ECR ETCHING OF GaP, GaAs, InP, and InGaAs in Cl_2/Ar, Cl_2/N_2, BCl_3/Ar, and BCl_3/N_2

*R. J. Shul, *A. G. Baca, *D. J. Rieger, * H. Hou, **S. J. Pearton, and ***F. Ren

* Sandia National Laboratories, Albuquerque, NM 87185-0603
** University of Florida, Gainesville, FL 32611
*** AT&T Bell Laboratories, Murray Hill, NJ 07974

ABSTRACT

Electron cyclotron resonance (ECR) etching of GaP, GaAs, InP, and InGaAs are reported as a function of percent chlorine-containing gas for Cl_2/Ar, Cl_2/N_2, BCl_3/Ar, and BCl_3/N_2 plasma chemistries. GaAs and GaP etch rates were faster than InP and InGaAs, independent of plasma chemistry due to the low volatility of the $InCl_x$ etch products. GaAs and GaP etch rates increased as $\%Cl_2$ was increased for Cl_2/Ar and Cl_2/N_2 plasmas. The GaAs and GaP etch rates were much slower in BCl_3-based plasmas due to lower concentrations of reactive Cl, however enhanced etch rates were observed in BCl_3/N_2 at 75% BCl_3. Smooth etched surfaces were obtained over a wide range of plasma chemistries.

INTRODUCTION

Plasma etching of InP, GaP, GaAs, and related compound semiconductor materials has significant impact on the fabrication of several photonic and electronic devices. Several different plasma chemistries have been used to etch these materials. The preference has been to etch Ga-containing films in Cl-based plasmas due to the high volatility of the Ga- and group-V-chlorides.[1-4] Etch rates are typically fast, with anisotropic profiles and smooth etch morphologies. CH_4/H_2-based plasmas have also been used to etch GaAs and AlGaAs, producing smooth anisotropic profiles at much slower etch rates than those obtained in Cl_2-based plasmas.[5-8] The preferred plasma chemistry for In-containing materials has been CH_4/H_2-based due to the formation of volatile $InCH_x$ etch products.[9] Etching In-containing compounds in room temperature Cl_2-based plasmas often results in roughened surfaces due to the low volatility of the In-chlorides and the preferential loss of the group-V species. Increasing the temperature to ~150°C improves the etch results due to higher volatilities of In-chlorides.[10, 11] Recently, low temperature Cl-based etching of In-containing materials with rates exceeding 1 μm/min have been reported in ECR etch systems.[12, 13] High etch rates were attributed to increased ion densities at high microwave power which increased the sputter desorption of non-volatile $InCl_x$ species formed at the surface. Etch rates were also increased with the addition of O_2 or N_2 to BCl_3 ECR-generated plasmas due to the generation of higher concentrations of reactive Cl and Cl ions or with the addition of Ar to increase the sputter desorption mechanism. In this paper, we report ECR etching of GaP, GaAs, InP, and InGaAs as a function of Cl-based plasma chemistries. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to evaluate surface morphology and etch profile.

EXPERIMENT

The GaP, GaAs, and InP samples etched in this study were semi-insulating, undoped substrates. The InGaAs sample was unintentionally-doped $In_{0.53}Ga_{0.47}As$ lattice-matched to a semi-insulating InP substrate. The InGaAs was grown at 580°C in a metal organic vapor phase epitaxy (MOVPE) reactor. The samples were patterned using a photoresist mask. The ECR plasma reactor used in this study was a load-locked Plasma-Therm SLR 770 etch system with a low profile Astex 4400 ECR source in which the upper magnet was operated at 165 A. Energetic ion bombardment was provided by superimposing an rf-bias (13.56 MHz) on the sample.

Samples were mounted using vacuum grease on an anodized Al carrier that was clamped to the cathode and cooled with He gas. Etch gases were introduced through an annulus into the chamber just below the quartz window. To minimize field divergence and to optimize plasma uniformity and ion density across the chamber, an external secondary collimating magnet was located on the same plane as the sample and was run at 25 A. Plasma uniformity was further enhanced by a series of external permanent rare-earth magnets located between the microwave cavity and the sample. ECR etch parameters held constant in this study were: 10°C electrode temperature, 1 mTorr total pressure, 30 sccm total gas flow, 850 W of applied microwave power, and 150 W rf-power with a corresponding dc-bias of -140 ± 10 V.

Etch rates were calculated from the depth of etched features measured with a Dektak stylus profilometer after removing the photoresist mask. Samples were approximately 1 cm^2 and depth measurements were taken at a minimum of three positions. Error bars for the etch rates represent the uniformity across each sample. Surface morphology, anisotropy, and sidewall undercutting were evaluated with a SEM. The root-mean-square (rms) surface roughness was quantified using a Digital Instruments Dimension 3000 AFM system operating in tapping mode with Si tips.

RESULTS AND DISCUSSIONS

The etch rates for GaP, GaAs, InP, and InGaAs in an ECR generated Cl_2/Ar plasma are shown in Figure 1 as a function of $\%Cl_2$. In general, the GaP and GaAs etch rates increased as the $\%Cl_2$ increased due to higher concentrations of reactive Cl and the strong chemical component of the etch mechanism. The sputter rates for all 4 materials in a pure Ar plasma were relatively slow (<250 nm/min). Under these conditions the material removal was purely physical. This data agrees with our earlier results[8] but are higher than InP and GaAs sputter rates reported by Pearton *et al.* using an ion milling instrument at -200 to -800 V dc-bias.[14] Faster sputter rates reported in the ECR were due to the generation of higher ion densities (3 to 4 orders of magnitude higher in the ECR). Etch rates for the In-containing materials were much slower than etch rates for Ga-containing materials and were relatively constant, independent of $\%Cl_2$. This was due to the low volatility of the $InCl_x$ etch products. The rms roughness for all samples was quite smooth, independent of the $\%Cl_2$. InP exposed to a pure Ar plasma showed the highest rms roughness,7.8 nm, as compared

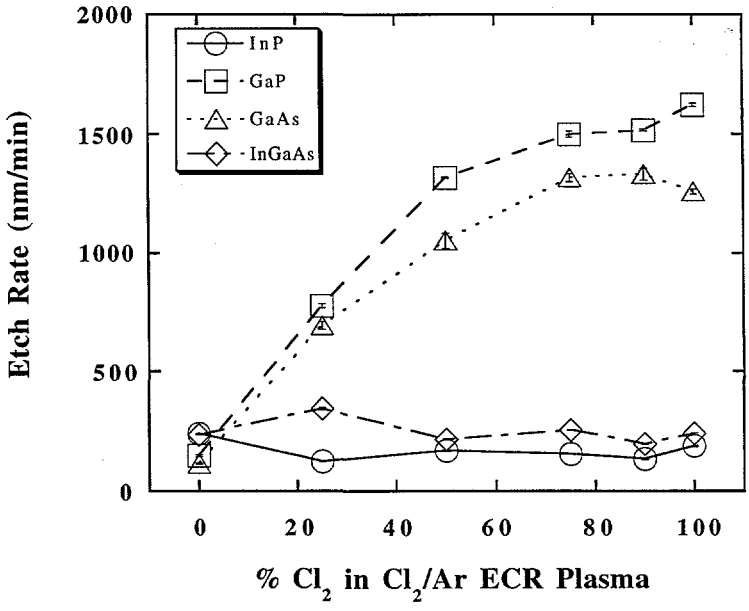

Figure 1. GaP, GaAs, InP, and InGaAs etch rates in an ECR-generated Cl_2/Ar plasma as a function of $\%Cl_2$.

to the InP control which had an rms roughness of 0.28 nm. Pearton *et al.* observed similar behavior during Ar ion milling where the surface morphology of InP was typically rougher than GaAs etched surfaces.[14]

In Figure 2, etch rates are shown as a function of $\%Cl_2$ in an ECR-generated Cl_2/N_2 plasma. Once again, the GaP and GaAs etch rates were faster than InP and InGaAs, however the increase occurred at much higher $\%Cl_2$ than that observed in the Cl_2/Ar plasma. The GaP and GaAs etch rates were slower in the Cl_2/N_2 plasma possibly due to the generation of less reactive Cl in the plasma or the formation of involatile nitride deposits on the semiconductor surface. The InGaAs etch rate reached a maximum value at 50% Cl_2 (~350 nm/min) and then decreased at higher Cl_2 concentrations, whereas the InP etch rate was fairly constant and slow, independent of $\%Cl_2$. The sputter rates were 2 to 3 times slower in pure N_2 as compared to pure Ar due to higher sputtering efficiency of Ar. The rms roughness was less than ~4 nm for all films, independent of $\%Cl_2$.

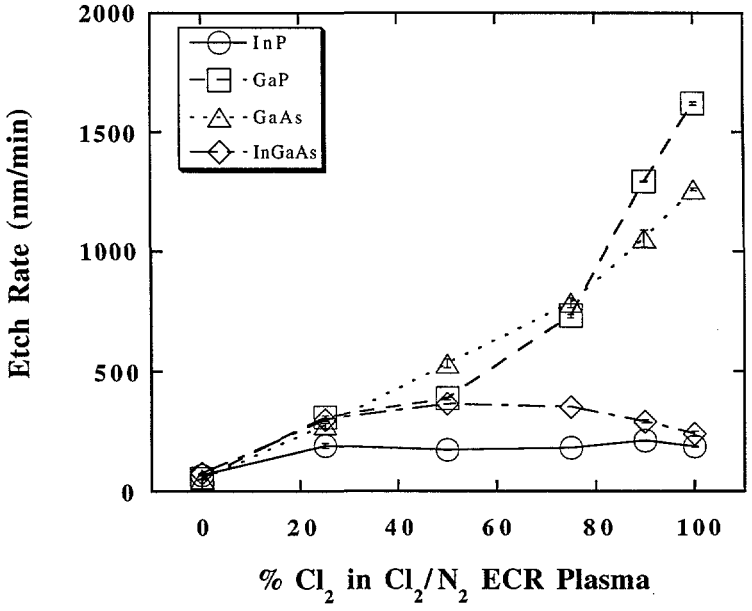

Figure 2. GaP, GaAs, InP, and InGaAs etch rates in an ECR-generated Cl_2/N_2 plasma as a function of $\%Cl_2$.

In Figure 3, etch rates are shown as a function of $\%BCl_3$ in an ECR-generated BCl_3/Ar plasma. The GaP and GaAs etch rates increased with higher $\%BCl_3$, however the etch rates were much slower than those obtained in the Cl_2/Ar plasma due to the generation of less reactive Cl in BCl_3-based plasmas. In this study, etch rates for In-containing materials in BCl_3-based plasmas were comparable to those obtained in Cl_2-based plasmas. The rms roughness for GaP, GaAs, and InGaAs remained smooth independent of $\%BCl_3$, whereas the InP rms roughness increased from ~8 nm in pure Ar to ~45 nm in pure BCl_3. This may be attributed to the preferential loss of P or micromasking effects at higher BCl_3 concentrations.

The dependence of etch rates on $\%BCl_3$ in a BCl_3/N_2 ECR-generated plasma is shown in Figure 4. With the addition of N_2 to the BCl_3 plasma the Ga-containing materials etched at much higher rates at 75% BCl_3. Using optical emission, Ren *et al.* observed increases in the intensity of atomic and molecular chlorine lines when N_2 was introduced into an ECR-generated BCl_3 discharge with a maximum intensity at 75% BCl_3.[12, 13] Nitrogen enhanced the dissociation of BCl_3 resulting in higher concentrations of reactive Cl and Cl ions. This resulted in faster etch rates due to enhanced chemical etching and physical ion bombardment where the sputter desorption of $InCl_x$ etch products improved. This trend was observed for GaP and GaAs etch rates in this study, however the InP and InGaAs etch rates remained relatively constant similar to those obtained in the BCl_3/Ar plasmas. Ren observed an InP etch rate of ~700 nm/min at 850 W applied microwave

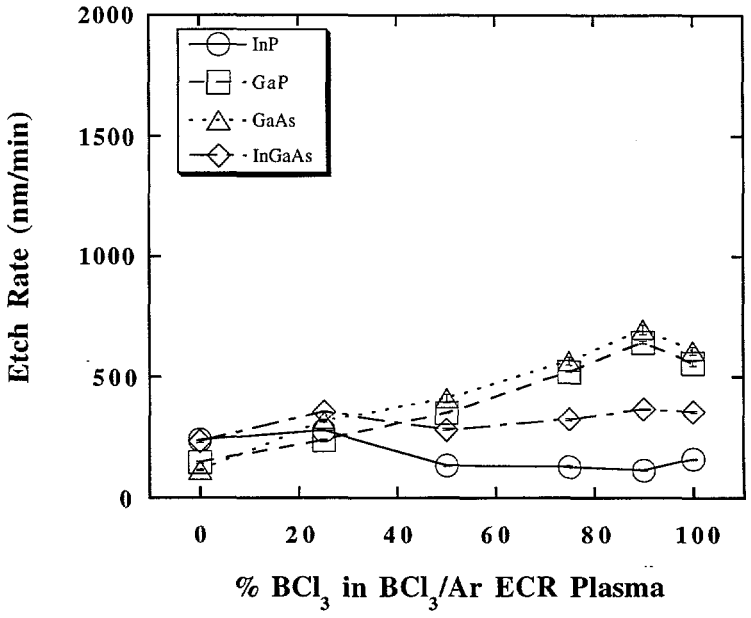

Figure 3. GaP, GaAs, InP, and InGaAs etch rates in an ECR-generated BCl_3/Ar plasma as a function of %BCl_3.

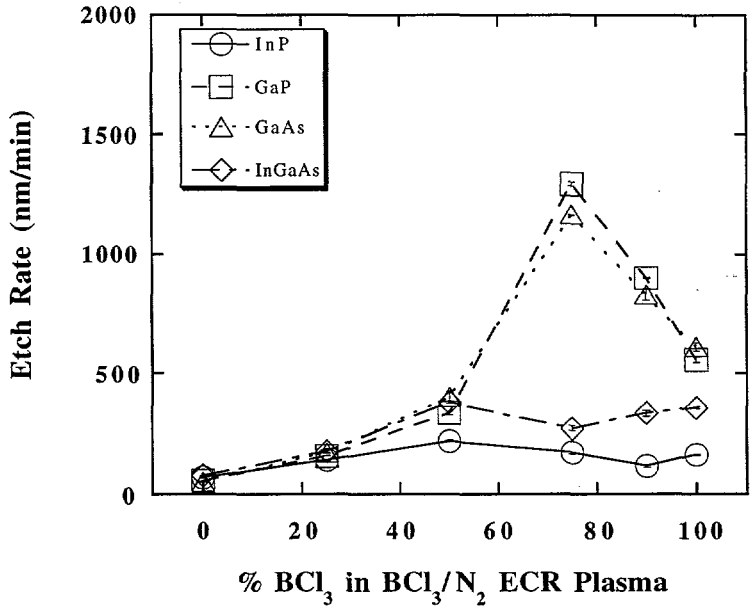

Figure 4. GaP, GaAs, InP, and InGaAs rms roughness in an ECR-generated BCl_3/N_2 plasma as a function of BCl_3 concentration.

power which was almost a factor of 5 faster than that observed in this study. This may be attributed to several differences in plasma conditions as well as the ECR source-to-sample distance which was ~30 cm greater in this report, thereby decreasing the ion density at the sample and the sputter desorption efficiency. Enhanced etch rates were not observed with the addition of N_2 to the Cl_2 plasma implying that N_2 did not liberate more reactive Cl under these plasma conditions.

In Figure 5, SEM micrographs of GaP, GaAs, InP, and InGaAs are shown as etched in an ECR-generated BCl_3/N_2 plasma at 75% BCl_3. The GaP and GaAs etches were anisotropic with

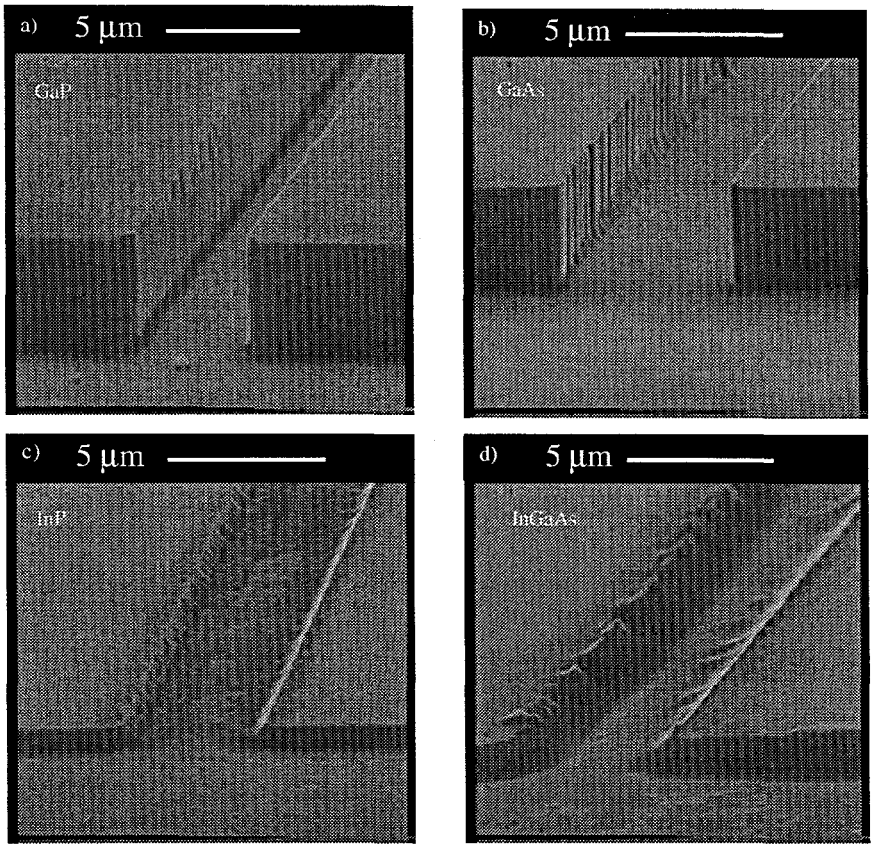

Figure 5. GaP, GaAs, InP and InGaAs SEM micrographs etched in an ECR-generated BCl_3/N_2 at 75% BCl_3.

smooth surface morphologies, however the GaAs showed some vertical striations in the sidewall possibly due to the striations in the mask which were replicated into the GaAs sidewall. There was also a slight "foot" at the base of the GaAs feature possibly due to mask-edge erosion. The InP and InGaAs etch profiles were severely overcut with poor dimensional control.

CONCLUSIONS

In summary, ECR etching of GaP, GaAs, InP, and InGaAs are reported as a function plasma chemistry. Etch rates for GaP and GaAs were faster in Cl_2-based plasmas as compared to BCl_3-based plasmas due to the generation of higher concentrations of reactive Cl. The InP and InGaAs etch rates were relatively slow, independent of plasma chemistry. This was due to the low volatility of $InCl_x$ etch products at 10°C, poor sputter desorption efficiency at 850 W microwave power, and the large source-to-sample spacing used in this etch system. Surface morphologies showed very smooth pattern transfer for a wide range of plasma conditions for all materials, however InP was more sensitive to changes in the plasma chemistry. Etch profiles were typically anisotropic with smooth sidewalls for GaP and GaAs, whereas the etch profiles were more overcut with poor dimensional control for InP and InGaAs.

ACKNOWLEDGMENTS

The authors would like to thank P. L. Glarborg, A. T. Ongstad, and L. Griego for their technical support. This work was performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract # DE-AC04-94AL85000.

REFERENCES

1. S. J. Pearton, F. Ren, A. Katz, J. R. Lothian, T. R. Fullowan, and B. Tseng, J. Vac. Sci. Technol. B **11**, 152 (1993).

2. E. L. Hu and R. E. Howard, Appl. Phys. Lett. **37**, 1022 (1980).

3. R. Cheung, Y. H. Lee, K. Y. Lee, T. P. Smith III, D. P. Kein, S. P. Beaumont, and C. D. W. Wilkinson, J. Vac. Sci. Technol. **B7**, 1462 (1989).

4. S. W. Pang, J. Electrochem. Soc. **133**, 784 (1986).

5. S. J. Pearton, U. K. Chakrabarti, A. P. Perley, and W. S. Hobson, J. Electrochem. Soc. **138**, 1432 (1991).

6. V. J. Law, M. Tewordt, S. G. Ingram, and G. A. C. Jones, J. Vac. Sci. Technol. B **9**, 1449 (1991).

7. J. Werking, J. Schramm, C. Nguyen, E. L. Hu, and H. Kroemer, Appl. Phys. Lett. **58**, 2003 (1991).

8. R. J. Shul, A. J. Howard, C. B. Vartuli, P. A. Barnes, and S. Weng, J. Vac. Sci. Technol. A, accepted.

9. S. J. Pearton, C. R. Abernathy, and F. Ren, Appl. Phys. Lett. **64**, 2294 (1994).

10. C. Constantine, C. Baratt, S. J. Pearton, F. Ren, and J. R. Lothian, Appl. Phys. Lett. **61**, 2899 (1992).

11. C. Constantine, C. Baratt, S. J. Pearton, F. Ren, and J. R. Lothian, Electron. Lett. **28**, 1749 (1992).

12. F. Ren, J. R. Lothian, J. M. Kuo, W. S. Hobson, J. Lopata, J. A. Caballero, S. J. Pearton, and M. W. Cole, J. Vac. Sci. Technol. **B14**, 1 (1995).

13. F. Ren, W. S. Hobson, J. R. Lothian, J. Lopata, J. A. Caballero, S. J. Pearton, and M. W. Cole, Appl. Phys. Lett. **67**, 2497 (1995).

14. S. J. Pearton, U. K. Chakrabarti, A. P. Perley, and K. S. Jones, J. Appl. Phys. **68**, 2760 (1990).