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Heterogeneous Reactions in Processing Plasmas[1]

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This talk will briefly review issues related to reactions of atoms and small molecules on substrates and chamber walls that are immersed in a plasma, a relatively unexplored, yet very important area of plasma science and technology. Emphasis will be placed on diagnostic methods, and in particular the "spinning wall" technique. With this method, a cylindrical substrate in the wall of the plasma reactor is rotated, and the surface is periodically exposed to the plasma and then to a differentially pumped diagnostics chamber and optionally to a beam of additional reactants or surface coatings. Reactants impinging on the surface can stick and react over time scales that are comparable to the substrate rotation period, which can be varied from ∼0.5 to 40 ms. Langmuir-Hinshelwood reaction probabilities can be derived from a measurement of the absolute desorption product yields as a function of the substrate rotation frequency. Auger electron spectroscopy allows the plasma-immersed surface to be monitored during plasma operation. Mass spectrometer cracking patterns are used to identify simple desorption products. In oxygen or chlorine plasmas, surfaces become coated with a layer containing Si, Al, and O, due to slow erosion of the reactor materials, in addition to Cl in chlorine plasmas. Low recombination probabilities were found for Cl and O on anodized Al and stainless steel surfaces, consistent with the similar chemical composition of the layer that forms on these surfaces after long exposure to the plasma. Weakly adsorbed Cl_2 was found to inhibit Cl recombination, hence the Cl recombination probability decreases with increasing Cl_2-to-Cl number density ratios in chlorine plasmas. In Cl_2/O_2 plasmas, Cl and O recombination occur, but in addition, ClO and ClO_2 form on the surface and desorb. These and other results, including a multi-site model and the catalytic enhancement of O recombination by monolayer amounts of Cu, will be discussed.

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