Plasma and gaseous etching of compounds of Groups III–V

Dale E. Ibbotson

AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA

ABSTRACT—Devices fabricated from III-V compound materials have become increasingly important to the communications and electronics industry. As design rules shrink to take advantage of the performance of III-V devices and as circuit integration approaches the sophistication of silicon technology, dry etching of these materials must replace many of the wet chemical etching techniques currently used to form certain microrelief structures. The high fidelity, resolution and control achieved with dry etching processes are critical for the realization of many devices. This paper will discuss the fundamental research and mechanistic understanding, the processing tools and their chemistry, recent device applications, and the current limitations associated with drying etch processing of III-V compound materials.

INTRODUCTION

Semiconductor devices fabricated from III-V compounds such as GaAs, AlGaAs, GaP, InP, InGaAsP and other ternary and quaternary alloy compositions have become increasingly important to the electronics and communications industries. The initial limitation associated with fabricating III-V devices was the growth of high quality substrates and active device and buffer layers; with the advent of molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), vapor phase epitaxy and their variations it has been possible to fabricate high quality lasers, LEDs, photodetectors, etc., which are now an integral part of lightwave communications, and other areas of optical signal processing. The concept of integrating logic and analog circuits with optically active devices has caused intense research and development in III-V materials and device processing.

As device analogs to silicon integrated circuits are fabricated from III-V materials, plasma-produced pattern delineation methods analogous to silicon device etch processing must be realized. However, III-V systems are considerably more complicated, since most of the device applications involve etching more than one III-V alloy composition. Binary, ternary, and even quaternary alloys may be encountered in one device structure. Suitable plasma etchants must be capable of selectively etching one alloy composition over another, while others must be capable of nonselectively etching multiple alloy layers to produce a smooth profile. For example, removal of the GaAs capping layer in the gate region on GaAs/Al_xGa_{1-x}As heterostructure transistors requires high selectivity, whereas GaAs/Al_xGa_{1-x}As laser structures require an anisotropic etch that erodes all layers at the same rate to produce featureless sidewall facets. Etchant and plasma conditions must be carefully chosen to realize these results.

Profile control is also an important consideration. III-V laser mirror facets must be smooth and vertical. This requires that the etching be anisotropic and nonselective. Although anisotropy is most often produced by directional removal of the product layer by ion bombardment, chemically induced anisotropy can also be produced by crystallographic-dependent plasma etching. However, since the etching is dominated by chemical reactions the masked features are undercut, and pattern fidelity may become an issue.

Finally, it is important to evaluate surface and bulk damage produced by plasma etching III-V materials. Many device structures are formed from thin active layers (<1000 Å) and ion induced degradation is a real concern. A tradeoff between the chemistry and ion bombardment effects must be considered in developing plasma etching systems.

ETCHING PARAMETERS

Group V halides are volatile, but group III halides, particularly the fluorides, have limited volatility at practical process temperatures (<300 °C). Therefore, the F-source plasma etch technologies entrenched in silicon device processing are not useful for patterning III-V’s. However, chloride products are sufficiently volatile below 300 °C so most investigations have used chlorine-containing plasmas. Although group III iodide and bromide products are also volatile, only one study was reported using Br_2 plasmas to etch GaAs and one has been documented for InP etching with iodine plasmas. Hydrogen plasma etching of InP and GaAs and its removal of native oxides on GaAs have been reported. Finally, there is one report of InP plasma etching with CH_4/H_2.
The feed gas mixture can be tailored to select radicals accompanying the halogen etchant that greatly influence the overall etching behavior. Species produced in CCI₄, CHCl₃, CCl₂F₂ and BC₁₃ discharges can remove surface oxides and may induce anisotropy by passivating the side walls not exposed to the clearing action of ion bombardment. The addition of Cl₂ to these gases increases the etch rate by providing more etchant. O₂ additions can free Cl radicals from the parent molecules to enhance etching and to balance the unsaturated chlorocarbon radicals so excessive polymer formation is avoided.

Practical etch rates (>1000 Å/min) and nearly total anisotropy can be obtained using halogen-containing plasmas with either low pressure (<50 mtorr) and high discharge frequency (13 MHz) RIE conditions or with high pressures (>100 mtorr) and low discharge frequency (<1 MHz, below the ion transit frequency) in parallel plate reactors. More exotic "reactive ion beam etching" (RIBE) systems utilizing an electron cyclotron resonance (ECR) plasma are typically operated below a few mtorr. ECR/RIBE etching is superior in many ways since ion flux and ion energy are independently controlled and low-damage, nonselective, anisotropic etching can be achieved simply with Cl₂. Some RIBE or ion assisted etching is performed using Kaufmann ion sources that generally supply inert ions (e.g. Ar⁺) and the reactive gas is directed (e.g. Cl₂) at the surface through a separate leak valve or beam nozzle. Under certain conditions rapid etching and vertical profiles are possible. In these cases ion bombardment induces anisotropy by accelerating material removal in unmasked areas. However, under conditions where ion effects do not dominate the reaction, GaAs etches "chemically" near room temperature, while temperatures above 200 °C are required for InP.

Substrate temperature increases the reaction rate and the evaporation rate of products, which influences the etch rate and surface morphology. If anisotropic profiles are desired the chemical reaction rate must be controlled by judicious choice of substrate temperature and pressure. In high pressure Cl₂ plasmas where chemical rates usually dominate, the GaAs and InP etch rates display Arrhenius-type temperature dependencies with apparent activation energies of 10.5 kcal/mole and 34 kcal/mole, respectively. At high pressures, plasmas utilizing chloro- and chlorofluorocarbons are more complicated because substrate temperature also affects the formation of polymer and unsaturates.

**RECENT PLASMA ETCHING STUDIES**

These studies are divided by the "mode" of the plasma source. Reactive ion etching (RIE) refers generally to parallel plate reactors operated below ~50 mtorr at 13 MHz, and many studies have utilized them because they are most amenable to production applications. However, RIE may also include higher pressure plasmas that are operated below the ion transit frequency region (<1 MHz). Reactive ion beam etching (RIBE) and ion beam assisted etching (IBAE) refer to lower pressure conditions (generally <10 mtorr). These sources offer the advantage of independent control over ion energy and ion current. Chemical plasma sources operate under reaction conditions that produce purely or mainly chemical etch rates and surface morphologies.

**RIE**

Chlorine-containing gas feed mixtures including SiCl₄, Cl₂ with inerts and O₂ additions, CCl₂F₂ with inerts and O₂, SiCl₄/H₂, COCl₂/O₂, CCl₄/O₂, and BC₁₃ with Cl₂ and Ar additions have been used to etch III-V materials under low pressure conditions. There is also one report of using CH₄/H₂ to etch InP.

**RIBE, IBAE**

Although IBAE and RIBE using a Kaufman ion source has been useful for studies of etching mechanisms, it is not amenable to production processes. InP has been etched with Cl₂ either introduced as a reactive ion (Cl⁺, Cl₁⁻) or as a neutral combined with inert ions. GaAs etching has also been studied with these combinations. Very smooth, flat walls can be obtained with this technique with minimal surface damage.

Electron cyclotron resonance (ECR) plasmas (10⁻⁶ – 10⁻³ torr) have been used as the ion and radical source in an ultrahigh vacuum system with loadlock and sample preparation chambers. Great care was taken to maintain the system with very low levels of H₂O and carbon-containing species, and the result was that they could achieve equal etching rates for GaAs and AlGaAs simply with a Cl₂ plasma. Moreover, very high aspect ratios were achieved using a hard-baked photoresist.

**Chemical Etching**

Since our initial studies of chemical plasma etching where we discovered that GaAs etching depends on the exposed crystal habit, others have reported similar crystallographic etching under other conditions. Crystallographic etching has been reported in a study of SiCl₄ RIE above 20 mTorr at low power, whereas at lower pressure anisotropic etching was achieved as the ion/neutral flux increased. A similar result was observed for Cl₂/Ar RIE where the etch rate increased and crystal faces were evident under masked features as the feed mixture became rich in Cl₂. GaAs and AlGaAs have also been crystallographically etched with chlorine radicals below 3 mtorr with ECR/RIBE. The sample was rotated away from the RIBE source and etched between 300 °C and 400 °C. At 400 °C the activation energy differences among the crystal planes were overcome thermally, the profile became isotropic and the surface morphology was rough.

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1 D. E. IBBOTSON

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This page contains a discussion on plasma etching, focusing on the use of halogen radicals and the effects of substrate temperature and pressure on etching rates. It highlights the differences between reactive ion etching (RIE) and reactive ion beam etching (RIBE), and the conditions under which anisotropic etching can be achieved. The text also mentions the role of chlorine-containing mixtures in etching III-V materials and the importance of substrate temperature in achieving smooth etched surfaces. The chemical etching of GaAs and AlGaAs is also discussed, emphasizing the role of crystallographic effects in the etching process.
MECHANISMS OF III-V ETCHING

Studies directed at the basic steps that govern III-V compound plasma etching may be divided into low pressure (<10 mtorr) and high pressure (>50 mtorr) regions. Most of the low pressure work has involved ion enhanced kinetic experiments and some studies of the chemical etch rate. Other investigations have focussed on the adsorption properties of CI/Cl₂ on III-V surfaces and the influence of gas additives on etching. These findings will be discussed and summarized here.

A relatively simple case is etching InP in a high pressure chlorine plasma where the rate limiting step appears to be sublimation of InCl₃. Sputter Auger analysis indicated that a multilayer film of InCl₃ is present on the surface during etching. The apparent activation energy for InP etching is close to the heat of InCl₃ sublimation (37 kcal/mol at 300 °C), which points to vaporization of InCl₃ as rate limiting. Moreover, the absolute etch rate is consistent with the InCl₃ sublimation rate calculated from thermodynamic equilibrium. Therefore, the anisotropy observed under high pressure and high temperature plasma etching conditions is controlled by the surface damage effect of ion bombardment. For low pressure and low temperature (<200 °C) ion bombardment probably enhances InCl₃ through localized heating or stimulated desorption. These ideas will be discussed in more detail in this section.

In chloro- and chlorofluorocarbon plasmas such as CCl₄, CCl₂F₂ and mixtures of these feed gases with O₂ or H₂, the situation is more complicated. Additional processes in the gas phase and on the surface must be considered. CCl₄ and CCl₃ can act as surface inhibitors to enhance anisotropy. Fluorine reactions with group III elements create products such as GaF₃, which have limited volatility. Thus ion enhanced desorption can promote anisotropic profiles. Moderate oxygen additions to these feed gases will produce more free Cl, thereby enhancing etch rates. Large amounts of oxygen suppress unsaturates completely and can promote surface oxidation. Hydrogen additions, however, promote oligomeric polymer formation by abstracting fluorine and chlorine from gas phase and surface species, so it is ensured that ion-induced etching dominates. This RIE plasma chemistry has been used to etch GaAs smoothly and anisotropically.

The use of oligomeric materials to produce smooth surfaces and anisotropic profiles has also been accomplished solely with hydrocarbon and hydrogen, CH₄/H₂, in reactive ion etching of InP, InGaAs and InGaAsP. Enhanced deposition of a carbonaceous polymer on SiO₂ and photosist masking materials prevented the mask erosion commonly associated with RIE chemistries. The InP etch rate increased with the CH₄ partial pressure for low pressures and produced undercut profiles for higher CH₄ partial pressure and total pressure, indicating a competing chemical rate. However the etch rate did not depend strongly on substrate temperature which suggests that removal rate is controlled by ion bombardment. Metal alkyl formation probably plays a role in this etching chemistry.

Fundamental studies of chemisorption effects in etching III-V surfaces have given us insight into the controlling phenomena. Even for high vacuum exposures, Cl₂ chemisorbs readily on clean III-V surfaces, and at monolayer coverages Cl atoms bond preferentially to group V atoms to enrich the topmost atomic layer with group V chlorides. Mayer used low energy ion scattering and mass spectrometry to study AsCl₂(GaAs) and PCI₃ (InP) surface segregation to the top of the product layer during Cl₂ etching. It has also been suggested that InP(110) exposure to Cl₂ depletes phosphorus from the top surface layer, leaving a surface enriched in indium. Thus, even in the absence of ion bombardment effects, such as preferential sputtering of the group V element, Cl₂ (and Cl) alters the surface concentration of In and P elements from that of the clean surface. Long exposures to Cl₂ or chlorine RIBE creates roughly a 50 Å layer enriched in indium, but the depletion of phosphorus is more severe with ion bombardment. A comparable product layer thickness was observed in high pressure Cl₂ plasma etching below 210 °C. For higher flux of reactant, lower ion flux and ion energy, and lower substrate temperature the rougher the resulting surface morphology. These phenomena can account for the roughening of III-V surfaces observed in reactive ion etching.

The reaction of chlorine with III-V surfaces produces a complex product layer whose composition depends on substrate temperature and reactant flux. Ion bombardment effects on these products layers, the evolved gas phase species and the kinetic mechanism of etching have been studied recently for GaAs and InP. GaAs gaseous etching with a modulated Cl₂ beam (~2×10⁻⁴ Torr) showed a maximum etch rate near 180 °C, corresponding to a maximum in the production of GaCl₃ and AsCl₂, and above 280 °C the monochlorides of Ga and As are favored. From modulated ion beam experiments MoNevin and Becker concluded that GaCl₃ is desorbed at high translational energy by impinging ions and that the temporal delay in the AsCl₂ signal they observed was related to the time needed to produce AsCl₃ by ion enhanced reaction. However the data and the mechanism developed by Balooch et al. are more convincing since they have satisfied detailed mass balance requirements and have accounted for the temporal response of chemical reactions in their modulation method. They conclude that ion bombardment stimulates the desorption of a GaCl₃-rich scale (roughly 10¹⁵ cm⁻²) to expose an underlying nonstoichiometric layer of Ga and As that can then react to form more AsCl₃, rather than accelerating AsCl₃ surface reactions.

Cl₂ (~2×10⁻⁶ Torr) gaseous etching of InP showed negligible etching below 160 °C but forms P₄, InCl₂ and monochloride above 160 °C. Similar products were observed for room temperature ion enhanced etching. These observations and others suggested that incident ions create a thermal pulse which causes desorption
of surface species. Although the experiments were done under rarified conditions, localized heating by charged species was also suggested for high pressure reactive ion etching of InP at higher temperatures. At this point it is not clear how ions stimulate desorption and enhance chemical etching. Large enhancements cannot be explained by physical sputtering of products, but surface heating or roughening of the product layer may accelerate the removal of these layers.

**DEVICE APPLICATIONS**

The plasma etching parametric and mechanistic studies presented here have been used to fabricate several devices from III-V compounds. These fabrication processes can be divided roughly into two general etching requirements—some form of anisotropy, and alloy selectivity. It is generally true that optically active elements require anisotropic etching, whereas transistor fabrication requires selective etching and, in some instances, anisotropic etching as well. Anisotropic etching can either mean crystallographic etching (chemically dominated reaction) or the more familiar directional etching that is dominated by ion effects. In some cases vertical facets are formed with both techniques, but undercutting can be a problem when the profile is controlled by the chemistry alone.

GaAs/AlGaAs heterostructures have been used in a wide range of electronic and photonic device applications. Electronic devices fabricated from heterostructures usually require thin active layers (80–500 Å) exhibiting high quality bulk and interfacial properties. Selectively doped heterostructure transistors (SDHT) are representative of this type of device structure. The structure, grown with MBE on semi-insulating GaAs substrates, typically consists of a 1 µm undoped GaAs barrier layer, a 20–25 Å AlGaAs spacer layer, a 400–600 Å heavily doped AlGaAs donor layer and finally a 500–1000 Å heavily doped GaAs capping layer. Fabrication of the SDHT's requires gate recess by highly selective etching of the GaAs capping layer over the AlGaAs donor layer while creating minimal damage to the underlying layers. Depletion mode and enhancement mode SDHT's differ in this structure only by the depth etched into the AlGaAs donor layer, typically 100–150 Å. Alternatively, 100–150 Å layers of an undoped AlGaAs/GaAs sandwich can be grown between the capping and donor layers to serve as a stopetch. In either case selectivity and damage-free surfaces are critical to device performance. Since the GaAs capping layer is thin (<1000 Å) compared to the typical gate width (~0.5–1 µm), anisotropy is not the prime consideration. Selectivity can be achieved by chemistry based either on the formation of involatile Al-oxide or Al-fluoride to passivate AlGaAs which stops the etching at the GaAs/AlGaAs interface.

RIE with CCl$_2$F$_2$, and CCl$_2$F$_2$/He mixtures selectively etches GaAs up to 1000 times faster than AlGaAs. Low bias conditions and Intermediate pressures (20–50 mtorr) are used so Al-fluoride formation is favorable, and so it is not rapidly removed by sputtering. Moreover, the higher pressures (50 mtorr) enhance chemical etching in order to slightly undercut the GaAs cap, thereby decreasing parasitic effects with the gate metallization. RIE with CCl$_2$/O$_2$ mixtures also shows a modest GaAs/AlGaAs selectivity (35:1). It was proposed that Al$_2$Ga$_{1-x}$As is more reactive to O$_2$ than GaAs, and the Al-oxide formed would depress the AlGaAs etch rate. However O$_2$ is not a sufficiently selective oxidant to obtain the high selectivities found for CCl$_2$F$_2$.

Room temperature oxidation studies of GaAs(110) show that H$_2$O reacts two to three orders of magnitude faster than O$_2$ to form thin oxides, and it is likely that AlGaAs displays similar behavior. However, AlGaAs is more susceptible to passivation by oxidation. We have taken advantage of this property by mixing a controlled partial pressure of H$_2$O vapor with Br$_2$ to spontaneously etch the GaAs cap and form a stopetch at AlGaAs layer on SDHT structures. This technique has also been applied to processing novel devices, constructed from SDHT GaAs/AlGaAs layers, which offer an attractive approach to the development of ultra-low power high-speed complementary logic circuits. An example of this device is shown in Figure 1. Prior to mesa formation, windows are opened where p-type SDHTs are to be fabricated by this selective gaseous etching technique. A stopetch is achieved at the p-Al$_2$Ga$_x$As layer with no degradation of surface morphology. Sample I-V curves from the completed complementary structure are shown in Figure 2. Excellent characteristics are observed with nearly complete saturation occurring at a drain-source voltage of 0.4 V. Although this is a purely chemical, gaseous-etch system, the concept can also be used in chemical plasma systems with the proper choice of feed gases.

The primary etch consideration for optically active devices, on the other hand, is anisotropy. In some cases alloy selectivity is desirable, but in all cases minimal mask erosion is important. Chlorine atoms are the primary reactive in all of the following device applications, but they are generated from various feed gas combinations. The desired etch profile is controlled by ion-enhanced product removal. Parallel plate reactors are the most common for these processes.

RIE with CCl$_2$F$_2$ at high bias (3 kV) has been used to form vertical mirrors in GaAs waveguide structures. Facet roughness is <0.1 µm and is mainly caused by mask erosion and mask irregularities. Curved GaAs waveguides have also been formed with SiCl$_4$/Ar mixtures under low power RIE conditions where Ar was a necessary additive to enhance sputter removal of products. More recently 100×100 arrays of GaAs optically bistable NOR/AND gate devices were fabricated from 1.5 µm high by 9 µm square pixels using CCl$_2$F$_2$/He/O$_2$ RIE that stopetched at the underlying Al$_2$Ga$_x$As layer. The etch uniformity and the high fidelity achieved with RIE were essential to form a good interferometer with a switch-off time of 200 ps. Finally, substrate via holes have been etched at >2 µm/min with CCl$_2$F$_2$. The hole profile was controlled by sidewall deposits formed in higher pressure RIE (75–150 mtorr).
Plasma and gaseous etching of compounds of Groups III-V

Fig. 1. Complementary P-MODFET/n-HB MESFET transistor pair. Prior to mesa fabrication, a window to the p-(Al,Ga)As layer is formed by selective gaseous etching. The gate length, gate width, and source-drain spacing in the test structure were 2, 100 and 5 μm, respectively.

Fig. 2. Current-voltage characteristic of the n-HB MESFET and p-MODFET at 77 K. The values are normalized for a 1-mm gate width.

Much attention has also focussed on etching active laser device structures. Early work by Coldren et.al. showed that RIE etched mirror facets could be successfully formed for GaInAsP/InP stripe lasers with C12/O2 mixtures, or with a combination of wet chemical etching (WCE) and RIE to improve the facet quality. GaInAsP/InP buried heterostructures have also been etched with CCl4/O2. However the facets sloped outward which decreased the efficiency of optical confinement, but these problems could possibly have been eliminated by careful adjustment of power and pressure. There have also been RIE facets formed for GaAs/AlGaAs double heterostructure (DH) lasers. WCE combined with CCl2F2/He/O2 RIE was used to circumvent the problem of etching AlGaAs with CCl2F2. Although the etch rate ratio of GaAs/AlGaAs reported was 4:1 using C2/Ar, sufficiently anisotropic conditions were found to produce vertical and smooth mirror facets.

Recently, GaAs/AlGaAs multiple quantum well structures have been etched by C12 ECR/RIBE and BCl3/Ar RIE. Smooth vertical facets and good quantum efficiencies were reported. The finest scale etching in III-V heterostructure devices (<500 Å lateral dimension) was done with BCl3/Ar RIE on specially masked multiple quantum wells. The etched features are referred to as "quantum disks" since their lateral dimension is close to the thickness of the quantum well structure and they exhibit different optical properties from the original layers. Ultrahigh resolution circular masks of 100 Å SrF2 were produced by electron beam lithography and liftoff. RIE was performed in a parallel plate configuration using a 9:1 Ar/BCl3 at 15 mtorr and 0.3 W/cm². Similar etch rates for GaAs and AlGaAs and no undercutting were obtained. The formation of 400 Å diameter by 2300 Å tall columns were demonstrated.

LIMITATIONS OF DRY ETCHING

There are a mix of etching requirements which preclude the use of one chemistry with different plasma conditions to achieve anisotropy or selectivity, in all III-V structures. Anisotropic profile formation, using RIE or RIBE, is now a rather well-developed technique. However, more studies are needed to characterize the effects of plasma etching on the electrical performance and materials properties of these devices. Highly selective etching is achieved in some cases, but etching AlGaAs selectively over GaAs or selective etching of alloys with one composition but with different doping levels has not been accomplished by the chemistries and plasmas explored so far. However the development of hybrid techniques such as coupling laser excitation with Cl radical etching holds some promise to obtain etch selectivity with doping level.
SUMMARY

Dry etching techniques for patterning III-V materials have been developed over the last several years. Although chlorine-based plasma chemistry, developed in the early studies, continues to be the mainstay, the process techniques and equipment have been improved tremendously since then. These plasma etching processes have been successfully applied to a number of III-V device applications.

REFERENCES