*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

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ABSTRACT

Electron cyclotron resonance (ECR) etching of GaP, GaAs, InP, and InGaAs are reported as a function of percent chlorine-containing gas for Cl₂/Ar, Cl₂/N₂, BCl₃/Ar, and BCl₃/N₂ 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 %Cl₂ was increased for Cl₂/Ar and Cl₂/N₂ plasmas. The GaAs and GaP etch rates were much slower in BCl₃-based plasmas due to lower concentrations of reactive Cl, however enhanced etch rates were observed in BCl₃/N₂ at 75% BCl₃. 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. CH₄/H₂-based plasmas have also been used to etch GaAs and AlGaAs, producing smooth anisotropic profiles at much slower etch rates than those obtained in Cl₂-based plasmas.⁵⁻⁸ The preferred plasma chemistry for In-containing materials has been CH₄/H₂-based due to the formation of volatile InCH_x etch products.⁹ Etching In-containing compounds in room temperature Cl₂-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 O₂ or N₂ to BCl₃ 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.

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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 cm² 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 Cl₂/Ar plasma are shown in Figure 1 as a function of %Cl₂. In general, the GaP and GaAs etch rates increased as the %Cl₂ 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 results⁸ 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 %Cl₂. 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 %Cl₂. 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 Cl₂/Ar plasma as a function of %Cl₂.

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 %Cl₂ in an ECR-generated Cl₂/N₂ plasma. Once again, the GaP and GaAs etch rates were faster than InP and InGaAs, however the increase occurred at much higher %Cl₂ than that observed in the Cl₂/Ar plasma. The GaP and GaAs etch rates were slower in the Cl₂/N₂ 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% Cl₂ (~350 nm/min) and then decreased at higher Cl₂ concentrations, whereas the InP etch rate was fairly constant and slow, independent of %Cl₂. The sputter rates were 2 to 3 times slower in pure N₂ 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 %Cl₂.

Figure 2. GaP, GaAs, InP, and InGaAs etch rates in an ECR-generated Cl₂/N₂ plasma as a function of %Cl₂.

In Figure 3, etch rates are shown as a function of %BCl₃ in an ECR-generated BCl₃/Ar plasma. The GaP and GaAs etch rates increased with higher %BCl₃, however the etch rates were much slower than those obtained in the Cl₂/Ar plasma due to the generation of less reactive Cl in BCl₃-based plasmas. In this study, etch rates for In-containing materials in BCl₃-based plasmas were comparable to those obtained in Cl₂-based plasmas. The rms roughness for GaP, GaAs, and InGaAs remained smooth independent of %BCl₃, whereas the InP rms roughness increased from ~8 nm in pure Ar to ~45 nm in pure BCl₃. This may be attributed to the preferential loss of P or micromasking effects at higher BCl₃ concentrations.

The dependence of etch rates on %BCl₃ in a BCl₃/N₂ ECR-generated plasma is shown in Figure 4. With the addition of N₂ to the BCl₃ plasma the Ga-containing materials etched at much higher rates at 75% BCl₃. Using optical emission, Ren *et al.* observed increases in the intensity of atomic and molecular chlorine lines when N₂ was introduced into an ECR-generated BCl₃ discharge with a maximum intensity at 75% BCl₃.^{12, 13} Nitrogen enhanced the dissociation of BCl₃ 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 BCl₃/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 BCl₃/Ar plasma as a function of %BCl₃.

Figure 4. GaP, GaAs, InP, and InGaAs rms roughness in an ECR-generated BCl₃/N₂ plasma as a function of BCl₃ 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 N₂ to the Cl₂ plasma implying that N₂ 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 BCl₃/N₂ plasma at 75% BCl₃. 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.

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