

Electron-Enhanced Atomic Layer Deposition (ALD) and Atomic Layer Etching (ALE)

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Electrons can be employed to enhance atomic layer deposition (ALD) and atomic layer etching (ALE). For electron-enhanced ALD (EE-ALD), the electrons can facilitate ALD nucleation, lower the ALD temperatures, and enable new ALD chemistry. The mechanisms for EE-ALD involve surface and gas phase activation. The surface can be activated by desorbing ligands from the surface by electron stimulated desorption (ESD). The gas phase can be activated by dissociating various gases to produce reactive radicals. The mechanisms for EE-ALE also involve surface and gas phase activation. Surface species can be removed by ESD. Reactive radicals can also be produced in the gas phase that enable the production of volatile etch products. The electron exposures for the EE-ALD and EE-ALE in this presentation were derived from a hollow cathode plasma electron source (HC-PES) that delivered electrons at ~100 eV.

Results for EE-ALD of amorphous titanium carbonitride (TiC_xN_y) demonstrated the EE-ALD of a ternary nitride with tunable carbon content. Amorphous titanium carbonitride is used as a diffusion barrier. TiC_xN_y EE-ALD was achieved using sequential exposures of tetrakis(dimethylamino) titanium (TDMAT) and low energy electrons in the presence of a continuous NH_3 reactive background gas (**Figure 1**). Carbon content in the TiC_xN_y films was tuned by varying the NH_3 background pressure and the electron exposure time. Nucleation occurred within the first two EE-ALD cycles (**Figure 2**) and the growth rates were in the range of 0.4-0.9 Å/cycle.

Results for controlled electron-enhanced etching of molybdenum (Mo) demonstrated the EE-ALE of a transition metal. Mo is a potential backend interconnect material for advanced nodes. Mo film etching was controlled using alternating O_2 and HCl pressures combined with simultaneous electron exposures. In addition, a positive sample voltage increased the Mo oxidation and Mo oxide removal as a volatile Mo oxychloride. The enhancement by positive sample voltage suggested that O^- and Cl^- gas phase anions were the dominant reactive species. Alternating oxidation and chlorination steps in a controlled digital fashion produced a Mo etch rate of 1.3 Å/cycle (**Figure 3**).

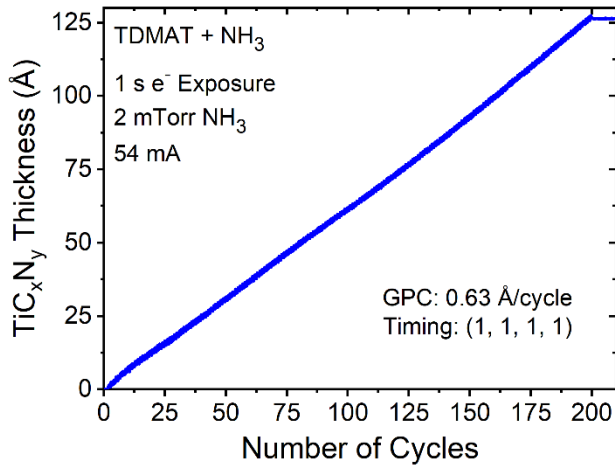


Figure 1. TiC_xN_y film thickness during 200 cycles of TiC_xN_y EE-ALD on Si native oxide measured by in situ ellipsometry. Growth rate of 0.63 Å/cycle was obtained using TDMAT with a NH₃ background pressure of 2 mTorr and timing sequence with time in seconds of (1, 1, 1, 1).

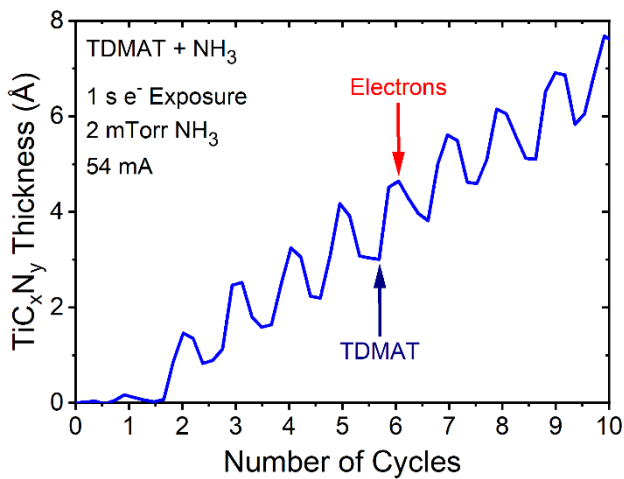


Figure 2. Initial growth during first 10 cycles of TiC_xN_y EE-ALD in Figure 1 showing rapid nucleation of TiC_xN_y film growth. In situ ellipsometry can monitor the digital nature of film growth resulting from sequential TDMAT and electron exposures.

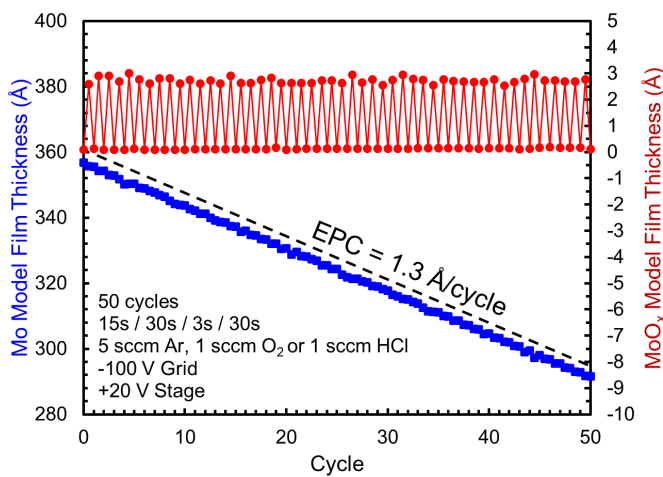


Figure 3. Mo and MoO_x model film thickness versus cycle during Mo etching using alternating exposures of O₂ and HCl background gases. Stage bias was +20 V. Grid bias was -100 V. Reaction sequence was 15 s O₂ + electrons, 30 s purge, 3 s HCl + electrons, 30 s purge. Etch per cycle was 1.3 Å/cycle.