

GaAs Etch Rate Enhancement with SF₆ Addition to BCl₃ PlasmasK. J. Nordheden,^{a,*} K. Upadhyaya,^{a,**} Y.-S. Lee,^{a,**} S. P. Gogineni,^a and M.-Y. Kao^b^aPlasma Research Laboratory, University of Kansas, Lawrence, Kansas 66045, USA^bTriQuint Semiconductor, Texas, Richardson, Texas 75083, USA

A dramatic increase in the GaAs etch rate has been observed with the addition of SF₆ to BCl₃ plasmas. The etch rate increases from 70 Å/min in pure BCl₃ to 4000 Å/min with 70% SF₆ in the total flow. Optical emission intensities of both molecular and atomic chlorine were observed to increase with SF₆ addition, and the peak intensity of the atomic chlorine emission coincided with the peak in the etch rate. Argon was added to the mixture as an actinometer, and the argon emission intensity at 750 nm increased significantly with the addition of SF₆. However, microwave measurements indicated that the average electron density decreases with increasing SF₆ addition. It is believed that the increased production of etch species is due to an increase in the average electron temperature as a result of electron attachment heating.

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Gas mixtures which contain both chlorine and fluorine are often used to selectively plasma etch GaAs cap layers over underlying layers of AlGaAs.¹⁻⁵ The AlGaAs layer acts as an etch stop due to the formation of a nonvolatile layer of AlF₃.⁶ While investigating selective etching in gas mixtures of BCl₃/SF₆, a dramatic increase in the etch rate of GaAs was observed while using this same gas mixture to etch GaN.^{7,8} Since fluorine is not known to etch GaAs (due to the low volatility of etch products), a change in the plasma dynamics must be responsible for the increase in etch rate. Optical emission actinometry of chlorine species and microwave measurements of the electron density were used to help determine the cause for the increase in etch rate.

Experimental

The etching experiments described in this work were performed in a PlasmaTherm 790 parallel-plate reactive ion etch (RIE) system. The 10 in. diam aluminum powered electrode was operated at a frequency of 13.56 MHz. The aluminum upper electrode and chamber walls were grounded, and the top of the chamber was located approximately 3 in. above the powered electrode. The chamber was evacuated around the outer diameter of the powered electrode by a 150 L/s water-cooled turbopump backed by a 32 cfm mechanical pump. Gases were introduced into the plasma chamber through a showerhead configuration in the top of the chamber and the flow rates of the gases were controlled by MKS mass-flow controllers. All etch gases used were semiconductor grade, and the argon was ultrahigh-pressure (UHP) zero grade. Prior to etching, the chamber was evacuated to a base pressure of less than 1×10^{-5} Torr, and during etching the chamber pressure was kept constant with a throttle valve. During each etch run, the powered electrode was cooled by a recirculator to a temperature of 20°C.

Investigations of etch rates were conducted on $1/2 \times 1/2$ in. full thickness GaAs mechanical wafers which were patterned with AZ 4210 photoresist. The samples were pretreated in a 1:30 solution of NH₄OH/H₂O for 15 s and then blown dry to remove native oxide prior to loading the samples into the RIE chamber. Etch runs were 10-30 min long, so any etch initiation delay which might occur due to this pretreatment would be insignificant.⁹ Etched depths were measured with a Dektak II surface profilometer after removal of the photoresist mask. Optical emission from the discharge was focused with a fused silica lens onto the slits (100 μm) of a Jobin Yvon Spex Triax 550 spectrometer and detected with a Hamamatsu R928 photomultiplier. The 750 nm argon emission line was chosen as an actinometer since it has been shown to be excited directly from the

ground state and does not have a significant contribution from the argon metastable state.¹⁰

The microwave measurement system used to monitor electron density consisted of a network analyzer (HP 8722C) which was used to generate and detect the microwave signal (see Fig. 1). The network analyzer operated as a bistatic step-frequency radar was used for phase measurements. The operating principle of a step-frequency radar is described elsewhere,¹¹ only a brief summary is provided here. In a step-frequency radar, amplitude and phase of the continuous wave at several discrete frequencies is measured in transmission (S21) mode over the desired bandwidth. These amplitude and phase data are then Fourier transformed to obtain a high-resolution range or time profile. These Fourier-transformed data are generally processed further by gating to select desired signal from clutter and to extract amplitude and phase of the gated signal.

The output from the network analyzer was coupled to a collimating antenna flush mounted with the Pyrex window of the plasma chamber with a high-quality radio frequency (rf) cable. A similar antenna mounted at the other end of the chamber collects transmitted signals through the chamber. These signals are coupled to the network analyzer input port through another high-quality rf cable. The phase of the transmitted signal was measured with and without a plasma and the difference of these was used to obtain the excess phase shift experienced by the signal in propagating through the plasma. The line-averaged electron density was then calculated from this excess phase shift.¹²

The network analyzer was operated over the frequency range from 26 to 40 GHz and the amplitude and phase information was

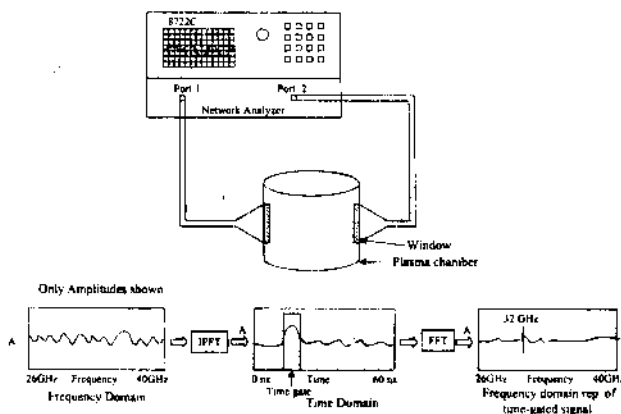


Figure 1. Schematic of microwave system for electron density measurements.

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collected at 801 discrete points over this frequency range. The internal fast Fourier transform (FFT) processor and time-gating capability of the network analyzer were used to obtain the time-domain representation of the signal and to select desired signal from unwanted clutter. The network analyzer internal processor was used to transform the time-gated signal into frequency domain and the phase at 32 GHz was measured. Several readings were averaged to obtain the phase shift experienced by the signal in propagating between the transmitter and receiver. The excess bandwidth was used to obtain fine range or time resolution needed to gate out unwanted signals. The approximate one-way range resolution is about 3 cm when the signal is weighted to reduce range or time sidelobes.

Results and Discussion

The GaAs etch rate at 15 mTorr as a function of SF₆ percentage in the flow with the bias voltage held constant at -100 V is shown in Fig. 2a. The total flow rate was held constant at 20 sccm, and the addition of SF₆ corresponded to a reduction in the amount of BCl₃ in the flow. The etch rate increased from 70 Å/min in pure BCl₃ to 4000 Å/min at 70% SF₆ in the total flow. The etch rate in pure SF₆ was less than 30 Å/min. The RF power to maintain this bias is also shown, and it increases with increasing SF₆ addition. Some of the enhanced etch rate is no doubt due to the increase in power necessary to maintain the constant bias. Figure 2b shows the etch rate at 50 mTorr as a function of SF₆ percentage in the flow with the power held constant at 150 W. The decrease in the bias voltage with SF₆

addition is also shown. The etch rate increases from 90 Å/min in pure BCl₃ to 5500 Å/min at 55% SF₆. This indicates that the large etch rate enhancement observed in Fig. 2a for a constant bias voltage is not merely due to the approximately twofold increase in power. Shul *et al.*,⁷ have observed an increase in the etch rate of GaN for this same gas mixture in an inductively coupled plasma (ICP) system, and the etch rate exhibited a maximum at 20% SF₆.

Argon was added to the gas mixture (2 sccm) as an actinometer for optical emission measurements. The gallium arsenide etch rates were remeasured with the argon addition and are shown in Fig. 2a. The addition of argon appears to dilute the mixture, giving an overall lower etch rate, but the peak in the etch rate still occurs at the same percentage of SF₆. The corresponding rf power with argon addition is also shown.

The normalized optical emission intensities for chlorine, fluorine, and argon are shown in Fig. 3 as a function of SF₆ percentage in the flow for a constant bias voltage of -300 V. The 750 nm argon emission line was chosen since it has been shown to be excited directly from the ground state and does not have a significant contribution from the argon metastable state.¹⁰ The excited state emission from atomic chlorine increases with increasing SF₆ percentage and exhibits a maximum at approximately 70% SF₆, which coincides with the peak in the GaAs etch rate in Fig. 2a. Molecular chlorine ion emission (Cl₂⁺) also increases with SF₆ addition. The optical emission from atomic fluorine increases slowly until about 70% SF₆ and then increases more rapidly thereafter. Excited state emission from argon increases significantly (by a factor of 12.5 from 0 to 90% SF₆) with the addition of SF₆. Since the ground state concentration of argon is constant (constant flow rate), the increase in its emission must have to do with a change in the electron density and/or the electron temperature.

The average electron density as a function of rf power with varying percentages of SF₆ in the flow is shown in Fig. 4. The data were taken at a frequency of 32 GHz. For each gas mixture, the electron density increases as a function of increasing rf power. For constant rf power, the magnitude of the average electron density in pure BCl₃ is the highest, and the average electron density decreases with increasing SF₆ addition. This decrease is most likely due to electron attachment. Sulfur hexafluoride is known to readily attach electrons and the peak in its attachment cross section occurs near 0 eV.¹³ Since the fewer remaining electrons must sustain the same power dissipation, their average energy must increase. The result is an increase in the average electron temperature due to electron attachment heating.¹³ It should be mentioned that although the pressure was kept constant at 50 mTorr for these data, the same trend was observed at 15 mTorr.

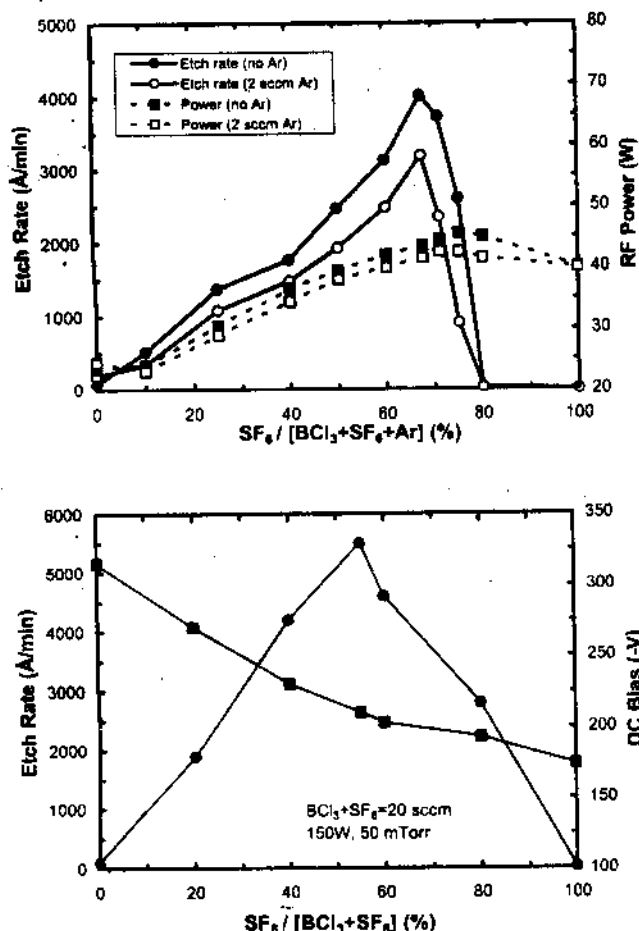


Figure 2. (a, top) Etch rate of GaAs as a function of percent SF₆ in the flow for constant bias voltage and with and without Ar as an actinometer (-100 V, 15 mTorr, 20 sccm BCl₃ + SF₆). RF power is also shown. (b, bottom) Etch rate of GaAs as a function of percent SF₆ in the flow for constant power (150 W, 50 mTorr, 20 sccm). DC bias is also shown.

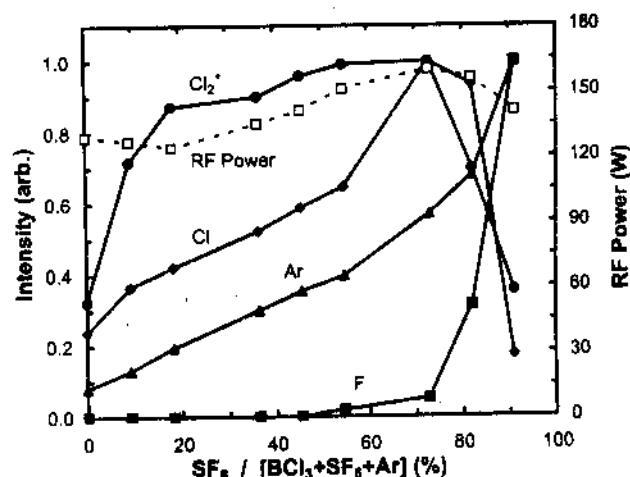


Figure 3. Normalized optical emission intensities of Cl₂⁺ (465.5 nm), Cl (725.6 nm), F (703.7 nm), and Ar (750.4 nm) as a function of SF₆ percentage in the flow (-300 V, 15 mTorr, 22 sccm). RF power is also shown.

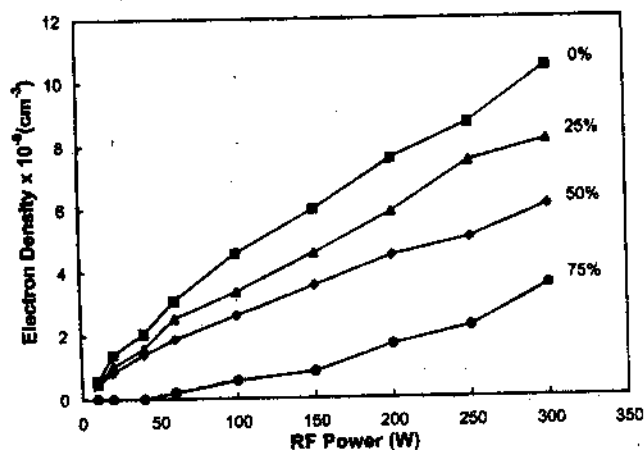


Figure 4. Average electron density as a function of rf power with SF₆ percentage a parameter (20 sccm, 50 mTorr).

Since the electron density is decreasing with increasing SF₆ addition, the increase in the argon emission must be due at least in part to an increase in the electron temperature and a subsequent increase in the rate coefficient. There must also be some contribution from the increase in power which occurs to maintain the constant dc bias voltage, however, it was observed that the trends in the optical emission for constant power were very similar to those for constant bias. Some of the increase in the chlorine emission is no doubt also due to this shift in the electron energy distribution function (EEDF). If one invokes simple actinometry and divides the chlorine emission intensities by the argon emission intensity, the Cl⁺ concentration goes through a maximum at 10% SF₆ and then decreases with further SF₆ addition. The atomic chlorine concentration holds steady up to 10% SF₆, then decreases, and has a local maximum at 70% SF₆. Since the electron density and electron temperature are changing with SF₆ addition, there are some doubts as to the validity of actinometry for this particular experiment. Actinometry is valid only if the rate coefficients of the two species change by the same amount as the EEDF changes.¹⁴ It has also been suggested that the similarity in excitation thresholds is more important than the shapes of the collision cross sections.¹⁴ The threshold energies for the two atomic excited states are different (10.6 eV for Cl*, and 13.5 eV for Ar*). Xenon, with an excitation threshold of 9.82 eV at 823 nm, might have been a more suitable choice for an actinometer but was not available on our system. Furthermore, it is possible for the myriad of molecular species present in the plasma to quench the upper levels of atomic species which would result in a reduction of their emission.

However, the large increase in the GaAs etch rate indicates that the increased chlorine emission is not merely due to enhanced exci-

tation but to a real increase in the concentration of chlorine species. In support of this, preliminary mass spectrometric results show that the mass signal for molecular chlorine increases with the addition of sulfur hexafluoride.¹⁵ Furthermore, Shul *et al.* also observed an increase in the atomic chlorine mass signal with SF₆ addition and concluded that SF₆ enhanced the dissociation of BCl₃, resulting in faster GaN etch rates.⁷ This increase in chlorine production occurs in spite of the fact that the amount of BCl₃ present in the flow is decreasing. The decrease in the etch rate at SF₆ percentages above 70% is probably due to a combination of a decrease in the amount of BCl₃ available to form chlorine etch species, and the possible formation of a layer of nonvolatile gallium fluoride.

Conclusion

The addition of SF₆ to BCl₃ plasmas results in a dramatic increase in the GaAs etch rate. Although the average electron density decreases with increasing SF₆ addition, the dissociation of the BCl₃ increases, resulting in an increase in the production of chlorine etch species. Based on the experimental results, it is believed that the enhanced dissociation is due to an increase in the electron temperature as a result of electron attachment heating.

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