Mechanism of Hydrogen Plasma Modified ALD Growth of Metal-enriched Oxides Studied by *In-Situ* Mass Spectrometry

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Modifying atomic layer deposition (ALD) growth by inserting argon/hydrogen plasma steps has been shown to alter the stoichiometry of oxides, driving metal-enriched films and lower oxidation states. Altering oxide stoichiometry is useful for changing the electrical conductivity, optical properties, bandgaps, and other device characteristics; often inaccessible from typical ALD growth. It has been unclear what the mechanism of the plasma-surface reactions and modifications to standard chemical (or "thermal") ALD growth has been in these processes, however. To elucidate this mechanism, a quadrupole mass spectrometer has been used to examine both reactant and product gas species during the ALD and plasma-modified ALD reactions of ZnO growth from diethyl zinc (DEZ), water, and H_2/Ar plasmas.

Comparison was made between thermal reactions, inserting H_2/Ar plasma after the metal precursor step, after the oxidant step, between sequential metal precursor steps before the oxidant step, and of argon-only plasma between sequential metal steps. Evidence for a mechanism involving metal-organic ligand desorption and further reaction with the plasma upon H_2/Ar plasma exposure is to be presented. No evidence demonstrating removal of oxygen atoms from the growing film, either by O_2 or H_2O gas evolution was found. Zinc metal enriching in ZnO growth occurs when the H_2/Ar plasma is inserted between sequential DEZ steps before the water steps. When the ethyl-terminated surface (after DEZ reaction) is exposed to plasma, primarily a small amount of methane (M/Z = 16) is produced, with a trace of ethane (M/Z = 28). This is due to ethane desorption and fast reaction with the large excess of hydrogen radicals from the plasma, cracking ethane to methane. After desorption of ethyl ligands, sites open up for additional adsorption of Zn in the second DEZ step. Plasmas containing hydrogen are required, as no ethane nor methane was observed with argon-only plasma.

To verify the generality of this mechanism for plasma-modified ALD using hydrogen plasmas to metal enrich ALD-grown oxides, additional modified oxide materials will also be presented (*i.e.* Nb_2O_5 to NbO_2, etc.).

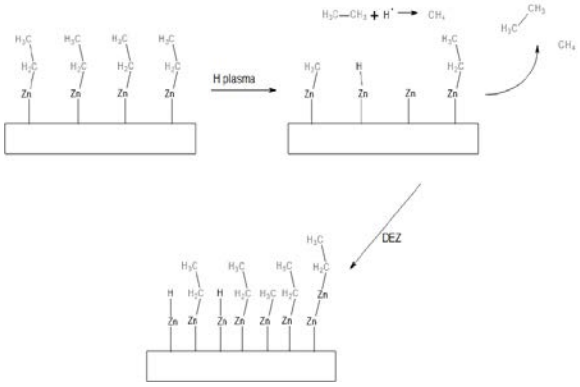

Figure 1 Scheme of chemical surface modification by H plasma and second metal precursor step.

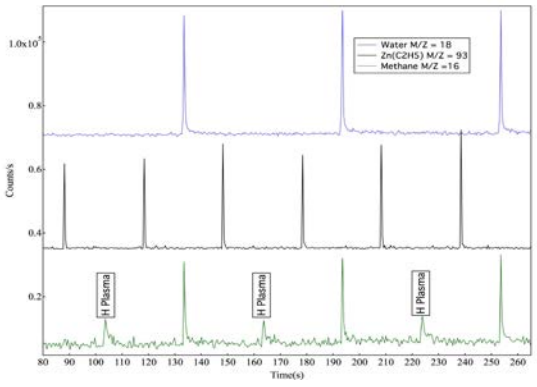

Figure 2 Mass spectral data demonstrating methane evolution upon H plasma reaction.

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