Laser-Induced Thermal Desorption as an *In Situ* Surface Probe during Plasma Processing

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We report a new technique for detecting adsorbates in real time during plasma processing. During etching of Si(100) in a Cl_2 plasma, pulsed XeCl excimer laser irradiation of the surface induces thermal desorption of $SiCl_x$ ($x = 0$–4). Desorbing products are detected by either laser-induced fluorescence (for SiCl) excited by the same laser pulse, or by plasma-induced emission (for SiCl and Si) from electron impact excitation. The technique has a time resolution of < 0.1 s and submonolayer sensitivity, and should be applicable to processes at high ambient pressure.

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Over the last decade, tremendous advances have been made in the application of *in situ* gas-phase diagnostic techniques for the monitoring and control of plasma etching and deposition processes used in the manufacturing of microelectronic devices [1]. Determining surface compositions in real time is also important in understanding and controlling these processes. Established surface science techniques, such as x-ray photoelectron spectroscopy (XPS), require high vacuum ($< 10^{-6}$ Torr) and so cannot be applied *in situ* at the higher pressures ($> 10^{-3}$ Torr) used in these processes, while the plasma environment precludes energy-resolved detection of electrons. Optical surface analysis techniques such as ellipsometry and total internal reflection Fourier transform infrared spectroscopy (TIR-FTIR) can be used at high pressures. However, the interpretation of ellipsometry data strongly depends on modeling and chemical analysis is not possible [2]. Though TIR-FTIR can be used for chemical analysis, it requires long collection times, special substrates, and can be complicated by substrate absorption [3].

In this study, laser-induced thermal desorption (LITD) was used for the first time to probe steady-state surface compositions *in situ* during plasma processing. Specifically, the steady-state chlorinated surface layer produced during the etching of Si(100) by a Cl_2 plasma was investigated. When LITD is used to study surface reaction kinetics in ultrahigh vacuum (UHV) [4], the species that desorb are normally detected by mass spectrometry. Here the plasma environment makes detection of the desorption products difficult. Instead, we use laser irradiation of the surface to desorb species that are then identified by their characteristic fluorescence after they have been excited near the surface by laser absorption or by electron-impact excitation in the plasma. Emissions from both SiCl and Si have been observed.

The Si(100) samples (n type, P doped, 5–50 Ω cm) were clamped to a stainless steel holder, and were etched in the downstream region of a helical resonator plasma reactor that is described elsewhere [5]. The plasma was operated at a Cl_2 pressure of 1 mTorr, a radio frequency (rf) of 11.2 MHz, and a net power of 300 W. The substrate holder was capacitively coupled to a second rf source operating at 14.5 MHz to impose a dc bias voltage of -32 V on the sample. The plasma potential was 50 V, hence the substrate was bombarded by 82 eV positive ions (mostly Cl_2^+). Two solenoid magnets (100 G each) confined the plasma near the substrate, where the positive ion density was $(1\text{-}2)\times 10^{11}$ cm^{-3}. A XeCl excimer laser (308 nm, 200 mJ/pulse, 20 ns pulse width, 5 Hz) was directed at the substrate surface at normal incidence to desorb the surface species. Absorption by $Cl_{2(g)}$ attenuated the laser by a negligible amount (∼0.05%) before it reached the surface. The same laser pulse excited some of the desorbed species. Optical emission excited by the laser, as well as by the plasma, was dispersed with a scanning monochromator (1.2 Å resolution) and detected with a GaAs photomultiplier tube. Imaging optics were used to detect light either directly from the near-surface region (within ∼4 mm), or from the discharge directly above the sample. A boxcar integrator with 1-3 μs wide gates was used to capture the prompt and delayed fluorescence.

Four distinct excitation processes can occur in the plasma, three of which were observed in this study. (1) Plasma-induced emission (PIE)—This is the optical emission excited by electron impact or other energetic processes that normally occurs in the plasma [1]. No laser excitation is involved. (2) Laser desorption-plasma-induced emission (LD-PIE)—In this process, pulsed laser irradiation of the substrate surface causes transient heating that leads to thermal desorption. These desorption products are excited by the PIE process as they enter the plasma. Emission persists until the products diffuse out of the discharge region (10-100 μs). (3) Laser-induced fluorescence (LIF)—This is the standard excitation process in which laser light promotes a gas-phase species to an electronically excited state that subsequently emits light. From spatially and temporally resolved measurements, and studies with substrate irradiation at fluences too low to cause thermal desorption, no LIF signal can be attributed here to species that could be present naturally during plasma etching. (4) Laser desorption-LIF (LD-LIF)—In this process, each laser pulse causes desorption and subsequent electronic excitation of gas-phase species, which then emit light.

Emission spectra from processes (1), (2), and (4) are

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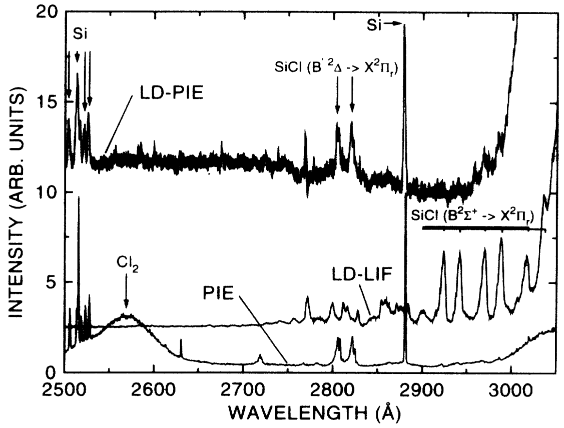

FIG. 1. Spectra during etching of Si(100) by Cl_2 showing plasma-induced emission (PIE) (bottom trace), laser-induced fluorescence of SiCl desorbed by the laser (LD-LIF) (middle trace), and plasma-induced emission after laser desorption (LD-PIE) (top trace). The laser fluence for LD-LIF and LD-PIE was 0.50 J/cm^2. The features at 2772 Å in the top and middle traces are artifacts caused by diffraction of laser light in the monochromator.

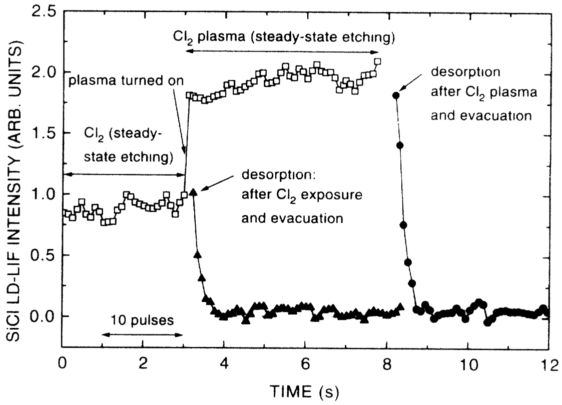

FIG. 2. LIF intensity of laser-desorbed SiCl (2930 Å) as a function of time. The □'s show steady-state laser-induced etching of Si by Cl_2, and then etching with the plasma suddenly turned on (at 3 s). The solid symbols show the time dependence of desorbed SiCl after chlorination with the plasma off (▲) and on (●), and subsequent pump down. For comparison, these last two traces have been placed immediately after the respective steady-state traces.

shown in Fig. 1. The PIE spectrum (bottom trace) recorded without laser irradiation consists of emission from a transition between two excited states of Cl_2 (centered at 2570 Å), from Si (lines from 2500–2530 and 2882 Å), and from SiCl($B'^2\Delta \rightarrow X^2\Pi_r$) [6,7] (at 2809 and 2823 Å). Transient increases in PIE from Si and SiCl($B'^2\Delta \rightarrow X^2\Pi_r$) are induced by an LD-PIE process (Fig. 1, top trace) when the laser irradiates the Si surface and the optics are aligned to collect light, integrated over a volume from 1 to 10 mm above the surface. At 1 mTorr, desorbing products will collide with few neutral species or ions over this distance. The LD-PIE Si signal at 2516 Å peaks within < 3 μs after the laser pulse when light < 4 mm above the surface is imaged into the spectrometer, while it peaks ~ 9 μs after the laser pulse when light ~ 12 mm above the surface is imaged. A reasonable explanation is that the laser is causing thermal desorption of $SiCl_x$ ($x = 0$–4) products that undergo subsequent electron-impact excitation (possibly including dissociation). The measured delay times indicate that the products desorb with a mean speed of $\sim 1 \times 10^5$ cm s^{-1}. This is in good agreement with the average speed of 9×10^4 cm s^{-1} expected for SiCl desorbing from Si near its melting point (1683 K). No LD-PIE signal due to Cl_2 (at 2570 Å) or Cl (7000–9000 Å region, not shown) is observed. This suggests that the steady-state Cl_2 coverage is negligible.

The spectrum observed with laser irradiation and the plasma on is different when light is collected from a volume near (< 4 mm) the surface (Fig. 1, middle trace). The only strong features are the SiCl($B^2\Sigma^+ \rightarrow X^2\Pi_r$) bandheads [6,7] that are excited by the XeCl laser [$B^2\Sigma^+(v'=0) \leftarrow X^2\Pi_r(v''=3,4)$] [7,8] in an LD-LIF process. LD-LIF of SiCl($B'^2\Delta$) is not expected since excitation of the $v'=0$ level with 308 nm radiation can occur only from the sparsely populated $v''=6$ and 7 levels of the ground state. Similar LD-LIF spectra of about half the intensity were observed with Cl_2 present and the plasma off. This laser-induced desorption process is actually laser-induced etching [8].

During excimer laser-induced etching of Si(100) by Cl_2, desorbed $SiCl_x$ ($x = 1$–4) with SiCl dominant has been detected by mass spectrometry [9] and LIF [10]. UHV LITD studies by Gupta *et al.* [11] of Cl-dosed Si(111), which employed a ruby laser, found a similar $SiCl_x$ product mass spectrum, but assigned $SiCl_2$ as the major product. In addition, $SiCl_2$ and $SiCl_4$ have been reported in thermal desorption studies of chlorinated Si(100) and Si(111) surfaces [11,12].

The LD-PIE SiCl emission peaks several mm above the surface and several μs after the laser pulse irradiates the surface, and comes from the $B'^2\Delta$ state, which has a ~ 1 μs lifetime [6]. In contrast, the LD-LIF SiCl emission peaks at the surface, with no delay with respect to the laser pulse, and comes from the $B^2\Sigma^+$ state (10 ns lifetime) [13]. Since the laser desorption process and LIF excitation of SiCl both occur within the same ~ 20 ns laser pulse, the LD-LIF spectrum must come directly from desorbed SiCl. The preferential electron-impact excitation of SiCl($B'^2\Delta$) in LD-PIE indicates that either the nearly isoenergetic, stronger optical transition $B^2\Sigma^+ \leftarrow X^2\Pi_r$ is not strongly favored in electron-impact excitation, or that $B'^2\Delta$ emission is a result of another process, most likely electron-impact dissociation of $SiCl_2$.

Figure 2 shows how this method can probe the surface layer in real time. The SiCl LD-LIF (2930 Å) signal observed with Cl_2 flowing and the plasma off remains constant for minutes, as the sample is exposed to several thousand laser pulses. Only a short portion of this measurement is shown in Fig. 2. When the plasma is turned on, the SiCl LIF signal immediately (i.e., within one or two pulses, ~0.2 s) increases to a new steady-state level that is also constant for at least several minutes. The SiCl LD-LIF signal with the plasma on is about twice that with the plasma off, at a saturation fluence of 0.6 J/cm^2 (see below). This suggests that the Cl coverage approximately doubles when the plasma is on. This is confirmed by *ex situ* XPS, with sample transfer under vacuum, and is described in more detail elsewhere [14]. The XPS measurements indicate that the layer formed during plasma etching corresponds to a coverage of 1×10^{15} Cl/cm^2 [14].

After steady-state chlorination without laser desorption, Cl_2 flow was stopped, the system was pumped to $< 1\times 10^{-7}$ Torr, and then the sample was irradiated with the laser. Figure 2 shows that the SiCl LD-LIF signal begins near the respective steady-state value, with the plasma either turned on or off, and then decays to zero within a few pulses. This indicates that the chlorine coverage on the surface does not decrease significantly ($< 10\%$) during the several-minute pump down. Therefore the surfaces of samples exposed to the plasma and then transferred under vacuum to an analysis chamber are stable and *ex situ* surface analysis (e.g., XPS) reflects the surface present during etching [5]. The decay of the LD-LIF signal indicates that $\sim \frac{1}{2}$ of the surface layer is desorbed by each laser pulse.

Figure 3 shows the fluence dependence of both LD-PIE and LD-LIF signals. The laser fluence controls both the degree of desorption and subsequent LIF excitation (for LD-LIF). With the plasma on, the SiCl LD-PIE and LD-LIF signals both depend on fluence in approximately the same way. (Intensities have been normalized at 0.65 J/cm^2.) Each has a threshold of 0.20 J/cm^2 and saturates at 0.6 J/cm^2. Si LD-PIE has a similar threshold, but saturates above 0.6 J/cm^2. The SiCl LD-LIF fluence dependence is different when the plasma is off. The threshold increases to 0.35 J/cm^2 and saturation is reached near 0.7 J/cm^2. These LD-LIF values with the plasma off are in good agreement with threshold and saturation fluences of 0.35 and 0.55 J/cm^2 reported by Aliouchouche *et al.* [8] for SiCl, detected by mass spectrometry. It has been reported that laser-induced etching of Si by Cl_2 occurs when the laser melts the surface ($T > 1683$ K), with laser wavelengths of 308 and 248 nm [8,9,15]. From one dimensional heat flow calculations [16], we estimate that the surface melts at a fluence of 0.45 J/cm^2 at 308 nm.

The lower fluence threshold observed when the plasma is on indicates that the surface species formed during plasma etching are more weakly bound than are those formed by exposing Si(100) to Cl_2 at 300 K. Heat flow calculations show that the surface reaches peak temperatures of ~800 and ~1300 K during laser heating at the observed fluence thresholds for desorption with the plasma turned on and off, respectively. A likely explanation for the different thresholds is that SiCl is more weakly bound to the surface in the more highly chlorinated and damaged layer that forms when the plasma is on [17].

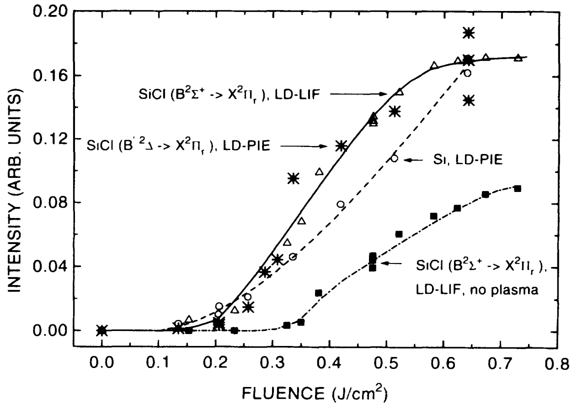

FIG. 3. Fluence dependences for LD-PIE of SiCl [2830 Å (∗)] and Si[2882 Å (○)], and for LD-LIF of SiCl [2930 Å (△)] with the plasma turned on, and of SiCl LD-LIF [2930 Å (■)] with the plasma off during chlorination of Si.

Si etches at a rate of ~40 Å/s under these plasma conditions, or 8 Å (5 monolayers) between laser pulses (5 Hz repetition rate). Consequently, each laser pulse probes a surface layer that is representative of steady-state etching and is not influenced by laser heating and, at high fluences, by melting of the surface from the previous pulse. In addition, the laser does not perturb the steady-state properties of the plasma because any transient effects due to a given pulse will have decayed away before the next laser pulse. The laser photon energy (4.0 eV) is less than the work functions of Si(100) (4.91 eV) [18] and the Cl-covered Si(100) (5.1 eV) [19]. Therefore, electron emission from the surface should be minimal.

LD-LIF measurements, made as a function of pressure, plasma source power, and substrate dc bias voltage, are described elsewhere [14]. Briefly, the SiCl LD-LIF signal, and therefore Cl coverage, increases with plasma power to a saturation level at ~100 W, and then is independent of power to 400 W. It depends weakly on negative dc substrate bias voltage, increasing linearly by ~25% between 0 and −125 V. The signal peaks near 1 mTorr, and falls by only 5% between 1 and 20 mTorr, and between 1 and 0.2 mTorr, indicating that Cl coverage saturates at a very low pressure, so that etching throughout this typical pressure range is limited by the ion flux, and not by chlorination by neutral Cl and Cl_2. Similar measurements in Cl_2/HBr plasmas are presented elsewhere [20]. Analogous LD-LIF signals were observed for SiBr.

Although the techniques described here are best suited to systems in which the surface layer reforms between laser pulses, they could also be used to monitor removal of surface contaminants such as native oxides and hydrocarbons on air-exposed substrates. Since laser-induced desorption may remove much of this thin layer, either the sample or the laser beam should be rastered. Rastering could also be used for real-time detection of adsorbates on temperature-sensitive substrates, to ensure that the previous laser pulse does not perturb the process and measurement. LD-LIF and LD-PIE should also be applicable to higher pressure processes such as chemical vapor deposition and catalysis. Species such as SiF, SiF_2, SiH, NH, NH_2, NO, P_2, As_2, and CH_3O have strong optical transitions with bound excited states in the accessible UV-visible region. At higher pressures, signals will be reduced by quenching. For example, a species with a 50 ns radiative lifetime and a gas-kinetic quenching rate constant of 1×10^{-10} cm^3s^{-1} will have a 1% fluorescence quantum yield at 1 atm pressure. Given the signal-to-noise in this initial study, the improvements in light collection and scattered light rejection that could be implemented, it is likely that the sensitivity would be sufficient for detecting adsorbates under these conditions.

In summary, we have demonstrated that laser-induced thermal desorption with optical detection can be used to quantitatively determine the coverage of surface species during plasma etching. This probe is comparable to other surface analysis techniques, e.g., XPS, in sensitivity, and has a time resolution, determined by the laser repetition rate, that is faster than the time required to etch one monolayer. During Si(100) etching in a Cl_2 plasma, Si-chloride products were desorbed from the surface by laser-induced heating. SiCl was detected through fluorescence excited by the same laser pulse, while SiCl and Si were also monitored by electron-impact emission as the $SiCl_x$ desorption products entered the plasma. The Si-chloride layer that forms during plasma etching reaches a self-limiting thickness of about a monolayer in a short time (<0.2 s) and is nearly independent of pressure, power, and substrate bias voltage over a wide range of conditions. Cl coverage is twice that found after dosing Si(100) with Cl_2, and the adsorbates are more weakly bound. Detailed applications to Si etching in Cl_2/O_2 plasmas [14] and Cl_2/HBr plasmas [20] are given elsewhere. Finally, the technique could be used to study other plasma/surface interactions and, with LIF detection, high pressure processes such as chemical vapor deposition and catalysis.

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