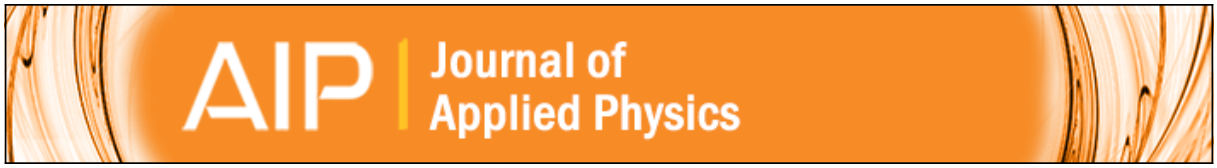

Mass spectrometric characterization of BCl 3 /SF 6 plasmas

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Mass spectrometric characterization of BCl_3/SF_6 plasmas

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Significant increases in the etch rates of both GaAs and GaN have been observed with the addition of SF_6 to BCl_3 plasmas. Mass spectrometric characterization of neutrals in these gas mixtures shows that increasing the SF_6 percentage in the flow enhances the dissociation of BCl_3, resulting in nearly 100% dissociation at 70% SF_6. This increased dissociation is believed to be due to electron attachment heating. Both Cl and Cl_2 mass intensities also maximize at 70% SF_6. The detection of BClF and BCl_2F suggest the possibility of reactions occurring between BCl and BCl_2 radicals and fluorine, which may inhibit the recombination of Cl. © *2000 American Institute of Physics.* [S0021-8979(00)07620-9]

I. INTRODUCTION

Boron trichloride (BCl_3) and sulfur hexafluoride (SF_6) plasmas have been used to selectively etch GaAs over AlGaAs for the fabrication of gallium arsenide based field effect transistors,[1,2] and to etch GaN.[3,4] For both applications, a significant increase in the etch rate has been observed with the addition of SF_6 to the BCl_3 plasmas. Previous microwave measurements on these gas mixtures showed that the electron density decreased with increasing SF_6 percentage, and optical emission actinometry with argon indicated an increase in the electron temperature due to electron attachment heating.[5] Although the optical emission from molecular chlorine (normalized to the argon emission) showed an increase in the ground state concentration for low percentages of SF_6, there was some doubt as to the validity of actinometry because of the shift in the electron density distribution function.[5] Shul *et al.* observed an increase in the atomic chlorine mass signal with the addition of SF_6 and assumed that the dissociation of BCl_3 was increasing.[3] In this article, mass spectrometric characterization of BCl_3/SF_6 plasmas is presented. The relative concentrations of BCl_3 and neutral radical species within the plasma are examined as functions of SF_6 percentage in the flow and dc bias (rf power).

II. EXPERIMENTAL PROCEDURE

The characterization of the BCl_3/SF_6 plasmas was performed in a 600 amu VG Quadropoles SXP Elite mass spectrometry system which was connected to the Plasma Therm 790 reactive ion etching plasma chamber via one of the viewports. Discharge species were sampled through a 100 μm diameter orifice, and sampling pressures within the mass spectrometer chamber were on the order of 10^{-7} torr to reduce recombination reactions within the analyzer. The emission current of the spectrometer was kept below 0.3 mA to minimize the effect of the thermal dissociation of neutral species caused by hot electron emission from the filament.

To be sure that the mass signals were originating only from neutrals in the plasma, and not from dissociative ionization within the mass spectrometer itself, the method of appearance mass spectrometry was employed.[6] This technique is based on the several electron volt energy difference between the appearance potentials for electron-impact ionization and the energy for dissociative ionization of parent molecules. For radicals such as BCl_2, Cl_2, and Cl, the electron energy was set below the threshold appearance energy needed to observe the mass signal with the plasma off. An electron energy of 35 eV was used to monitor BCl_3 for the dissociation measurements.

III. RESULTS AND DISCUSSION

The GaAs etch rate at 50 mTorr as a function of SF_6 percentage in the flow is shown in Fig. 1. The rf power and total flow were held constant at 150 W and 20 sccm, respectively. The decrease in the bias voltage with increasing SF_6 addition is also shown (and is consistent with the fact that the electron density decreases due to attachment with an increasing SF_6 percentage in the flow[5]). The etch rate increases from 90 Å/min in pure BCl_3 to 5500 Å/min at 55% SF_6. Shul *et al.* have also observed an increase in the etch rate of GaN as a function of SF_6 percentage in an inductively coupled plasma system.[3,4]

The quadrupole mass spectrometer (QMS) intensities of BCl_3, BCl_2, Cl_2, and Cl as a function of SF_6 percentage in the flow are shown in Fig. 2. No mass signal corresponding to BCl was apparent. The rf power, pressure, and total flow were held constant at 200 W, 50 mTorr, and 20 sccm, respectively. The curves for both Cl_2 and Cl exhibit maxima at approximately 70% SF_6. The Cl_2 intensity increased by a factor of 38 and the Cl intensity increased by about 5 times. The increase in etch rate observed in Fig. 1 is no doubt due to the increased chlorine production. As expected, both Cl_2 and Cl intensities decrease to zero for 100% SF_6 (0% BCl_3). Overall, the Cl_2 intensity is significantly higher than the Cl intensity. Recombination of Cl to form Cl_2 during transport to the mass spectrometer could account for the low Cl inten-

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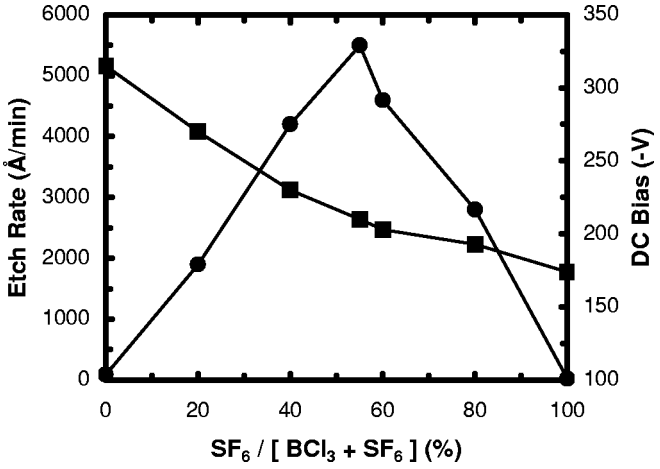

FIG. 1. Etch rate of GaAs (●) as a function of percent SF_6 in the flow for constant power (150 W, 50 mTorr, and 20 sccm). dc bias (■) is also shown.

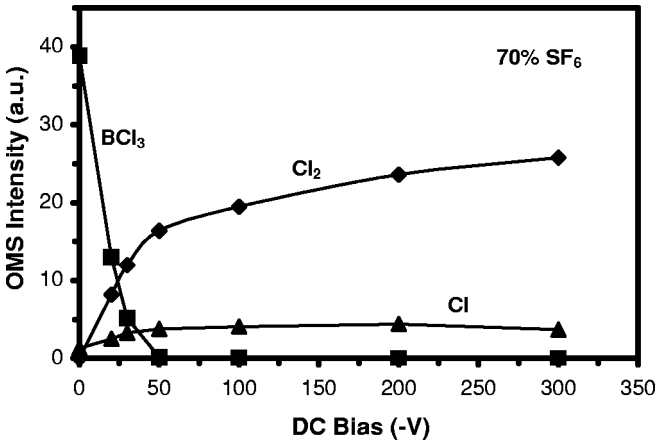

FIG. 3. QMS intensities of BCl_3, Cl_2, and Cl as functions of dc bias (20 sccm and 50 mTorr).

sity. Figure 2 also shows that the BCl_2 intensity is very small for low SF_6 percentages, and essentially nonexistent for SF_6 percentages above 30%.

The dependence of the mass intensities of neutral species as a function of dc bias was also investigated and is shown in Fig. 3. The SF_6 percentage in flow was 70%, the total flow was 20 sccm, and the pressure was maintained at 50 mTorr. The intensity of BCl_3 decreases sharply with increasing dc bias and drops to almost zero at -50 V, indicating significant dissociation of BCl_3. The Cl_2 mass signal increases rapidly for this same range and then increases at a much slower rate for higher biases. The Cl intensity also increases initially and then saturates. The initial increases in both the Cl and Cl_2 mass intensities can be attributed to increased dissociation of BCl_3. The slower increase in the Cl_2 intensity at biases above -50 V may be due to dissociation of radicals such as BCl_2. The observed saturation region for Cl may be due to the recombination of Cl radicals to form Cl_2.

The dissociation of BCl_3 was measured as a function of rf power with SF_6 percentage as a parameter and the results are shown in Fig. 4. The pressure in the system was 50 mTorr. The dissociation of BCl_3 was defined as the QMS intensity difference of the BCl_3 peak with plasma on and off divided by the intensity while off. The dissociation of BCl_3 increased with increasing rf power regardless of the percentage of SF_6 in the flow. This is consistent with the fact that higher rf power results in higher electron densities, which should enhance the BCl_3 dissociation. For the 0% SF_6 curve, the dissociation of BCl_3 is very low and shows only a slight increase with increasing rf power. This explains the very low etch rate of GaAs in pure BCl_3 plasmas observed in Fig. 1. For constant rf power, the dissociation of BCl_3 increases with increasing SF_6 percentage. At 70% SF_6 and an rf power of 200 W, there is nearly 100% dissociation of the BCl_3. For constant power, the electron density decreases with increasing SF_6 percentage as a result of electron attachment.[5] In order to dissipate the same amount of power the average energy of the remaining electrons must increase (a phenomenon known as electron attachment heating). The enhanced dissociation of BCl_3 is most likely due to this increase in average electron energy.

The appearance of mass signals for BClF and BCl_2F for different chlorine and boron isotopes were observed with the addition of SF_6. The mass intensities of BClF ($^{10}B^{35}ClF$ at $m/e=63.98$, $^{11}B^{35}ClF$ at $m/e=64.98$, and $^{11}B^{37}ClF$ at m/e

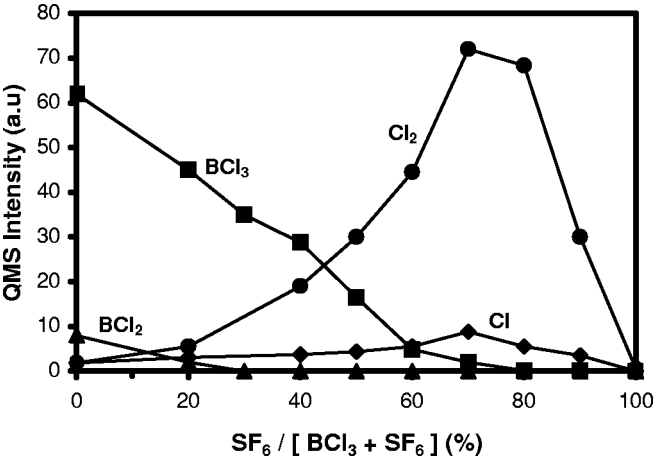

FIG. 2. QMS intensities of BCl_3, BCl_2, Cl_2, and Cl as functions of SF_6 percentage in the flow (200 W, 50 mTorr, and 20 sccm).

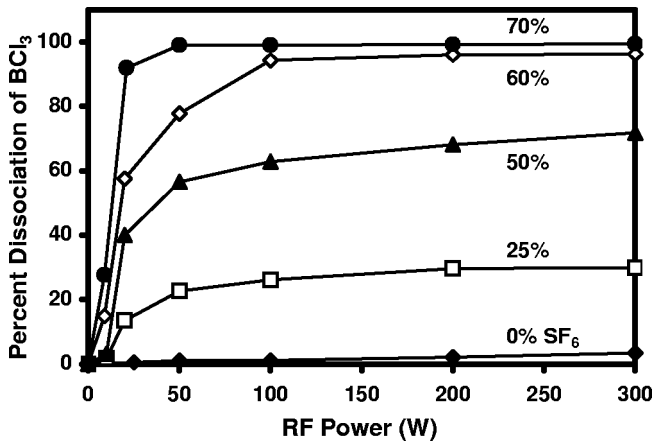

FIG. 4. Dissociation of BCl_3 as a function of rf power with SF_6 percentage a parameter (50 mTorr and 20 sccm).

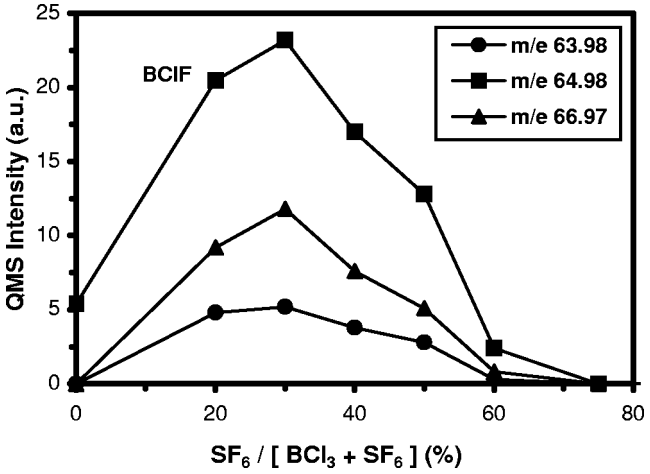

FIG. 5. QMS intensities of BClF for different isotopes of chlorine and boron as functions of SF_6 percentage in the flow (200 W, 50 mTorr, and 20 sccm).

$=66.97$) as a function of SF_6 percentage in the flow are shown in Fig. 5. The BCl_2F mass signals ($^{10}B^{35}Cl_2F$ at $m/e=98.94$, $^{11}B^{35}Cl_2F$ at $m/e=99.95$, and $^{10}B^{35}Cl^{37}ClF$ at $m/e=100.94$) were also monitored as a function of SF_6 percentage in the total flow and are shown in Fig. 6. The rf power, pressure, and total flow were held constant at 200 W, 50 mTorr, and 20 sccm, respectively. The occurrence of any BClF or BCl_2F signals at 0% SF_6 is believed to be due to residual fluorine in the chamber. A significant increase in the mass peak intensities of BClF and BCl_2F were observed as the SF_6 percentage increased and both exhibited maxima at 30% SF_6. It is possible that fluorine from SF_6 reacts with the BCl and BCl_2 radicals to form BClF and BCl_2F. This could explain why the BCl_2 mass peak intensity in Fig. 2 is almost zero at 30% SF_6, and why no BCl mass signal was observed.

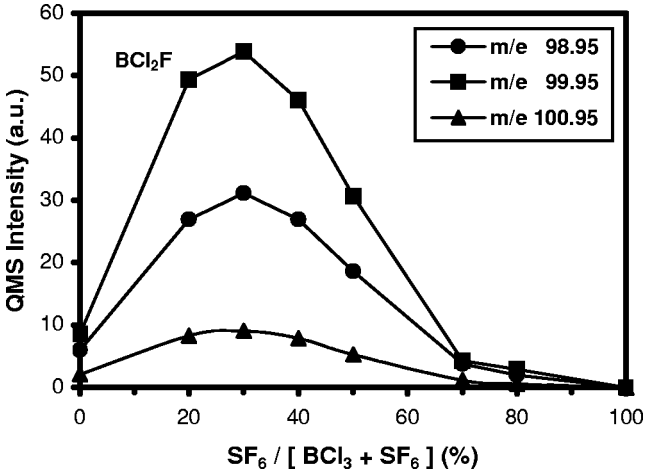

FIG. 6. QMS intensities of BCl_2F for different isotopes of chlorine and boron as functions of SF_6 percentage in the flow (200 W, 50 mTorr, and 20 sccm).

There is some uncertainty as to whether these reactions occur in the plasma chamber or between the chamber and the mass spectrometer. However, previous experimental results have indicated that the F* optical emission intensity is essentially zero until the SF_6 percentage is increased to 70%.[5] At 70% SF_6, the mass peak intensities of both BClF and BCl_2F approach zero (see Figs. 5 and 6). Since these trends are consistent with one another, it would appear that the formation of BClF and BCl_2F occurs in the plasma chamber. The formation of BClF and BCl_2F would help to prevent BCl and BCl_2 radicals from recombining with chlorine, thus reducing two possible loss mechanisms for chlorine radicals.

The addition of SF_6 results in an increase in the dissociation of BCl_3 and a subsequent increase in chlorine radical concentrations, hence accounting for the increase in the GaAs etch rate observed in Fig. 1. The dissociation of BCl_3 and the chlorine radical densities exhibit maxima at 70% SF_6 but the GaAs etch rate peaks near 55% SF_6. The shift between the maxima in etch rate and the peaks in the chlorine radical densities could be attributed to the formation of nonvolatile GaF_3 which would compete with the etch process.

IV. SUMMARY

Mass spectrometric analysis of BCl_3/SF_6 plasmas has shown that the dissociation of BCl_3 increases with the addition of SF_6, and results in nearly 100% dissociation of BCl_3 for 70% SF_6 in the flow. The enhanced dissociation is believed to be due to an increase in the average electron temperature as a result of electron attachment heating. Both the Cl_2 and Cl concentrations also exhibited maxima for 70% SF_6 in BCl_3. The increase in the dissociation of BCl_3 and subsequent increase in chlorine radical concentrations accounts for the observed increase in etch rate. In addition, two new species, BCl and BCl_2F, were detected in these gas mixtures. Their formation might help to prevent BCl and BCl_2 radicals from recombining with chlorine, thus reducing two possible loss mechanisms for chlorine radicals.

ACKNOWLEDGMENTS

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