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An experimental study of the reactive ion etching (RIE) of GaP using BCl_3 plasma processing

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Abstract

A detailed study of the reactive ion etching (RIE) of GaP, through BCl_3 based plasma processing is reported. We discuss the effects on the etch rate through the studies of RF power, reactant and carrier gas (Ar) flow and chamber pressure. Atomic force microscopy (AFM) characterization, along with photoluminescence (PL) spectroscopy, is used to investigate the surface quality and correlate the material damage. Compared to previous dry etching studies, we find that the etching rate is enhanced to 850 nm/min with slight increase in surface roughness. PL spectroscopy indicates a progressive degradation of the surface quality with increased RF power, which is not due to increased surface roughness but presumably due to either a change of the surface state density or depletion layer thickness in GaP.

Keywords: GaP; Semiconductor processing; Photoluminescence; Plasma processing; Atomic force microscopy

1. Introduction

GaP is a promising material for optoelectronic devices in the visible range of electromagnetic radiation, due to its band gap of ~2.3 eV (~550 nm), and has been adapted for photo-detectors [1], light emitting diodes [2,3], lasers [4], and even for photonic crystals [5]. For device processing and fabrication, especially at the micro- and nano-scales, dry etching techniques are preferred over wet etching processes due to the advantages of anisotropic etch characteristics and high selectivity.

In this paper, we report on the development of a high throughput reactive ion etching (RIE) technique for GaP processing. While dry etching on GaP has been previously reported [6], there has been no systematic study on the effects of process variables such as chamber pressure, power, and gas flow rate, which we address here. We study specifically the RIE processes based on BCl_3 plasmas, under various conditions, and the concomitant effects on the surface roughness and quality. BCl_3 gas has been chosen for its ability to provide a smoother surface than elemental Cl_2, as B is known to help [7] in surface oxide removal. While BCl_3 reacts with the GaP surface forming volatile chemical products, Ar is used as a carrier gas to stabilize the plasma and Ar ions help in the physical removal of material from the surface.

2. Experiments

n-doped GaP (from University Wafers Inc., Si Doped, $\rho \sim 0.05\ \Omega$ cm) was used for the RIE experiments. Prior to etching, the sample was ultrasonically cleaned in trichloroethylene, acetone, isopropanol, and deionized water with a dry nitrogen blow in between each clean. Etch masks were fabricated by spinning on electron-beam resist (4 wt.% 495 K PMMA dissolved in chlorobenzene) onto the GaP sample and subsequently electron-beam lithography was used to etch rectangular and circular patterns, in the range of 0.1–10 μm. Ni metal was deposited by electron beam evaporation in the patterned areas and the PMMA removed. The Ni metal lines/mesas serve as etch masks and delineate the etch profiles.

The etching was performed at room temperature in a Trion RIE/ICP etching system (with a base pressure of <1 mTorr) equipped with a 13.56 MHz RF source, under various conditions of BCl_3 and Ar pressure, flow rate, and RF power. The etch rate was determined by a surface profiler (Dektak 3030), which measures the step height, and the RMS surface roughness was probed by Atomic Force Microscopy (Nanoscope IIIA, from

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Digital Instruments). Photoluminescence (PL) spectroscopy was performed, at room temperature, on the etched surfaces to diagnose the surface damage resulting from etching. A blue laser (from LaserGlow, $\lambda = 462$ nm) was incident on the GaP surfaces etched under various conditions, and the resulting luminescence dispersed through an Oriel Cornerstone 130 (1/8 m) monochromator, and measured through photo-detectors.

3. Results and discussion

Several parameters pertinent to the GaP etching, such as BCl_3 flow rate, chamber pressure, and RF power were investigated in order to determine the optimal conditions. The dependence of the etching rate on the BCl_3 flow rate is shown in Fig. 1a. An increasing flow rate corresponds to a decreased residence time for the reactive etching radicals, with the chamber pressure being maintained constant ~10 mTorr. While the initial peak (in the range of 0–10 sccm) corresponds to a reaction rate limited regime where the reactive radicals (such as $(BCl_n)^-$ ($n = 1, 2, 3$) and Cl^- interacting with the GaP sample surface) can fully react with GaP [8]; beyond 10 sccm, the etch rate is relatively constant at ~850 nm/min. In the higher flow rate regime, the dominant etch mechanism appears to be physical sputtering. The linear variation of the etch rate with the RF power (Fig. 1b), and the chamber pressure (Fig. 1c), also support the above conclusion. It is remarkable that the etch rate could be increased to >1 μm/min, at an RF power ~300 W. However, such high powers result in considerable surface damage as was quantified through PL spectroscopy (Fig. 4). On the other hand, increasing the chamber pressure reduces the mean free paths of the etching ions/radicals and lowers the physical sputtering, which decreases the etch rate. Similar flow rate dependencies were observed in the RIE of other compound semiconductors such as InGaN and GaN [8]. It is to be noted that, in comparison to a previous study [6] of GaP dry etching, using $SiCl_4$ based plasma processing, with an etch rate of ~75 nm/min (at 20 mTorr, 60 W), the etching rate in our work is approximately a factor of 5 higher (~500 nm/min, at 20 mTorr, 100 W).

To enhance the physical sputtering of GaP, Ar was added to the BCl_3 plasma but it was noticed that the etch rate was decreased (Fig. 2a). This could be explained by positing that Ar has a dilution effect, causing a net reduction in the amount of reactive species reaching the surface. However, it was observed that the net roughness of the GaP surface increases with increased Ar flow rate, which might point to its physical influence (Fig. 2b). Consequently, the use of Ar is not advocated for GaP etching where smooth surfaces are of paramount importance. Instead of argon, using carrier gases such as helium, neon, or even hydrogen could have less impact on surface smoothness [9].

Surface damage is a critical parameter for photonic device fabrication as it can cause light scattering and power loss. A detailed AFM characterization of the GaP surface etched under various conditions was performed. There is generally an increased roughness with various etching treatments (Fig. 3b and c) compared to the un-etched sample (Fig. 3a), with the most

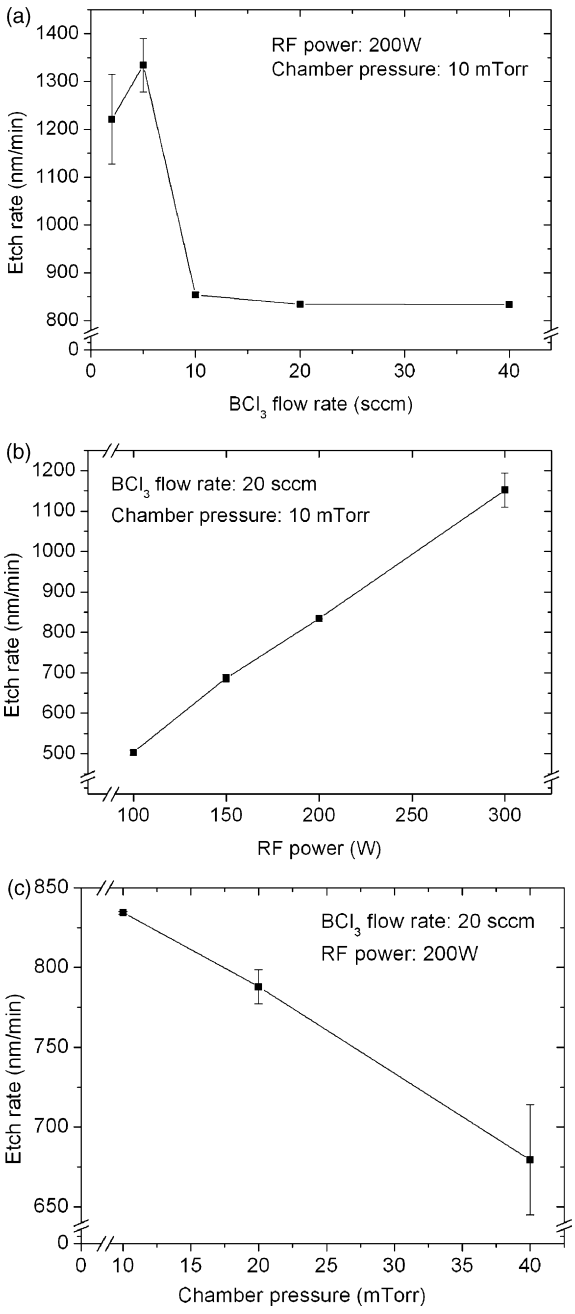

Fig. 1. A comparison of the etch rate of GaP as function of the (a) BCl_3 flow rate, (b) RF power, and (c) chamber pressure (six measurements on different samples were taken to determine the error).

significant effect arising from the use of Ar (Figs. 2b and 3c). We also think that subsequent wet etching chemical treatments, similar to those used for InP [10] and GaAs [11], of the surface might help to alleviate the surface roughness to <1 nm [12]. We specifically point to the use of α-hydroxy acids, that has been pioneered by one of the co-authors [10], for metal phosphide semiconductors, in conjunction with a $HCl:CH_3COOH:H_2O_2$ mixture [13] to be pertinent.

Photoluminescence (PL) spectroscopy is often used as a sensitive, non-destructive, probe of the surface quality [14], and was used to study the concomitant effects of increased etch rate and

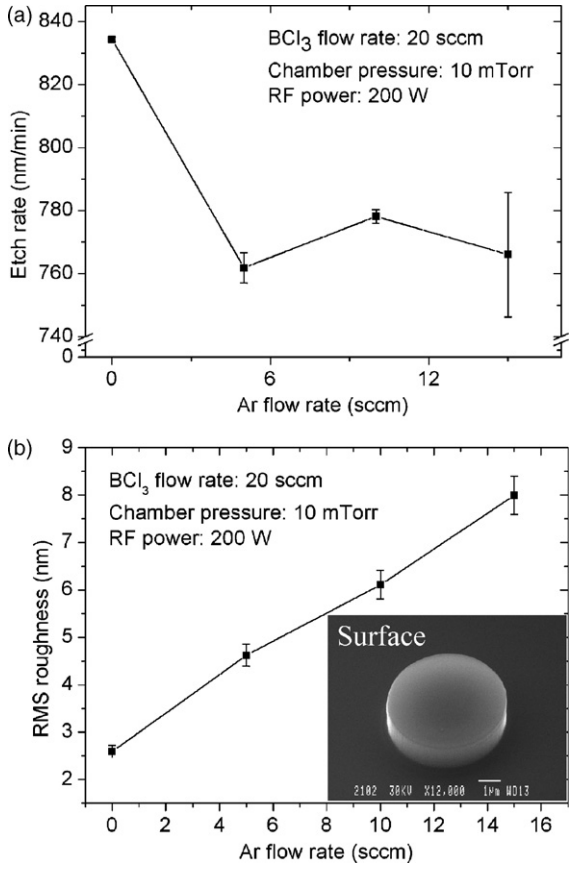

Fig. 2. The effects of Argon, as a carrier gas addition, on the GaP etch rate, as a function of the (a) flow rate, and (b) surface roughness (the insert show the circular etching profile of a GaP mesa, for the 10 sccm sample).

RF power on radiative efficiency. It is to be noted, however, that in indirect bandgap semiconductors, such as GaP, non-radiative recombination tends to dominate the PL efficiency. The PL spectra of the bare and etched GaP under various RF powers are shown in Fig. 4, where inverse relationship between the peak intensity and the RF power is observed. Additionally, while there is no peak shift from the unetched sample case (~2.23 eV), it is noted that the peak width decreases. Generally, a decrease in the PL intensity is correlated with poor interface properties and surface damage [15]. However, the rms surface roughness, as determined through AFM, was relatively constant (Fig. 4

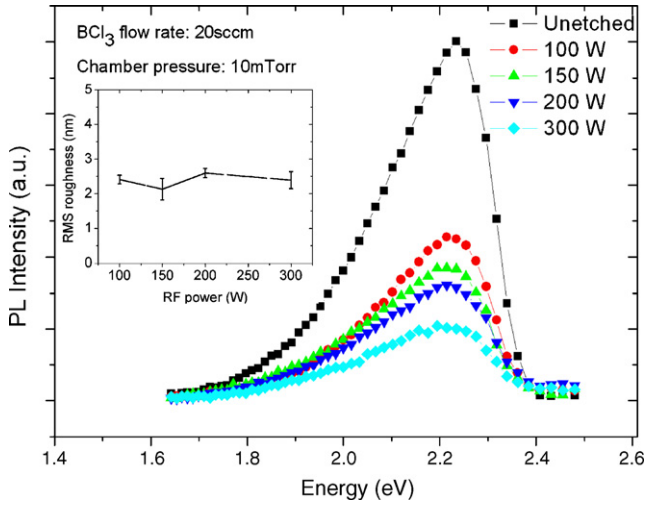

Fig. 4. A comparison of the photoluminescence (PL) spectra of GaP surface as a function of applied BCl_3 plasma RF power. The inset shows that the surface roughness is unchanged which points to charging of the GaP surface, and increased surface recombination as a source for the decreased PL intensity.

inset). The PL intensity decrease is then hypothesized to be either due to a change in the surface state density or changes in depletion thickness [12], brought about through increased RF power. In either case, the non-radiative surface recombination [16] is enhanced which leads to a quenching of the photoluminescence [17]. In the absence of a peak shift, our results (Fig. 4) seem to indicate a negative charging of the surface implying a reduced depletion width and narrower peak width. It is to be noted [18] that GaP has a surface energy level $\sim 0.66 \pm 0.2$ eV, which can be altered through surface treatment. If our proposed mechanism for the PL quenching is valid, then the effects of surface charging could be nullified by electrical means, and our study points to such possibilities. It would also be interesting to study the effect of surface adsorbates, in affecting charge transfer to/from the surface, to tune the PL intensity. For example, functional groups incorporating –OH and –OR, in conjunction with α-hydroxy acids can be used [10] to modify the surface potential by electron abstraction from the GaP surface. Further investigations involving Capacitance (*C*)–Voltage (*V*) measurements on the GaP are necessary to confirm these conclusions.

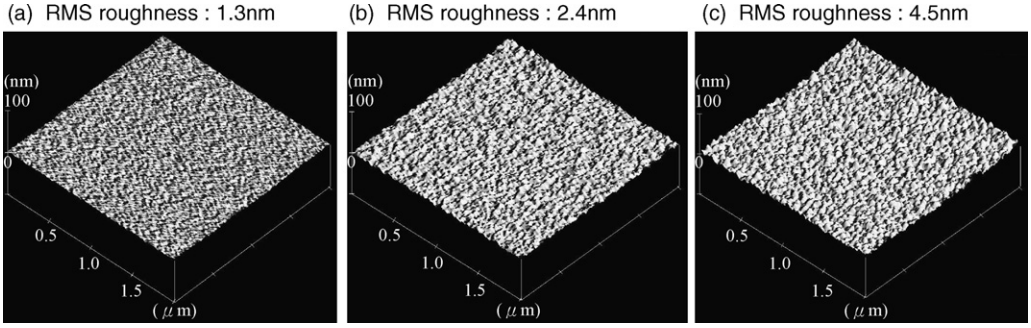

Fig. 3. Atomic force microscopy (AFM) images of the GaP surface topography. The figures in the brackets indicate the RMS roughness: (a) Prior to etching (rms roughness: 1.3 nm), and GaP etched at 200 W RF power, 20 mTorr chamber pressure and (b) 20 sccm of BCl_3 (rms roughness: 2.4 nm), and (c) with additional 5 sccm of Ar gas (rms roughness: 4.5 nm).

4. Summary

We have conducted a through investigation into the reactive ion etching (RIE) processes in GaP using BCl_3 based plasmas. The effects of flow rate, chamber pressure, and RF power on the etch rate has been studied. An increase in the RF power was shown to linearly increase the etch rate and physical sputtering of the surface (beyond a minimal BCl_3 flow rate). The use of Argon as a carrier gas leads to considerable surface roughening with a decreased etch rate and we consequently do not advocate the use of Ar, for BCl_3 plasma etching of GaP. AFM study has been used to correlate surface roughness with etching treatment. PL spectroscopy indicates that a change in the depletion region thickness, due to surface charging by negatively charged $(BCl_n)^-/Cl^-$ species is dominant and could account for the reduced PL intensities with etching.

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