (1), assuming the values for several parameters to be those cited in the text. Experimental results are indicated by open circles and error bars reflect the estimated uncertainty in each measurement. The broken line demonstrates that theory and experiment differ by a factor of ~3.

Au islands was measured and found to correlate well with a diode model for DC sputtering and deposition in parallel plate geometry. Integration of a low temperature plasma with a TEM presents new opportunities in the science of plasma-materials interactions. Extending the present experiments to RF excitation of the plasma, and alternative window materials, will permit oxidizing environments to be investigated and, specifically, offers the ability to explore reaction pathways in specific materials systems. Furthermore, lattice images have already been obtained in the absence of the electric field imposed on the microplasma device. Continued effort to screen the microscope from spurious field effects will undoubtedly yield high-resolution lattice images in real-time and provide a window onto the microscopic history of the plasma-induced deposition process. Gold contact pads were patterned onto the outside (rear) face of both windows and Au wires were subsequently bonded onto the windows by a deionized water rinse, thereby exposing regions in which the window was uncoated. Polystyrene spheres were placed onto several of the windows to act as deposition masks. These circular openings in the gold film proved to be ideal for observing the temporal distributions of as-grown single-walled carbon nanotubes by tuning Ni₆Fe₁₋ₓ nanoparticles. Nature Mat. 8, 882 (2009).

Methods

Design of plasma cell. A cross-sectional diagram of the design for the plasma microcell developed for the present experiments is illustrated in Fig. 6. Commercially-available, Si-supported Si₃N₄ membranes having Si grid and Si₃N₄ thicknesses of 200 nm and 50 nm, respectively, served as the windows for the cell. Gold films, 25–50 nm in thickness, were deposited onto the interior faces of both windows by electron beam evaporation. Prior to the Au film growth process, ~1 μm diameter polystyrene spheres were placed onto several of the windows to act as deposition masks. After the Au films were deposited, the spheres were removed with acetone and a deionized water rinse, thereby exposing regions in which the window was uncoated. These circular openings in the gold film proved to be ideal for observing the temporal history of the plasma-induced deposition process. Gold contact pads were patterned onto the outside (rear) face of both windows and Au wires were subsequently bonded onto the pads. The Au-coated Si/Si₃N₄ windows were separated by 75 μm with spacers and the planar region between the windows was filled with 1 atm (~760 Torr) of Ar in a glovebox prior to sealing the structure. Before finalizing the assembly, the windows were placed in the Ar-filled glovebox for 24 h. Tests showed that this procedure yields microcells containing either a gas or a liquid that are stable in the vacuum environment of the TEM. For all of the experiments described here, the windows/electrodes were driven by a power supply delivering 350–800 VDC through a 1 MΩ resistor in series with the anode. Current supplied to the plasma was determined from the voltage developed across a 1 kΩ resistor. When the microcell was powered, the violet glow characteristic of Ar was readily visible through the 1.5 mm apertures at the top and bottom of the cell structure (S6).

Completed microcell assemblies were installed in a JEOL-2010 LaB₆ microscope having a video capture system. Morphology of the anode and cathode gold films was examined at several stages of the sputtering and deposition process by ex situ atomic force microscopy (AFM).

Monte Carlo simulations (Electron Flight Simulator) predict that ~3% of the 200 keV electrons incident on the microcell scatter elastically. Based upon the electron fluxes utilized in these experiments (beam current density of ~1.5 mA·cm⁻²), the fraction of the gas atoms in the cell ionized by the particle beam is ~10⁻⁴ which is negligible compared to that generated by the plasma itself (~10⁻¹ for an estimated electron density of ~10¹⁴ cm⁻³).

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