Surface chemistry during plasma etching of silicon

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<u>Abstract</u>: 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-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. The LD-LIF measurements on unmasked Si(100) samples were performed *in-situ* during etching. In these experiments, 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. The subsequent fluorescence signal from this state is proportional to Cl-coverage, verified by XPS. In HBr-containing plasmas, analogous LD-LIF detection was used for SiBr, providing a measure of Br coverage. The major findings of these studies are that Si surfaces rapidly become covered with a stable (in vacuum), saturated layer of about 2 monolayers of halogens during plasma etching. The layer consists of silicon mono-, di-, and tri-halides. In Cl$_2$ plasmas, the Cl coverage increases with increasing ion energy, but is nearly independent of pressure (0.5-20 mTorr). 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 are discussed.

INTRODUCTION

Despite considerable effort, plasma etching mechanisms are still not well understood. In particular, deviations from ideal anisotropic etching are often observed and are the subject of many current investigations. Most experimental and theoretical studies have dealt with the gas-phase plasma physics and chemistry. Fewer studies have been performed on plasma-surface interactions, and most of these have either carried out surface analysis after etching, or have simulated plasma conditions in high-vacuum beam experiments. This high vacuum, non-plasma environment is necessary to allow conventional electron-detection-based surface analysis techniques to be used. To understand and better control etching processes, real-time surface diagnostic techniques are required that are not based on electron spectroscopy. Infrared (IR) optical absorption is one possible technique that can be applied, and one study of etching of Si in a chlorine plasma has recently been published (1). Surface IR absorption is weak, however, and Si-Cl vibrational frequencies are low, so that special wedged substrates with buried metal layers are required to obtain sufficient sensitivity. Recently, we reported a laser desorption-laser induced fluorescence (LD-LIF) technique for measuring Cl and Br coverages on Si during etching in high-density HBr/Cl$_2$ plasmas (2)-(4). Laser pulses are used to rapidly heat the surface and desorb Si-monohalide which is in turn detected by laser-induced fluorescence. The LD-LIF technique can be

applied at the pressures typically used in plasma etching, as well as at higher pressures and is capable of detecting coverages of <0.1 monolayers with a time resolution of less than 0.02 s. A description of this technique and selected applications from recent reports (2)-(4) are summarized here.

EXPERIMENTAL PROCEDURE

The plasma reactor consists of a helical resonator source and a stainless steel downstream chamber (2)-(6). The substrate stage is radio-frequency (rf) biased to achieve DC bias voltages of 0-120 V. The charge density above the Si substrate in the downstream chamber was 1-2 x 10^{11} cm^{-3}. Cl_2/HBr total flow rates of 2-17 sccm and pressures of 0.6-20 mTorr were used. The Cl_2/(HBr+Cl_2) ratio was varied from 0 to 1. Polycrystalline Si (poly-Si) and single crystal Si(100) substrates were used. A UHV load-lock chamber connects the plasma reactor to a UHV analysis chamber, allowing samples to be transferred to this chamber after etching, without exposure to air. Angle-resolved x-ray photoelectron spectroscopy (XPS) measurements are performed in this analysis chamber. The LD-LIF detection apparatus is mounted on the plasma chamber. It consists of a XeCl excimer laser, imaging optics to collect the fluorescence, and a monochromator equipped with a photomultiplier tube. The laser beam passes through a viewport at the top of the plasma source and irradiates the sample at normal incidence. The fluorescence from the near-surface region is imaged onto the entrance slit of the monochromator.

RESULTS AND DISCUSSION

After etching, angle-resolved XPS measurements on masked samples used shadowing of photoelectrons by adjacent features and differential electrostatic charging (5), (6), (7) to distinguish adsorbates on the photoresist (PR) -masked surfaces from those on etched Si sidewalls and trench bottoms. These results are discussed in detail elsewhere (5), (6). In pure Cl_2 plasmas, about 2 monolayers of Cl was found on all 4 surfaces (i.e. PR and poly-Si vertical and horizontal surfaces). No carbon was detected on the poly-Si surfaces, however, a thin coverage of Si was found on the PR sidewall. Analogous results were obtained in pure HBr plasmas. High resolution Si(2p) spectra revealed that Si- mono, di, and tri-halides were present. A sample spectrum recorded after etching in a Cl_2 plasma is shown in Figure 1.

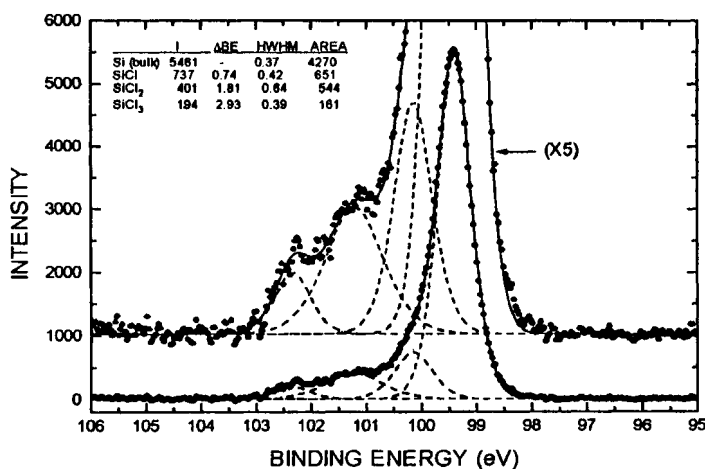|	I	ΔBE	HWHM	AREA
Si (bulk)	5461	-	0.37	4270
SiCl	737	0.74	0.42	651
SiCl₂	401	1.81	0.64	544
SiCl₃	194	2.93	0.39	161

Fig. 1. Si(2p 3/2) XPS spectrum recorded after etching in a Cl_2 plasma without laser irradiation. (from ref. 3). The 2p 1/2 spin-orbit component has been removed. The relative areas for SiCl:SiCl₂:SiCl₃ are 1.0:0.84:0.25.

The LD-LIF measurements on unmasked Si(100) samples were performed *in-situ* during etching. In this process, 15 ns 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 from the v=3,4 vibrational levels of the ground electronic state to the v=0 level of the (B$^2\Sigma^+$) state in the gas-phase. Subsequent fluorescence from this state is detected with the monochromator and photomultiplier tube detector. The (B$^2\Sigma^+$) state has a lifetime of 10 ns, so the fluorescence is confined to a region within about 10 μm from the surface. The fluorescence spectrum recorded with the plasma on and off are presented in Fig. 2. The strong bands are due to transitions from the v=0 level of the (B$^2\Sigma^+$) state to vibrational levels of the ground state. The factor of two increase in signal when the plasma is on is due to an increase in Cl coverage. Both the plasma on and plasma off signals depend on laser fluence in a manner that suggests a thermal desorption process. They have distinct threshold fluences and they
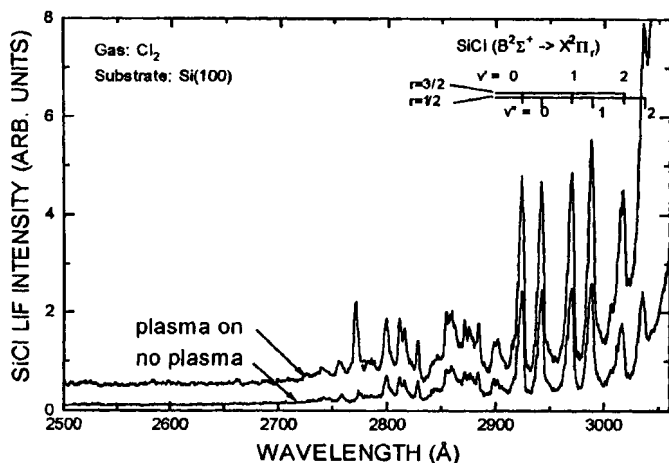
Fig. 2. Steady-state LD-LIF spectra (from ref. 3) recorded during exposure of Si(100) to Cl_2 gas (no plasma, bottom trace) and a 280 W plasma (top trace).

saturate at fluences above about 0.5 J/cm^2. The threshold fluence for the signal with the plasma on (0.15 J/cm^2) is lower than that observed with the plasma off (0.35 J/cm^2), indicating that a more weakly bound layer forms when Si(100) is exposed to a Cl_2 plasma. These layers (plasma on or off) are stable after the laser desorption is interrupted, the plasma is extinguished and gas pumped away, and the laser irradiation is resumed minutes later. The LD-LIF signals observed on the first pulse are close to the respective steady-state levels. Continuous irradiation under these conditions leads to a rapid decay of signal to an undetectable level. Roughly 1/e of the Cl is removed per laser pulse. These observations suggest that the $SiCl_x$ adsorbed layer is stable after the plasma is extinguished, so the XPS analysis in Fig. 1 is indicative of the steady-state surface during etching.

The SiCl LIF signal is proportional to Cl-coverage as verified by XPS. This was shown by transferring samples to the analysis chamber after exposure to the plasma (no laser irradiation for the last segment of the exposure), or after exposure to the laser and Cl_2 with no plasma. The Cl(2p)-to-Si(2p) ratio was 1.9 X higher after plasma exposure than with just exposure to the laser and Cl_2, in good agreement with the 2.2-fold increase in the LD-LIF signal when the plasma is on. Thus, at low laser repetition rates the LD-LIF method provides an instantaneous measure of chlorine coverage at steady state. Cl-coverage was measured as a function of discharge power, pressure, and bias voltage. The power dependence is reproduced in Fig. 3. The total Cl-coverage increases rapidly with power and reaches a saturated level at a substantially lower power than does the etch rate or ion flux (saturated ion current in Fig. 3). This is ascribed to the increase in the formation of Cl-atoms with increasing power, which is shown elsewhere to depend on power in a similar manner. (8) The etch rate increases both with Cl-coverage and ion flux at low power, and then is proportional to ion flux at the higher powers that at more typical of standard conditions in commercial high-density plasmas. Consequently, the etch rate under these latter conditions is limited by the ion-bombardment removal of product rather than by the supply of Cl to the surface. This is further supported by a pressure-independent Cl-coverage and etch rate as a function of pressure (0.6-20 mTorr).
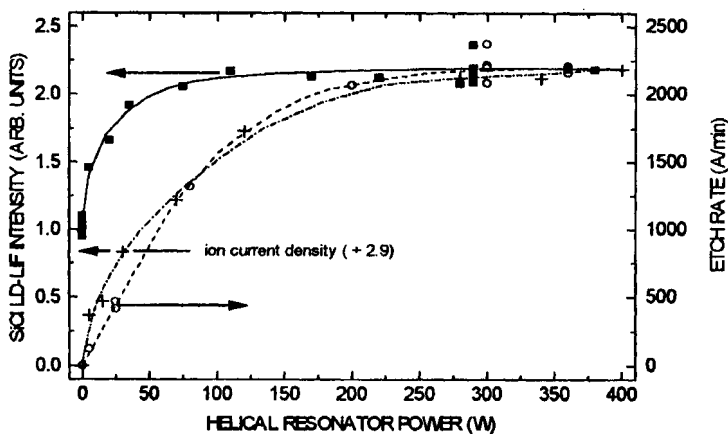

Fig. 3. LD-LIF signal intensity (1 arb. unit = 5 x 10^{14} Cl/cm^2), saturated ion current, and Si etch rate vs. Cl_2 discharge power (from ref. 3).
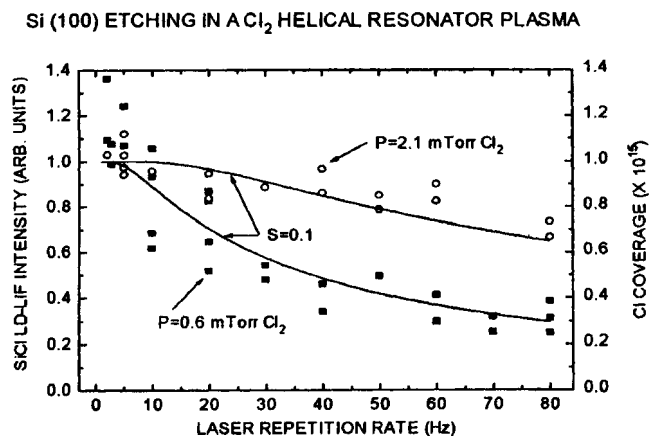
Si (100) ETCHING IN A Cl₂ HELICAL RESONATOR PLASMA

Fig. 4. LD-LIF signal intensity (converted to Cl-coverage on the right-hand axis) vs. laser repetition rate during Cl₂ plasma etching of Si(100) (adapted from ref. 3).

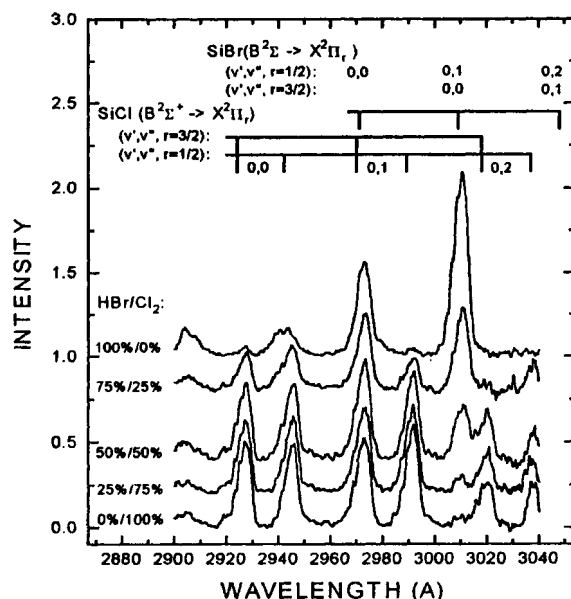Fig. 5. LD-LIF spectra of SiCl and SiBr in Cl₂/HBr plasmas as a function of gas ratio during plasma etching of Si(100) (from ref. 4).

At high laser repetition rates, the approach to steady state Cl-coverage can be followed. A plot of Cl-coverage as a function of repetition rate is shown in Fig. 4 for two pressures. At low pressure and high repetition rate the laser irradiation is removing Cl faster than the plasma can supply it. A first-order rate coefficient of 8.1×10^4 s^{-1} Torr^{-1} was derived from the dependence of the LD-LIF signal on laser repetition rate and pressure. This indicates that chlorination occurs rapidly with respect to the time required to etch one monolayer, at pressures as low as 0.5 mTorr. The predominant species impinging on the surface is believed to be Cl-atoms (8). If we ignore the other chlorine species, then using a simple Langmuir adsorption model, we can derive a sticking coefficient of ~0.1 (fits indicated by the solid curves in Fig. 4).

In HBr-containing plasmas, an analogous detection scheme can be used to detect SiBr by LD-LIF, providing a measure of Br coverage (4). In mixed Cl₂/HBr plasmas, both species can be detected simultaneously, as shown in Fig. 5. In Cl₂/HBr plasmas, the coverages of Cl and Br are simply proportional to the total respective halogen content of the feed gas. The total halogen coverage decreases with increasing HBr, reaching a saturated Br coverage in pure HBr plasmas of 0.6 X the saturated Cl-coverage in Cl₂ plasmas. The similar reduction in the etch rate in HBr plasmas is likely due to this reduced halogen coverage.

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