SURFACE CHEMISTRY DURING PLASMA ETCHING OF SILICON, V. M. Donnelly, I. P Herman[a], C-C. Cheng[b], and K. V. Guinn, AT&T Bell Laboratories, 600 Mountain Ave. Murray Hill, NJ 07974.

Angle-resolved x-ray photoelectron spectroscopy (XPS) and laser-induced thermal desorption (LD), combined with laser-induced fluorescence (LIF) detection, were used to study the etching of polycrystalline Si (poly-Si) and single crystal Si(100) in high density (1-2 x 10^{11} ions/cm^3), low pressure (0.5-10 mTorr) $Cl_2/HBr/O_2$-containing, helical resonator plasmas. The XPS measurements on both unmasked Si(100) and fine-line masked poly-Si samples were performed after the sample was etched and then transferred under high vacuum from the plasma reactor to the ultrahigh vacuum (UHV) analysis chamber. Shadowing of photoelectrons by adjacent features and differential electrostatic charging were used to distinguish adsorbates on the photoresist-masked surfaces from those on etched Si sidewalls and trench bottoms. The LD-LIF measurements on unmasked Si(100) samples were performed *in-situ* during etching. When Si is etched in a Cl_2 plasma, XeCl excimer laser pulses rapidly heat the Si surface to near the melting point, causing thermal desorption of SiCl. The tail of the same laser pulse excites SiCl to the ($B^2\Sigma^+$) state in the gas-phase near the surface. Subsequent fluorescence from this state is detected with a monochromator and photomultiplier tube detector. The SiCl LIF signal is proportional to Cl-coverage, verified by XPS. Thus, at low laser repetition rates the LD-LIF method provides an instantaneous measure of chlorine coverage at steady state, while at high laser repetition rates, the approach to steady state can be followed. In HBr-containing plasmas, an analogous detection scheme can be used to detect SiBr by LD-LIF, providing a measure of Br coverage. In mixed Cl_2/HBr plasmas, both species can be detected simultaneously. The major findings of these studies are that Si surfaces rapidly become covered with a saturated layer of about 2 monolayers of halogens during plasma etching. The layer consists on silicon mono-, di-, and tri-halides. Once formed, this layer is stable indefinitely under UHV conditions. In Cl_2 plasmas, the Cl coverage increases with increasing ion energy, but is nearly independent of pressure (0.5-10 mTorr). A first-order rate coefficient of 8.1 x 10^4 s^{-1} $Torr^{-1}$ was derived from the dependence of the LD-LIF signal on laser repetition rate. This indicates that chlorination occurs rapidly with respect to the time required to etch one monolayer, at pressures as low as 0.5 mTorr. Consequently, the etching rate is limited by the ion flux, and not the neutral flux under these conditions. In mixed Cl_2/HBr plasmas, the coverages of Cl and Br are simply proportional to the total respective halogen content of the feed gas. Other implications for etching mechanisms will be discussed.

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