

Acknowledgments

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Reactive Ion Etching of GaInP, GaAs, and AlGaAs

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ABSTRACT

We have investigated the reactive ion etching of GaInP, GaAs, and AlGaAs. High etching selectivity of GaAs to AlGaAs (or to GaInP) can be achieved due to the formation of aluminum fluoride (AlF_3) and indium fluoride (InF_3) using a BCl_3/SF_6 mixture. By using a CH_4/H_2 mixture, a polymer film is accumulated on the GaAs surface after reactive ion etching. This polymer film inhibits the reactive ion etching of GaAs. There is no polymer film accumulated on the surface of GaInP. The polymer deposited on the surface of GaInP is removed as the etching products are being removed. Hence, a high etching selectivity of GaInP to GaAs can be achieved by using a CH_4/H_2 mixture.

Introduction

The critical processing issues of heterojunction bipolar transistor (HBTs) include (i) emitter-base self-alignment, (ii) surface passivation for current gain enhancement, (iii) etching control, (iv) ohmic contact formation, (v) reduction of capacitive parasitics, and (vi) interconnection.¹ To access the base, etching through 0.15 ~ 0.2 μm of emitter layer and stopping within 0.01 μm after reaching the base layer (thickness < 0.1 μm) is necessary. This task can be greatly simplified with the availability of a composition-selective etching process. A composition-selective etching is also important for the fabrication of the single lateral mode laser to control precisely the difference of the refractive index in the ridge waveguide structure.

The lattice-matched AlGaAs/GaAs, GaInP/GaAs, AlInAs/GaInAs/InP have been the most important material systems for the HBT fabrications. For the AlGaAs/GaAs heterostructure, the GaAs etching rate can be higher than that of AlGaAs by using an ammonium-hydroxide/hydrogen peroxide solution^{2,3} or a citric acid/hydrogen peroxide solution.⁴ For the GaInP/GaAs heterostructure, the etching characteristics can be influenced by varying the amount of H_2O_2 in a mixture of $1\text{HCl}:20\text{CH}_3\text{COOH}:x\text{H}_2\text{O}_2$, with $0 \leq x \leq 5$.⁵

Reactive ion etching (RIE) is an alternate to wet etching. The most common gases used for the etching of III-V semiconductors are based on chlorine. In the past, Freon-12 was commonly used for the fabrication of GaAs-based devices.^{6,7} The etching selectivity of GaAs to AlGaAs is over 100 by using CCl_2F_2 .⁸ However, the use of chlorofluorocarbon (CFC) gases will be banned because of their undesirable influences on the environment. There are several possible mixtures for the CFC replacement.⁹⁻¹¹ Salimian *et al.*

used SF_6 and SiCl_4 to achieve a selective etching of GaAs to AlGaAs.¹²

We report the results using boron trichloride (BCl_3) and sulfur hexafluoride (SF_6) to achieve a selective etching of GaAs to AlGaAs (or to GaInP). By using a methane/hydrogen (CH_4/H_2) mixture, a selective etching of GaInP to GaAs can be achieved.

Experimental

A parallel-plate-type RIE system was used for this study. The diameter of the plate is 11 in. The $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}/\text{GaAs}$ epi-wafers were grown by molecular beam epitaxy (MBE). The $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{GaAs}$ epi-wafers were grown by metallorganic chemical vapor deposition (MOCVD). A positive photoresist AZ6112 was used for lithography. After the pattern was defined, the samples were dipped in a NH_4OH solution for a few seconds and then rinsed in DI water. After rinsing, the samples were immediately put into the RIE chamber. The RIE system is equipped with a rotary pump and a turbo pump. The chamber temperature is cooled (or heated) by water. The base pressure of the chamber is below 5×10^{-6} Torr. The gas flow rate is regulated by a mass flow controller. A glow discharge occurs between the parallel plates when the RF power is applied. The volatile etching products will be removed by the pumping system. The surface morphology and the etching depth of the samples are characterized by field emission scanning electron microscopy and Sloan Dektok.

Results and Discussions

Selective dry etching of GaAs to AlGaAs.— BCl_3 is used to etch both AlGaAs and GaAs. The pressure dependencies of the GaAs and AlGaAs etching rates at different power levels are shown in Fig. 1 and 2. The flow rate of BCl_3 is 10 sccm (standard cubic centimeter per minute) for both

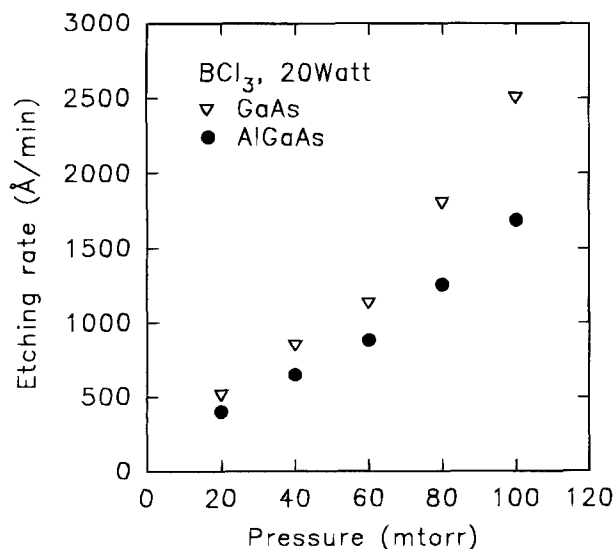


Fig. 1. The pressure dependencies of GaAs and AlGaAs etching rates using BCl₃ at 20 W RF power.

cases. As shown in these figures, the etching rates of GaAs and AlGaAs increase as the chamber pressure increases. The etching selectivity of GaAs to AlGaAs also increases when the chamber pressure increases. In general, the developed self-bias voltage, which is the average dc potential of the electrode surface with respect to ground and gives a measurement of the ion bombardment that the electrode surface experiences, increases as the applied RF power increases. A chemical etching process is dominant in the case of low RF power (20 W, as shown in Fig. 1). At high RF power levels (100 W), high energetic ions physically bombard the surface of the sample. The etching rate is slightly increased. The surface morphology is smooth and the etching profile is sharp, but the etching selectivity is reduced (as shown in Fig. 2).

By using a mixture of BCl₃ and SF₆, the etching selectivity of GaAs to AlGaAs is better than the above cases. Figure 3 illustrates the pressure dependences of GaAs and AlGaAs etching rates. The flow rates of BCl₃ and SF₆ are 50 and 10 sccm, respectively. The RF power is 20 W. The etching depth of the AlGaAs layer is less than 300 Å even after etching for 30 min. The etching selectivities of GaAs to AlGaAs are very high (200 ~ 500). The role of SF₆ is to provide F⁻ radicals that react with AlGaAs and form AlF₃.

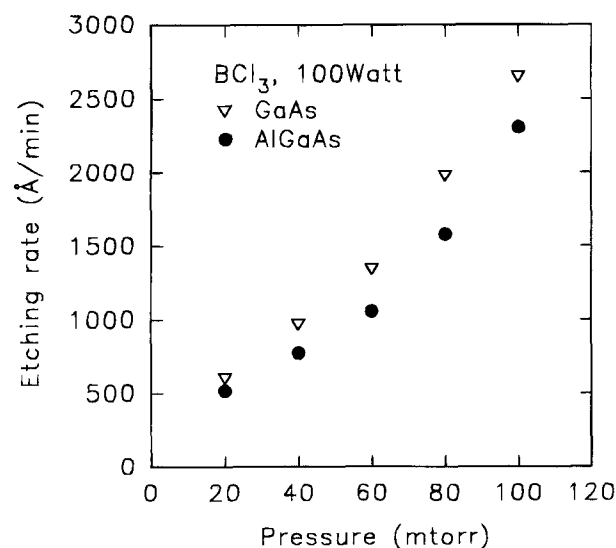


Fig. 2. The pressure dependencies of GaAs and AlGaAs etching rates using BCl₃ at 100 W RF power.

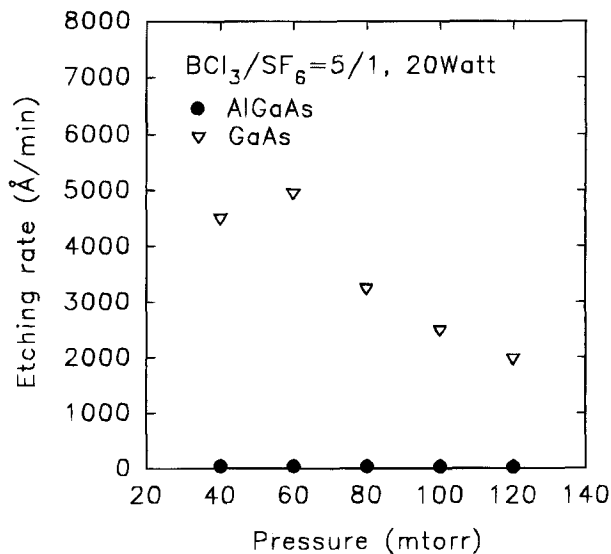


Fig. 3. The pressure dependencies of GaAs and AlGaAs etching rates using BCl₃/SF₆ = 5/1 at 20 W RF power.

Since the boiling point of AlF₃ is high (~1291°C),¹⁴ it is a nonvolatile substance. As in the case of using Freon-12, AlF₃ inhibits the dry etching of AlGaAs layer. Therefore, the etching rate of AlGaAs using BCl₃/SF₆ is low (<10 Å/min).

At high RF power levels (120 W), the sputtering effect plays an important role in the etching process. The nonvolatile AlF₃ film can be removed by energetic ions physically bombarding the surface. Thus the etching rate of AlGaAs at high RF power levels is faster when compared to the etching rate at low RF power levels (as shown in Fig. 4). However the etching selectivity of GaAs to AlGaAs decreases to less than 100.

Selective dry etching between GaAs and GaInP.—Similarly, a slow etching rate of GaInP can be achieved by using a mixture of BCl₃ and SF₆. The role of SF₆ is to provide the F⁻ radicals that react with GaInP and produce InF₃. Since the boiling point of InF₃ is very high (above 1200°C),¹⁴ it is a nonvolatile substance. The InF₃ layer protects the GaInP layer from being etched. Figure 5 illustrates the pressure dependences of GaInP and GaAs etching rates at 20 W RF power. The flow rates of BCl₃ and SF₆ are 50 and 10 sccm, respectively. As shown in Fig. 5, the etching selectivities of GaAs to GaInP are excellent (200 ~ 500). The etching rates

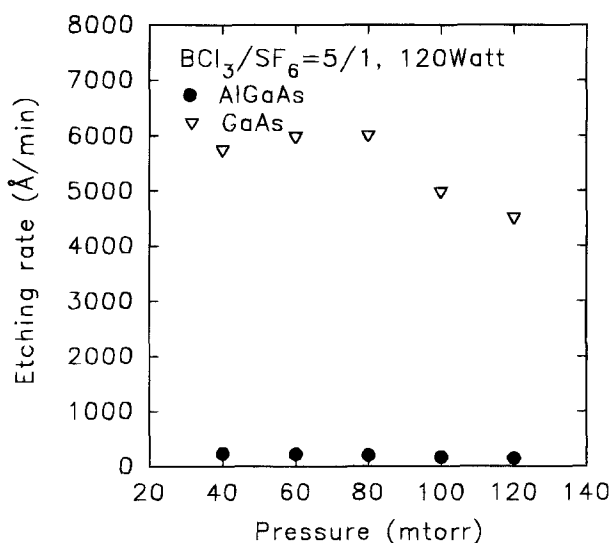


Fig. 4. The pressure dependencies of GaAs and AlGaAs etching rates using BCl₃/SF₆ = 5/1 at 120 W RF power.

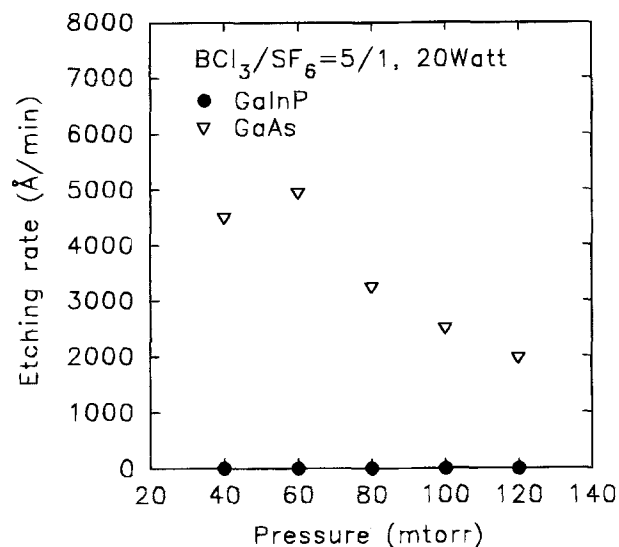


Fig. 5. The pressure dependencies of GaAs and GaInP etching rates using $\text{BCl}_3/\text{SF}_6 = 5/1$ at 20 W RF power.

of GaInP under such circumstances are low (<10 Å/min). Similarly, at high RF power levels, the sputtering effect plays an important role in the etching process. The InF_3 layer is removed by the bombardment of highly energetic ions. Thus the etching rate of GaInP increases at high RF power levels (as illustrated in Fig. 6).

Since the boiling point of indium chloride is higher (600°C) than those of other chlorine-based products,^{13,14} the etching rates of In-containing compounds cannot be higher than that of GaAs by using Cl-based gases. In order to overcome the limitations of chlorine-based mixtures, a CH_4/H_2 mixture is introduced for the dry etching of In-containing compounds.¹⁵ The role of the CH_4 is to remove the group III species (A) as $(\text{CH}_3)_m\text{A}_n$ type compounds, while the H_2 removes the group V species (B) as BH_3 . The major drawback of using CH_4 is the deposition of polymer. If the deposition rate of polymer is faster than the etching rate, the sample will be covered with polymer. In our study, the GaAs surface is covered with polymer while using a CH_4/H_2 mixture. Thus, the etching depth of GaAs using a CH_4/H_2 mixture is almost zero. However, no polymer is accumulated on the GaInP surface. The removal of polymer film on the GaInP is accompanied by the removal of volatile etching products. In other words, the etching rate of GaInP

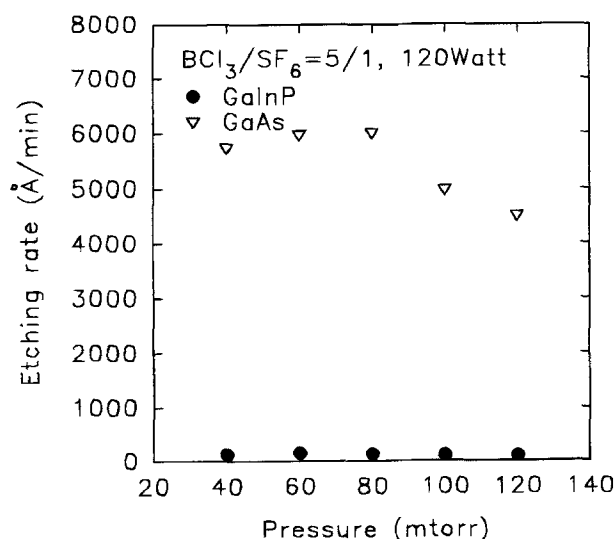


Fig. 6. The pressure dependencies of GaAs and GaInP etching rates using $\text{BCl}_3/\text{SF}_6 = 5/1$ at 120 W RF power.

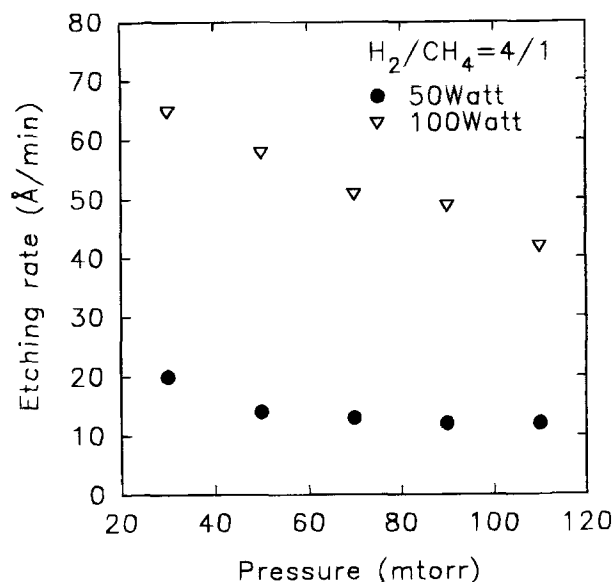


Fig. 7. The pressure dependencies of GaInP etching rates using $\text{H}_2/\text{CH}_4 = 4/1$ at 50 and 100 W RF power (the etching rate of GaAs is zero).

using a CH_4/H_2 mixture is higher than the deposition rate of polymer. Figure 7 shows the pressure dependence of the GaInP etching rate at 50 and 100 W RF power levels. The flow rates of CH_4 and H_2 are 10 and 40 sccm, respectively, because the deposition rate of polymer increases as the chamber pressure and CH_4 flow rate increases.¹³ Therefore, as shown in Fig. 7, the etching rate of GaInP decreases while the chamber pressure increases.

Conclusions

The gas mixture of BCl_3 and SF_6 was used in our study. The etching rates of AlGaAs and GaInP using such a gas mixture are very low due to the formation of the non-volatile substances AlF_3 and InF_3 . A high etching selectivity of GaAs to AlGaAs (or GaInP) can be achieved by using a BCl_3 and SF_6 mixture. In addition, the handling of BCl_3 is easier than that of SiCl_4 , because the boiling point of SiCl_4 is 57.5°C and that of BCl_3 is 12.5°C . The SiCl_4 vapor usually condenses into liquid type when it touches a cold surface. It is more difficult to arrange the SiCl_4 piping system as compared with BCl_3 . Therefore, BCl_3 is more suitable than SiCl_4 for the replacement of Freon-12 (CCl_2F_2).

High etching selectivity of GaInP to GaAs can be achieved by using a CH_4/H_2 mixture. There is essentially no etching of GaAs. A polymer film accumulates on the GaAs surface. The etching rate of GaInP is higher than the deposition rate of polymer, and no polymer film accumulated on the GaInP surface. The deposition rate of the polymer is different at various chamber pressures, CH_4 flow rate, and RF power. Therefore, the etching rate of GaInP can be changed by adjusting the chamber pressure, CH_4 flow rate, and RF power.

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Correlations Between the Electrical Characteristics of Metal-Oxide-InP Tunnel Diodes and the Nature of Thin Interfacial Oxides

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ABSTRACT

Thin native oxides with different compositions were grown on InP before metal deposition to increase the Schottky barrier height and the behavior of the metal-oxide-InP tunnel diode. Three types of interfacial oxides were compared: they were obtained by thermal, anodic, and UV-assisted oxidation, their composition being close to InPO_4 , $\text{In}(\text{PO}_3)_3$, and $\text{InP}_{0.5}\text{O}_3$, respectively. The diode parameters (barrier height, ideality factor) were extracted from the electrical characteristics and correlated with the nature of the interfacial oxide. Particular attention was devoted to the study of diode stability under forward and reverse bias voltage. The best results were obtained with UV-assisted oxides which reached a barrier height of about 0.74 eV, an ideality factor of 1.17, very high stability, and a breakdown voltage of 20 V. These characteristics meet the requirements of metal semiconductor field effect transistor realization.

Introduction

Indium phosphide is becoming an important material for electronic devices. The main reasons for such an interest are its high electron peak velocity and its direct bandgap which makes it suitable for the realization of high speed and optoelectronic devices. The pioneering studies on InP have demonstrated that the barrier height of the metal-InP is too low to be used directly in a device. Moreover, as the insulator-InP interface was obtained with a relatively low interface state density, much of the research work on the InP transistor has been devoted to the metal insulator semiconductor field effect transistor (MISFET) with encouraging results. Recently, transistors with a high transconductance have been realized.¹ However, the main drawback of these devices is the very poor time stability of the drain current under gate bias voltage.² The principal reason is that under electrical stress the charges move to fill the interface states producing a change in the band bending and consequently of the current. As a result of this drift of the current during polarization, InP MISFET cannot be widely used.

An alternative way for developing InP transistor technology is to use a metal semiconductor field effect transistor (MESFET) based on a Schottky barrier. At first, this scheme was hindered by the inherently low InP Schottky barrier height (0.43 eV)³ resulting in large reverse leakage current. On the other hand, these devices should be more stable than MISFETs since the electric charges can be removed through the Schottky barrier. A thin interfacial oxide can be used to increase the Schottky barrier height. Moreover, this oxide layer can reduce transmission of electrons by the tunneling effect and decrease the interface states leading to relative unpinning of the Fermi level. Since the pioneering work of Cardwell *et al.*,⁴ several oxidation techniques have been used: chemical oxidation,^{5,6} plasma oxidation,⁷ and P_2O_5 deposition.⁸ More recently,

high performance Schottky diodes and FET were realized on InP by UV/ozone oxidation^{9,10} resulting in improved stability. All these studies have shown that the behavior of MIS tunnel diodes are intrinsically correlated with the nature of the interfacial layer.

An extensive study of the chemical, structural, and electrical properties of native oxides on InP has been carried out in our group.¹¹ This has shown in particular that condensed phosphates electrochemically grown on InP are good candidates for the passivation of the InP surface, but these oxides have not been studied in relation to Schottky diodes.

In this paper we report on a comparative study of the electrical characteristics of metal-oxide-InP tunnel diodes obtained with different native oxides. The relationship between chemical composition and electrical properties are discussed. The native oxides were grown by thermal oxidation, anodic oxidation, and UV-photoassisted oxidation. The device parameters (barrier height, ideality factor) were evaluated from *I-V* measurements. Emphasis is also placed on their current stability under polarization.

Experimental

Single-crystal (100) InP wafers of n-type ($5 \cdot 10^{15} \text{ cm}^{-3}$) provided by Sumitomo were used. The sample surface was cleaned by sequential baths in boiling trichloroethylene, acetone, methanol followed by a 1 min etch in 5% HF/water.

Anodic oxidation was performed with a 0.02 to 0.2 mA/cm² constant current under white light illumination to assist the oxidation process. In this work, two electrolytes were used for electrochemical oxidation: deionized water, to reduce contamination, and methanol. A small quantity of phosphate salts was added to the alcohol to ensure the electrical conduction. These oxide films have been described as a two-layer system: close to the semiconductor an inner phosphorus-rich layer with a composition close to $\text{In}(\text{PO}_3)_3$, and near the surface an indium-rich layer.^{12,13} The final oxidation thickness ranged from 100 to 150 nm. In

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