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Bailey I I I, A.D.; van de Sanden, M.C.M.; Gregus, J.A.; Gottscho, R.A.

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Scaling of Si and GaAs trench etch rates with aspect ratio, feature width, and substrate temperature

A. D. Bailey III, M. C. M. van de Sanden, a) J. A. Gregus, and R. A. Gottscho b)
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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The scaling of etch rates with feature dimensions is an important issue in the fabrication of microelectronic and photonic devices. Because etch rates depend on circuit layouts and design rules, considerable effort is spent to modify processes each time changes in design are made. Knowing how etch rates scale with design parameters should accelerate the introduction of new designs into manufacturing while minimizing the cost of doing so. Recently it has been shown that etch rates for a variety of conditions scale with the depth/width or aspect ratio and not on width or depth alone. While various mechanisms might be responsible for such scaling, isolating one mechanism from another is not straightforward. Nonetheless, it is important to understand the underlying mechanisms so that differences in etch chemistry and etch reactor design can be accounted for when scaling plasma processes from one design or reactor to another. To assess the effects of etch chemistry alone, the trench etch rates of Si and GaAs are compared under constant plasma conditions. Substrate temperature is varied to further assess the relative importance of surface vs transport phenomena during the etching process. At higher temperatures, both Si and GaAs trench etch rates scale only with aspect ratio in an Ar/Cl2 electron cyclotron resonance plasma. The results are consistent with an ion-neutral synergy model based on Langmuir adsorption kinetics where the scaling can be explained by the aspect ratio dependence of the neutral reactant transport into the trench: charging effects, ion shadowing, and Knudsen transport are not consistent with the data. At −45 °C, the etch rate no longer scales with aspect ratio alone, but now also depends on trench width. The data at this lower temperature are well described by a model incorporating the deposition of an etch inhibiting layer. While the trench etch rates for GaAs and Si scale in similar ways with aspect ratio and trench width, the dependence on feature dimensions of the Si etch rate is much stronger than that for GaAs at all substrate temperatures because the steady-state surface coverage of Cl is smaller for Si. This results in a greater sensitivity to the incoming, aspect ratio dependent, neutral fluxes. The implications of the models on the goal of aspect ratio independent etching are also discussed. © 1995 American Vacuum Society.

I. INTRODUCTION

Microscopically uniform anisotropic etching of semiconductor layers is a necessary step in ultralarge scale integrated (ULSI) circuit fabrication. Plasma etching is widely used today and is the most mature technology for future ULSI production. However, incomplete understanding of many of the important physical and chemical processes affecting product yields leads to difficulties in applying plasma process technology. As critical dimensions of circuit patterns approach the submicron regime, smaller contact windows and narrower trenches tend to etch more slowly than their larger counterparts. As pointed out in a recent review,1 such phenomena have been referred to as RIE lag,2–4 microloading,5–9 aperture effect10 aspect-ratio-dependent etching (ARDE),1,11 and pattern factor.12 Such dependencies of etch rates on circuit design complicate the successful and cost effective fabrication of devices containing a range of feature sizes and desired aspect ratios (etched depth divided by feature width). Overetching is required to completely clear the slowly etched features while the features already cleared are exposed excessively to the potentially damaging effects of the plasma environment. This problem is especially critical when the underlying layer is a very thin gate dielectric.13 Overetch times used to optimize device yields must be determined on a costly case by case basis. Small changes in device cell design, design rules, or wafer layout can result in unexpected, time consuming and expensive plasma process development.14–16

The microscopic nonuniformity of etching rates has been observed under a wide range of plasma conditions and with a variety of reactor systems such as symmetric rf diodes (plasma etch mode), asymmetric rf diodes at low pressure (reactive ion etch or RIE mode), magnetically enhanced RIE (MERIE), and electron cyclotron resonance (ECR) reactors. Similar observations have been made using chemistries ranging from Cl2 and SF6 to CHF3/O2/H2 gas mixtures and substrate materials ranging from polymers and metals to Si and III–V compounds (cf. Ref. 1 and references therein). Although the general nature of plasma etching processes are now reasonably well understood, current theoretical models are no substitute for experimental exploration of possible mechanisms responsible for etch rate scaling and their dependence on operating conditions such as feature sizes, plasma conditions, etch chemistry, and etched material. Understanding when these phenomena are the result of generic or specific etch conditions will lead to better control of etch

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a)Eindhoven University of Technology, The Netherlands.
b)Author to whom correspondence should be addressed.
processes, to reduced cost and time for introduction of new processes on established equipment, and to the development of next generation, lower cost-of-ownership production tools.

It has been shown in numerous studies that etch rates depend on the instantaneous aspect ratio rather than the absolute feature width.\textsuperscript{17,18} Gottsch\textit{e} et al.\textsuperscript{1} introduced a consistent nomenclature connected to the possible physical mechanisms playing a role in these phenomena and highlighted the aspect ratio dependence of the most important mechanisms. Chin \textit{et al.}\textsuperscript{17} showed that the etch rate of 2.5–0.2 \textmu m wide trenches in Si scaled with aspect ratio alone. Although their initial proposal that deflection of ions by the trench or window electric field does not appear reasonable,\textsuperscript{19} the aspect ratio scaling alone permits many other mechanisms without such scaling to be eliminated as well. In another study, Fujiwara \textit{et al.}\textsuperscript{5,6} reduced RIE lag in the Cl\textsubscript{2} etching of poly-Si by reducing the width of the ion angular distribution, but they did not clearly demonstrate that etch rates scaled with aspect ratio alone as implied by the ion shadowing mechanism.\textsuperscript{1} In an extensive study of Al etch rates with different plasma conditions and masks, Boyer and Henry\textsuperscript{18} observed strong aspect ratio scaling of Al etch rates dominated by neutral flux shadowing assuming ad hoc angular distributions. Differences between the aspect ratio dependence using insulating or conducting masks could be explained by assuming ion angular distributions with different breadths. It is unclear whether the proposed mask charging mechanism is aspect ratio dependent. In the same study,\textsuperscript{18} the aspect ratio dependence with a conductive mask was observed to increase as the substrate temperature was lowered contrary to the trend with an insulating mask.\textsuperscript{18,20} and also contrary to previously reported results in (Al)GaAs (Refs. 21 and 22) and SiO\textsubscript{2} (Ref. 23) etching.

Overall, a clear understanding of the influence of chemistry on etch rate scaling has not yet emerged. Sato \textit{et al.}\textsuperscript{24} report more pronounced Si etch rate scaling when fluorinated chemistries are used instead of chlorinated chemistries. Fujiwara \textit{et al.}\textsuperscript{5} attributed weaker scaling of poly-Si etch rates with heavier halogens (HBr and HI to Cl\textsubscript{2} and HCl) to the narrower ion angular distribution function in the heavier reactive gases; however, they made these comparisons without keeping other potentially important process parameters constant, such as substrate temperature which was −20 °C for the chlorine experiments and 50 °C for the HBr and HI experiments. Keeping conditions more similar, Aoki \textit{et al.}\textsuperscript{20} report stronger etch dependence on pattern spacing with HBr compared to Cl\textsubscript{2} at 40 °C, seemingly at odds with Fujiwara \textit{et al.}'s results. Generally, confusion abounds when one tries to determine the dominant physical and chemical mechanisms responsible for etch rate variations with feature dimensions. Compounding the inherent difficulties of isolating such strongly coupled mechanisms is the lack of systematic experimentation where only one parameter is varied at a time.

Since many of the likely mechanisms for microscopic nonuniformity depend on aspect ratio alone,\textsuperscript{1} it is informative to study the data within the framework of aspect ratio scaling. Of the articles mentioned, only Chin \textit{et al.}\textsuperscript{17} and Boyer \textit{et al.}\textsuperscript{18} plot etch rate versus aspect ratio when presenting and interpreting their data. Often limited etch rate data are shown as a function of feature width which has, to our knowledge, not yet been shown to be an invariant scaling parameter.\textsuperscript{1,17,18} Moreover, most of the papers seem to neglect that more than one physical mechanism can influence etch rate scaling and that they may be synergistically related.\textsuperscript{1} Physical phenomena that can play a role in etch rate nonuniformity include deposition of etch inhibitors,\textsuperscript{20,23–25} ion shadowing,\textsuperscript{5,6,9,18} ion deflection,\textsuperscript{19,26–30} neutral shadowing,\textsuperscript{18} Knudsen transport of neutrals,\textsuperscript{31} surface diffusion,\textsuperscript{24} and bulk diffusion.\textsuperscript{1} The fact that many of these mechanisms may be important to varying degrees in every plasma etching situation has been repeatedly shown in profile simulations.\textsuperscript{11,32–34} The plethora of possible mechanisms is also evident in the difficulty process engineers have in determining optimum etch conditions for next generation design rules.

The experiments reported here are designed to study differences in etch scaling caused by surface chemistry. To isolate fundamental mechanisms of etch scaling, identically patterned Si and GaAs samples are etched under identical plasma conditions at three different substrate temperatures, $T_{\text{sub}}=85$, 20, and −45 °C. Since the plasma conditions are identical, differences in etch rate scaling from Si to GaAs or from one temperature to another cannot be ascribed to ion and neutral transport effects. Since identical features are etched in both substrate materials, geometrical factors are also held constant.

We show below that aspect ratio scaling is dominant at the higher temperatures in both substrates, but the effects are noticeably stronger in Si. For both GaAs and Si, a more complicated, time-dependent scaling is observed at the lowest temperature. Again, the effect is more apparent in the Si than in the GaAs etch rates. The data are well described by an ion-neutral synergy model\textsuperscript{35,36} with pure neutral flux shadowing. At low temperatures, the model is extended to include deposition of an etch inhibitor that accounts for the nonaspect ratio scaling. The model provides a framework within which differences in etch rate scaling can be related to properties of the surface etching reactions. In the following section, the experiment and the procedures used to analyze the data are described. The results and models are presented next. Before concluding, the implications of these results for minimizing etch rate scaling effects and the importance of other nonuniformity mechanisms are discussed.

Before discussing our results and the analysis employed it is important to remember that in any kinetic study the strongest conclusions are those drawn from a failure of the model to explain the data. When the model does not fail, one can only say that the model is consistent with the observations. While one can always include the effects of more complicated models, we employ Ockham’s razor: the simplest model consistent with the data is adopted. We place emphasis on evaluating the rationality of the model in terms of not only our own experimental data, but also those data found in the literature.
II. EXPERIMENT

A. The plasma source and substrate electrode

Experiments are performed using an electron cyclotron resonance (ECR) plasma reactor with a temperature controlled electrode described in detail previously.\(^{37}\) The ECR plasma source consists of an etching chamber, a load-lock chamber and a sample transfer chamber (Fig. 1). A commercially available ECR source (ASTeX HS1500) with a single magnet (12 layers of 14 windings) and a 2.45 GHz power supply are used to generate a high density Ar/7.5% Cl\(_2\) plasma (\(n_e\approx 10^{13}\) cm\(^{-3}\)). The plasma extends from the ECR plasma zone towards the substrate platen 19 cm away following the diverging magnetic field lines. A quartz liner conforming to the magnetic field lines in the source region helps to minimize sputtering of the chamber wall. Reflected microwave power is reduced to less than 1% of the 700 W incident power using a three stub tuner (ASTeX TS-1000). Gas flow into the source region is regulated using mass flow controllers (MKS 2159B). During processing, the chamber pressure of 2 mTorr is controlled by feeding back the output from a capacitance manometer to a throttle valve limiting the pumping speed of a 1500 l/s turbomolecular pump. The quartz liner temperature is used to approximate the gas temperature,\(^{38}\) which increases by ~200 K during the longest etches in this study and can reach as high as 750 K. Changes in neutral pressure are expected (It will be shown later with the ion-neutral synergy model that 10% changes in the neutral flux lead to <10% changes in etch rates for the aspect ratios in this experiment) to cause changes in etch rate <10% as confirmed by the observation of no significant changes in blanket etch rates monitored in situ by infrared interferometry.\(^{39}\) These operating conditions avoid regions of parameter space where multiple steady states with different plasma conditions exist.\(^{40}\) The wall temperature is also maintained at 45 °C using heat tape to minimize water contamination and provide reproducible boundary conditions. An additional cryopump is used to achieve low base pressures (~2×10\(^{-7}\) Torr), consisting mainly of HCl, prior to every processing run.

A 13.56 MHz rf signal resulting in ~40 V dc bias is applied to the substrate electrode by feeding the amplified (ENI 3200L) output from a function generator into a matching network (rf plasma products AMN 1000). The electrode is covered with a 0.125-cm-thick quartz shield to minimize sputtering of electrode material. Current and voltage waveforms are obtained using a current transformer and high-voltage probe. The electrode temperature is measured using a type K thermocouple in a boron nitride block press fit into a groove on the back of the electrode. The temperature is set by simultaneously cooling from a LN\(_2\) reservoir and heating from an ohmic heater within the electrode itself. Using feedback control of the heating element, the substrate temperature \(T_{sub}\), measured by infrared interferometry,\(^{39}\) is maintained within ±3 °C of the set temperature during processing.

The experimental conditions used for all experiments are as follows: 700±1 W microwave power into the ECR source, 37 sccm Ar, 3 sccm Cl\(_2\) at 2.00±0.05 mTorr, 10 W of 13.56 MHz power applied to the substrate electrode to achieve a dc bias of ~42±1 V. (These conditions represent a compromise made to obtain etch anisotropy, selectivity to photoresist, and high etch rate for both Si and GaAs under the same conditions. If one were to optimize the conditions independently for either Si or GaAs etching, the operating parameters would be different from those cited here and would be different from each other.) Although this work is exclusively concerned with the etch rate at the center of Si and GaAs trenches, conditions were chosen that produced simultaneously the most vertical profiles as possible for trenches in both materials (see Figs. 2 and 3). The Cl\(_2\) fraction, for example, is chosen to balance excessive microtrenching with bottom bowing in Si and undercutting of the mask in GaAs. In both cases, etch rate is sacrificed. The electrode bias is adjusted to avoid micromasking on GaAs and yet maintain marginal etch selectivity with respect to resist.

B. Sample handling and preparation

The transfer chamber and load lock are independently pumped below 10\(^{-8}\) Torr using a turbo pump and a cryopump, respectively. Samples are transferred from the load lock into the transfer chamber and then into the etching chamber by means of a magnetically coupled arm. Typically six samples are loaded and then serially transferred and etched between load-lock ventings. Etch samples of ~1 cm\(^2\) are cleaved from either GaAs or Si(100) wafers that are patterned using the same photolithographic mask and procedures. The initial (type J1350) photoresist thickness is 0.7 µm on Si and 0.8 µm on GaAs. The pattern consists of pairs of trenches having widths varying from 5 to 0.6 µm, i.e., 5, 3, 2, 1.5, 1.2, 1, 0.8, and 0.6 µm with each trench separated by 1 µm. The pattern is replicated over the entire wafer. Selectivity with respect to resist in GaAs and Si is 5:1 and 3:1, respectively, at 20 °C for 5 µm trenches. The difference
in selectivity between GaAs and Si is purely a result of the difference in the GaAs and Si etch rates under these conditions. Samples are held by two stainless steel clips on 2.54-cm-diam Ni plated Cu or stainless-steel sample holders using In foil for good thermal contact. So that the back of sample is flush with the electrode surface, the holders are pneumatically pulled into cylindrical wells in the electrode where they compress another In gasket to provide efficient heat transfer between the substrate holder and the electrode.

No pretreatment of the patterned samples is performed prior to insertion into the reactor. To see if the effects of native oxide are significant, we dipped samples in 3% NH₄ OH/H₂O and compared the results to samples without a dip. No etch inhibition is observed for either patterned or blanket etches implying that any native oxide is easily removed by the etching plasma.

C. Experimental procedure and data analysis

A disappointing aspect of most published work on etching microuniformity is the lack of detailed description of the analysis used to present the results. Since there are many ways to analyze the data, the lack of information confounds comparisons between data from different studies. Commonly, average etch rate data obtained for a single etch time is plotted as a function of feature width despite strong evidence that the etch rate is a function of aspect ratio alone. Such scaling cannot be deduced without measuring etch rates as a function of time as well as width. Furthermore, under RIE lag conditions with aspect ratio scaling, etch rates obtained by simply dividing the etched depth by the etch time overestimates the actual etch rate for the final aspect ratio.

Lacking the capability to measure instantaneous etch rate at the bottom of a trench directly, the following procedure is used to determine the etch rate as a function of time.

(1) For each sample temperature and material, 10 to 15 etches are performed for 6 to 8 different etch times. The differences between etch times are chosen large enough to generate easily measurable differences in etched depths. The maximum etch time is limited by the selectivity to the photoresist mask.

(2) Etched samples are cleaved and then analyzed using a scanning electron microscope (SEM): the 5 and 3 μm trenches are photographed using a magnification of 8 K, the 2 and 1.5 μm using 15 K, the 1.2 and 1.0 μm using 20 K, and the 1 μm and 0.8 μm using 22 K (Figs. 2 and 3). The 0.6 μm trenches are not used since the resist pattern did not uniformly clear after development. The linearity of the SEM is checked by comparing the measured etched depth of the 5 and 3 μm trenches at 8 and 22 K magnification. Measurements are made in the center of the sample only since the regions near the holding clips do not etch uniformly.

(3) The deepest point in the center of the trench, \( D = M + L \), where \( M \) is the remaining mask thickness and \( L \) is the etched depth in the substrate, is measured from the SEM photographs [see Fig. 3(c)]. Occasionally in high aspect ratio GaAs features evidence of (re)deposition exists in the form of contrast differences between (re)deposited material and...
the original sample material. In such cases, two etch depths are measured at the top and bottom of the (re)deposited layer to bracket the range of $D$. The thickness of the remaining photoresist mask $M$ is measured from the micrograph with a magnification of 22 K. Although mask erosion could be observed in some of the etched profiles, changes in trench width $W$ are negligible and the initial resist patterned feature width (top width) is used throughout.

(4) The etched depth $L$ and the aspect ratio $A= D/W$ are calculated from the measured values of $D$ and $M$ ignoring specific profile shapes. The uncertainty in $A$, $L$, and $M$ are calculated using the magnification of the SEM micrographs and a 0.5 mm uncertainty in readings of the ruler used to measure the photographed features.

(5) For a given width, $L$ is plotted as a function of the etch time $t$. At least-mean-squares fit is made using a second order polynomial as shown in Fig. 4. The uncertainties in $a_1$ and $a_2$ are typically $<10\%$ and $<50\%$, respectively.

(6) The etch rate $E$ is now calculated by taking the derivative of $L(t): E = a_1 + 2a_2t$. The choice of the second-order polynomial fit of $L(t)$ to $t$ is arbitrary. We perform this fit merely to smooth the data and thereby obtain less noisy values for $E(t)$.

(7) So-derived etch rates are plotted as a function of the corresponding measured aspect ratios for the experimental etch times.

(8) Blanket etch rates are measured using infrared interferometry. Double side polished GaAs and Si(100) samples are etched under the same plasma conditions and at the same three sample temperatures. The values of the blanket etch rates correspond to $A=0$.

Due to the ex situ and destructive nature of the data acquisition method, data from different plasma etches must be used to determine the etch rate as a function of time. Conceivably, fluctuations in experimental conditions, e.g., plasma parameters, reactor wall conditioning, or sample material, may affect the measured etch rates. Every effort was made to minimize these variations by following a regimented experimental procedure including wall conditioning in a Cl$_2$ plasma, sacrificial etches prior to an experimental run, and H$_2$ plasma cleaning at the end of each day. With these procedures, etched depths are reproducible to within 10% over a period of two months.

III. EXPERIMENTAL RESULTS AND MODELING

A. Comments on trench profiles

The trench profiles in GaAs tend to be more tapered than those in Si (compare Figs. 2 and 3). The tapering in GaAs is most pronounced at lower $T_{\text{sub}}$ and in higher aspect ratio features independent of feature width [compare Figs. 3(a) and 3(b) to 3(c) and 3(d)] whereas in Si there appears to be little variation with aspect ratio (see Fig. 2). If this tapering in GaAs is due to redeposition, the redeposited material is likely to be Ga and As since no contrast is observed between the redeposited material and the original GaAs. Deposition of photoresist material may also affect the profiles, but a thin residue would be difficult to observe with the SEM. The profiles in Si often show small microtrenching for all trench widths, sample temperatures, and aspect ratios. As mentioned earlier, these profile effects are ignored when calculating the aspect ratio from deepest point in the center of the trench. For the neutral shadowing model, the side-wall slope does not affect the flux to the center of the trench.

B. Scaling of etch rate data

In the rest of this section the experimental results are presented within the framework of an ion-neutral synergy etching model\cite{1,35,36} based on Langmuir adsorption kinetics\cite{41} that is consistent with the data at $T_{\text{sub}}=85$ and 20 °C. We extend this model to include deposition of an etch inhibitor at the lowest temperature, $T_{\text{sub}}=-45$ °C. Independent measurements of sticking coefficients and chemical sputtering yields from the literature are used to constrain fits to the data and validate parameters derived from such fits.

Figure 5 displays the trench etch rates for Si and GaAs as a function of aspect ratio for substrates at $T_{\text{sub}}=20$ and 85 °C. Etch rates at these temperatures are clearly aspect ratio dependent. Features with different widths, but identical aspect ratios etch at the same rate. By contrast, when the same data are plotted as a function of trench width, the etch rates are also found to depend on etch time (Fig. 6). At $T=-45$ °C, the etch rates show no simple scaling with either aspect ratio or width (Fig. 7).

C. Ion-neutral synergy model with Langmuir adsorption and no inhibition: Treatment of data at 20 and 80 °C

The etch rate scaling for the higher temperature can be understood by considering the surface coverage of Cl during etching. Assuming it is the only etchant in these experiments, the rate of change in the Cl coverage $\theta_e$ is determined by a balance between the incoming flux of Cl neutrals and the ion enhanced etching and sputtering that removes Cl from the surface. Ignoring spontaneous desorption,
where the surface site areal density \( s_e \) is approximately equal to the number of atoms on the crystallographic plane and the removal of etchant coverage is proportional to the ion flux \( J_i \), and the number of surface sites \( n_e \) cleared per ion impact. [Spontaneous etching would appear as a term \( \varepsilon \theta_e \) subtracted from the right-hand side of Eq. (1), identical in form to the ion enhanced etching term. Under the current experimental conditions Si does not etch spontaneously and \( \varepsilon=0.02 \). Considering all the Cl as molecular or atomic, spontaneous etch rates of GaAs in Cl\(_2\) in Cl\(_2\) is 10\(^{-5}\) \( \mu \)m/min and in Cl\(_2\) is 0.01 \( \mu \)m/min implying \( \varepsilon<7 \times 10^{14} \) cm\(^{-2}\) s\(^{-1}\).

Thus ignoring spontaneous etching is a good approximation.] The neutral source term is assumed proportional to the aspect-ratio-dependent neutral flux, \( J_n(A) \), the sticking coefficient for \( A=0 \), \( s_e \), and the number of unoccupied surface sites \( (1-\theta_e) \).

The aspect ratio dependence of the neutral flux to the center of the trench, \( n(A) \),

\[
\frac{\sigma_e}{\partial \theta_e} = J_n(A)s_e(1-\theta_e) - \eta_s J_i \theta_e, \tag{1}
\]

is assumed to be governed by line-of-sight shadowing by the side walls of the trench\(^1\) with the open field neutral flux \( J_{n0} \). [Note that in Ref. 1 there is a typographical error in Eqs. (7) and (8). Each of the arctan (A/2) terms should be arctan (1/2A) which would then make those equations correct and consistent with Eq. (2) of this work.] This assumption implies that reactants stick or are lost to all other surfaces with unit probability and that the surface reaction probabilities at the bottom of the trench are not angle or energy dependent.

Recent UHV molecular Cl\(_2\) beam measurements of the zero coverage sticking coefficients on well-defined Si and GaAs surfaces by Kummel and co-workers\(^{50,51}\) indicate that \( s_e \) does vary with angle and energy albeit weakly (\(<20\%\) variation) over an energy range of a few tenths to a few eV.
Given the range of aspect ratios in this study, the ion angular spread would have to be significantly greater than \( \arctan(2A_{\text{max}})^{-1} = 9.5^\circ \) to affect the center trench etch rate scaling. In turn, such a large ion angular spread would imply that the perpendicular ion temperature \( T_{i\perp} > 3 \) eV. But, laser-induced fluorescence measurements of ion temperatures in similar reactors\(^{52}\) showed that \( T_{i\perp} < 1 \) eV. This previous work combined with the absence of bowed sidewalls\(^{53}\) leads us to conclude that the ion angular spread can be neglected when considering the etch rate scaling. Such a conclusion is further justified by considering that under our operating conditions, the ion collisional mean-free path is much larger than the accelerating sheath thickness, so \( J_i \) is nearly unidirectional and monoenergetic.\(^{54}\) Thus, the aspect ratio dependence to \( J_i \) is neglected and \( \eta_e \) is assumed to be constant, independent of \( A \).

Assuming quasisteady state, Eq. (1) can be solved for the reactant surface coverage,

\[
\theta_e^0(A) = \left(1 + \frac{r_j}{n(A)}\right)^{-1}, \tag{3}
\]

where the 0 superscript will be used later to denote this model without etch inhibition and \( n(A) \) is given by Eq. (2). [Quasisteady state can be shown \textit{a posteriori} to be a valid assumption. Since the two terms on the right-hand side of Eq. (1) are an order of magnitude larger than the term on the left-hand side they nearly balance each other.] The etchant surface coverage is related to the ion-enhanced etch rate according to

\[
E^0(A) = \frac{YJ_i\theta_e^0(A)}{\rho_{\text{sub}}}, \tag{4}
\]

where \( Y \) is the chemically enhanced ion sputtering yield and \( \rho_{\text{sub}} \) is the substrate atom density. The effective ion to neutral flux ratio,

\[
r_j = \frac{\eta_jJ_i}{s_Jn_0} \tag{5}
\]

in Eq. (3) determines the magnitude of the aspect ratio scaling induced by the neutral shadowing. Within the framework of this model, the data are well described by pure neutral shadowing. [Note that for \( A = 0 \) (blanket films), etch rates are slightly higher than predicted from the model (Fig. 5). A reasonable explanation for this observation is the absence of photoresist on the blanket films. Clearly, photoresist could be sputtered and redeposited in the trenches and thereby reduce the etching rates. If the inhibitor (photoresist) coverage is small or has a weak dependence on \( A \), the aspect ratio dependence of the inhibitor will not be apparent in the etch rate, and \( E_g^0(A) \approx E^0(A)/(1 - \delta) \), where \( E_g^0(A) \) is the etch rate in the presence of an inhibitor and \( \delta \) is a small, nearly constant surface coverage of the inhibitor. This appears to be the case at the higher temperatures where the blanket etch rates are higher than predicted. Such an effect alters only slightly the meaning of \( Y \) deduced from the aspect ratio dependent data. We consider such contamination effects in greater detail in Sec. III D, where they are required to interpret the lower-temperature data.] The curves in Fig. 5 are derived by varying \( \eta_e \) and \( Y \) for each material at each temperature (Table I) as the data are fit to Eq. (4). It is clear by comparing normalized etch rates (plotted in Fig. 8 for \( T_{\text{sub}} = 20^\circ \text{C} \)) that the aspect ratio scaling is much stronger in Si than in GaAs. We now consider the significance of the parameters deduced from the fit and thereby assess the rationality of the simple model adopted.

**Constraints and implications of the model parameters:** Since both Si and GaAs are etched under identical plasma conditions, the absolute ion and neutral fluxes to the substrate are the same in all cases. Differences in aspect ratio scaling are clearly intrinsic to the substrate material. The ion flux in Table I is determined from Langmuir-probe ion saturation current measurements made in Ar plasmas in this reactor.\(^{40}\) The neutral flux is estimated from the 0.15 mTorr partial pressure of Cl\(_2\) at 700 K. Though there is some un-

| Table I. Parameters used for model without etch inhibition. |
|------------------|------------------|------------------|
|                  | \( T_{\text{sub}} \) (°C) |                  |
|                  | 85               | 20               | -45              |
|                  | \( J_i (10^{16} \text{ cm}^{-2} \text{ s}^{-1}) \) | 1.2 | 1.2 | 1.2 | Ref. 40 |
|                  | \( J_{\text{m}} (10^{16} \text{ cm}^{-2} \text{ s}^{-1}) \) | 4.7 | 4.7 | 4.7 | Est. from part. pressure |
|                  | \( \rho_{\text{Si}} (10^{22} \text{ cm}^{-3}) \) | 5.0 | 5.0 | 5.0 | Fixed |
|                  | \( \rho_{\text{GaAs}} (10^{22} \text{ cm}^{-3}) \) | 4.4 | 4.4 | 4.4 | Fixed |
|                  | \( s_J (\text{Si}) \) | 0.52 | 0.55 | 0.66 | From Ref. 50 |
|                  | \( s_J (\text{GaAs}) \) | 0.46 | 0.56 | 0.65 | From Ref. 51 |
|                  | \( \eta_i (\text{Si}) \) | 3 | 3 | 3 | Varied |
|                  | \( \eta_i (\text{GaAs}) \) | 0.48 | 0.47 | 0.47 | Varied |
|                  | \( r_J (\text{Si}) \) | 1.47 | 1.47 | 1.2 | Calculated from Eq. (5) |
|                  | \( r_J (\text{GaAs}) \) | 0.27 | 0.21 | 0.19 | Calculated from Eq. (5) |
|                  | \( Y (\text{Si}) \) | 0.37 | 0.37 | 0.38 | Varied |
|                  | \( Y (\text{GaAs}) \) | 0.52 | 0.51 | 0.72 | Varied |
|                  | \( \theta_{e=1} (\text{Si}) \) | 0.23 | 0.23 | 0.27 | Calculated from Eq. (3) |
|                  | \( \theta_{e=1} (\text{GaAs}) \) | 0.63 | 0.68 | 0.71 | Calculated from Eq. (3) |
|                  | \( \eta_e (\text{Si}) \) | 8.2 | 8.2 | 8.2 | Calculated |
|                  | \( \eta_e (\text{GaAs}) \) | 0.93 | 0.92 | 0.63 | Calculated |
certainty in the degree of Cl₂ dissociation and the gas temperature, $J_{20} = 4.7 \times 10^{10}$ cm$^{-2}$ s$^{-1}$ is fixed as a reasonable number. The sticking coefficients used are for the Cl₂ with 0.038 eV translational energy and come from measurements on Si(100) (Ref. 51) and GaAs(100) (Ref. 50) as a function of temperature. Thus, the data are fit by varying only $\eta_1$, which determines the aspect ratio scaling, and $Y$, which is determined by the absolute etch rate.

The number of Si atoms removed per Ar$^+$ impact on a partially chlorinated surface ranges from 0.25 (Ref. 55) to 1.1 (Ref. 56) for 50 eV ions and 0.9 (Ref. 55) to 1.5–3 (Ref. 56) for 100 eV ions depending on the Cl₂ pressure. Under RIE conditions for similar ion energies, $Y$ can range from 0.3 to 0.94 (Ref. 56). For GaAs, $Y$ has not been reported for ion energies below 100 eV. At 300 eV Ref. 57 and 500 eV Ref. 58, $Y$ is estimated to be as large as 10. For the low ion energy conditions of our experiment, it is reasonable to expect $Y \approx 1$ for both substrates as deduced (Table I).

Since the ion and neutral fluxes are the same in both the Si and GaAs experiments, only differences in the ratios of substrate dependent parameters $s_j/\eta_1$ can be responsible for differences in the aspect ratio scaling of etch rates. The absolute value of the etch rate depends on both the ratio $r_j$, which determines the equilibrium coverage during etching, and $Y$, the stronger aspect ratio dependence of the Si etch rate is evident in the larger effective ion to neutral flux ratio (found by varying $\eta_1$ and fixing $s_j$) for Si, $r_j \approx 1.5$, compared $r_j \approx 0.25$ for GaAs (see Table I). The equilibrium coverage during etching of GaAs is high $\theta_j(A = 1) \approx 0.7$, so that the etch rate is not as readily affected by the aspect ratio dependent neutral flux. But for Si, where the equilibrium coverage is much less, $\theta_j(A = 1) \approx 0.2$, the aspect ratio scaling of the neutral flux is more clearly evident. For high density plasma etching as employed here, where the ion angular spread can largely be ignored, it is best to minimize aspect ratio dependent etching by making $r_j$ small, i.e., using large neutral to ion flux ratios. As the etch data for GaAs show, however, having $r_j$ simply less than one is not sufficient to avoid significant aspect ratio dependent etching.

Assuming all Cl removed from the surface by an impacting ion is bound to a substrate atom, the average stoichiometry of the etch products can be estimated from the ratio $\eta_j/Y$. From the fits to the GaAs etch rates, $\eta_j/Y \approx 0.9$ is deduced and suggests that etch products have little Cl content. For example, GaCl₁ ($x = 1.2$) and As₂ would give an average product stoichiometry $\approx 1$. Etch product analysis in the literature spans a range of stoichiometries depending on the surface temperature and ion energy. The etch products of ion-assisted etching of GaAs in Cl₂ have been reported as AsCl₁ and GaCl₁ with 3.5 keV Ar$^+$ ions, AsCl₂, GaCl₁, and possibly GaCl₂ ($x = 1.2$) with 3 keV Ar$^+$ ions, GaCl₂, and AsCl₃ with 500 eV Ar$^+$ ions. But, in recent digital etching experiments by Aoyagi et al., a monolayer of Cl is adsorbed on a GaAs surface and then bombarded with a 20 eV Ar$^+$ beam. The resulting molecular layer etching implies GaCl and As₂ as etch products. At temperatures above 650 K, As₂, GaCl, and As₂ are observed as the dominant reaction products in molecular beam scattering experiments. It appears that for the lower ion energies used here lower stoichiometry products may dominate.

The most likely products resulting from low-energy ion-assisted etching of Si are SiCl₂ and SiCl₄. However, from our analysis, not even the desorption of tetrachloride products is consistent with the value of $\eta_j/Y \approx 8.2$ derived. This large ratio implies that direct sputtering of Cl from the Si surface is important, which is consistent with results from Sanders et al. who state that Cl is a major product of the SiCl₂, 1 keV Ar$^+$ system. Similarly, Vitkavage et al. measured a total removal yield of $\approx 10$ Cl atoms per 1 keV Ar$^+$ compared to a chemical sputter yield of 3 Si per ion under similar conditions. Mayer et al. inferred that 600 eV Ar$^+$ sputters at least 50% more Cl from the surface than appears directly in etch products. It is further interesting to note that Rosen and Sawin found physical sputtering to be favored over chemically enhanced sputtering at lower Cl coverages. This seems likely in our experiments since the chlorinated surface is predominantly SiCl₄ and the average product is probably SiCl₂, with $x > 1$. Thus, an ion impact resulting in an etch product must pull additional Cl from nearby Si surface atoms, but the low coverage ($\theta_j = 0.23$ in Table I) implied by the ion-neutral synergy model may be a situation more favorable to Cl sputtering rather than Si product desorption, explaining the high $\eta_j/Y$ ratio.

Finally, let us consider the effect of temperature on the surface parameters. The small decline in absolute GaAs etch rates between 20 and 85 °C is due to an 18% drop in sticking coefficient (see Table I). This leads to a lower surface coverage and thus smaller etch rate for nearly the same chemical sputter yield. The Si etch rates do not noticeably change in absolute magnitude or in aspect ratio scaling over this temperature range. This result is consistent with the already low Cl surface coverage on Si at the lower temperature.

In short, the aspect ratio scaling of etch rates for Si and GaAs is consistent with a simple ion-neutral synergy model based on Langmuir adsorption kinetics and neutral shadowing. The two parameters, reactive sputter yield, $Y$, and num-

![Fig. 8. Normalized etch rates as a function of aspect ratio for Si and GaAs at $T_{\text{sub}} = 20$ °C.](image-url)
D. Ion-neutral synergy model with etch inhibition: Treatment of data at \(-45\) °C

The simple model discussed above is clearly not adequate to account for the nonaspect ratio scaling at \(T_{\text{sub}}=-45\) °C (see Fig. 7). It was expected that lowering the substrate temperature would change the surface reaction rates and thereby reduce the aspect ratio dependence of the etch rates. However, the etch rates plotted in Fig. 7 still show an aspect ratio dependence as well as an apparent dependence on trench width. The variation in etch rate with trench dimensions is clearly more severe at this lower temperature. While the model discussed above appears to account qualitatively for the aspect ratio dependence of all feature widths early in time, i.e., the lowest aspect ratios for each trench (dashed lines in Fig. 7); one parameter \(r_J\) is clearly insufficient to capture the etch rate scaling with trench dimensions.

Given the lower temperature, a natural explanation might lie in the effects of a reaction inhibitor. To account for such an effect, we extend the model above by considering the deposition of an etch inhibiting layer which competes with reactant for the same surface sites and which follows the same Langmuir adsorption kinetics.

\[
\frac{\partial \theta_g}{\partial t} = J_g(A)\sigma_g(1 - \theta_g - \theta_e) - \eta_g J_e \theta_e, \quad (6)
\]
\[
\frac{\partial \theta_e}{\partial t} = J_e(A)\sigma_e(1 - \theta_g - \theta_e) - \eta_e J_e \theta_e, \quad (7)
\]

where \(\sigma_g, \theta_g, J_g, \) and \(\eta_g\) are the etch inhibitor surface site density (\(\sigma_g = \sigma_e\)), coverage, open field \(A=0\) sticking coefficient, and ion removal constant, respectively. \(J_g(A)\) is the aspect-ratio-dependent flux of the etch inhibitor. (The subscript \(g\) is used to denote “gunk,” a piece of English slang which loosely means dirt.) Invoking the steady-state approximation for Eqs. (6) and (7), we obtain

\[
E_g(A) = \frac{Y J_e \theta_e(A)}{\rho_{\text{sub}}} \approx E^0(A)[1 - \theta_g(A)].
\]

In other words, the etch rate still scales with aspect ratio alone, which is clearly inconsistent with the low-temperature data shown in Fig. 7. Since etch rates are still sizable at low temperature, the inhibitor flux and the inhibitor sticking coefficient should be small. Furthermore, by definition of an important inhibitor, the inhibitor removal rate by ions should also be small. Thus, we expect all three terms in Eq. (6) to be comparable and the steady-state approximation for the inhibitor should not be valid at low temperature. This is the key point. Because the inhibitor surface coverage is time dependent, the etch rate scaling cannot be dependent on aspect ratio alone. Note that we can still invoke steady state for the etchrate coverage,

\[
\theta_e \approx \theta^0_e(1 - \theta_g), \quad (9)
\]

since the terms on the right-hand side of Eq. (6) are still large and comparable to one another when the etch rate is significant.

Before numerically solving Eqs. (6) and (7) for the inhibitor coverage and resultant etch rate, it is useful to approximate the solution to clarify the effects of slow deposition. Assuming no initial inhibitor coverage, \(\theta_g(t=0) = 0\), the aspect ratio changes slowly compared to the change in inhibitor coverage [so \(A\) is approximately constant in Eq. (6)], and that \(\theta_e\) is given by Eq. (9)

\[
\theta_e \approx \frac{s_g J_g e}{s_g J_g e + \eta_g J_e} \left[1 - \exp\left(-\frac{s_g J_g e + \eta_g J_e}{\sigma_g}\right)t\right], \quad (10a)
\]

where \(\varepsilon = 1-\theta^0_e\). Further assuming that \(s_g J_g\) and \(\eta_g J_e\) are small compared to \(\sigma_g\), Eq. (10a) can be simplified so that the inhibitor surface coverage is proportional to time,

\[
\theta_e \approx \frac{s_g J_g e}{\sigma_g} t, \quad (10b)
\]

while the etch rate is a linear function of time,

\[
E_g(A,t) = E^0(A)[1 - q_g n(A)e(A)t], \quad (11)
\]

where \(J_e = J_{\text{in}} n(A)\) is assumed, \(q_g = s_g J_g / \sigma_g\), and the aspect ratio dependence is explicitly indicated. Thus, this time-dependent model predicts trench etching initially at a rate governed by the no-inhibition model (surface sites have not yet been inhibited), but as the inhibitor layer deposits in time the etch rate will slow. The rate at which the etching slows depends not only on the inhibitor parameters, but also on the etchant coverage, \(\varepsilon\) or \(\theta^0_e\). The higher the etchrate coverage, the slower the decrease in etch rate. This is consistent with the data where the etchant coverage is higher and the nonaspect ratio scaling is less pronounced for GaAs when compared to Si (Fig. 7).

To plot the time-dependent inhibitor model predictions as a function of aspect ratio, time must be expressed as a function of the aspect ratio. Again, we invoke the approximation of small \(s_g J_g\),

\[
\int_0^t dt \approx E^0(A) t \approx W(A - A_0),
\]

where \(A_0\) is the initial aspect ratio. Substitution into Eq. (11) gives an approximate relation that explicitly shows both the aspect ratio \(A\) and the trench width \(W\), dependence of the etch rate when inhibition is important:

\[
E_g(A,W) \approx E^0(A) - q_g n(A)e(A)(A-A_0)W. \quad (12)
\]

As observed, this approximation predicts that etch rates for wider trenches decrease more rapidly with increasing aspect ratio than do narrower trenches (Fig. 7).

While this approximation is used to illustrate how a time-dependent etch rate caused by the build up of a small amount of inhibitor can produce an apparent width dependence to the etch rates, in fact we have no need to invoke the approximations of small \(s_g J_g\) and \(\eta_g J_e\), but can solve Eqs. (6) and (7) exactly using numerical methods. In so doing, we need to adjust \(\eta_g / \sigma_g\), which determines how long the above approximations remain valid, in addition to the chemical sputter yield \(Y\), the ion-induced etch removal \(\eta_e\), and the etch inhibitor parameter \(q_g\). To the extent that the etch rate does
vary linearly with time [Eqs. (11) and (12)], $\eta_e/\sigma_g$ will be undetermined. The modeled data are shown in Fig. 7 and the parameters so-deduced are given in Table II. We see that the approximations of small $s_eJ_{e0}$ and $\eta_eJ_i$ are excellent and $\eta_e/\sigma_g$ is too small to be determined. The $T_{\text{sub}} = -45 ^\circ C$ data graphically demonstrate the nonaspect ratio dependence resulting from increasing inhibitor coverage during the etch.

Since the blanket etch rates ($A = 0$) show no time dependence and in some cases are higher than the low aspect ratio trenches, we suspect that photore sist is the source of etch inhibitor. We note that $s_eJ_{e0} \approx 10^{12}$ cm$^{-2}$ s$^{-1}$, four to five orders of magnitude lower than the etchant neutral or ion fluxes. This is not an unreasonable number since the photore sist with a 1 nm/s etch rate and density $\approx 10^{22}$ cm$^{-3}$ could be a local source of C and O on the order of $10^{15}$ cm$^{-2}$ s$^{-1}$. It is well known that the Cl$_2$ chemistry is selective with respect to oxide. A wide range of initial sticking coefficient values for O$_2$ on Si at 300 K have been reported (cf. Ref. 67 and references therein) and appear to increase with decreasing temperature. It has also been reported that room temperature etching of poly-Si in pure Cl$_2$ plasmas stopped altogether with the addition of O$_2$ at the 6% to 20% levels.

### IV. DISCUSSION

#### A. Aspect ratio scaling mechanisms

Without regard to the ion-neutral synergy model, the fact that etch rates for $T_{\text{sub}} > -45 ^\circ C$ scale with aspect ratio implies that the important etching mechanisms in this system must be aspect ratio dependent. Although many aspect ratio dependent etching mechanisms can be considered, neutral shadowing appears to be dominant under our experimental conditions. Since the plasma and photore sist mask are the same during the etching of both Si and GaAs, mask shadowing cannot be responsible for the differences between the aspect ratio scaling for the two materials. Moreover, since the Si used has a small resistivity compared to GaAs (respectively 4 and $10^7$ Ω cm at 20 °C, both n type), the effects of differential charging on aspect ratio scaling are expected to be more pronounced for GaAs than for Si, contrary to our observations. As already mentioned, ion shadowing should be insignificant under these conditions where the sheath is virtually collisionless.

**Knudsen transport:** Knudsen transport is an important aspect ratio scaling mechanism that highlights an interesting conundrum implicit in our use of neutral shadowing in the ion-neutral synergy model. Since the sidewall etch rate is small, the sidewalls should be nearly saturated with Cl. Thus, incident Cl$_2$ and Cl should not stick with high probability, contrary to the assumption of neutral shadowing. Coburn and Winters$^{31}$ first considered this situation where neutrals bounce from the sidewalls as they Knudsen diffuse to the bottom of trenches and contact windows. They assumed perfect ($s_e^{\text{wall}} = 0$) diffuse scattering from the walls to calculate the average neutral flux incident on the bottom of a feature with sticking coefficient $s_e^{\text{bot}} > 0$,

$$J_n = \frac{k J_{n0}}{1 - (1 - s_e^{\text{bot}})(1 - k)},$$  

where $k$ is the probability that a particle entering the top of the trench will Knudsen diffuse to the bottom.$^{72}$ Incorporating the coverage-dependent sticking coefficient actually expected on the trench bottom $s_e^{\text{bot}} = s_e(1 - \theta_e)$, Gottscho et al.$^1$ incorporated Knudsen diffusion into the ion-neutral synergy model. Equation (13) is substituted in the equation for the etchant coverage Eq. (1) giving a quadratic equation for the coverage $\theta_e$, which is solved and plugged into the expression for the etch rate Eq. (4),

$$E_{\text{Knud}} = \frac{1 + r_j}{2ar_j}\{1 + r_j(1 + a) - \sqrt{[1 + r_j(1 + a)]^2 - 4ar_j}\},$$  

where $r_j$ is the effective ion-neutral flux ratio defined before and $a = (1 - k)s_e/k$. We tried to apply this model to the interpretation of our data, but as the calculations in Fig. 9 show, Knudsen diffusion is not consistent with our observations. For example, to obtain even close agreement with experiment (Fig. 9) we used $s_e = 0.56$, the same $J_i$ and $J_{n0}$ as before and an extreme value of $\eta_e = 20$ in the Knudsen model. The predicted coverage is quite low $\theta_e(A = 0) = 0.1$, implying a factor of 3–7 increase in chemical sputter yield to match the absolute etch rate. Further increases in $\eta_e$ continue to reduce the coverage, but have little effect on the aspect ratio scaling. Knudsen diffusion simply does not give a sufficiently strong aspect ratio scaling to match the experimen-
tal observations. Although a recent, more detailed, iterative etching model including Knudsen transport does not explicitly model a case with the ion/neutral flux ratio appropriate for these experiments, it is clear that Knudsen diffusion significantly weakens aspect ratio dependence of the neutral flux. This leaves open the question of what happens to the chlorine atoms and molecules that hit the wall, but do not stick.

It seems likely that little Cl would Knudsen diffuse to the bottom of a deep trench since it would have to scatter many times from the highly chlorinated walls without recombining. So, for deep trenches, the assumption of neutral shadowing seems reasonable. Perhaps Knudsen scattered neutrals do reach the bottom in the form of Cl$_2$, but since Cl atoms are the more important etchant the Knudsen diffusion of Cl$_2$ appears to have only a minor influence on the etching.

Another possibility is that the walls are not as chlorinated as presumed. It is possible Cl atoms and etch products combine with Cl on the walls to form Cl$_2$ or more highly chlorinated products keeping the walls less than fully saturated and thus more reactive. Knudsen diffusion depends on the neutrals making numerous bounces. If $\delta_{\text{wall}} < 0$ the Knudsen flux will drop significantly. Sputter yields of Cl on Si also increase more quickly than chemically enhanced Si yields as a function of ion angle of incidence. This means a relatively smaller flux of ions may keep the sidewalls below saturation coverage. Sputtering of Cl from the sidewalls would provide additional neutral flux to the corners of the trench that may contribute to the microtrenching phenomenon.

While we have considered only etch rates in the center of the trench and there we find neutral shadowing to be consistent with the data, it is likely that for other parts of the trench other mechanisms such as Knudsen diffusion may play a more important role. Consider low aspect ratio trenches where the Knudsen flux in the trench corners is likely more important than the shadowed neutral flux; the opposite should be true in the center of the trench. Such effects may help to explain why the trench bottom etches uniformly when pure neutral shadowing would predict significantly slower etch rates in the corners. Clearly, more work examining the scaling of the trench shape would help to unravel some of the competing mechanisms.

### B. Nonaspect-ratio scaling

The more complicated dependence of the etch rates observed at $T_{\text{sub}} = -45$ °C cannot be caused by any of the aspect ratio scaling mechanisms. However, there are numerous mechanisms other than etch inhibition that could be invoked to explain the data: image force deflection, bulk diffusion from the plasma to the surface, field curvature near conductive topography and surface diffusion. Image force deflection gives rise to an increasing RIE lag with decreasing feature size, contrary to our observations. Bulk diffusion can be neglected since all mean free paths of importance are much larger than the feature sizes etched. Field curvature can also be ruled out because the Debye length is about 10 $\mu$m leading to a typical sheath thickness of 100 $\mu$m, which is much less than ion-neutral or ion-ion mean-free paths. Thus, most of the ion energy is gained crossing the sheath and the field curvature in the trench will not significantly affect the ion trajectory. This leaves surface diffusion as a possible candidate to consider for the breakdown of aspect ratio scaling. Surface diffusion has been incorporated in a number of profile evolution models, but the aspect ratio dependence has not been explicitly explored. To simply model the instantaneous etch rate at the bottom of a trench, one can add a diffusion term $\rho J D \partial^2 \theta / \partial x^2$ to the coverage equation (without deposition) Eq. (1), where $x$ is a curvilinear spatial coordinate along the trench profile. Assuming quasisteady state and solving the differential equation along the walls of the trench gives $\theta_e$ at the center of the trench that can be used to calculate the etch rate as before. Assuming pure neutral shadowing, there exists a narrow range of diffusion coefficients for which the neutral flux gradients along the bottom of the trench reduce the etch rate at the center of the trench. This is a small effect, however, that is largest for the narrowest trenches, contrary to our observations. Most choices of $D$ large enough to cause significant variation from the $D = 0$ ion-neutral synergy model cause the etch rate in the center of the trench to increase. This is due to the added source of etchant diffusing from the walls. The scaling does not depend simply on width or aspect ratio. At a given aspect ratio, smaller width features have a larger increase in etch rate since identical variations in neutral flux occur over shorter absolute distances along the trench profile giving rise to steeper gradients in coverage. Coupled with the expectation that $D$ would decrease as a function of temperature, becoming less important, surface diffusion is not considered significant over the range of temperatures considered in this work.

### C. Reducing the sensitivity of etch rates to trench geometry

In semiconductor processing, it is desirable to have as high an etch rate as possible. Using the ion-neutral synergy model, this implies going to regimes of high ion flux and high chemical sputter yields, i.e., large $r_j$. But in this regime, aspect ratio effects due to neutral shadowing should be more pronounced. The obvious way to reduce $r_j$ is to operate with a much higher Cl$_2$ flux. Since the sticking coefficients are already quite large, reducing the substrate temperature to increase $s_e$ would have minimal effect and could lead to more severe problems as shown by the data for $T_{\text{sub}} = -45$ °C. One might also consider decreasing $\eta_c$, but this cannot be accomplished without reducing etch rate. However, recent laser desorption measurements in Cl$_2$ plasmas indicate that Cl$_2$ plays a significant role in chlorinating the surface and providing Cl needed for etch product formation. The ions need not remove as much surface Cl to etch, making $\eta_c$ very small. Thus, the etch rate may be increased by increasing the ion flux while $r_j$ stays small. Since ion shadowing is a much smaller effect than neutral shadowing under high density, low-pressure plasma conditions, the etch rate could be maintained while aspect ratio scaling is reduced.
polymer film (often used to enhance anisotropy and selectivity in oxide etching) would produce a larger inhibitor flux in higher aspect ratio features. The results for such a case (taking the inverse of the neutral shadowing expression in Eq. (2)) show etch rates as a function of time that are qualitatively consistent with the data of Joubert et al.25 and Kato et al.76 eventually etching stops, but does so much sooner for the narrower (higher aspect ratio) trenches. Since it was assumed that the etchant and inhibitor coverage both compete for surface sites [see Eqs. (6) and (7)], the inhibitor coverage in the model is limited to a monolayer which stops the etching. In oxide etching, however, multilayer deposition can occur during etching.25 Deposition of a thick inhibitor layer can be included by modeling the inhibitor source term in Eq. (7) as \( s_v J_p (1 - \theta_v) \), i.e., the inhibitor competes only with the etchant for sites. In this case, the higher aspect ratio features are filled by inhibitor material as shown by the lines in Fig. 10 and the etch rates may reverse sign, i.e., deposition may become dominant after etching stops. The results are in good agreement with the experimental observations of contact hole etching by Joubert et al.25 using the inverse of neutral shadowing for circular contact holes. More work must be done to definitively determine the mechanisms actually at work in these experiments.

V. CONCLUSIONS

Detailed etch rate data for trenches in Si and GaAs under identical plasma conditions have been presented. At substrate temperatures \( T_{sub} = 20 \) and 85 °C etch rates are aspect ratio dependent and well described using an ion-neutral synergy model with Langmuir adsorption kinetics. The scaling of the etch rates with aspect ratio can be explained solely in terms of neutral shadowing. Differences observed between the scaling for Si and GaAs are attributed to differences in Cl surface coverage: for Si, the surface coverage is less than that for GaAs leading to a stronger dependence of the Si trench etch rates on the neutral flux and hence the aspect ratio. For \( T_{sub} \sim 45 \) °C, etch rates show a more complicated dependence on both aspect ratio and trench width. These data are well described by positing a small flux of etch inhibitor whose surface coverage increases slowly in time during the etch. Although definitive identification of the inhibitor remains unresolved, evidence points to the influence of photoresist.

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3Y. H. Lee and Z. H. Zhou, in Ref. 2, p. 34.