CHEMICAL TOPOGRAPHY OF Si ETCHING IN A Cl_2 PLASMA, STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY AND LASER-INDUCED THERMAL DESORPTION

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ABSTRACT

This paper describes x-ray photoelectron spectroscopy (XPS) studies of etching of Si in high-density Cl_2 plasmas. Polycrystalline Si films, masked with photoresist stripes, are etched and then transferred in vacuum to the XPS analysis chamber. Shadowing of photoelectrons by adjacent stripes and differential charging of the photoresist and poly-Si were used to separate contributions from the top of the mask, the side of the mask, the etched poly-Si sidewall, and the bottom of the etched trench. In pure Cl_2 plasmas, surfaces are covered with about one monolayer of Cl. If oxygen is introduced into the plasma, either by addition of O_2 or by erosion of the glass discharge tube, then a thin Si-oxide layer forms on the sides of both the poly-Si and the photoresist. Laser-induced thermal desorption (LITD) was used to study etching in real time. LITD of SiCl was detected by laser-induced fluorescence. These studies show that the Si-chloride layer formed during plasma etching is stable after the plasma is extinguished, so the XPS measurements are representative of the surface during etching. LITD measurements as a function of pressure and discharge power show that the etching rate is limited by the positive ion flux to the surface, and not by the supply of Cl_2, at pressures above 0.5 mTorr and for ion fluxes of $\sim 4 \times 10^{16} cm^{-2} s^{-1}$.

INTRODUCTION

With the advent of high charge density ($10^{11} - 10^{12} cm^{-3}$), low ion energy (<100 eV), low pressure (0.3-10 mTorr) plasmas for anisotropic etching of microelectronics materials, mechanisms for etching need to be re-examined. At ion energies of several hundred eV traditionally used in higher pressure processes, etching is generally believed to occur by an ion-enhancement of surface reactions with species (e.g. Cl-atoms) formed from the etchant gas (e.g. Cl_2) in the plasma [1,2]. The chemically enhanced ion sputtering yields exceed one Si atom-per-ion, and the flux of neutrals is orders of magnitude larger than the ion flux. In low pressure, high density plasmas, however, the low ion energies cause the yields to be less than one, and the ion flux is comparable to the neutral flux.

In this paper, we describe *ex situ* x-ray photoelectron spectroscopy (XPS) studies of anisotropic etching of photoresist-masked polycrystalline Si in a high-density helical resonator Cl_2 plasma. The XPS analysis uses shadowing of photoelectrons by adjacent features to spatially resolve adsorbate coverages. This principle was first reported by Fadley [3,4], and was more recently adapted by Oehrlein and co-workers to study etched features [5-8]. We also use *in situ* laser induced desorption measurements performed in real time during etching to determine Cl-coverages as a function of time and plasma conditions. More detailed accounts of this work are reported elsewhere [9-11].

EXPERIMENTAL PROCEDURE

The apparatus described in detail previously (Figure 1) [9-12], consists of a plasma reactor and an ultrahigh vacuum chamber equipped with an X-ray photoelectron spectrometer (XPS). The plasma reactor contains a high-density helical resonator source with magnetic confinement.

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Samples used for XPS analysis consist of SiO_2-covered Si(100) substrates on which are deposited 3000Å of undoped polycrystalline Si. These samples are then masked with patterned photoresist (PR). Samples are clamped to a stainless steel holder so that after etching they can be moved under high vacuum to the analysis chamber. Etching was carried out at a pressure of 1 mTorr Cl_2. The plasma density was $1-2x10^{11}$ positive ions/cm^3, and the ion current was 6.3mA/cm^2 ($3.9x10^{16}$ions/cm^2/s) [11]. A radio frequency bias was applied to the sample stage to obtain a DC bias of -35 V in most experiments, or 0 to -100 V in experiments that investigated the effects of bias. The plasma potential was 50 V, so the energy of ions bombarding the substrate was 85 eV, when the DC bias voltage was -35V.

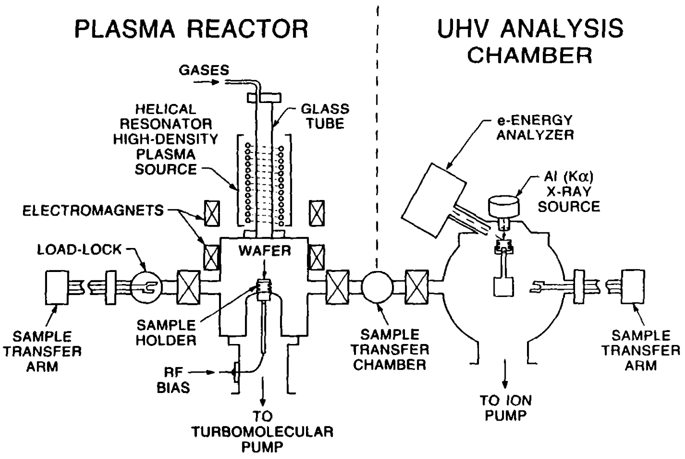

Figure 1. Schematic depiction of the plasma etching chamber and XPS analysis chamber.

After etching, samples were transferred under vacuum to the XPS chamber. In XPS analysis, the sample is irradiated with an X-ray beam that penetrates several microns into the material. Photoelectrons are detected at different take-off angles, θ. When θ=90°, the top of the mask and the bottom of the trench are mainly detected. When θ=30°, the top of the mask and the side of the features are seen. Also, since PR is an insulator, the XPS peaks are shifted, allowing adsorbates on PR and Si to be resolved. We can also flood the surface with low energy electrons, neutralizing the charge and shifting the peaks back to their normal binding energies to aid in making assignments.

Laser-induced desorption measurements were performed *in situ*, both during and after etching of bare Si(100) substrates. The excimer laser (XeCl, 308 nm 0.2−0.6J/cm^2, 15 ns pulses at 1-80 Hz) irradiated the surface at normal incidence and caused transient heating of the surface. Products are thermally desorbed and are excited both by the tail of the laser pulse and by electron impact excitation in the plasma. The former, laser-induced fluorescence (LIF) method was used to detect laser-induced thermal desorption of SiCl, and is described elsewhere [11,12]. The latter method was not used in the study reported here and is discussed in another report [12].

RESULTS AND DISCUSSION

X-Ray Photoelectron Spectroscopy

Figure 2 shows an example of Si(2p) spectra for 0.75μm lines and spaces after etching in a Cl_2 plasma. Etching was stopped before reaching the SiO_2 layer. At $\theta = 90°$, we see elemental Si (Si(2p) peak at 99.5 eV) at the bottom of the poly-Si trench. Since the poly-Si does not charge up, the flood gun has no effect on the electron kinetic energy and hence apparent binding energy. At $\theta = 30°$, photoelectrons from the top and side of the mask and a small amount from the poly-Si sidewall can reach the electron energy analyzer. The small Si signal at 99.6 eV comes from the poly-Si sidewall. In addition, with the charge neutralizer off, a broad feature is observed between 100 and 114 eV. This apparent binding energy is too high to be due to a chemical shift. When the flood gun is turned on, the broad feature shifts to the position expected for SiO_2. Therefore this feature originates from oxidized Si (SiO_xCl_y, see below) on PR. Since the broad feature is not observed at $\theta = 90°$, this SiO_xCl_y adsorbate is only on the side and not on the top of the PR.

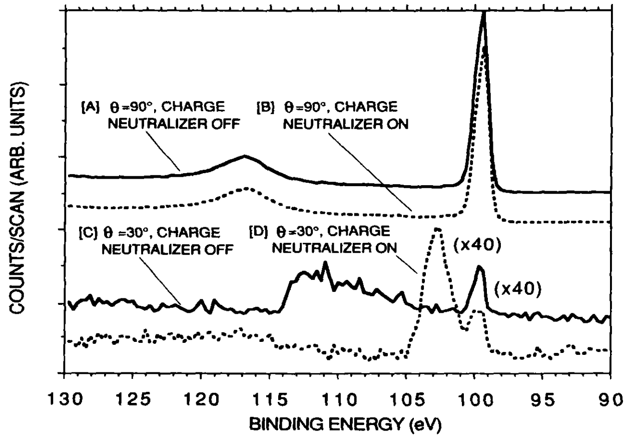

Figure 2. Si(2p) spectra for the region of 0.75μm lines and spaces, recorded after etching. (a): Charge neutralizer off, $\theta = 90°$. (b): Charge neutralizer on, $\theta = 90°$. (c): Charge neutralizer off, $\theta = 30°$. (d): Charge neutralizer on, $\theta = 30°$.

We can perform similar analyses for the other elements to derive separate XPS signals for elements on poly-Si and PR. We then use measurements at $\theta = 90°$ to determine atomic concentrations for species on top of the PR and at the bottom of the poly-Si trenches. This information, in conjunction with measured θ dependences and the angle response function of the analyzer, and modelling of geometric shadowing of photoelectrons and X-ray absorption, is used to determine the atomic concentrations of adsorbates on the PR and poly-Si sidewalls. These concentrations are then converted into a two-dimensional bar graph or "chemical topography" of the etched surface, as shown in the example in Figure 3. In this method of presenting the results, the atomic concentration of each surface species is ratioed to that of the main bulk component (i.e. Si for poly-Si regions, and C for PR regions). In this example, the bottoms of etched poly-Si features are covered with roughly a monolayer of Cl and not much else. There appears to be somewhat less Cl on the poly-Si sidewall, in addition to some O. In contrast, PR picks up much more Cl on the side and less on top. The PR sidewalls are also covered with a thin layer of oxidized Si (SiO_xCl_y). The O on the poly-Si sidewall and SiO_xCl_y on the side of the PR come from deposition of products from erosion of the glass tube where the helical resonator plasma is formed. [9] When the reactor was modified to minimize this erosion, etching in a pure Cl_2 plasma produced about a monolayer of Cl on etched surfaces, and much less O (on poly-Si) and Si (on PR). One of the more striking conclusions is the lack of C on the Si over a wide range of conditions, even though the mask was also etching. It is often speculated that C eroding from PR produces a thin film that protects poly-Si sidewalls and prevents undercutting. We find no evidence for this process under the etching conditions used in this study.

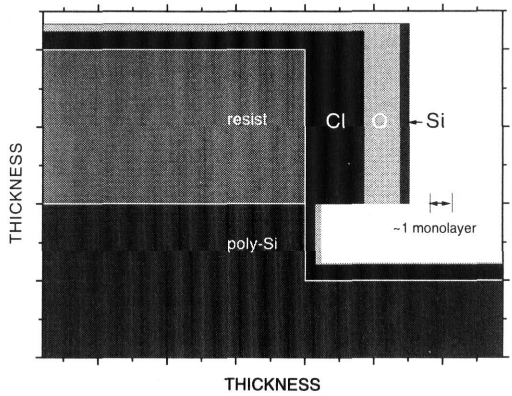

Figure 3. Chemical topography plot of the photoresist/poly-Si structure after etching with a pure Cl_2 plasma, under conditions where the glass tube containing the high-density plasma was eroding at an accelerated rate. The thickness of each of the bands is proportional to the atomic concentration of adsorbates on that surface, ratioed to the major component for the bulk material (i.e. Si for the poly-Si regions and C for the photoresist regions).

Laser-Induced Thermal Desorption

One question frequently asked in post-processing analysis is whether the analyzed surface is representative of the one present during etching, i.e. do adsorbates desorb in the time that it takes to move the sample to the XPS chamber, or is the surface further chlorinated during the pump down and transfer period. To address these issues, we have developed an *in situ* analysis technique. We use laser pulses to thermally desorb and detect adsorbates present during etching. In the present case, the same pulse excites LIF of SiCl [11-14], unambiguously identified from the observed fluorescence spectrum corresponding to the transition ($B^2\Sigma^+_o \rightarrow X^2\Pi$). The signal observed as a function of time (Figure 4) at a fixed wavelength (2930Å) is a real-time, relative measure of the coverage of Cl during exposure to Cl_2 with the plasma either on or off [11]. We see that the Cl coverage from exposure to Cl_2 immediately doubles and then remains nearly constant when the plasma is turned on. When the plasma is turned off with the laser blocked, the Cl_2 is pumped away, and laser irradiation is resumed (~5min later), the signal observed on the first laser pulse is nearly equal to (about 90% of) the steady-state signal during etching, indicating that the surface has changed little during this 5 min period. Consequently, the chemical topographies derived form XPS measurements are a good reflection of the surfaces during etching.

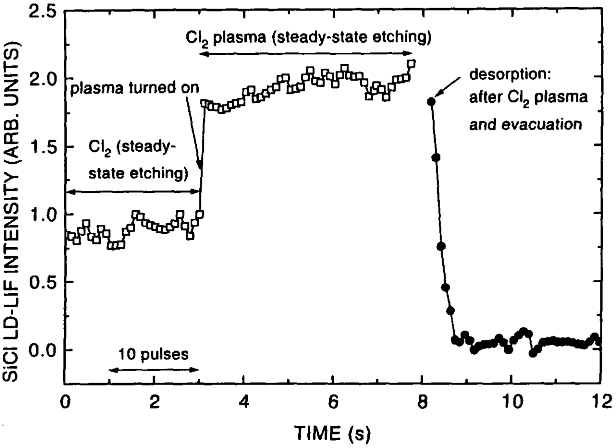

Figure 4. LIF intensity of laser-desorbed SiCl (2930Å) as a function of time. The open squares show steady-state laser-induced etching of Si by Cl_2, and then etching with the plasma suddenly turned on (at 3 s). (●): Time dependence of desorbed SiCl after chlorination with the plasma and subsequent pump down. For comparison, this trace has been placed immediately after the steady-state measurement. Laser repetition rate = 5 Hz, laser fluence=0.5J/cm^2.

We have also used the laser-desorption method to determine Cl coverage in real time as a function of discharge power, sample bias, and pressure. These results are reported elsewhere [11]. We show the power and bias dependences in Figures 5 and 6. Also plotted in Figures 5 and 6 are the poly-Si etch rates and (in Figure 6) the saturated ion current density. The Cl coverage increases rapidly with power and saturates at ~100W. The etch rate rises less steeply with power, and saturates at the same power (~200W) at which the ion current density saturates. These results indicate that the etching rate is limited by the flux of ions to the surface, and not by the neutral chlorine flux, under typical etching conditions (a pressure of 1-10 mTorr, and a power density of ~1W/cm^3 (~400W in our plasma source)). This is also substantiated by an etching rate that is nearly independent of pressure. From etch rate measurements as a function of DC bias voltage (Figure 6) and saturated ion current density measurements (3.9×10^{16} cm^{-2}s^{-1}, independent of bias), we determined that the chemically enhanced ion sputtering yield (Si atoms-per-positive ion) is 0.38 at an ion energy of 50 eV and 0.60 at 120 eV.

CONCLUSIONS

We have used *ex situ* x-ray photoelectron spectroscopy, with vacuum sample transfer, to study etching of Si in a high-charge-density ($1-2 \times 10^{11}$ ions/cm^3), low pressure (0.3-10 mTorr) Cl_2 plasma. After etching in a pure Cl_2 plasma, polycrystalline Si films, masked with photoresist stripes, are covered with about one monolayer of Cl on the top of the mask, the side of the mask, the etched poly-Si sidewall, and the bottom of the etched trench. When oxygen is

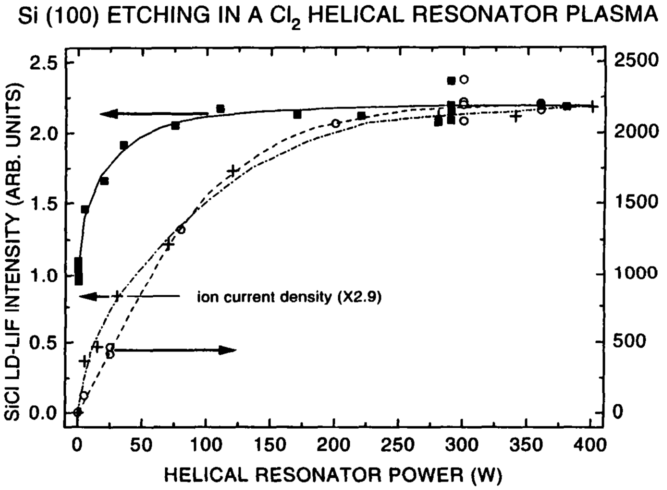

Figure 5. SiCl LD-LIF signal intensity (__■__), etch rate (— — O — —), and I_{sat}, the saturated ion current density (.-.-+-.-.) *vs.* helical resonator power. I_{sat} can be obtained by multiplying the left y-axis scale by 2.9 (i.e. $I_{sat}=6.3 mA/cm^2$ at 400 W). Other conditions are the same as for Figure 4.

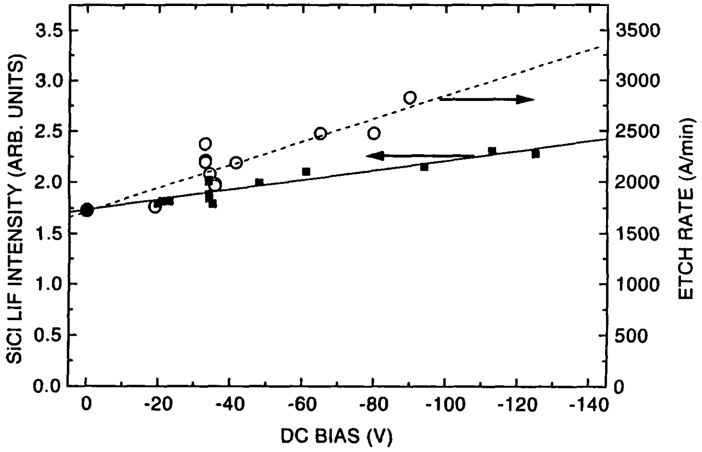

Figure 6. SiCl LD-LIF signal intensity (■) and etch rate (O) *vs.* substrate bias voltage. Other conditions are the same as for Figure 4.

present in the plasma, either by addition of O_2 or by erosion of the glass discharge tube, then a thin Si-oxide layer forms on the sides of both the poly-Si and the photoresist.

Using *in situ* laser-induced thermal desorption, combined with laser-induced fluorescence detection of SiCl, we have shown that the Si-chloride layer formed during etching is stable after the plasma is extinguished, so the XPS measurements are representative of the surface during etching. Laser-desorption measurements as a function of pressure and discharge power also show that the etching rate is limited by the positive ion flux to the surface, and not by the supply of Cl_2 at pressures above 0.5 mTorr, and ion fluxes of $\sim 4 \times 10^{16} cm^{-2} s^{-1}$. The chemically enhanced sputtering yield is 0.38 Si atoms-per-ion at 50 eV ion energy and 0.60 at 120 eV.

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