

# A multi-sensor study of Cl<sub>2</sub> etching of polycrystalline Si

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Cl<sub>2</sub> chemistries are the basis for etching of polycrystalline Si and other conductive gate materials in Si CMOS integrated circuit fabrication. It is now well-known that recombination of atomic Cl neutrals on the chamber walls influences the etch rate and thus leads to manufacturing reproducibility problems. In this work, we make use of multiple real-time

measurements to improve the understanding of the physical mechanisms for this effect. In particular, real-time spectroscopic ellipsometry is used as both a poly-Si etch rate monitor and as a virtual SiCl<sub>4</sub> flow rate sensor. This aids in the quantitative interpretation of the optical emission spectroscopy data.

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**1 Introduction** The wall-state of reactive ion etch tools is known to strongly affect etch results, and previous studies show that neutral species concentrations vary with chamber seasoning [1, 2]. In this paper, we will show data from simultaneous, real-time, in situ measurements of etch rates (using spectroscopic ellipsometry), plasma electron density (using broadband RF reflectometry), and Cl neutral actinometry data during high-density Cl<sub>2</sub> reactive ion etching of poly-Si in a Lam 9400 SE TCP system. All of these quantities are found to vary over time after a seasoned chamber is cleaned by exposure to a fluorine-containing plasma. Following chamber cleaning/fluorination, variations in real-time poly-Si etch rates correlate closely with electron density transients. Proportional-integral (PI) feedback control of the plasma density using the TCP power restores both the nominal density and poly-Si real-time etch rate. Using corresponding chlorine actinometry measurements, we suggest that the compensation mechanism is accomplished by increasing the electron temperature,  $T_e$ , and therefore the ionization rate. Neutral Cl concentrations,  $n_{Cl}$ , are found to drift as the chamber walls season in a Cl<sub>2</sub> environment, and PI feedback control of density may compensate for some of the  $n_{Cl}$  losses. These results are fully consistent with a significant body of experimental and theoretical work suggesting that high density plasma Cl<sub>2</sub> etching of Si is ion-dominated and is sensitive to chamber wall state. However, they are the first to clearly demon-

strate these connections to real-time etch rate variations and provide the first demonstration mechanism for feedback control correction to wall-state drift. Our in situ spectroscopic ellipsometry measurements allowed us to: (1) connect the data of the plasma density and chemical species concentrations to the real-time etch rates; and, (2) accurately estimate the concentration of etch by-product (SiCl<sub>4</sub>) present in the chamber. With the estimated SiCl<sub>4</sub> concentration, we were able to correct for gas dilution effects and improve the actinometric estimate of the neutral Cl concentration. The simultaneous use of multiple real-time process and wafer state sensors allowed us to get an improved overall qualitative and quantitative understanding of this etch process.

## 2 Experimental

All experiments all used unpatterned 150 mm Si (100) orientation wafers coated with ~500 nm of LPCVD polycrystalline Si on 31.7 nm of thermally grown SiO<sub>2</sub>. Reactive ion etches were performed in a Lam 9400 SE TCP high density, inductively coupled etch system. The inductive source and bias supplies operated at 13.56 MHz. During poly-Si etch, the chamber pressure was 10 mTorr and the gas flows consisted of 100 sccm Cl<sub>2</sub> and 5 sccm Ar. The source power was nominally 250 W (but was automatically varied during the PI control experiments) and the bias supply power was 100 W.

The etch system was equipped with a high speed rotating polarizer spectroscopic ellipsometer with a prism spectrometer/CCD detection system (Sopra RTSE). SE data were collect at a 1 sample/0.18 s rate. It was also equipped with a broadband RF reflectometry system (BBRF) for plasma density measurements [1], and a two wavelength optical emission spectroscopy (OES) system. The OES system used two SPEX 500M grating monochromators with cooled photomultiplier detectors monitored using a chopper/lock-in amplifier configuration. This approach allowed simultaneous high speed, high signal to noise monitoring of two spectral lines (the 750.4 nm Ar line and the 822.2 nm atomic Cl line) for performing Cl neutral actinometry. The BBRF and OES data were collect at 1 sample/0.25 s rate. All data was collected using a LABVIEW™-based collection system with careful attention to maintaining a synchronized, accurate time base for all data.

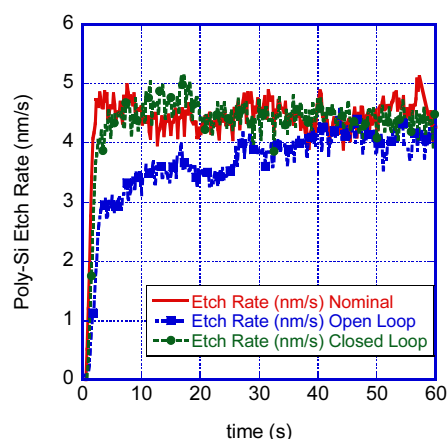
We also collected data on etch byproducts from an Online Technologies Fourier transform infrared spectrometer (FTIR) in the foreline of the vacuum system. The sampling of this system was slower (typically 1 sample/4 s depending on desired SNR). This data was used for corroboration of our results rather than for quantitative real-time analysis.

### 3 Results and discussion

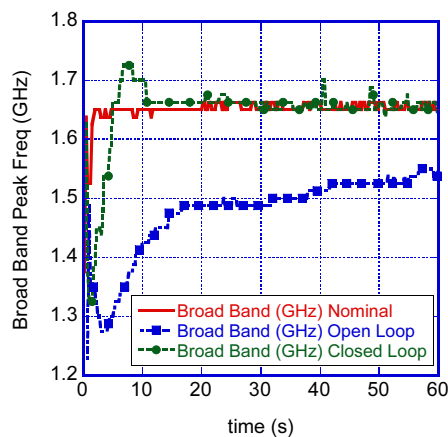
In our earlier work of [1], we showed that when the etch chamber had been “seasoned” following ~10 minutes of Si etching (several separate wafer etch runs), the poly Si etch rate (measured by RTSE) was constant as was the plasma density (BBRF). If the chamber was “cleaned” using CF<sub>4</sub> to remove SiO<sub>x</sub>Cl<sub>y</sub> etch byproducts from the chamber walls, the poly-Si etch rate decreased and became time-dependent. The plasma density also showed similar time dependence. Using a PI controller which adjusted the TCP source power to maintain a constant target plasma density, the poly-Si etch rate was stabilized. The results of one of these sets of experiments are shown in Figs. 1 and 2. The actinometry ratio (Cl OES emission intensity  $I_{Cl}$ /Ar OES emission intensity  $I_{Ar}$ ) for these experiments is plotted in Fig. 3. This ratio is often taken to be proportional to the neutral atomic Cl concentration ( $n_{Cl}$ ). This point will be addressed further in this paper. Since the poly-Si etch rates follow the trends of the BBRF plasma density measurements and the closed loop results do not follow the actinometry ratio, we conclude that the poly-Si etch rate is dominated by the ion density rather than neutral Cl concentration. In quasi-neutral plasmas, the ion and electron concentrations are nearly equal, so the BBRF signal (which is proportional to the electron density) provides a indicator for both. We conclude that in all tested cases, there is sufficient neutral Cl to chemically saturate the Si surface, and that the etch rate is controlled by the Cl<sup>+</sup> ion concentration. While we feel these conclusions well supported by this data, there are important details that were unresolved. The most notable are: (1) the Ar OES signal  $I_{Ar}$  is nearly constant with time in the open loop experiments even though

the plasma density is varying; and (2) the actinometry ratio is the same for the open loop and closed loop experiments (why does the extra TCP power in the closed loop case not raise the apparent neutral Cl concentration?).

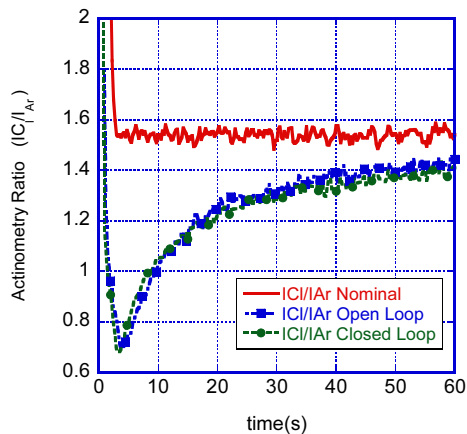
Careful simultaneous analysis of the real-time sensor data shows that both of these effects are explained by time-varying chamber gas composition. While the input gas flows are held virtually constant by mass flow controllers, the time varying dissociation rate of Cl<sub>2</sub> into Cl (due to plasma density changes), the time varying recombination rate of Cl into Cl<sub>2</sub> (due to chamber wall “seasoning”), and the time-varying evolution of SiCl<sub>4</sub> etch byproduct (due to



**Figure 1** Real-time poly-Si etch rates measured with RTSE: (solid line) nominal/seasoned, (dashed/dots) closed loop/clean, (dashed/squares) open loop/cleaned.



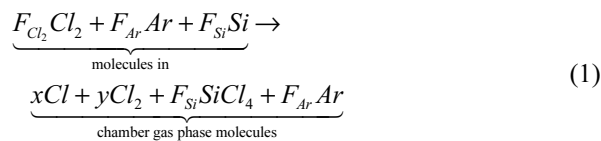
**Figure 2** BBRF reflectometry data ( $\propto$  to plasma density) for the experiments of Fig. 1. (solid line) nominal/seasoned, (dashed/dots) closed loop/clean, (dashed/squares) open loop/cleaned.



**Figure 3** Cl/Ar actinometry ratio for the 3 representative etch runs. (solid line) nominal/seasoned, (dashed/dots) closed loop/clean, (dashed/squares) open loop/cleaned.

the varying poly-Si etch rate) all contribute strongly to the actual relative concentration of Ar present in the chamber and thus to the quantitative interpretation of the OES/actinometry results.

To model the OES data, we assume the following simplified etch reaction:



where  $F_{Cl_2}$  and  $F_{Ar}$  are the flow rates of  $Cl_2$  and Ar into the chamber (measured by mass flow meters), and  $F_{Si}$  is the flow rate of Si into the etch chamber gas environment (as  $SiCl_4$ ). This quantity is derived from the poly-Si etch rate and the area of the wafer. We assume that the density of the poly-Si is that of single crystal silicon (this introduces a negligible systematic error). With an etch rate of 4 nm/s, there is an effective flow rate of  $\sim 7.9$  sccm of Si byproduct ( $SiCl_x$ ) into the etch chamber. Mass balance requires that:

$$\frac{1}{2}x + y + 2F_{Si} = F_{Cl_2} \quad (2)$$

and

$$y = (1-d)F_{Cl_2} \quad (3)$$

where  $d$  is the net fraction of  $Cl_2$  which is dissociated into Cl. This is affected by both dissociation in the plasma, bulk recombination, and wall recombination. These two mass balance equations yield:

$$x = [2dF_{Cl_2} - 4F_{Si}] \quad (4)$$

The OES signal can be modelled as:

$$I_{Ar} = C_{Ar} n_e n_{Ar} = K_{Ar} \omega_n^2 n_{Ar} \quad (5)$$

$$I_{Cl} = C_{Cl} n_e n_{Cl} = K_{Cl} \omega_n^2 n_{Cl} \quad (6)$$

since the electron density ( $n_e$ ) is proportional to the BBRF frequency squared ( $\omega_n^2$ ). The constants  $C$  and  $K$  are sensitive to the electron energy distribution function (sometimes simplified to an electron temperature,  $T_e$ ). For actinometry, we assume that the ratio  $K_{Cl}/K_{Ar}$  is approximately constant with  $T_e$  variations. The following set of mass balance equations, with  $n_g$  representing the total gas particle concentration in the chamber, allows us to create a time varying model for the OES data:

$$\begin{aligned} n_g &\propto x + y + F_{Si} + F_{Ar} \\ &\propto 2dF_{Cl_2} - 4F_{Si} + (1-d)F_{Cl_2} + F_{Si} + F_{Ar} \\ &\propto (1+d)F_{Cl_2} + F_{Ar} - 3F_{Si} \end{aligned} \quad (7)$$

$$n_{Cl} = \left[ \frac{x}{x + y + F_{Si} + F_{Ar}} \right] n_g = \left[ \frac{2dF_{Cl_2} - 4F_{Si}}{(1+d)F_{Cl_2} + F_{Ar} - 3F_{Si}} \right] n_g \quad (8)$$

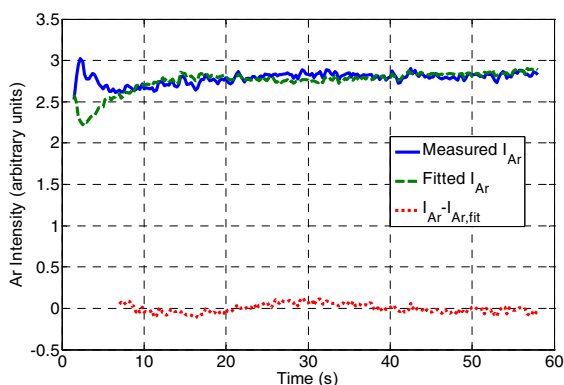
$$\begin{aligned} n_{Ar} &= \left[ \frac{F_{Ar}}{x + y + F_{Si} + F_{Ar}} \right] n_g = \left[ \frac{F_{Ar}}{(1+d)F_{Cl_2} + F_{Ar} - 3F_{Si}} \right] n_g \end{aligned} \quad (9)$$

Thus the measured actinometry ratio is:

$$\left[ \frac{I_{Cl}}{I_{Ar}} \right]_m = \frac{K_{Cl} n_{Cl} n_e}{K_{Ar} n_{Ar} n_e} = \frac{K_{Cl}}{K_{Ar}} \left[ \frac{2dF_{Cl_2} - 4F_{Si}}{F_{Ar}} \right] \quad (10)$$

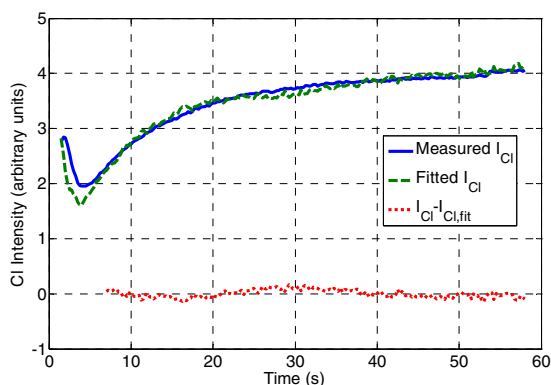
For low dissociation fraction ( $d$ ) and low etch rates (thus low  $F_{Si}$ ), the actinometry ratio given in the last equation will be proportional to the neutral Cl concentration  $n_{Cl}$ . However, in high density plasma etch systems, both of these assumptions are violated and more detailed analysis is required.

Assuming a constant chamber gas temperature yields a constant  $n_g$ . Thus we now have a model with only 2 adjustable time-constant parameters ( $K_{Cl}$  and  $K_{Ar}$ ). The time-varying  $Cl_2$  dissociation fraction  $d(t)$  is found from the last equation using the measured actinometry ratio. Regression analysis of the open loop data allows estimation of both unknown constants. These fits are shown in Figs. 4 and 5.



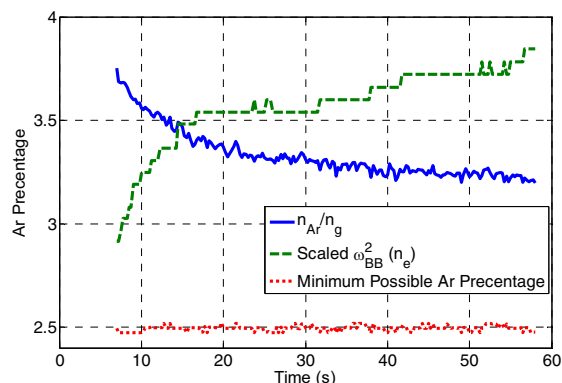
**Figure 4** Measured (solid) Ar OES line intensity, fit (dashed) and error (dotted).

The resulting relative Ar concentration in the chamber is shown in Fig. 6 along with a scaled plot of the BBRF signal. This plot shows that the nearly constant  $I_{Ar}$  signal (Fig. 4) observed in the open loop case is the result of a decreasing Ar fraction in the gas (due to dilution effects) and an increasing plasma density (with the resulting product being nearly constant). This cancellation effect had lead prior researchers to conclude that the plasma density was constant [2, 3]. With a time-varying etch rate (and thus SiCl<sub>4</sub> evolution rate) and a time-varying Cl recombination rate, the Ar concentration cannot be constant and thus using the nearly constant behaviour of  $I_{Ar}$  as a plasma density indicator is incorrect.



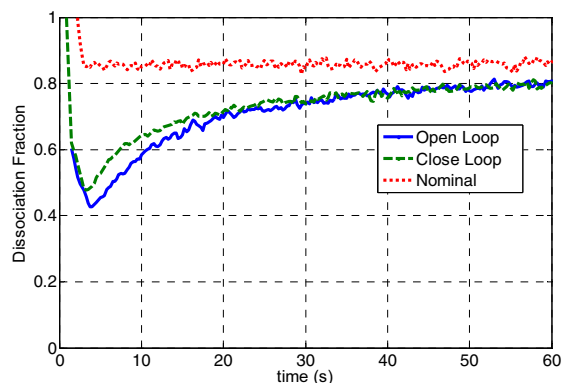
**Figure 5** Measured (solid) Cl OES line intensity, fit (dashed), and error (dotted).

Assuming that these constants hold for the conditions of the nominal and closed loop runs, we can then estimate the net dissociation fraction  $d$ . This is illustrated in Fig. 7. Based on our estimated corrections, we again assert that the poly-Si etch rate is controlled by the Cl<sup>+</sup> ion concentration (directly related to plasma density). Neutral atomic Cl recombination on the chamber walls reduces this species concentration in the open loop case, and the lack of atomic neutrals reduces the ionization rate, leading to a lower plasma density. In the closed loop case, the BBRF PI



**Figure 6** Ar fraction (solid), scaled BBRF signal (dashed), and minimum possible Ar fraction (dotted) showing the opposing actions of Ar dilution and plasma density increase.

controlled increase in the TCP power yields a constant plasma density approximately the same as that of the open loop case. This leads to only a small observable increase in the net Cl<sub>2</sub> dissociation fraction ( $d$ ). Thus, the stabilization of the plasma density (and thus etch rate) must be the result of an increase in the electron temperature  $T_e$  with TCP source power (this is certainly physically reasonable). Thus the Cl ionization and Cl<sub>2</sub> dissociation rates are both increased, but the net dissociation fraction is still suppressed by the wall recombination. Also, most of the newly generated atomic neutral Cl is consumed by the increase in the poly-Si etch rate, leading to another interesting balance of effects resulting in no apparent difference in the actinometry results of two very different cases (the open and close loop experiments).



**Figure 7** Net Cl<sub>2</sub> dissociation fraction  $d$  for the open loop (solid), closed loop (dashed) and nominal seasoned chamber (dotted) cases.

**4 Conclusions** We have self-consistently analyzed the results of simultaneous real-time measurements of plasma, neutral chemical, and wafer state data to develop a more complete picture for the factors that lead to time-varying poly-Si etch rates in Cl<sub>2</sub> plasmas. Use of *in situ*, real-time spectroscopic ellipsometry was critical to both link the plasma and neutral chemistry data to the etch rates,

as well as to provide a critical quantitative estimate for the amount of etch byproduct gas ( $\text{SiCl}_4$ ) being released into the chamber.

We also developed a test for validating the constant  $T_e$  assumption. Due to space constraints, this cannot be discussed in detail in this report. We will state without proof that examining the BBRF to Cl OES signal ration ( $\omega_n^4/I_{Cl}$ ) provides an indicator of variation in  $T_e$ . For the open loop and nominal cases, we find this ratio to be approximately constant. For the closed-loop case, it varies significantly with time. Our work could be further improved if an independent measure of  $T_e$  (such as by Langmuir probe or multiple species rare gas OES methods) were also included.

### References

- [1] P. I. Klimecky, J. W. Grizzle, and F. L. Terry, Jr., *J. Vac. Sci. Technol. A* **21**, 706 (2003).
- [2] S. J. Ullal, A. R. Godfrey, E. Edelberg, L. Braly, V. Vahedi, and E. S. Aydil, *J. Vac. Sci. Technol. A* **20**, 43 (2001)
- [3] V.M. Donnelly, *J. Vac. Sci. Technol. A* **14**, 1076 (1996).