Characteristics of III-V Dry Etching In HBr-Based Discharges


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ABSTRACT

Electron cyclotron resonance (ECR) discharges of HBr/Ar, HBr/H2, or HBr/CH4, were used for dry etching of Ga-based (GaAs, GaSb, and AlGaAs) and In-based (InP, InAs, InSb, InGaAs, and InAlAs) III-V semiconductors. The effects of variations in pressure (1-20 mTorr), gas composition, and additional RF-induced bias on the sample were examined. At least 100 V of dc bias is required to initiate etching under all conditions, with the etch rates found to be fastest with CH4 addition, followed by H2 and then Ar. The etched surface morphologies are smooth with HBr/Ar and HBr/CH4 discharges, but tend to become increasingly rough as the microwave power into HBr/H2 discharges is increased, particularly with the In-based materials. The surfaces are chemically very clean after dry etching, with no evidence of Br-containing contamination remaining on any of the materials. The HBr/Ar and HBr/CH4 discharges produce the smallest changes in the electrical properties of the semiconductors, while HBr/H2 plasma exposure may cause dopant passivation and changes in barrier height under some conditions.

III-V semiconductors may be dry etched using several different classes of discharges. The most common gas mixtures are those based on chlorine (e.g. Cl2, SiCl4, BCl3, and CCl3F2), often diluted with Ar, He, or O (1-13). The etch rates obtained depend on the material itself and the exact plasma conditions, but in general the etch rates are quite high for Ga-based compounds such as GaAs, AlGaAs, and GaSb. The sole exception is when fluorine is present in the discharge, in this case AlGaAs displays a very slow etch rate due to formation of the relatively involatile AlF3 on the surface (14-16). The use of CCl3F2 or the addition of fluorine-containing gases (usually SF6) to a Cl2-based discharge therefore provides an etch stop at an underlying AlGaAs when etching through GaAs (7, 12). The other class of gas mixtures used are based on CH3H2 largely introduced to overcome the limitations of Cl2-based discharges for etching In-containing materials such as InP, InGaAs, and related compounds (17-21). In the latter cases, the removal of indium chlorides is difficult at conventional etch temperatures (<100°C) (10) and preferential loss of the group V element (P, As, or Sb) will generally lead to surface morphologies which are somewhat rough. The CH3H2 mixtures, on the other hand, will etch all of the In-based compounds in a slow but very smooth manner under the right conditions.

The third general class of gas mixtures are those based on Br2 or I2. Little information is available on the etching characteristics of III-V semiconductors, particularly under the ion-enhanced conditions necessary for production of small feature sizes (2, 22, 23). Ibbotson et al. (22) have reported extremely fast etch rates for GaAs (60 μm · min⁻¹) in high pressure (0.3 Torr) Br2 plasmas. Temperatures in excess of 200°C were required to achieve etching of InP in similar plasmas. Takimoto et al. (23) fabricated etch-facet lasers using Br2/N2 and Br2/Ar reactive ion etching to obtain rates of 2 μm · min⁻¹ for power densities of 0.78 W cm⁻² at a pressure of ~4 mTorr. Also, HBr plasma etching has recently attracted attention for deep feature fabrication in Si technology (24). It is of interest to see whether Br-based discharges will provide faster etching than CH3H2 plasmas while retaining smooth surface morphologies.

In this paper we report on the etching characteristics of III-V semiconductors in electron cyclotron resonance (ECR) discharges of HBr/H2, HBr/CH4, and HBr/Ar. All of the common Ga-based (GaAs, Al0.5Ga0.5As, and GaSb) and In-based (InP, InAs, InSb, InGaAs, and InAlAs) materials have been examined. The etch rates have been measured as a function of microwave power pressure and dc bias on the samples, while the surface morphology was examined.
by scanning electron microscopy (SEM). Auger electron spectroscopy (AES) was used to monitor changes in surface composition as a result of the etching, while capacitance-voltage (C-V), current-voltage (I-V), and photoluminescence (PL) measurements were used to measure changes in the electrical and optical quality of the material. Finally, transmission electron microscopy (TEM) was used to check for lattice disruption in some of the samples due to the ion bombardment present during the dry etching.

Experimental

A variety of different types of material was used for these experiments. For etch rate measurements, semi-insulating InP, undoped (p = 10^{16} cm^{-3}), (100) bulk GaSb, n-type (n = 10^{16} cm^{-3}) bulk InAs and n-type (2 x 10^{14} cm^{-3}), bulk InSb wafers were patterned with Hoescht Celanese 5209 E photosresist to yield a test pattern with various opening sizes. Epitaxial layers (~1 μm thick) of n-type (n = 10^{16} cm^{-3}), Sn-doped Al_{0.5}Ga_{0.5}As were grown by metal organic molecular beam epitaxy (MOMBE) on semiinsulating substrates, while undoped (n = 10^{16} cm^{-3}) epitaxial layers (~1 μm thick) of InAs_{0.5}Ga_{0.5}As and InSb_{0.5}As were grown by metal organic chemical vapor deposition (MOCVD) on Fe-doped, seminsulating InP substrates. Some of these samples were lithographically patterned as described above. After etching, the resist was removed in acetone and the etched depth of removals was determined by stylus profilometry measurements. The anisotropy and smoothness of the etching were examined by SEM. Unpatterned GaAs and InP were used for AES and PL measurements. The AES primary electron beam voltage was 10 kV at a beam current of 0.5 μA, with a primary spot size of 5 μm diam. Depth profiling was accomplished by sputtering the samples with a 5.3 keV Ar^{+} ion beam at a rate of ~30 Å·min^{-1}, rastered over 3 x 3 mm^{2}. The AES analysis was performed after removal from the etch chamber since we wish to know the state of the surface that would be presented for further processing, rather than the intrinsic changes caused by plasma exposure. The PL measurements were performed at 300 K using an Ar^{+} ion laser as the excitation source.

For C-V and I-V measurements, n-type InP (n = 6 x 10^{15} cm^{-3}) and GaAs (n = 10^{17} cm^{-3}) bulk Si-doped wafers were contacted on the rear face with alloyed (400°C, 20 s) AuGeNi/Al metallization to provide ohmic contact. After the dry etching treatments, TiPdAu (for GaAs) or Au (for InP) was evaporated onto the front face for Schottky contacts. Unpatterned sections of InSb were also prepared for contact formation by chemical thinning and iodine ion milling. Multibeam bright-field imaging with seven beams included within the objective aperture was utilized to obtain lattice imaging.

The dry etching was performed in the hybrid ECR-radio frequency (RF, 13.56 MHz) Plasma Therm SL 720 system described in detail previously (25, 26). In brief, this utilizes a 2.45 GHz microwave excitation source (WaveMat Model 300) with the resonant cavity designed to include additional ECR beams superimposed at the sample position. The electronic grade HBr, H_{2}, CH_{4}, and Ar were introduced into the microwave source via mass flow controllers. Typical flow rates were 15 standard cubic centimeters per min (scm) for HBr, and 5 scm for the other gases. These ratios were chosen specifically to compare the efficiency of the etching with CH_{4} in the mixture, in which the CH_{4}/H_{2} ratio is typically ~3:1. We also used total flows of one-half and three times these values but the same general trends were observed regardless of the absolute flow rates. We also found that neat HBr discharges were difficult to initiate at the low end of our pressure range (1.5 mTor), while initiation of the three mixtures listed above was straightforward. Prior to loading the samples into the system, the sample chamber was purged with 100 cm^{3} of pure He to remove native oxides. The samples were then dried in filtered N_{2} and transferred via the load-lock into the Plasma Therm system.

Results and Discussion

Figure 1 shows the etching rate of the eight materials investigated as a function of the dc bias at fixed pressure (1 mTorr) and microwave power (150 W) for the 15 HBr/5 H_{2}, 15 HBr/5 CH_{4}, and 15 HBr/5 Ar discharges. The etching rates are all generally slow, and have the same trend for each different semiconductor in that the HBr additive produces faster rates than H_{2} which in turn is faster than Ar addition. The role of the CH_{4} is primarily to aid removal of group III species (X = Ga, In, or Al) by formation of volatile species of the form CH_{x}X_{y}m, where n = 1-3 and m is probably unity (17-21). These species appear to be more readily removed than the group III bromides. For the latter, the BR_{x} has a far greater probability of forming a volatile compound at 81°C, whereas GaBr_{3}, GaBr_{2}, InBr_{3}, and InBr_{2} boil at 27°C and 66°C, respectively (InBr_{2} sublimes) (1). These values, while not always a reliable indicator of etch rates since there is the volatility under ion-enhanced conditions that is important, are all higher than their Cl substituted counterparts. We stress however that the vapor pressures are to be used as qualitative guides only. The role of the H_{2} is to enhance removal of the volatile group V species as PH_{3}, AsH_{3}, or SbH_{3} (17-21), and these appear to be somewhat more volatile than their counterparts PBr_{2}, PBr_{3}, AsBr_{3}, and SbBr_{3} under our conditions. This trend is indeed borne out by a consideration of the melting points: PBr_{2} (106°C) and PBr_{3} (173°C) vs. PH_{3} (~88°C), AsBr_{2} (221°C) vs. AsH_{3} (~55°C), and SbBr_{3} (280°C) vs. SbH_{3} (~17°C) (1). The vapor pressures for these species show a similar hierarchy. The predominant role of the Ar is to enhance the ion bombardment component of the etching, and as the dc bias, and hence the energy of the incident ions, is increased, the etch rate also increases, as expected. Of the Ga-based materials, the etch rates increase in the order AlGaAs < GaSb, whereas for the In-based semiconductors it increases in the order InAlAs < InP < InAs < InSb-InGaAs. Rather high dc biases are needed to initiate etching for all of the materials relative to C-based mixtures where even 10-20 V will cause etching of the Ga-based semiconductor (~80 V for In-based under similar flow rates, 20 scm, and pressure 1 mTorr) (13) and CH_{4}/H_{2}
mixtures where the In-based materials will etch at ~40 V (InAlAs requires ≥120 V) and Ga-based materials at ≥80 V (27). The requirement for high dc biases is certainly a disadvantage in terms of utility for etching electronic devices because of the introduction of damage to the semiconductor and possible mask erosion during longer plasma exposures.

Features etched into GaAs (top and bottom left), InAs (top right) and InP (bottom right) with 15 HBr/5 CH₄, 1 mTorr, –250 V dc, 150 W (microwave) discharges.

Fig. 2. SEM micrographs of features etched into GaAs (top and bottom left), InAs (top right), and InP (bottom right) with 15 HBr/5 CH₄, 1 mTorr, –250 V dc, 150 W (microwave) discharges.

Fig. 3. SEM micrographs of features etched into InSb in 1 mTorr, –250 V dc (top left) or –350 V dc (bottom left), 150 W (microwave) 15 HBr/5 Ar discharges. At right are micrographs of InGaAs etched in 15 HBr/5 H₂, 150 W, –250 V dc plasmas at 20 mTorr (top right) or 1 mTorr (bottom right).

Fig. 3. SEM micrographs of features etched into InSb in 1 mTorr, –250 V dc (top left) or –350 V dc (bottom left), 150 W (microwave) 15 HBr/5 Ar discharges. At right are micrographs of InGaAs etched in 15 HBr/5 H₂, 150 W, –250 V dc plasmas at 20 mTorr (top right) or 1 mTorr (bottom right).

Fig. 3. SEM micrographs of features etched into InSb in 1 mTorr, –250 V dc (top left) or –350 V dc (bottom left), 150 W (microwave) 15 HBr/5 Ar discharges. At right are micrographs of InGaAs etched in 15 HBr/5 H₂, 150 W, –250 V dc plasmas at 20 mTorr (top right) or 1 mTorr (bottom right).

In Fig. 3 we show SEM micrographs from InSb etched in HBr/Ar discharges at 1 mTorr pressure, 150 W of microwave power, and –250 V dc bias (top left) or –350 V bias (bottom left). While the surface morphology is quite smooth in the former case, some degree of surface roughening is evident at the higher bias. This is most likely a result of the preferential sputtering of Sb, leaving the surface In-rich. This is a common occurrence with In-based binary semiconductors (28). The right hand side of Fig. 3 shows SEM micrographs of features etched into InGaAs with HBr/H₂ discharges with –250 V dc bias at a pressure of
ternary onset near 0.1 mTorr. The results for InAlAs with HBr/Ar discharges are shown in Fig. 4. The etching rate is sensitive to changes in microwave power, with a threefold increase observed as the power is increased from 75 to 150 W. The etch rate is also sensitive to the gas composition, with a decrease of 20% observed when the HBr/Ar ratio is decreased from 1:5 to 1:2. The etching rate is insensitive to the gas pressure, which is consistent with the absence of STM features etched into InAlAs with 150 W microwave power and either -250 (top) or -400 V (bottom) dc bias. In both cases the etched surface morphologies are smooth and indicate that ternary materials are more resistant to preferential sputtering of the group V element than binaries such as InAs, InSb, and InP. This is evident from a comparison of the InAlAs results with those from InSb in the previous figure and also from the micrograph at the bottom of Fig. 4, which shows InP etched in 1 mTorr, 150 W (microwave), -400 V dc HBr/H₂ discharge. In this case there are In droplets evident on the surface due to the preferential loss of P. With a combination of high bias (-400 V) and high pressure (20 mTorr), the HBr/H₂ etching produces sputtering of the resist mask and undercutting of the feature sidewalls leading to the sidewall profile shown at the top right of Fig. 4.

The dependence of semiconductor etching rates in HBr/H₂ and HBr/CH₄ discharges (150 W microwave power, -200 V dc bias) are shown in Fig. 5. For GaAs and AlGaAs, the etch rates show little change with pressure in the range 1-20 mTorr, indicating that the etching is not reactant-limited for these materials under these conditions. For GaSb, InGaAs, InP, InAs, and InSb, the etching rates increase at higher pressures as more active Br, H, and CH₃ species are supplied to the semiconductor surfaces. By contrast, the etch rate of InAlAs decreases at the higher pressures, even though the dc bias is left constant. This may be due to an increase in coverage of the surface with gas molecules which impede release of volatile etch products, particularly those of the Al.

The dependence of etching rate for each of the materials on applied microwave power is shown in Fig. 6. In all cases the etching rates increase as the respective discharges become more dissociated at the higher microwave powers. Based on preliminary measurements of the average electron densities 4 cm downstream from the baseplate of the microwave source using a plasma density monitor, the typical electron density increased from \(10^{11}\) to \(8 \times 10^{11}\) cm\(^{-3}\) in a 15 HBr/5 Ar, 1 mTorr discharge when the microwave power was increased from 100 to 700 W. As more active species are incident on the surface at higher microwave powers, the etching rates also increase.

The benefits of operating at high microwave powers must, however, be balanced against the effect on the resultant etched surface morphology. The Ga-based materials appear relatively insensitive to the introduction of surface roughness at high microwave powers. The left-hand side of Fig. 7 shows features etched into GaAs with HBr/H₂ discharges (1 mTorr, -200 V dc) at either 500 (top) or 20 mTorr (bottom).
150 W (bottom). In both cases the surfaces are quite smooth. By contrast, the In-based materials, with the exception of InAlAs, generally displayed rougher surfaces at high power. The right-hand side of Fig. 7 shows InGaAs surfaces after etching in HBr/H₂ discharges (1 mTorr, -200 V dc) at either 150 (top) or 500 W (bottom). Based on our past experience (21, 26) and that of others (24-33), in the effects of hydrogen-containing plasmas on In-containing compounds, we ascribe this surface roughening to the preferential loss of As from the material. This was confirmed by AES analysis, which showed enrichment of In and Al to a depth of ~160 Å in the sample of Fig. 7. This roughening is evident from short plasma exposures for high microwave powers and not, we believe, due to heating of the surface and subsequent evaporation of the group V species. Similarly, thermal bonding of the samples directly to the water-cooled cathode did not prevent the surface roughening. We estimate the temperature of our sample to be ≤80°C at all times for thermally unbounded sections and ≤40°C for those bonded to the cathode, based on fluoro-optic probe measurements.

Further examples of the effects of high microwave power levels on the surfaces of binary materials, InP and InAs, are shown in the SEM micrographs of Fig. 8. In both cases the samples were etched in 20 mTorr, -200 V, 15 HBr/5 H₂ discharges with 500 W of microwave power. The combination of undercut, due to the higher pressure, and roughening, due to the preferential loss of P or As, leads to very poor etch characteristics. Similar results were obtained with both HBr/CH₄ and HBr/Ar discharges.

Figure 9 shows AES surface scans and depth profiles from GaAs samples etched in 1 mTorr, -200 V, 150 W (microwave) 15 HBr/5 H₂ or HBr/5 CH₄ discharges for 15 min, as well as comparable data from an unetched GaAs control sample. Under these conditions there are no significant changes caused to the GaAs surface by the dry etching. For these moderate bias and microwave power levels there is no preferential loss of As, and there are no Br-containing species remaining on the surface. This is somewhat surprising given the relatively low etch rates with the HBr-based mixtures, in that one might expect to find Br-containing compounds remaining on the surface. However these compounds might only be found for very low bias conditions, for which we have no AES data. Moreover, the CH₄-containing plasma does not add significant carbon contamination to the GaAs surface. Indeed, the HBr-based etching is quite clean relative to some gas mixtures (e.g., CF₅Br or CCl₃F₂ with additives) which are proven to polymer deposition.

Similar data for InP samples etched under the same conditions are shown in Fig. 10. Once again, the etching is remarkably clean, with no Br-containing species detected by the Auger analysis. In the case of HBr/H₂ dry etching, however, there is a slight deficiency of P present to a depth of ~100 Å. This again is most likely due to preferential removal of P by active hydrogen from the discharge. This could be countered by altering the HBr/H₂ ratio of the gas.
mixture to reduce the amount of free hydrogen in the plasma.

Changes in the optical quality of the semiconductors as a result of HBr-based dry etching were examined by room temperature PL measurements. Figure 11 shows PL spectra from GaAs and InP samples before and after a 15 min exposure to 1 mTorr, -250 V, 150 W discharges of 15 HBr/5 H2 or 15 HBr/5 CH4. In the case of the GaAs, the dry etching reduces the luminescent efficiency of the material for both mixtures. The decrease however is less for the H2 addition to the HBr. The most likely explanation for this is that there is a greater relative concentration of atomic hydrogen available in this case to passivate some of the deep levels created by ion bombardment of the GaAs near-surface region. This is a common feature of experiments in-

Fig. 8. SEM micrographs of features etched into InP (top, left and right) or InAs (bottom, left and right) in 15 HBr/5 H2 20 mTorr, 500 W (microwave), -200 V dc discharges.

Fig. 9. AES surface and depth profiles of GaAs samples before and after etching in 1 mTorr, -200 V dc, 150 W (microwave) discharges of 15 HBr/5 H2 or 15 HBr/5 CH4.

Fig. 10. AES surface and depth profiles of InP samples etched under the same conditions as in Fig. 9.
Fig. 11. Room temperature PL spectra from GaAs and InP samples etched in 1 mTorr, −250 V dc, 150 W (microwave) discharges of 15 HBr/5 H₂ or 15 HBr/5 CH₄ for 15 min.

Forward and reverse I-V characteristics from Au contacted, n-InP Schottky diodes after etching for 15 min prior to contact deposition in 1 mTorr, −250 V dc, 150 W (microwave) discharges of 15 HBr/5 H₂ or 15 HBr/5 CH₄.

Forward and reverse I-V characteristics from Au contacted, n-InP Schottky diodes after etching for 15 min prior to contact deposition in 1 mTorr, −250 V dc, 150 W (microwave) discharges of 15 HBr/5 H₂ or 15 HBr/5 CH₄.

Fig. 12. Forward and reverse I-V characteristics from Au contacted, n-InP Schottky diodes after etching for 15 min prior to contact deposition in 1 mTorr, −250 V dc, 150 W (microwave) discharges of 15 HBr/5 H₂ or 15 HBr/5 CH₄.

Fig. 13. Carrier profiles in n-type GaAs etched for 15 min in 1 mTorr, −150 V dc, 200 W (microwave) discharges of 15 HBr/5 CH₄, 15 HBr/5 H₂, or 15 HBr/5 CH₄.
causes only a minor change. The greater effect present in the first two cases appears to be a result of the more significant hydrogen passivation of the Si donors in the material, as one would expect due to the relatively greater amount of hydrogen available (33). These results are consistent with both the PL and I-V measurements described earlier.

TEM cross-sectional micrographs from InSb samples etched in either HBr/H₂ (top and bottom left) or HBr/CH₄ (top and bottom right) discharges at the same pressure (1 mTorr), dc bias (-250 V), and microwave power (400 W) are shown in Fig. 14. The low-resolution images at top show that, as expected, the surface morphology is much smoother with the HBr/CH₄ mixture under these condi-
tions. The lattice images at bottom show that there is no perceptible disorder visible at this resolution in either sample. Usually we do not observe defects visible by TEM in dry etched samples unless the dc bias during the plasma exposure was \(-350\) V. The oxide thickness is \(30-40\) Å in the case of the HBr/CH₄ etched sample, consistent with the value found by AES analysis. An expanded view of the lattice-image of this InSb sample is shown in Fig. 15. Again, there is no visible disorder introduced by the dry etching.

**Summary and Conclusions**

The etch rates of III-V semiconductors in HBr-based discharges are quite slow under the conditions needed for smooth anisotropic etching. Relatively high self-biases are needed to initiate etching with any of the three mixtures (HBr/Ar, HBr/He, and HBr/CH₄) we investigated. At high dc biases, the binary In-based materials show surface roughening due to preferential sputtering of the group V element, and at high microwave power levels the surfaces of all the In-based semiconductors (except InAlAs) become rough. For these materials, the HBr/CH₄ mixture provides smooth etching over the widest range of conditions. Changes in the electrical and optical properties of the semiconductors are generally not as severe as might be expected at the high (-250 V) dc biases used in many of our experiments because of the passivation of deep-levels by hydrogen from the discharges.

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