

Transition between two states of surface coverage and etch rate during Si etching in inductively coupled Cl₂-Ar plasmas with changing mixtures

N. C. M. Fuller and Donald A. Telesca, Jr.

Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027

Vincent M. Donnelly

Department of Chemical Engineering, University of Houston, Houston, Texas 77204

Irving P. Herman^{a)}

Department of Applied Physics and Applied Mathematics, and the Materials Research Science and Engineering Center, Columbia University, New York, New York 10027

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The etch rate and surface SiCl and SiCl₂ concentrations abruptly increase and the surface Si concentration abruptly decreases as the chlorine fraction is increased above a threshold value during Si etching by an inductively coupled Cl₂-Ar mixture plasma. The surface species are detected by laser desorption of the chlorinated adlayer using laser-induced fluorescence and plasma-induced emission of the desorbed species. This threshold chlorine fraction is 75% for 80 eV average ion energy, and increases with the average energy of ions incident on the surface. This unexpected observation is attributed to a phase transition between two states of surface chlorination and morphology. © 2003 American Institute of Physics. [DOI: 10.1063/1.1585124]

The density of surface adsorbates during plasma etching has usually been treated using simple Langmuir kinetics, as in describing the degree of surface chlorination during etching of Si by chlorine plasmas.^{1,2} In contrast, there are many instances in studying adsorption on well-prepared surfaces where such simple analysis is not possible due to a reconstruction that occurs to lower the surface energy.³⁻⁶ Analogous morphological and chemical changes to the surface have rarely been considered during plasma processing because they were thought unimportant given the irregular nature of the ion-bombarded surface. This letter reports that the surface chlorination and etch rate unexpectedly increase abruptly and enter a different state of operation when increasing the composition of Cl₂-Ar mixtures during the inductively coupled plasma (ICP) etching of Si(100) above a threshold Cl₂ fraction that depends on substrate bias. As such, this observation suggests such morphological changes are possible even with plasma-exposed surfaces.

The ICP reactor was operated in the inductively coupled mode with 18 mTorr pressure and rf power delivered to the coil (500 W, 13.56 MHz). The rf power delivered to the substrate holder was varied to tune the substrate bias. The Si(100) substrate was well bonded to the water-cooled holder. The surface coverage of chlorine was measured with the laser desorption (LD) surface probe (XeCl laser, 308 nm, 20 ns pulse length, 36 mJ/pulse, 2 pps), in tandem with plasma-induced emission (PIE) detection of desorbed SiCl₂ and Si and laser induced fluorescence (LIF) detection of desorbed SiCl.⁷⁻⁹ SiCl LD-LIF was excited by the same 308 nm laser and detected at 292.4 nm, both $B^2\Sigma_+ \rightarrow X^2\Pi_r$ transitions.^{7,8} The SiCl₂ and Si LD-PIE signals were moni-

tored at 327.0 and 288.2 nm, corresponding to the $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$ and $4s^1P_1^0 \rightarrow 3p^2^1D_2$ transitions.⁹

The first-order chlorination constants 70 ms (30% Cl₂) and 40 ms (75% Cl₂), from SiCl LD-LIF as a function of the laser repetition rate, indicate the laser desorbed regions were fully chlorinated between laser pulses at 2 pps.

Figure 1 shows that for -60 V bias, both the SiCl LD-LIF and SiCl₂ LD-PIE signals increase with Cl₂ fraction and are constant near 50%. Between 75% and 83% Cl₂ fraction, the SiCl LD-LIF intensity increases abruptly by a factor of ≈ 2.1 and the SiCl₂ LD-PIE signal increases by a factor of ≈ 1.3 . Further increases in the Cl₂ fraction cause negligible

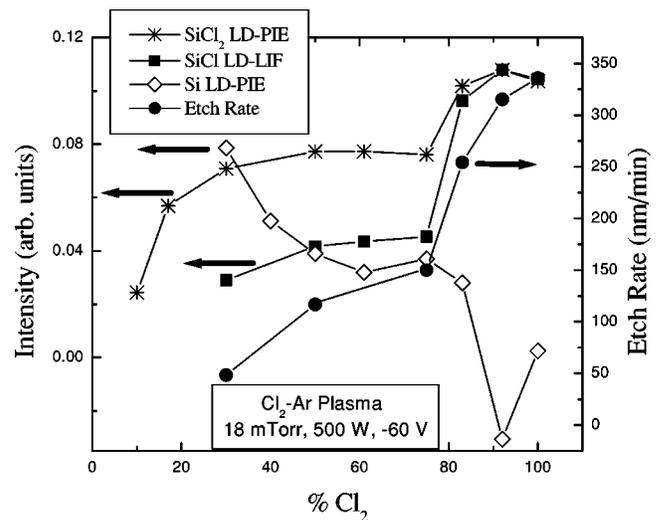


FIG. 1. SiCl LD-LIF and SiCl₂ and Si LD-PIE intensities at 292.4, 327.0, and 288.2 nm, respectively, and etch rates vs Cl₂ fraction in an 18 mTorr Cl₂-Ar plasma (500 W rf power, -60 V bias, 36 mJ/pulse, and 2 pps). LD-PIE measures the transient change in PIE and so can be negative, as for the 92% Si LD-PIE datum point.

^{a)}Electronic mail: iph1@columbia.edu

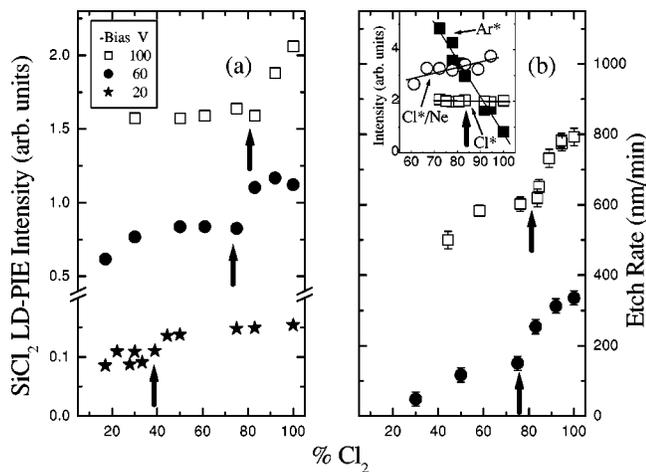


FIG. 2. (a) SiCl₂ LD-PIE intensity at 327.0 nm vs Cl₂ fraction and substrate bias (-20, -60, and -100 V); (b) etch rate vs Cl₂ fraction and substrate bias (-60 and -100 V), inset of Ar* (750.4 nm) and Cl* (822.2 nm) emission intensity, and that of Cl⁺* (482.0 nm) normalized by that of Ne* (585.2 nm).

change in either signal. The Si LD-PIE intensity decreases by a factor of ≈ 2 as the Cl₂ fraction is increased from 30% to 50%, is fairly constant up to 75% fraction, and then decreases suddenly to negligible values for larger fractions. The etch rate (ER) increases slowly with increasing Cl₂ fraction, and then abruptly increases at 75% fraction.

Figure 2(a) shows the abrupt increase in SiCl₂ LD-PIE intensity occurs at a Cl₂ fraction that increases with ion energy, respectively at $\approx 39\%$, 75% , and 83% Cl₂ fractions for substrate biases of -20, -60, and -100 V, corresponding to average ion energies of ≈ 40 , 80, and 120 eV. Figure 2(b) shows the abrupt change in etch rate versus Cl₂ fraction also for -100 V. No hysteresis was noted, which is expected since many layers are etched between measurements.

Transitions between multiple plasma processing modes have been seen previously between the inductively coupled and capacitively coupled modes of ICP operation and between competing etching and deposition of adlayers.^{10,11} Neither occurs here since the reactor operates at rf powers way above the ICP mode transition and competition between deposition and etching, while occurring in several fluorocarbon plasmas, does not occur in these chlorine plasmas. The plasma operates stably in the inductive mode, with net rf power, $P_{\text{net}} = P_{\text{incident}} - P_{\text{reflected}} = 500$ W, far above the threshold for pure Ar (~ 200 W) and Cl₂ (~ 300 W). There was no observed change in $P_{\text{reflected}}/P_{\text{incident}}$ at the transition, indicating no abrupt changes in plasma dynamics.

Since the SiCl₂ LD-PIE intensity depends on SiCl₂ coverage θ_{SiCl_2} (and θ_{SiCl_3} to a lesser extent), θ_{SiCl_2} increases abruptly above the observed threshold.⁸ Likewise, since the SiCl LD-LIF intensity monitors desorbed SiCl possibly from both surface SiCl and laser-induced dissociation of surface SiCl₂, a sudden increase in θ_{SiCl} and/or θ_{SiCl_2} is possible. The decrease in Si LD-PIE likely reflects a decrease in desorbed Si, due to a decrease in θ_{Si} or possibly θ_{SiCl} (if the SiCl LD-LIF is due mostly to adsorbed SiCl₂).

In Cl₂-Ar ICPs operating in the inductively coupled (H-, bright-) mode, chlorination is mainly due to Cl atoms and sputtering is due to Cl⁺ and Ar⁺. The Si etch rate ER

$= \Gamma_i \theta_{\text{SiCl}_x} Y$, where Γ_i is the ion flux to the wafer and Y is the Si atom sputter yield per incident ion. $\Gamma_i \propto n_i \sqrt{T_e}$, where n_i is the ion density and T_e the electron temperature. $n_i \propto P_{\text{dep}} / \sqrt{V_p}$, where P_{dep} is the deposited rf power. $Y \propto \sqrt{V_p - V_{\text{bias}}}$, where the plasma potential $V_p \approx 5T_e$. The yield is expected to be different for different types of surface coverage, e.g., SiCl vs SiCl₂. The coverage θ_{SiCl_x} depends on the number of sites available, which depends on Γ_i , the chlorine flux Γ_{Cl} , the final average ion speed $\propto \sqrt{V_p - V_{\text{bias}}}$, and other factors. Overall, the change in ER and θ_{SiCl_x} could be due to changes in n_i , T_e , P_{dep} , or other parameters that change the density or types of surface chlorination sites.

Abrupt changes in T_e (and V_p) and in the Cl, Cl⁺, and Ar⁺ densities with mixture concentration were not seen in previous studies where the etch rate was negligible (silicon dioxide atop Si) in this^{12,13} and other¹⁴ reactors; they do not occur during etching here, as confirmed by the measurements in Fig. 2(b) of Ar*, Cl*, Ar⁺* (not shown), and Cl⁺* emission intensities (the last normalized by Ne* emission actinometry). (A 5% rare gas mixture was added for this last measurement, which did not change the observed abrupt changes.) Given this and that each plasma parameter is only weakly affected by substrate bias, no sudden changes in Γ_i are expected. To account for the change in the ER at the transition solely by increased ion speed to the surface would require V_p to increase by an unreasonably high 151 V (70 V) caused by an impossible increase in T_e by 30 eV (14 eV) for 60 V (100 V) substrate bias. Any sudden change in the recombination rate of the walls would have been indicated by a change in Cl* emission in Fig. 2(b). There is no optical emission at 844.6 nm from O atoms, so large pressures of oxygen impurities that could change SiCl LD-LIF and ER¹⁵ are unimportant. Lack of hysteresis rules out systematic effects due to plasma heating of the well-cooled substrate.

This two-state behavior of ER and θ_{SiCl_x} appears to be due to a change in surface morphology and composition. On a local basis it may parallel the adsorbate repulsive interaction in the adsorption and thermal etching of H₂ on Si(100)^{3,4} and Br₂ on Si(100).^{5,6} Steric interactions¹⁶ between SiH and SiH₂ (SiBr and SiBr₂) adsorbates lead to reconstructions causing the coverage of SiH (SiBr) to abruptly decrease and SiH₂ (SiBr₂) to abruptly increase. Comparable studies for Cl adsorption on Si(100)-(2 \times 1)⁵ show that the Si surface maintains its (2 \times 1) reconstruction and is, as such, only covered by SiCl species and steric interactions are small.

The crystallinity and flatness of the initial Si(100) surface is greatly changed due to the bombardment by 40–120 eV ions. The layers near the surface are more amorphous than crystalline and they are rough with crevices.^{17,18} SiCl₂ and SiCl₃ are on the plasma-treated surface and there might be steric interactions between neighboring SiCl_x ($x \geq 2$) that could interact locally in a way similar to the more global reconstruction on well-prepared surfaces. An increase in ion energy is known to increase the number of surface sites,²⁰ which is consistent with the observed increase in threshold chlorine fraction with increasing bias.

The kinetics of this transition are modeled by the steady-state solutions to the rate equations interrelating the surface coverages of Si, SiCl, and SiCl₂ for a total density of sites

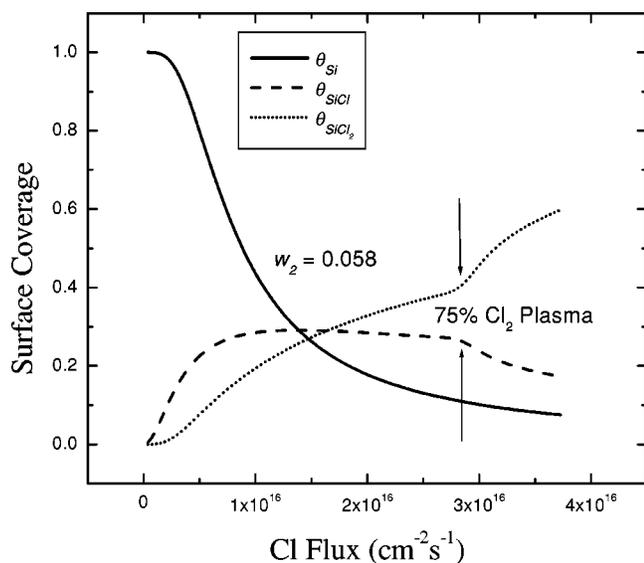


FIG. 3. Surface coverage of Si, SiCl, and SiCl₂, as a function of Cl atom flux to the surface during Si etching in ICP Cl₂-Ar plasmas, as determined by a kinetics model.

θ_{total} ; the coverage of SiCl₃ is ignored for now. It is assumed that Γ_i is independent of chlorine fraction and the sputtering rates of Cl⁺ and Ar⁺ are about the same:

$$d\theta_{\text{Si}}/dt = -a_0\Gamma_{\text{Cl}}\theta_{\text{Si}} + k_1\Gamma_i\theta_{\text{SiCl}} + k_2\Gamma_i\theta_{\text{SiCl}_2}, \quad (1)$$

$$d\theta_{\text{SiCl}}/dt = a_0\Gamma_{\text{Cl}}\theta_{\text{Si}} - a_1\Gamma_{\text{Cl}}\theta_{\text{SiCl}} - k_1\Gamma_i\theta_{\text{SiCl}}, \quad (2)$$

$$d\theta_{\text{SiCl}_2}/dt = a_1\Gamma_{\text{Cl}}\theta_{\text{SiCl}} - k_2\Gamma_i\theta_{\text{SiCl}_2}, \quad (3)$$

where a_0 and a_1 are the reaction rate constants for the chlorinating surface Si to SiCl and SiCl to SiCl₂, and k_1 and k_2 are the desorption (sputter) rate constants of surface SiCl and SiCl₂; all are chosen to produce \sim a monolayer for a chlorine-dominant plasma.

Only smooth variations of θ_{Si} , θ_{SiCl} , and θ_{SiCl_2} with chlorine fraction are seen for a_0 , a_1 , k_1 , and k_2 that are constant or polynomial expansions of $\theta_{\text{Si}}^\alpha\theta_{\text{SiCl}}^\beta\theta_{\text{SiCl}_2}^\gamma$ terms. Abrupt changes in SiCl and SiCl₂ surface coverage are seen when repulsive interactions are included. Reference 16 shows the equilibrium constant for adsorption and desorption in systems with such repulsive terms has the form $\exp(-cw\theta/k_B T)$, so the chlorination rate constants can be expressed as $a_0 = b \exp(-c_1 w_1 \theta_{\text{SiCl}}/k_B T)$ and $a_1 = b \exp(-c_2 w_2 \theta_{\text{SiCl}_2}/k_B T)$, where c_1 and c_2 are the number of adsorbate nearest-neighbor sites (three for SiCl and two for SiCl₂ for an ideal planar surface), and w_1 and w_2 are the repulsive interaction terms between pairs of adsorbates, SiCl-SiCl and SiCl₂-SiCl₂.^{5,16} The total number of surface sites decreases in such a surface transition.¹⁶

Figure 3 shows the coverage of SiCl_x predicted assuming $w_1 = 0$ (i.e., no SiCl repulsive interaction⁵) and a SiCl₂-SiCl₂ repulsion term $w_2 = 0.058$ (for 10^{15} sites/cm²). There is an abrupt increase in θ_{SiCl_2} and a decrease in θ_{SiCl} , with little or no change in θ_{Si} for a 75% Cl₂ plasma. Using the same value of w_2 the model shows that the threshold chlorine fraction increases with θ_{total} . Since θ_{SiCl_2} increases with increasing ion energy,^{19,20} this model is consistent with the increased transition chlorine fraction with bias (Fig. 2).

Such an abrupt increase in θ_{SiCl_2} would cause the observed abrupt increase in the SiCl₂ LD-PIE. The predicted decrease in θ_{SiCl} could be consistent with the SiCl LD-LIF data in Fig. 1, since the SiCl LD-LIF signal originates from both adsorbed SiCl and SiCl₂. The desorption energy for SiCl from a chlorinated surface is ~ 6.1 eV.²¹ Given the smaller desorption energy of SiCl₂, 3.4 eV, and SiCl-Cl bond energy, ~ 4.6 eV,²² desorption of SiCl₂ to give SiCl_(g) and Cl_(g) would require more energy, ~ 8.0 eV, unless the Cl returns to the surface, and then the energy required would be 4-5 eV.²¹ The observed sudden decrease in the Si LD-PIE intensity would also be predicted by the model by including the expected decrease in θ_{total} after such a reconstruction.¹⁶ Qualitatively similar abrupt increases in surface chlorination are seen when including SiCl₃ on the surface and SiCl₃-SiCl₃ repulsion. This smaller desorption energy of the more chlorinated adsorbates $E_{d,\text{SiCl}_3} < E_{d,\text{SiCl}_2} < E_{d,\text{SiCl}}$ also explains the concomitant sudden increase in etch rate.²¹

A phase transition between two states of surface chlorination and etch rate during Si etching in Cl₂-Ar mixtures is observed that appears to be due to a change in surface morphology and bonding. This phenomenon may be more widely important in plasma processing than previously thought and may be of general importance in the etching, even thermal etching, of rough surfaces.

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