

# Photo-assisted etching of silicon in chlorine- and bromine-containing plasmas

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Cl<sub>2</sub>, Br<sub>2</sub>, HBr, Br<sub>2</sub>/Cl<sub>2</sub>, and HBr/Cl<sub>2</sub> feed gases diluted in Ar (50%–50% by volume) were used to study etching of p-type Si(100) in a rf inductively coupled, Faraday-shielded plasma, with a focus on the photo-assisted etching component. Etching rates were measured as a function of ion energy. Etching at ion energies below the threshold for ion-assisted etching was observed in all cases, with Br<sub>2</sub>/Ar and HBr/Cl<sub>2</sub>/Ar plasmas having the lowest and highest sub-threshold etching rates, respectively. Sub-threshold etching rates scaled with the product of surface halogen coverage (measured by X-ray photoelectron spectroscopy) and Ar emission intensity (7504 Å). Etching rates measured under MgF<sub>2</sub>, quartz, and opaque windows showed that sub-threshold etching is due to photon-stimulated processes on the surface, with vacuum ultraviolet photons being much more effective than longer wavelengths. Scanning electron and atomic force microscopy revealed that photo-etched surfaces were very rough, quite likely due to the inability of the photo-assisted process to remove contaminants from the surface. Photo-assisted etching in Cl<sub>2</sub>/Ar plasmas resulted in the formation of 4-sided pyramidal features with bases that formed an angle of 45° with respect to  $\langle 110 \rangle$  cleavage planes, suggesting that photo-assisted etching can be sensitive to crystal orientation. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4878895]

# I. INTRODUCTION

Energetic ion bombardment plays a critical role in plasma etching used in manufacturing of ultra large-scale integrated circuits.<sup>1,2</sup> It is inevitable that, over the coming decades, plasma etching will be employed for pattern delineation at the atomic scale. Shrinking of device dimensions predicted by Moore's Law, however, brings substantial complexity to plasma etching. For example, much lower ion energies (10 s of eV) are desired to improve selectivity and reduce damage as the feature size shrinks below 20 nm. At such low ion energies, other processes such as spontaneous chemical etching and photo-assisted etching rate, which is greatly reduced.

Photo-assisted (or photo-induced) etching of metals and semiconductors with halogens in the *absence of a plasma* has been studied by several researchers. Jackman *et al.*<sup>3</sup> investigated the effect of ultraviolet (UV) radiation on the interaction of chlorine with Si (100). They found that in the presence of UV irradiation, strongly adsorbed species on the surface could be converted into species with weaker bonds, leading to an enhancement of desorption and higher etching rates. Okano *et al.*<sup>4</sup> observed that in the presence of photodissociated Cl radicals, etching of undoped and p<sup>+</sup> poly-Si occurred only when UV light was directed at the surface of the sample. Etching was attributed to field-assisted diffusion<sup>5–7</sup> of Cl<sup>-</sup> ions, which are formed in the near surface region through the combination of Cl atoms and photo-electrons generated by UV irradiation. Field-assisted diffusion of Cl<sup>-</sup> has also been proposed to cause etching of p-Si in Cl<sub>2</sub> under irradiation by XeC1, KrF, and ArF excimer lasers.<sup>8</sup>

Other researchers have proposed that etching is induced by photo-generated carriers. Houle<sup>9</sup> studied photo-assisted etching of Si by  $XeF_2$  with an Ar<sup>+</sup> laser (514.5 nm, 6 W, unfocussed). She showed that photo-generated carriers enhanced etching by inducing a surface process causing desorption of SiF<sub>3</sub>. She also argued that there is no evidence of field-assisted etching. Etching of p-type Si induced by photo-generated carriers in a Cl<sub>2</sub> atmosphere was also obtained using a pulsed 308 nm XeCl excimer laser<sup>10</sup> and cw Ar<sup>+</sup> and K<sup>+</sup> lasers with various wavelengths.<sup>11</sup> Schwentner et al. systematically investigated photo-induced etching of  $Cu^{12-15}$  and  $GaAs^{16}$  with  $Cl_2$ , and etching of Si with  $\mathrm{XeF_2}^{17-19}$  using synchrotron radiation in the vacuum UV (VUV) range. They found that photo-induced etching was strongly wavelength-dependent, with the maximum yield exhibited around 120 nm. They claimed that substrate atoms can be removed with an efficiency of 10 s-per-photon for GaAs and Si, and 100s to 1000s-per-photon for Cu. They attributed such high-yields to the photo-excitation of a reactive surface layer, which can initiate a chain reaction, with amplification of the order of  $10^5$ . Samukawa *et al.*<sup>20</sup> showed that 220-380 nm radiation increased the etching rate of Si in a Cl atom beam at UV lamp power densities  $>20 \text{ mW/cm}^2$ . They claimed that the increased etching was due to UV light-induced crystal defects.

Photo-assisted etching (PAE) of p-Si in Cl<sub>2</sub>/Ar plasmas

was first reported in Ref. 21. The photo-assisted etching rate

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was substantial compared to the ion-assisted etching rate at very low ion energies, causing complications for processes that require low ion energies. Under such condition, PAE might play an important role in the evolution of features with sloped sidewalls, during Si etching in chlorine-containing plasmas.

In the present work, the feed gas dependence of PAE of p-type Si(100) was investigated using Cl<sub>2</sub>, Br<sub>2</sub>, HBr, Br<sub>2</sub>/Cl<sub>2</sub>, and HBr/Cl<sub>2</sub> diluted with Ar (50%–50% by volume) in a Faraday-shielded inductively coupled plasma (ICP). The photon energy dependence of PAE was studied by filtering incident light with different wavelengths to the substrate. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to survey surface morphology after photo-assisted etching.

# **II. EXPERIMENTAL**

The experimental system (Fig. 1) was described in a previous publication.<sup>22</sup> An ICP source, consisting of an alumina tube, Faraday shield, and 3-turn copper coil, was connected to a chamber below. The sample was inserted, via a load lock, through this chamber and into the ICP region. The sample could be transferred, in vacuum, to an ultrahigh-vacuum chamber containing an X-ray photoelectron spectrometer (XPS). The base pressure in the plasma chamber was  $1 \times 10^{-7}$  Torr.

Plasmas were operated in a continuous power mode. Fig. 2 shows normalized ion energy distributions (IED) in Ar plasmas at 300 W radio frequency (rf) power for different pressures. As reported previously,<sup>22</sup> IEDs of ions bombarding the substrate, measured by a retarding field ion energy analyzer, consisted of a single peak, as expected, since the Faraday shield prevented capacitive coupling that would impose a large rf oscillation on the plasma potential



FIG. 1. Schematic of the Faraday-shielded, inductively coupled plasma reactor. A periscope was used to collect optical emission near the sample surface. Samples could be transferred under vacuum to ultrahigh-vacuum chamber containing an x-ray photoelectron spectrometer. More details of the experimental apparatus can be found in Ref. 21 and 22.



FIG. 2. Normalized IED measured in continuous wave argon plasmas (300 W, 40 sccm), for 7, 14, 28, and 50 mTorr. Boundary electrode and sample stage were grounded. Details of the IED measurements can be found in Ref. 22.

and a bimodal (or at least broadened) IED. Fig. 2 shows that the IEDs maximize at an energy that decreases with increasing pressure. The maximum is  $\sim 5T_e$ , as expected, where  $T_e$  is the electron temperature. Since  $T_e$  decreases when halogens are added to an Ar ICP (lower ionization potentials), IEDs for the mixed gas plasmas will peak at still lower energies. Note that there are very few ions with energies above the lowest reported threshold of 16 eV for ion-assisted etching of Si.<sup>23–25</sup>

Unless otherwise stated, 50% halogen/50% Ar gas mixture plasmas were operated at 400 W rf power and 60 mTorr. When two halogen-containing gases were used, they were mixed in equal amounts (e.g., the HBr/Cl<sub>2</sub>/Ar plasma was 25% HBr, 25% Cl<sub>2</sub> and 50% Ar by volume). The sample and stage were connected to a pulsed dc power supply, operated at varied negative square wave pulses at a frequency of 10 kHz and a duty cycle of 50%. Even though the plasma power was on continuously, pulsed dc bias was employed to be able to compare with a previous study in which pulsed power and synchronous pulsed dc bias in the afterglow was used. Although a pulsed plasma with synchronous dc bias in the afterglow would provide narrower IEDs, the emphasis here was not to provide a careful measurement of the threshold for ion-assisted etching, but instead to study photo-assisted etching. Operating the plasma continuously provided faster etching rates for both photo-assisted etching (more light per unit time) and ion-assisted etching (higher  $T_e$ , ion Bohm velocity and hence flux). Pulsing the bias also reduced ion-assisted etching relative to PAE, which was helpful for some cases where PAE was found to be small. The ion energy during application of pulsed bias was assumed to be equal to the bias voltage plus the plasma potential,  $V_p$ , with no bias, as was found previously.<sup>22</sup>  $V_p$  was taken as the energy at which the IEDs in Ar plasmas (Fig. 2) maximize. (maxima as a function of pressure between 7 and 50 mTorr were extrapolated to obtain  $V_p = 6 V$  at 60 mTorr.) Plasma potentials may be 1 or 2 V lower than these values because of the lower ionization potential (and lower  $T_e$ ) when halogens are introduced into an Ar plasma.

As shown in Fig. 1, a periscope with UV transmitting prisms was attached to the sample holder to direct light from

the plasma near the substrate surface to an optical emission spectrometer, which consisted of a scanning monochromator and a cooled GaAs photomultiplier tube (PMT). The monochromator had 1200 grooves/mm and, with a slit width of  $100 \,\mu\text{m}$ , provided a resolution of 2.2 Å. When the plasma was ignited, Si optical emission at 2882 Å was recorded for different Ar/halogen chemistries, and was used to obtain relative etching rates.

Si (100) substrates (p-type, dopant density  $2.5 \times 10^{14}$  $-2.6 \times 10^{15} \text{ cm}^{-3}$ ) were exposed to a UV-ozone process for 45 min to remove carbon and form a thin oxide layer. Samples were cleaved into  $1 \text{ cm} \times 2 \text{ cm}$  pieces, dipped into HF solution for  $5 \min$ , and then dried with N<sub>2</sub>. They were then placed on a 2.54 cm-diameter stainless steel sample puck, using double-sided carbon tape to hold them in place and aid in thermal and electrical contact. The sample holder was then placed in a load-lock chamber and transferred to the plasma chamber or to the XPS chamber. Before etching, XPS analysis showed that samples contained  $\sim 1\%$  O and  $\sim$ 3% C. Si optical emission at 2882 Å, (shown previously<sup>21</sup> and in the present work to be proportional to the etching rate when only the bias was varied), was recorded for different Ar/halogen plasmas. Absolute etching rates were also obtained by measuring the step height on masked samples using a stylus profilometer. A  $2 \times 2 \text{ mm}$  piece of silicon wafer was used as a mask, held onto the sample by a minimum amount of silicone paste.

The roughness and surface morphology of etched silicon samples were studied using a Veeco model CP-ii atmospheric pressure AFM operating in contact mode using high resolution silicon nitride probes (Veeco model MSCT-AUNM, k = 0.01-0.6 N/m, tip radius = 10 nm). Some images were also obtained in non-contact mode of operation using silicon probes (Veeco model RTESPA, k = 20-80 N/m).  $5 \times 5 \mu m^2$  images were obtained at four different locations on etched silicon samples. The images were flattened using a second-order polynomial curve fit to compensate for bowing of the piezo tube. Root Mean Square (RMS) roughness was obtained from the AFM images as follows:

RMS roughness (R) = 
$$\sqrt{\sum_{n=1}^{N} \frac{(z_n - \bar{z})^2}{N - 1}}$$
, (1)

where,  $\bar{z}$  denotes the mean height of the data defined by the region and N is the number of data points in the region. RMS roughness was obtained by averaging over 4 different locations on the sample.

### **III. RESULTS AND DISCUSSION**

Fig. 3 shows the silicon etching rate as a function of the square root of ion energy for all the gas mixtures used in this study. The open star symbols indicate absolute etching rates measured at 0 V, -40 V, and -60 V substrate bias. These were used to calibrate the rest of the data (solid points) which were obtained by recording the optical emission intensity of Si at 2882 Å. The calibration constant for each mixture is given in parenthesis in the figure label.



FIG. 3. Absolute etching rates of blanket p-type Si (solid symbols) obtained by calibration of the relative intensity of Si 2882 Å emission (relative proportionality constants are given in parentheses in the figure labels), and measured absolute etching rates (hollow stars), as a function of  $E^{1/2}$  (E = ion energy), in different continuous wave argon/halogen plasmas. Pulsed dc bias at 10 kHz and 50% duty cycle was applied on the sample stage. The boundary electrode was grounded. Double headed arrow lengths indicate photoassisted etching rates obtained by subtracting any isotropic (chemical) etching rate (dotted lines) from the total sub-threshold etching rate (dashed lines).

For each mixture, etching rates remain constant but non-zero as ion energy increases from its minimum value, until reaching a threshold that corresponds to the onset of ion-assisted etching. The dashed lines in Fig. 3 represent a constant etching rate that is due to processes other than those stimulated by energetic ion bombardment. Above the threshold, etching rates increase linearly as a function of square root of ion energy.

## A. Ion-assisted etching

The ion-assisted etching threshold energy  $(E_0)$  may be found by fitting a straight line to the ion-assisted etching regime in Fig. 3, and extrapolating this line to zero etching rate. A more representative threshold  $(E_1)$  may be found as the intersection of this line with a horizontal line fitted to the sub-threshold etching regime. Both thresholds are indicated in Fig. 3 for 50% Br<sub>2</sub>/50% Ar plasmas. The larger the contribution of sub-threshold etching, the more  $E_0$  will deviate from  $E_1$ . Table I lists the values found for  $E_0$  and  $E_1$ .  $E_1 = 40$ , 29, and 28 eV for Br<sub>2</sub>, HBr, and Cl<sub>2</sub>, respectively.

The ion-assisted etching threshold of  $E_1 = 28 \text{ eV}$  for the Cl<sub>2</sub>/Ar plasma found in this work is between the value of 42 eV reported by Levinson *et al.*,<sup>25</sup> for  $Ar^+$  and  $Cl_2$  beams, and the 16 eV threshold found by Chang *et al.*<sup>23</sup> for  $Ar^+$  and Cl beams. This could be due to the fact that, in the present work, both Cl and Cl<sub>2</sub> are impinging of the surface. Vitale et al.<sup>26</sup> reported yields as a function of ion energy, using a plasma to form a beam of ions and neutral radicals that were directed at a substrate in a differentially-pumped chamber. Species (including photons) exited through a grid. Their thresholds were 44, 10, and 9 eV for pure Br<sub>2</sub>, HBr, and Cl<sub>2</sub>, respectively. The  $E_1$  value for Br<sub>2</sub> in Table I ( $E_1 = 40$  eV) is in reasonable agreement with their threshold, but the  $E_I$  values for HBr and Cl<sub>2</sub> are much higher than their thresholds. Vitale et al.<sup>26</sup> showed no data below their quoted threshold energies, where, in the absence of other energetic species, it

TABLE I. Ion-assisted etching thresholds  $E_0$  and  $E_1$  (defined in Fig. 3), optical emission intensities (arbitrary units) from Ar 2p<sub>1</sub> at 750.4 nm, and normalized elemental chemical composition (excluding H), measured by XPS at a take-off angle of 30°, for blanket p-Si samples after etching in different Ar/halogen plasmas with no bias voltage.

	$E_0 (eV)$	$E_1 \left( eV \right)$	Ar 750.4 nm (a.u.)	Cl (2p)	Br (3d)	O (1s)	C (1s)	Si (2p)
50%Cl <sub>2</sub> /50%Ar	3	28	0.221	0.181	0	0	0	0.819
50%Br <sub>2</sub> /50%Ar	34	40	0.138	0	0.091	0	0.008	0.901
50%HBr/50%Ar	5	29	0.205	0	0.103	0	0	0.897
25%Cl <sub>2</sub> /25%Br <sub>2</sub> /50%Ar	12	30	0.262	0.107	0.025	0	0	0.868
25%Cl <sub>2</sub> /25%HBr/50%Ar	$\sim 1$	$\sim \! 40$	0.272	0.109	0.027	0	0	0.864

would be expected that the etching rate would be zero. Therefore, it is possible that their apparent thresholds were too low because photons emerging from their beam could cause etching as well, hence the thresholds were extrapolated to zero *total* etching rate and not zero *ion-assisted* etching rate.

Total etching rates in  $Cl_2/Ar$  plasmas are higher than those in HBr/Ar plasmas, but the ion-assisted component is about equal above threshold. Faster etching rates have been reported previously<sup>26,27</sup> for  $Cl_2 vs$ . HBr plasmas, ascribed to a chemical sputtering rate in proportion to the halogen coverage<sup>27</sup> or lower ion densities in HBr plasmas.<sup>26</sup> Faster etching rates for  $Cl_2$  plasmas could also be due to contributions from photo-assisted etching.

# B. Below the threshold for ion-assisted etching

The constant sub-threshold etching displayed in Fig. 3 for 50%Cl<sub>2</sub>/50% Ar plasmas was found previously for pure Cl<sub>2</sub> and 1%Cl<sub>2</sub>/99% Ar plasmas and was shown to be due to photo-assisted etching by light generated in the plasma.<sup>21</sup> Other mechanisms such as isotropic etching (chemical etching) by Cl atoms, metastable-induced etching, or ion-assisted etching by a mechanism different that chemical sputtering, were ruled out in that study.

#### 1. Isotropic chemical etching

Isotropic etching by reactive species can be distinguished from anisotropic processes such as photo-assisted etching by examining the profiles of features etched through a mask. A compilation of scanning electron micrographs for SiO<sub>2</sub>-masked, p-type Si with different halogen feed gas plasmas is shown in Fig. 4. In these experiments, both the boundary electrode and the substrate were grounded, resulting in a mean energy of 6 eV and a maximum energy of  $\sim 10 \text{ eV}$  for ions bombarding the substrate. The white lines and black arrows indicate the amount of horizontal etching immediately below the mask, as well as the extent of vertical etching. The horizontal etching rates derived from the SEMs of Fig. 4 are denoted as dotted lines in Fig. 3. For Br<sub>2</sub>/Ar plasmas, there was no detectable undercutting below the mask. This is in agreement with previous studies of Br atom etching of p-Si, which showed that the etching rate is exceedingly slow at room temperature.<sup>28</sup> 50% Cl<sub>2</sub>/50% Ar plasmas exhibited perhaps a slight amount of horizontal etching; in previous studies of 1%Cl<sub>2</sub>/99% Ar plasmas, no undercutting was found. As discussed previously,<sup>21</sup> etching by Cl atoms in the absence of a plasma has also been reported to be very slow near room temperature for p-type Si.<sup>29–31</sup>

The little or no isotropic etching in Cl<sub>2</sub>/Ar and Br<sub>2</sub>/Ar plasmas is very different from what was found in HBr-containing plasmas. Both HBr/Ar and Cl<sub>2</sub>/HBr/Ar plasmas exhibited a substantial amount of isotropic etching. This is likely due to purely chemical etching by H atoms, which etch Si at room temperature with a nearly isotropic profile.<sup>32–38</sup> Undercutting in HBr-containing plasmas is usually not observed.<sup>39–44</sup> Perhaps this is a result of the erosion of photoresist and chamber materials (with no Faraday shield, as in most commercial etching tools), resulting in





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passivating layers on the Si sidewalls<sup>42</sup> that could slow or block isotropic etching by H atoms. Haverlag *et al.*<sup>42</sup> reported undercutting of poly-Si beneath a photoresist mask exposed in an electron cyclotron resonance 5 mTorr HBr plasma at a modest substrate temperature (48 °C) and low rf bias voltage (50 V). They found that some time (~200 s) elapsed before enough carbon and/or oxygen passivated the sidewall, stopping lateral etching.

# 2. PAE

When the isotropic etching rates in Fig. 3 were subtracted from the total sub-threshold rates, the remaining, vertical etching was due to another anisotropic process that has been ascribed to PAE.<sup>21</sup> These PAE rates are represented in Fig. 3 as the length of the double-headed arrows. The rates are also presented in the bar graph in Fig. 5. PAE is fastest for Cl<sub>2</sub>/HBr, fast and nearly the same for Cl<sub>2</sub> and Cl<sub>2</sub>/Br<sub>2</sub>, slower for HBr, and slowest for Br<sub>2</sub> containing-plasmas, all diluted with 50% Ar.

It would be expected that regardless of the mechanism, photo-assisted etching of Si should scale with the intensity of light striking the surface, provided of course that the light is capable of inducing etching (e.g., at an energy above the bandgap, if etching is caused by photo-generation of electron-hole pairs). Previously (and in this study, described below) it was found that VUV radiation was more effective in inducing PAE. In Ar plasmas, strong VUV emission occurs at 104.8 and 106.6 nm (photon energies of 11.8 eV and 11.6 eV). In Cl<sub>2</sub> plasmas, Cl emits at 134.7 nm (9.2 eV) and 137.9 nm (8.9 eV). Strong Br emission occurs at 148.8 nm (8.35 eV) and 157.5 nm (7.9 eV). The VUV spectrum was not recorded, however, it is expected that emission from these high-energy states would be proportional to emission from the Ar  $2p_1$  state at 13.48 eV (that emits at 750.4 nm). Emission at this wavelength for the five gas compositions used in this study is also given in Table I. Emission is most intense and similar for Cl<sub>2</sub>-containing plasmas, weakest for Br<sub>2</sub>/Ar and second weakest for HBr/Ar plasmas. These trends are consistent with the ionization potentials that determine the magnitude of the electron temperature,  $T_e$ . The ionization potential (IP) of Ar (15.8 eV) is higher than any of



FIG. 5. Etching rate of blanket p-type Si measured by stylus profilometer in different 50% Ar/50% halogen plasmas with no bias voltage (solid columns). The products of optical emission intensities of Ar 750.4 nm and total halogen surface coverages (Cl + Br) measured by XPS are indicated by the cross hatched columns.

the feed gases or atomic fragments, hence  $T_e$  will be largely determined by the lower IPs of 11.5, 10.5, and 11.7 eV for Cl<sub>2</sub>, Br<sub>2</sub> and HBr, respectively, and 12.96, 11.8, and 13.6 eV for Cl, Br and H, respectively. Since Br<sub>2</sub> has the lowest IP of the feed gases employed, and Br the lowest fragment IP, the Br<sub>2</sub>/Ar plasma should have the lowest  $T_e$  and hence the lowest Ar 750.4 nm and VUV emission intensities. HBr has nearly the same IP as Cl<sub>2</sub>, but again, the low IP for Br should lower  $T_e$  some.

Any conceivable mechanism for PAE from light incident on the Si surface in the presence of a halogen feed gas would be expected to scale with the coverage of halogens on the surface. Table I shows the surface composition, measured by XPS, after etching with no bias voltage. It should be noted that no C was detected on Si surfaces after etching in Cl<sub>2</sub>-containing plasmas while 1%-3% C remained on the surface after Br<sub>2</sub>/Ar and HBr/Ar plasma exposures. While PAE rates correlate somewhat with the Ar 750.4 nm emission intensity as well as the total XPS halogen atom percent, the correlation with the product of emission intensity and total halogen coverage, represented by the cross hashed (green color online) columns in Fig. 5, is noteworthy.

# 3. Photon energy dependence of photo-assisted etching

Previously, it was shown that by placing a pair of grounded grids above the sample and applying positive bias to the substrate in excess of the plasma potential, all ions were blocked from reaching the surface, yet etching persisted.<sup>21</sup> When a quartz disc was placed above the surface the etching rate greatly slowed but a small residual etching remained. These results indicated that photo-assisted etching is most efficient by VUV light that would be blocked from reaching the substrate by the quartz window, but would of course be transmitted by the grids. In the present investigation, a MgF<sub>2</sub> window was also used to allow some VUV light to reach the sample.

VUV emissions from the 1s<sub>2</sub> and 1s<sub>4</sub> levels of Ar at 104.8 and 106.6 nm are expected to be a major source of VUV radiation in Ar-containing plasmas. No window material transmits at these wavelengths, but the analogous emissions from the 1s<sub>2</sub> and 1s<sub>4</sub> levels of Kr at 116.5 nm (10.64 eV) and 123.6 nm (10.03 eV) are partially transmitted by MgF<sub>2</sub>. Therefore, 50% Cl<sub>2</sub>/50% Kr plasmas were used to further investigate the photon energy dependence of PAE. Since Kr has a lower IP (14.0 eV) than Ar, the Cl<sub>2</sub>/Kr plasma will have a somewhat lower  $T_e$  and plasma potential compared to the Cl<sub>2</sub>/Ar plasma, and hence the maximum ion energy at 60 mTorr is expected to be slightly lower than  $\sim 10 \,\text{eV}$ . Consequently, ion assisted etching without bias will be eliminated in Cl<sub>2</sub>/Kr plasmas, just like in Cl<sub>2</sub>/Ar plasmas, since the energy of ions bombarding the substrate is less than the threshold energy.

A 38 mm diam. window of different materials was placed 10 mm above the sample to block photons of selected wavelengths that are emitted from the upper dense plasma (see schematic in Fig. 6). Etching rates of masked p-Si under the window were obtained with a stylus profilometer. Fused



FIG. 6. (left) Measured ion current to the substrate during the application of 10 kHz (50% duty cycle) pulsed dc bias (60 V amplitude, applied during 50  $\mu$ s–100  $\mu$ s) on the boundary electrode in a continuous wave 50% Cl<sub>2</sub>/50% Kr ICP (400 W rf power, 60 mTorr) for different window materials and no window. (right) Schematic of window placed above the sample to block photons of selected wavelengths that are emitted from the upper dense plasma.

TABLE II. Measured ion current density, optical emission of Cl at 792.4 nm, optical emission of Kr at 768.5 nm, Cl-to-Kr emission ratio, and etching rate of p-Si in a 50%Cl<sub>2</sub>/50%Kr plasma, with no applied bias voltage, underneath different windows or no window.

Window	Ion current density (mA/cm <sup>2</sup> )	Cl 792.4 nm (a.u.)	Kr 768.5 nm (a.u.)	Cl/Kr	Etching rate (nm/min)	
No window	13.1	1.3	2.79	0.465	235	
MgF <sub>2</sub>	2.4	0.143	0.308	0.464	$19.4 \pm 2.3$	
Quartz	2	0.181	0.498	0.363	$13.5 \pm 0.8$	
Opaque	1.8	0.134	0.388	0.345	$11.4\pm0.9$	

silica transmitted wavelengths  $>\sim 170$  nm, while the MgF<sub>2</sub> window allowed photons with wavelengths  $>\sim 120$  nm to reach the sample. An opaque window was also used to block all wavelengths. The ion density above the sample was determined in separate experiments by measuring ion currents during a 50  $\mu$ s, 60 V dc bias pulse applied on the boundary electrode. This raised the plasma potential and prevented electrons from reaching the substrate, thus, solely ion current was collected. (It should be noted that the bias pulse was used only to measure the positive ion density above the sample. It was assumed that this would equal the ion density during etching experiments with the window in place and the boundary electrode continuously at ground potential, leading to only low energy, <10 eV, ion bombardment.) Ion current densities near the end of the bias pulse are summarized in Table II. Ion current density dropped by nearly the same factor of  $\sim 6$  with the window in place and exhibited little dependence on window material.

Emission from Cl (792.4 nm) and Kr (768.5 nm) was also recorded below and parallel to the window (see Fig. 7 and Table II). Both emissions dropped by similar factors, comparable to the drop in ion current density and thus approximately electron density (the amount of Cl<sup>-</sup> and how much it drops below the window was not determined). The Cl-to-Kr emission ratio is expected to be proportional to Cl number density ( $n_{Cl}$ ), since the Cl<sub>2</sub> number density ( $n_{Cl2}$ ) should not be much greater than  $n_{Cl}$  under the high-plasma-density conditions of the present study. (Cl emission from dissociative excitation of Cl<sub>2</sub> cannot be neglected when  $n_{Cl2} \gg n_{Cl}$ ) Therefore, it appears that the Cl number density is unaffected by the presence of the window. Since Cl atoms have a low recombination coefficient on dielectrics such as quartz<sup>45–47</sup> and probably MgF<sub>2</sub>, this is not surprising. Si etching rates determined by measuring step heights on masked samples are given in Table II for the different windows and without the window. Etching rates dropped from 235 nm/min with no window to  $11.4 \pm 0.9$  nm/min with the opaque window. Since the Cl atom density was hardly affected by the window, the sub-threshold etching with no window is conclusively shown not to be due to purely chemical etching by Cl atoms. The 21-fold reduction in etching rate is much more than the 7-fold reduction in ion density above the substrate, ruling out some type of low-energy ionstimulated mechanism or electron assisted etching, in agreement with a previous study.<sup>21</sup>

The small but measurable etching beneath the opaque window is likely due to photo-assisted etching from light that scatters off the bottom of the window and from other



FIG. 7. Optical emission of Kr 768.5 nm (solid columns), Cl 792.4 nm (hatched columns) and Cl-to-Kr emission ratio (cross hatched columns) measured below the opaque, quartz and MgF<sub>2</sub> windows, compared with the measurements with no window in 50% Cl<sub>2</sub>/50% Kr ICPs.

line-of-sight reactor parts. PAE would also be caused by light generated in the low-density plasma between the window and the sample. Since the pathlength above the sample to the window is much shorter (10 mm) than the pathlength across the plasma ( $\sim$ 100 mm), the light intensity generated in this region that reaches the Si surface should be much less than 7-fold lower plasma density, causing the PAE rate to be reduced much more than 7-fold, as observed.

When the opaque window was replaced by a quartz window and light with wavelength >170 nm was allowed to reach the sample, the etching rate with zero bias voltage was  $13.5 \text{ nm/min} \pm 0.8 \text{ nm/min}$ , statistically no higher than that with the opaque window. This indicated that photons with wavelengths > 170 nm are not efficient for inducing PAE. With a MgF<sub>2</sub> window, the Si etching rate was  $19.4 \pm 2.3$  nm/min, about 10% of the rate with no window. The MgF<sub>2</sub> window transmits >90% at >200 nm, about 50% at 125 nm and falls off rapidly to 0% transmission at  $\sim <110$  nm. The longest wavelength Kr VUV lines at 116.5 and 123.6 nm are therefore in the transmission fall-off region. Cl has VUV lines in the 120–140 nm region. The VUV spectrum of the plasma was not measured in the present study. The factor of  $\sim 10$  fall-off in etching rate is more consistent with the Kr emission being dominant over the Cl emission. Estimates of quantitative reduction in VUV-induced etching are also complicated by the fact that the MgF<sub>2</sub> window formed color centers that attenuated transmission. (After the MgF<sub>2</sub> window was removed, following  $\sim 1 h$  of plasma operation, a yellow tint was observed in the window. Annealing the window for 8h at 400 °C removed the absorbing color centers.) Nonetheless, it appears that VUV light is more effective than UV-visible light in photo-assisted etching.

Absolute etching rates as a function of the square root of ion energy without a window (right y-axis) and below the opaque, quartz and MgF<sub>2</sub> windows (left y-axis) are shown in Fig. 8. These rates were also derived from a calibration of the Si 2882 Å emission. In this calibration, the PAE rates determined from step height measurements of masked samples beneath the opaque and quartz windows were used, since the transmission of the MgF<sub>2</sub> window could have



FIG. 8. Absolute etching rates of p-Si etched in 50% Cl<sub>2</sub>/50% Ar plasmas (based on the Si emission and calibrations described in the text) below the opaque (triangles), quartz (squares) and MgF<sub>2</sub> (circles) windows (left y-axis), along with a set of measurements with no window (diamonds, right y-axis).

changed as a function of time. The calibration factor relating etching rate to Si emission obtained from these experiments was 2.5 times higher than the experiment with no window, i.e. for a given etching rate, the plasma beneath the window was 2.5 times less efficient in exciting Si emission than the plasma with no window. This is less than the factor of  $\sim$ 7 decrease in Kr emission and plasma density and could perhaps be due to some enhancement in the concentration of Si-containing etching products beneath the window.

Consistent with the absolute etching rates, the relative rates below the opaque and quartz windows in Fig. 8 do not differ significantly, and the etching rates below the MgF<sub>2</sub> window at low ion energies are well above those found with the opaque window, due to the action of VUV light. The ion-assisted etching rates at 80 eV, obtained by subtracting off the photo-assisted rate at energies below threshold, were about 255 nm/min with no window, and 33, 37, and  $31 \pm 3$  nm/min beneath the opaque, quartz and MgF<sub>2</sub> windows, respectively (Table III). This indicates that there is little or no synergistic enhancement in the ion-assisted etching yield caused by VUV photons. In fact, as discussed below, there is some evidence for a negative synergy in which ion bombardment suppresses photo-assisted etching. Otherwise the ion-assisted rate beneath MgF<sub>2</sub> would be larger than beneath quartz or the opaque window. The factor of 7.7 reduction in ion-assisted etching beneath the windows is consisted with the reduction in ion flux to the Si surface.

It must be pointed out that the etching rates measured through step heights on masked samples are not consistent with rates determined from Si emission for all cases. There could be several factors causing these factor-of-about-two discrepancies. First, there is a strong proximity effect in etching rates near the edge of masked regions, especially when PAE dominates.<sup>21</sup> Hence, it is unclear at what distance from the mask should step heights be taken. Second, the PAE process produces a rough surface. This leads to some difference between the amount of material removed (proportional to Si emission) and the step height. Step height measurements were always taken as the maximum difference between the relatively smooth masked region and the fluctuating height of the rough etched regions, and hence will overestimate the average etching rate, given by Si emission, when surfaces are rough. Given the measured uncertainty in Si emission intensities and in step height measurements, the consistency between the two methods is reasonable.

Interestingly, the threshold for ion-assisted etching (colored arrows in Fig. 8, defined as the energy at which the ion-assisted etching rate drops to the photo-assisted etching rate) appears to be lower ( $\sim 16 \text{ eV}$ ) when fewer VUV

TABLE III. Ion-assisted etching rates at 80 eV, obtained by subtracting off the photo-assisted rate at energies below threshold, for p-Si underneath different windows or no window.

Window	Etching rate (nm/min)		
No window	255		
$MgF_2$	$31 \pm 3$		
Quartz	37		
Opaque	33		

photons reach the surface than when these photons are allowed to reach the surface (threshold of  $\sim$ 36 eV). One possible explanation is that ion bombardment begins to suppress photo-assisted etching at an energy similar to the threshold for ion-assisted etching. Just above threshold, ion-enhanced etching could be nearly balanced by ion-bombardment suppressed photo-assisted etching until the PAE rates go to zero and the ion-assisted etching dominates. The net result would be an apparent increase in the threshold for ion-assisted etching. One mechanism that would lead to this is disruption of the sub-surface crystalline Si, which would cause an increase in electron-hole pair recombination, and hence a loss of etching due to photoelectrons and/or holes. This type of ion-damageinduced loss of electron-hole pairs is responsible for the loss of laser-induced photoluminescence measured in situ in BCl<sub>3</sub> plasma etching of GaAs.48

# 4. Surface morphology after photo-assisted etching

As can be seen in the cross-sectional SEMs in Fig. 4, surfaces are very rough after etching under conditions where ions do not have enough energy to induce etching. A plausible explanation is that small patches of native oxide and/or carbonaceous contamination mask small regions on the wafer surface and prevent them from etching. XPS analysis of a preetched blanket samples revealed 3%-5% oxygen, presumably due to native oxide which was not completely removed after HF treatment, and 3%-5% of carbon. Erosion of reactor materials when etching commences could lead to the deposition of additional micro-masking material on the sample surface.

With no bias, the very low ion energies (i.e.,  $\sim 6 \text{ eV}$ ) used to study PAE are well below the threshold for sputtering of oxide and carbonaceous material, hence, even monolayer thick patches are expected to remain, assuming no chemical or photo-assisted reactions for their removal. Contaminant-masked regions will therefore etch with sloped sidewalls similar to those found for the lithographicallydefined masked regions. This roughening mechanism is analogous to the process believed to be responsible for the formation of needles, or so-called "black silicon," a problem that, early on, plagued reactive ion etching of silicon.<sup>49,50</sup> By improving cleaning procedures for wafers prior to etching, moving away from gases such as CCl<sub>4</sub>, and choosing reactor materials that erode very slowly, micromasking and needle formation have been eliminated in ion-stimulated etching processes, no doubt made easier by the fact that sputtering helped to remove contaminants, preventing them from forming islands that then act as masks.

Etched blanket Si(100) samples were examined by atmospheric pressure atomic force microscopy. Samples etched without bias in 50% Cl<sub>2</sub>/50% Ar plasma were found to have relatively smooth surfaces, except for a few interspersed pyramid-shaped hillocks, as can be seen in Fig. 9. Starting with an initial RMS roughness of 0.44 nm, samples etched for 30, 60, and 120 s exhibited RMS roughness of 0.65, 0.83, and 1.53 nm (excluding the hillocks), after etching away 175, 350, and 700 nm, respectively.

The hillocks are much taller than the RMS roughness, and are likely the result of contaminants that mask the tips of



FIG. 9. 5  $\mu$ m × 5  $\mu$ m AFM images of the surface of p-Si (100) etched in a 50% Cl<sub>2</sub>/50% Ar plasma for 120 s (corresponding to a depth of 700 nm) without substrate bias. (a) Top down view of the etched surface showing the orientation of the crystallographic facets with respect to the {110} cleavage planes. (b) 3-dimensional image showing pyramid like features. (c) The {110} crystal planes that form the faces of the pyramid shaped features.

the pyramids. The bases of the pyramids are oriented at  $45^{\circ}$ angles with respect to the {110} cleavage planes, and are therefore along  $\langle 100 \rangle$  directions, as seen in the top-down and tilted images in Figs. 9(a) and 9(b). The angles measured with respect to the sample surface for the pyramid facets and along the edge between two facets were  $47.4^{\circ} \pm 4.8^{\circ}$ and  $39.2^{\circ} \pm 3.7^{\circ}$ , respectively, for a sampling of several pyramids. These angles are close to the  $45^{\circ}$  and  $35^{\circ}$  angles expected if the pyramid facets are {110} planes, as depicted in Fig. 9(c). It therefore appears that photo-assisted etching rates, at least in chlorine-containing plasmas, depend strongly on the crystallographic plane. Specifically, {100} planes etch much faster than {110} planes, leaving behind micro-masked features with {110} facets. Crystallographic etching of silicon by atomic chlorine has been observed before. The (100) plane of p-type Si etched  $\sim 10$  to 100 times faster (depending on dopant concentration) than the (111) plane.<sup>51</sup> This was attributed to steric hindrance on a closely packed Si(111) surface which reduced the number of favorable adsorption sites and penetration of relatively large Cl atoms into the Si lattice.<sup>51</sup> Okano et al.<sup>4</sup> also reported slower etching for Si(111), relative to Si(100) when lightly doped p-type Si was exposed to UV light and  $Cl_{2(g)}$ , though they also observed that, under the same conditions, this difference disappeared for heavily-doped p-type Si. Apparently, etching of Si(110) by Cl atoms, or through the interaction of chlorine and light, has not been studied.

Every other feed gas mixture plasma investigated (with zero bias) resulted in rougher surfaces than in Cl<sub>2</sub>/Ar plasmas, with HBr/Cl<sub>2</sub>/Ar exhibiting twice the roughness after 30 and 60 s of etching, and HBr/Ar maintaining a nearly constant RMS roughness of ~4 nm after 30, 60, and 120 s of etching. Br<sub>2</sub>/Ar was the worst, exhibiting a RMS roughness of nearly 20 nm in the first 30 s of etching (37.5 nm removed), and then remaining at a nearly constant level of roughness after 60 and 120 s of etching (removing a total of 75 and 150 nm, respectively). The most likely explanation for the increased roughness with Br-content in the feed gas is the formation of oxygen and carbon-containing residues.<sup>52–54</sup>

This leads to increased micro-masking and hence increased density of needle-like and/or faceted features that crowd together (Fig. 10).

# C. Mechanisms for photo-assisted etching

Photo-assisted etching with visible or UV light is often attributed to a charge transfer process in which photoelectrons are captured by Cl (or F). Houle proposed that photoassisted etching of Si by F is a result of photo-generated electron-hole pairs that react to form F<sup>-</sup> and -Si<sup>+</sup>-SiF<sub>3</sub>, which then combine to form -SiF and SiF<sub>3</sub>, with the SiF<sub>3</sub> promptly desorbing.<sup>9</sup> Negative ions on the surface produce an electric field across the halogenated surface layer and into the underlying Si that assists sub-surface penetration by negative ions. It has also been proposed<sup>55</sup> that under photon irradiation, the flat-band condition that moves the Fermi level toward the conduction band for p-type and lightly-doped n-type Si, and increases the difference between the Fermi level and the electron affinity level, will cause an increase in the etching rate, as would be expected if etching proceeded by the Mott-Cabrera mechanism.<sup>6,7</sup>

It has been suggested that the mechanism for photoassisted etching of Si by Cl is different than that for F because the chlorinated surface layer consists of a single monolayer of SiCl.<sup>56</sup> This clearly is not the case with exposure to ion (and simultaneous photon) bombardment,<sup>57–59</sup> and may not even be the case for photo-assisted etching in the absence of ion bombardment after many monolayers of Si have been etched away. The primary desorption products are SiCl and SiCl<sub>2</sub><sup>60</sup> Field enhanced diffusion of Cl<sup>-</sup> (i.e., the Mott-Cabrera mechanism) has also been invoked to explain etching.<sup>4</sup> Photon-stimulated desorption from chlorinated Si(111) by picosecond-pulsed laser irradiation at 400 nm (3.1 eV) has been reported.<sup>61</sup> The authors suggested that etching was due to multiple excitations caused by hot carriers, since the photon energy of 3.1 eV was not enough to remove monochlorides (SiCl), whose bond energy to the Si substrate is 4.2 eV. Chen et al. observed a linear dependence



FIG. 10.  $5 \,\mu m \times 5 \,\mu m$  AFM image of the surface of p-Si (100) after 50% Br<sub>2</sub>/50% Ar plasma exposure for 1 min without applied bias. The darkest region corresponds to 0 nm, and the brightest regions corresponds to a height of 110 nm.

on fluence in etching of monochlorinated adatom on a Si (111) surface, using 193 nm (6.3 eV photon energy) nanosecond pulsed laser irradiation. They concluded that a single-photon absorption induced etching of a single adatom.<sup>62</sup> The amount of etching was  $3.4 \times 10^{-8}$  atoms per photon for the 33% chlorinated surface, corresponding to an effective cross-section of  $\sigma = 1.8 \times 10^{-22}$  cm<sup>2</sup> for the capture of a photon in an etching event.

The most striking aspect of the present study is the large enhancement in photo-assisted etching at the short VUV wavelengths. Radiation transmitted by a quartz window at wavelengths >170 nm causes little or no detectable etching. Photons passed by the MgF<sub>2</sub> window at wavelengths >120 nm are responsible for about 10% of the total photo-assisted etching, with the remaining  $\sim 90\%$  apparently being caused by radiation at wavelengths <120 nm. Electron-hole pairs are created in a region near the surface, within a characteristic depth of 1/k, where k is the absorption coefficient. If photo-generated electron-hole pairs mostly recombine before reaching the surface, then the photo-assisted etching rate should scale inversely with absorption depth and hence should be proportional to k, if etching is simply due to the reaction of an electron or hole with the chlorinated surface layer. k reaches a maximum of 2.2  $\times~10^{6} \rm cm^{-1}$  at 4.3 eV (288 nm) and falls to 1.2  $\times~10^{6} \rm cm^{-1}$  at 10 eV (124 nm),<sup>63</sup> hence *fewer* carriers per incident photon should be created near the surface at wavelengths shorter than 288 nm. It is quite possible that there is relatively little light between 123.6 nm (the strong Kr line) and the onset of low absorption coefficients at wavelengths > 376 nm (i.e. below the direct bandgap of Si at 3.3 eV). This could explain the substantial etching beneath MgF<sub>2</sub>, compared with little or no PAE (above the scattered light background) beneath quartz - the shortest wavelengths of plasma emission passing through quartz may be at energies below the direct bandgap energy of Si, thus these photo-generated carriers are created in a much thicker layer and much fewer of them reach the surface.

There is, however, some indirect evidence that the yields could fall off abruptly at wavelengths > 120 nm, meaning that even if there is a substantial amount of light passing through quartz between  $\sim 170$  and  $\sim 350$  nm, it may not be very effective in causing etching. While photo-assisted etching of Si in the presence of chlorine has apparently not been studied at VUV wavelengths, VUV radiation-induced etching of GaAs with  $Cl_{2(g)}$  and Si with  $XeF_{2(g)}$  have been reported. For GaAs, yields of  $\sim 70$  were found between 117 and 128 nm, while between 130 and 135 nm much smaller yields ( $\sim 0-10$ ) were observed.<sup>19</sup> For Si etching with XeF<sub>2</sub>, yields of  $\sim 100$  were found near 112 nm,  $\sim 1$  between 130and 170 nm, and near zero between 170 and 200 nm.<sup>19</sup> Even more surprising, these authors concluded that most photons are not absorbed, but when one is, it initiates a chain reaction that causes  $\sim 10^5$  Si-containing products to desorb.

In the present study, the etching rates appear to be very high. The VUV intensity was not measured, but it is likely to be a small fraction of the power delivered to the plasma. The surface area of the cylindrical discharge tube was about 600 cm<sup>2</sup>, hence the input power density was about 0.67 W/cm<sup>2</sup>. Woodworth *et al.*<sup>64</sup> reported an absolute photon flux of  $3.5 \times 10^{16}$  cm<sup>-2</sup>s<sup>-1</sup>, integrated over the region between 70

and 130 nm. The power in their experiment (200 W), spread over the 345 cm<sup>2</sup> area of their cylindrical plasma boundary, corresponds to nearly the same input power density  $(0.6 \text{ W/cm}^2)$  as for the current study. An etching rate for 50%Cl<sub>2</sub>/50% Ar plasmas of 350 nm/min (Fig. 3) corresponds to a Si-containing product flux of  $2.9 \times 10^{16} \text{ cm}^{-2} \text{s}^{-1}$ . If the VUV flux in the present work was equal to that measured by Woodward et al., then the corresponding yield would be 0.8 Si atoms/photon. Reported photo-assisted etching yields are much lower for Si (100) in the presence of  $Cl_{2(g)}$  with longer wavelength light.<sup>10,11,65,66</sup> For example, the yield was  $3.34 \times 10^{-4}$  Si atoms/photon at 248 nm and  $6.46 \times 10^{-6}$  Si atoms/photon at 308 nm using pulsed excimer lasers at a Cl<sub>2</sub> pressure of 525 mTorr.<sup>66</sup> The yield was  $2.88 \times 10^{-6}$  Si atoms/photon at 488 nm and  $2.13 \times 10^{-6}$  Si atoms/photon at 514.5 nm under continuous Ar<sup>+</sup> laser irradiation in a 750 Torr Cl<sub>2</sub> atmosphere.<sup>11</sup> Kullmer and D. Bäuerle<sup>10</sup> found that with low laser fluence, etching was non-thermal and ascribed the process to the reaction between photoelectrons and Cl radicals on the surface to form Cl<sup>-</sup>, which then penetrates the sub-surface region.

The large increase in yields at shorter wavelengths suggests some energy threshold for this process. One possibility is that direct excitation occurs that leads to the prompt desorption of a SiCl<sub>x</sub> product. It is not likely, however, that the absorption cross section for such a process would be so large that every VUV photon would be absorbed in the  $\sim 1$  nm thick surface layer. Even if this were to happen, photon absorption would need to lead to desorption of a product molecule nearly 100% of the time.

Another possibility is that energetic carriers play a role in PAE. Carriers created by VUV absorption are initially quite energetic. Energy conservation requires that the photon energy hv divides according to:<sup>67</sup>

$$\Delta E_e = \frac{h\nu - E_g}{1 + \frac{m_e^*}{m_h^*}}, \quad \Delta E_h = \frac{h\nu - E_g}{1 + \frac{m_h^*}{m_e^*}}, \quad (2)$$

where  $m_e^*$  and  $m_h^*$  are the effective masses of the electron and hole, respectively, and  $E_g$  is the bandgap (1.12 eV for Si at room temperature).  $m_e^*/m_e$  and  $m_h^*/m_e$  for Si, based on the density of states, are 1.08 and 0.56, respectively,<sup>68</sup> with  $m_e$ being the electron rest mass. Hence,  $\Delta E_e = 0.34(h\nu - E_g)$ and  $\Delta E_h = 0.66(h\nu - E_g)$ .

Carrier-carrier collisions quickly thermalize these initially hot carriers and then carriers transfer energy to phonons and cool to the lattice temperature. These substrate-temperature carriers are then lost by recombination on much longer time scales. Hence, in the short time during which the carriers possess high energies, they may induce chemistry that does not occur for thermalized carriers that form more quickly with lower energy photons.

If surface states pin the Fermi level energy  $(E_F)$  near mid-gap, as is widely found to occur,<sup>69</sup> then the conduction and valence band edges (energies  $E_C$  and  $E_V$ ) bend downward for p-type material. Hence, to reach the surface chlorinated layer, holes traveling toward the surface would need an energy normal to the surface in excess of a barrier energy,

$$E_b \approx 1/2E_g + k_B T \ln[N_A/N_v], \qquad (3)$$

where  $N_V = 1.8 \times 10^{19} \text{ cm}^{-3}$  is the density of states at the top of the valence band,  $k_B$  is the Boltzmann constant, and *T* is the substrate temperature. The acceptor number density,  $N_A = 2.7 \times 10^{14}$  to  $2.7 \times 10^{15} \text{ cm}^{-3}$  for the Si samples used, hence  $E_b = 0.27 - 0.33 \text{ eV}$ . Very few holes created with low energy photons would therefore be able to reach the surface, while those created with VUV photons could lose most of their energy and still be energetic enough to reach the Si surface region. Photoelectrons will see an attractive potential of  $E_b$  pulling them toward the surface.

While electrons generated by 120 nm light initially possess barely enough energy (3.1 eV, from Eq. (2)) to break Si-Si bonds, it is unlikely that such "electron impact" dissociation would occur with unit efficiency, let alone with yields approaching 100 etching products per photon that have been reported.<sup>19</sup> Photo-electrons that do not recombine with holes would be pulled toward the surface and obtain at most an additional  $E_b = 0.3 \text{ eV}$  due to band bending. It is expected that electrons born with 3.1 eV translational energy have a higher probability of reaching the surface before recombining with holes at defect sites via the Shockley-Read-Hall (SRH) mechanism.<sup>70</sup> Unlike low energy electrons, hot carriers that would have sufficient energy to avoid being trapped by the mid gap states created by these defects. Fardi *et al.*<sup>71</sup> saw evidence for this in AlGaAs/GaAs p-i-n photodiodes. They found that hot carriers were much more likely to avoid SRH recombination, allowing them to escape quantum well layers and be injected into adjacent layers. Perhaps these electrons are efficient at inducing surface reactions leading to etching.

If energetic holes reach the chlorinated surface layer, they could lead to the irreversible breaking of Si-Si bonds. This could occur via several types of processes. For example, if a hole reaches the near-surface and resides on a Si atom that has bonds to 3 Si atoms and a SiCl<sub>3</sub> group, the Si-SiCl<sub>3</sub> bond could be weakened enough that SiCl<sub>3</sub> desorbs. Holes can also migrate to a Si atom with one or more tensile-strained bonds to adjacent Si atoms, then the weakened single-electron bond, formed when the hole moves to one of the strained Si atoms, could rupture and the two Si atoms recoil from each other to relieve the strain. Once the hole migrates to another Si atom, the two dangling bonds on nearby Si atoms would not reform a bond because they are too far apart. These Si atoms would then readily react with 2Cl and/or Cl<sub>2</sub> to form two SiCl species. In both of these examples the hole is not lost in the process, hence it could catalyze more than one Si-containing etching product to form. Photo-assisted hole-catalyzed reactions have been reported. Ghosh and Bauld have found that electron acceptors (holes) in zeolites catalyze cyclo-addition reactions.<sup>72</sup> They report catalytic factors (products per hole) of 10<sup>18</sup> or higher! Because photo-assisted etching of Si is confined to the surface, and band bending would likely push the hole into the bulk, it is difficult to envision how such a process could lead to yields of 50, let alone  $10^5$ , as has been reported.<sup>19</sup>

An unresolved issue with the above explanation is the lack of hole-catalyzed reaction when low energy ions

neutralize upon impinging on the silicon surface. When an ion approaches the surface, it is widely believed to be neutralized nearly 100% of the time, at a very close distance from the surface. In this process, an electron is removed from the valence band and, to conserve energy, a second, Auger electron is generated, along with another hole. Most of the time the Auger electron does not escape the solid, but occasionally it does. The substantial amount of energy divided between the electron and two holes created at the surface is rapidly dissipated until the carriers thermalize with the lattice and relax to the top of the valence band (holes) or bottom of the conduction band (Auger electron). One would expect these holes to play the same important role in accelerating etching as might the photo-excited holes. However, in a previous study it was shown that when all ion bombardment was blocked from the surface, relatively fast etching persisted with no change in rate. Hence ions with energies below the threshold for ion-assisted etching ( $\sim < 15 \text{ eV}$ ) did not cause any etching. The reason may be that the Augergenerated holes have low energy compared to the VUV photo-generated "hot" holes. Again, low energy holes can't overcome the potential barrier to be able to reach the surface and possibly catalyze etching.

# IV. SUMMARY AND CONCLUSIONS

Etching of p-type Si (100) was studied in a rf inductively coupled plasma in Cl<sub>2</sub>, Br<sub>2</sub>, HBr, Br<sub>2</sub>/Cl<sub>2</sub> and HBr/Cl<sub>2</sub> gases diluted with Ar (50%-50%). A Faraday shield prevented capacitive coupling to the plasma, allowing for a low dc plasma potential (<10 V) and control of the energy of ions bombarding the substrate. Above a threshold value, the Si etching rate increased with the square root of ion energy. Below that threshold, the etching rate was independent of ion energy and was determined to be due to PAE, except for a small contribution of isotropic chemical etching by H atoms in HBr-containing plasmas. Isotropic etching was observed as mask undercut in SEM cross sections of patterned wafers. For the gas mixtures investigated, HBr/Cl<sub>2</sub>/Ar and Br<sub>2</sub>/Ar exhibited the fastest and slowest PAE etching rate, respectively. Experiments using a window of different materials above the sample to selectively allow different wavelengths to strike the surface, as well as etch rate measurements based on the calibrated intensity of the 2882 Å Si emission line, showed that photo-assisted etching at VUV wavelengths was much more effective in etching Si compared to longer wavelengths. The PAE rate scaled with the product of the intensity of the Ar 750.4 nm emission line and the halogen (Cl and/or Br) surface coverage, determined by XPS. SEM and AFM images revealed that PAE results in rough surfaces, probably due to the inability of low energy ions in removing surface contaminants that act as micromasks. Cl<sub>2</sub>/Ar and Br<sub>2</sub>/Ar plasmas resulted in the smoothest and roughest surface, respectively. In general, the surface roughness increased with increasing exposure to the plasma. Photo-assisted etching in Cl<sub>2</sub>/Ar plasmas resulted in the formation of 4-sided pyramidal features with bases along (100)directions and facet corresponding to {110} planes, suggesting that photo-assisted etching can be sensitive to crystal

orientation. The most striking feature of this work was the strong enhancement of the PAE rate at the short VUV wavelengths, with photon yields estimated to approach or even exceed unity. This may be due to the generation of hot carriers (specifically holes) at these short wavelengths. Such holes must have enough energy to overcome the potential barrier due to band bending and reach the chlorinated surface where they can initiate a chain reaction with a high overall yield.

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