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Inductively Coupled Plasma Etching of III-V Antimonides in BCl_3/Ar and Cl_2/Ar

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Abstract

Inductively coupled plasma (ICP) etching characteristics of GaSb and AlGaAsSb have been investigated in BCl_3/Ar and Cl_2/Ar plasmas. The etch rates and selectivity between GaSb and AlGaAsSb are reported as functions of plasma chemistry, ICP power, RF self-bias, and chamber pressure. It is found that physical sputtering desorption of the etch products plays a dominant role in BCl_3/Ar ICP etching, while in Cl_2/Ar plasma, the chemical reaction dominates the etching. GaSb etch rates exceeding 2 μm/min are achieved in Cl_2/Ar plasmas with smooth surfaces and anisotropic profiles. In BCl_3/Ar plasmas, etch rates of 5100 Å/min and 4200 Å/min are obtained for GaSb and AlGaAsSb, respectively. The surfaces of both GaSb and AlGaAsSb etched in BCl_3/Ar plasmas remain smooth and stoichiometric over the entire range of plasma conditions investigated. This result is attributed to effective removal of etch products by physical sputtering. For a wide range of plasma conditions, the selectivity between GaSb and AlGaAsSb is close to unity, which is desirable for fabricating etched mirrors and gratings for Sb-based mid-IR laser diodes.

Introduction

Semiconductor lasers emitting in the 2-5 μm wavelength range are potential sources for various applications including, laser radar (LADAR)[1], chemical sensing[2], and infrared countermeasures (IRCM).[3] The predominant materials in devices operating at these wavelengths are the group-III antimonides, from which broad area laser diodes emitting from 1.6–4.5 μm have been demonstrated.[4–6] Fabrication of more sophisticated device structures requires well-controlled etch techniques to achieve reliable pattern transfer. Compared to wet chemical etching, dry etching provides a more anisotropic profile, greater repeatability, improved etch depth control, and higher aspect ratio. Dry etching is especially important for patterning III-Sb's with high Al concentration because wet etching of these materials yields slow etch rates and rough surfaces.[7] Since wet etching of AlGaAsSb commonly leaves a heavily oxidized surface, only single-step etching is achievable with any predictability. There is surprisingly little in the literature concerning dry etching of III-Sb compounds except the binaries, InSb and GaSb. Pearton, *et. al.*, have investigated electron cyclotron resonance (ECR) etching and reactive ion etching (RIE) of InSb and GaSb using various chemistries.[8–11] GaSb etch rates of 5000Å/min, 3000Å/min, and 2500Å/min were reported in Cl_2/Ar, BCl_3/Ar, and CH_4/H_2/Ar ECR discharges, respectively. This paper presents results of inductively coupled plasma (ICP) etching as an attractive alternative to ECR techniques for patterning antimonides.

Compared to ECR sources, it is believed that ICP sources are easier to scale-up, more economical in terms of cost and power requirements, and have more mature automatic tuning technology.[12] ICP plasmas are formed in a dielectric vessel encircled by an inductive coil into which RF power is applied. The alternating electrical field between the coils induces a strong alternating magnetic field that confines electrons and enhances ion density. Anisotropic etch profiles are obtained by superimposing an RF-induced DC self-bias on the sample to control the ion energy independent of the ion density. In this paper, ICP etch results of GaSb and AlGaAsSb in BCl_3/Ar and Cl_2/Ar plasmas are presented. The etch rate and selectivity are reported as a function of ICP power, DC self-bias, plasma chemistry, and chamber pressure.

Experiment

The samples used in this study are undoped GaSb and undoped $Al_{0.9}Ga_{0.1}As_{0.07}Sb_{0.93}$ grown lattice-matched to GaSb by molecular beam epitaxy (MBE). Etching is performed in a load-locked Plasma-Therm SLR 770 ICP reactor with the ICP source operating at 2 MHz. Energetic ion bombardment is provided by superimposing a DC self-bias (13.56 MHz) on the sample. For all experiments, the automatic matching network is set to the DC self-bias control mode that varies the input RF power to match the set point of the DC self bias. Etch gases are introduced through an annular region at the top of the chamber. All samples are mounted using vacuum grease on an anodized Al carrier that is clamped to the cathode and backside-cooled with He gas. The temperature of the electrode is set to 10 °C. Samples are patterned with AZ 4330 photoresist and etched for 2.5 min in the plasma. The etch depth is measured using a Dektak stylus profilometer after the photoresist is removed. Surface morphology, anisotropy, and sidewall undercutting are evaluated with a scanning electron microscope (SEM). Unless otherwise mentioned, the baseline etch parameters are 750 W ICP power, 100 V DC self-bias, 2 mTorr chamber pressure, 25 sccm BCl_3 or Cl_2 flow rate, and 5 sccm Ar flow rate.

Results

Fig. 1 shows ICP etch rates for GaSb and AlGaAsSb and etch selectivity between them as a function of DC self-bias in a BCl_3/Ar discharge. Etch rates increase near linearly with increasing DC bias voltage, indicating physical sputtering desorption plays a significant role in BCl_3/Ar ICP etch of these materials. Etch rates of GaSb and AlGaAsSb rise by a factor of 2.5 as DC bias increases from 50 to 300 V. This result is attributed to enhanced ion bombardment and sputter desorption of etch products due to higher ion energies at higher DC bias. The simultaneous increase in the GaSb and AlGaAsSb etch rates yields a relatively constant etch selectivity between the two materials of approximately 1.34 ± 0.12.

In Fig. 2, ICP etch rates and the selectivity are plotted as a function of percent composition of BCl_3 in the chemistry. The total flow rate of BCl_3 and Ar is held constant at 30 sccm. The data shows a relatively small variation in the GaSb etch rate over the entire range of BCl_3 composition. This observation suggests that in a BCl_3/Ar ICP mixture, the effect of a higher concentration of reactive Cl on the GaSb etch rate (at a higher BCl_3/Ar ratio) is compensated by the effect of a lower Ar ion sputtering rate. To further verify this assumption, an ICP etch of GaSb and AlGaAsSb in BCl_3/N_2/Ar is carried out to decouple the physical and chemical component of the etching mechanism. Generally, adding N_2 to a BCl_3/Ar plasma enhances the dissociation of BCl_3, resulting in a higher concentration of reactive Cl and, consequently, a higher etch rate.[13][14] Based on a previous study of GaN ICP etching in BCl_3/N_2 which shows a peak GaN etch rate at 40% N_2,[15] a chemistry of 15 sccm BCl_3/10 sccm N_2/5 sccm Ar was chosen to etch GaSb. An etch rate of 5536 Å/min is obtained for GaSb and 4428 Å/min for AlGaAsSb, much higher than the rates obtained in the 25 sccm BCl_3/5 sccm Ar ICP discharge shown in Fig. 2. This outcome indicates that the etching is limited by the reactive Cl supply. It also confirms that the physical and chemical component are balanced in the BCl_3/Ar ICP etch, producing a relatively small variation in the GaSb etch rate with changes in BCl_3 composition. In contrast, the AlGaAsSb ICP etch rate shows a significant increase when BCl_3 is first introduced into the pure Ar plasma. The etch rate grows by a factor of more than 5 when the BCl_3 concentration is raised from 0 to 33%, indicating that BCl_3 removes Al more efficiently than Ar due to the high volatility of $AlCl_3$ etch product. A further increase in the BCl_3 concentration shows little effect on the etch rate of AlGaAsSb. The etch selectivity between GaSb and AlGaAsSb is ~ 6:1 for pure Ar plasma and drops to ~ 1.2:1 as BCl_3 is introduced into the plasma.

The etch rates and selectivity in BCl_3/Ar as a function of ICP source power are displayed in Fig. 3. The rates rise significantly with increasing ICP power since a larger ICP power creates more chlorine radicals and a higher ion flux, enhancing both the chemical and physical etch components of the process. The selectivity decreases from 4.2 to 1.3 as the ICP power is increased from 250 W to 500 W, then stays relatively constant for higher powers. The higher selectivity at low ICP power is attributed to a low etch rate of AlGaAsSb due to fewer chlorine radicals.

The dependence of the etching on the process pressure is shown in Fig. 4. An initial etch rate increase as pressure rises from 1 mTorr to 5 mTorr is followed by a decrease at pressures greater than 5 mTorr. The initial increase is attributed to a higher reactive Cl concentration at higher pressure, implying a reactant limited etch regime at low pressure. The decrease in the high pressure range is caused by lower kinetic energy of the ions due to more collisions, suggesting a sputtering desorption limited etch mechanism. The selectivity remains low for the entire pressure range that is studied. Fig. 5 shows scanning electron micrographs of GaSb and AlGaAsSb after patterning in a BCl_3/Ar plasma. For a wide range of conditions, the etch yields smooth surfaces, anisotropic profiles, and roughly equal etch rates between GaSb and AlGaAsSb. This process is most favorable for making dry etched facets for laser mirrors or deep gratings.

In contrast to the BCl_3/Ar ICP etch of III-V antimonides which shows physical sputtering dominated etch characteristics due to a limited reactive Cl supply, the Cl_2/Ar ICP etch mechanism is strongly dominated by chemical reaction. Due to the surface roughness of AlGaAsSb etched in Cl_2/Ar plasmas, an accurate measurement of etch depth on these samples is unachievable; therefore, only GaSb etch rates in Cl_2/Ar plasmas are available. In Fig. 6, the GaSb etch rate is plotted as a function of DC bias. Note that the GaSb etch rate is much higher in a Cl_2/Ar plasma than in a BCl_3/Ar mixture for similar process conditions, suggesting a much higher concentration of reactive Cl in a Cl_2 plasma as compared to a BCl_3 plasma. Despite a significant change in DC bias from 50 to 200 V, the rate increases only ~20%. As the DC bias is increased further to 300 V, the etch rate actually decreases slightly. This weak dependence of etch rate on DC bias indicates that the physical sputtering is not a dominant factor in Cl_2/Ar ICP etching. The decrease in etch rate at 300 V may be related to sputtering desorption of reactive species before they have time to react with the III-V antimonides at the surface.

Fig. 7 shows the etch rate as a function of %Cl_2 in a Cl_2/Ar chemistry. The etch rate increases monotonically with increasing Cl_2 percentage as would be expected from the increased reactive chlorine density in the chamber. Notice that the GaSb etch rate is substantially enhanced (by a factor of > 6) as the Cl_2 percentage increases from 0 to 100%, indicating that the chemical reaction dominates the ICP etching of GaSb in the Cl_2/Ar chemistry. In Fig. 8, the etch rate of GaSb is plotted as a function of ICP source power. The etch rate increases significantly with increasing ICP power up to 750 W, caused by a higher concentration of reactive species in the plasma and higher ion flux. However, the etch rate remains relatively constant above 750 W, possibly due to saturation of the reactive species at the surface or creation of an adsorption-limited regime. In Fig. 9, the GaSb etch rate is shown as a function of process pressure. At high pressure, the mean free path decreases and the collisional frequency increases. This causes a loss of ion kinetic energy and, typically, lowers the etch rate as a result of a decreased physical sputtering effect. However, the GaSb etch rate in Cl_2/Ar increases monotonically up to 10 mTorr. This data indicates that the physical sputtering has little effect on the etch rate, that the chemical reaction completely dominates the process, and that the etching is probably reactant-limited.

Fig. 10 shows scanning electron micrographs of GaSb etched in Cl_2/Ar ICP discharges at different Cl_2 percentage concentrations and pressures. The etched surface remains smooth for all the samples etched at 2 mTorr (a, b, and c). A smooth and vertical sidewall is obtained at 10 sccm Cl_2 and 20 sccm Ar. However, as the Cl_2 concentration increases, sidewall roughness and undercutting is observed due to lateral etching. This effect becomes more obvious in Figure 10 (d), which shows the surface and profile of GaSb etched at 10 mTorr. At high pressure, the sidewall profile is severely undercut and poorly defined because of a lower mean free path, collisional scattering of ions, and increased lateral etching of GaSb. Surface roughness is also observed at 10 mTorr.

Conclusions

ICP etching characteristics of GaSb and AlGaAsSb have been studied in BCl_3/Ar and Cl_2/Ar plasmas. The Cl_2/Ar ICP etching of GaSb exhibits a strong chemically dominated etching behavior. A GaSb etch rate as high as 4.6 μm/min is achieved. In BCl_3/Ar plasmas, due to a limited reactive Cl supply, the etching mechanism is dominated by ion bombardment and physical desorption of etch products. Smooth, anisotropic, and non-selective etching of GaSb and AlGaAsSb has been achieved in BCl_3/Ar ICP discharges, which is desirable for making dry-etched facets as laser mirrors. Maximum etch rates of 5100 Å/min and 4200 Å/min are obtained for GaSb and AlGaAsSb, respectively. Compared to Cl_2/Ar, BCl_3/Ar ICP etching yields much smoother etched surfaces on AlGaAsSb, indicating that BCl_3 removes the Al in AlGaAsSb more efficiently, possibly due to improved sputtering (higher mass ions) or the O_2 gettering effect of BCl_3 which reduces surface oxidation.

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Figure Captions

Fig. 1. DC bias dependence of the GaSb and $Al_{0.9}Ga_{0.1}As_{0.07}Sb_{0.93}$ etch rate and selectivity in a BCl_3/Ar plasma. Unless otherwise noted the plasma conditions are: 750 W ICP power, 2 mTorr pressure, 25 sccm BCl_3 or Cl_2 flow rate, 5 sccm Ar flow rate, and 100 V DC self-bias.

Fig. 2. Etch rates and selectivity of GaSb and $Al_{0.9}Ga_{0.1}As_{0.07}Sb_{0.93}$ as a function of % BCl_3 in a BCl_3/Ar plasma. The total gas flow rate is 30 sccm.

Fig. 3. Etch rates and selectivity versus ICP power in a BCl_3/Ar plasma.

Fig. 4. Etch rates and selectivity of GaSb and $Al_{0.9}Ga_{0.1}As_{0.07}Sb_{0.93}$ as function of process pressure in a BCl_3/Ar plasma.

Fig. 5. Scanning electron micrographs of GaSb and $Al_{0.9}Ga_{0.1}As_{0.07}Sb_{0.93}$ features etched in BCl_3/Ar plasma. The plasma conditions are: 750 W ICP power, 2 mTorr pressure, 25 sccm BCl_3 flow rate, 5 sccm Ar flow rate, and 100 V DC self-bias.

Fig. 6. The etch rate of GaSb in a Cl_2/Ar plasma vs. DC self-bias.

Fig. 7. GaSb etch rate as a function of %Cl_2 in the Cl_2/Ar plasma.

Fig. 8. The GaSb etch rate versus ICP power in a Cl_2/Ar plasma.

Fig. 9. The process pressure dependence of the GaSb etch rate in a Cl_2/Ar mixture.

Fig. 10. Scanning electron micrographs of GaSb etched in Cl_2/Ar ICP discharges at (a) 2 mTorr, 10 sccm Cl_2/20 sccm Ar; (b) 2 mTorr, 20 sccm Cl_2/10 sccm Ar; (c) 2 mTorr, 25 sccm Cl_2/5 sccm Ar; (d) 10 mTorr, 25 sccm Cl_2/5 sccm Ar. The other etch parameters are 750 W ICP power and 100 V DC bias.

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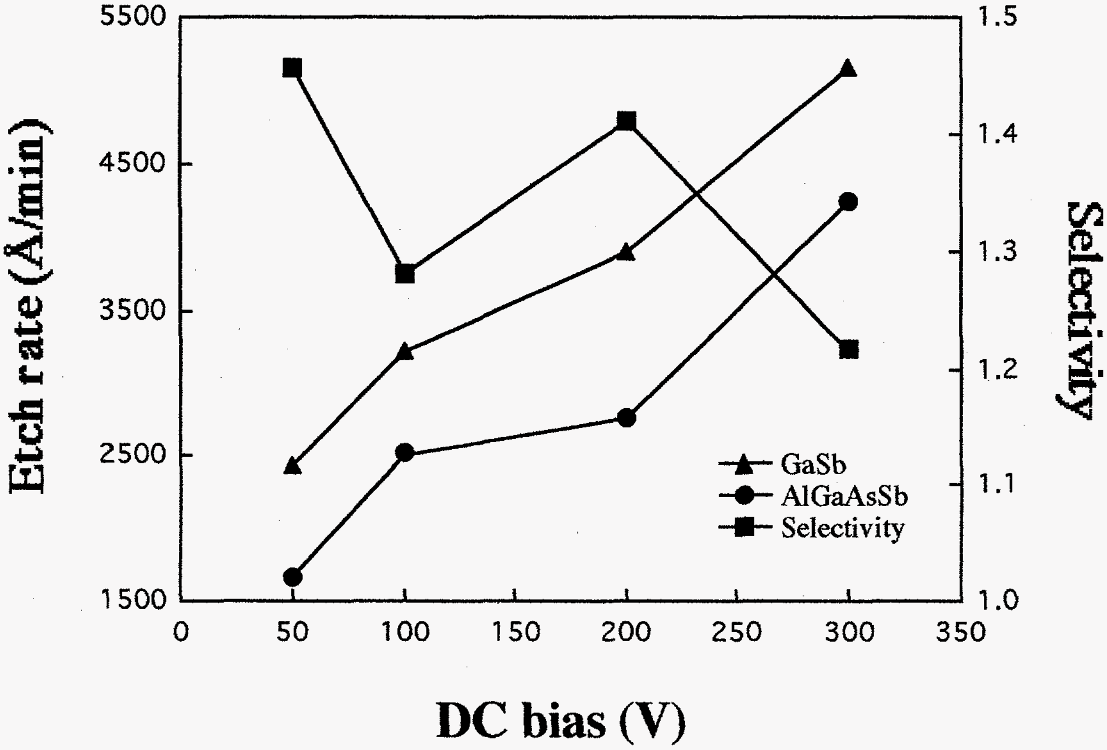
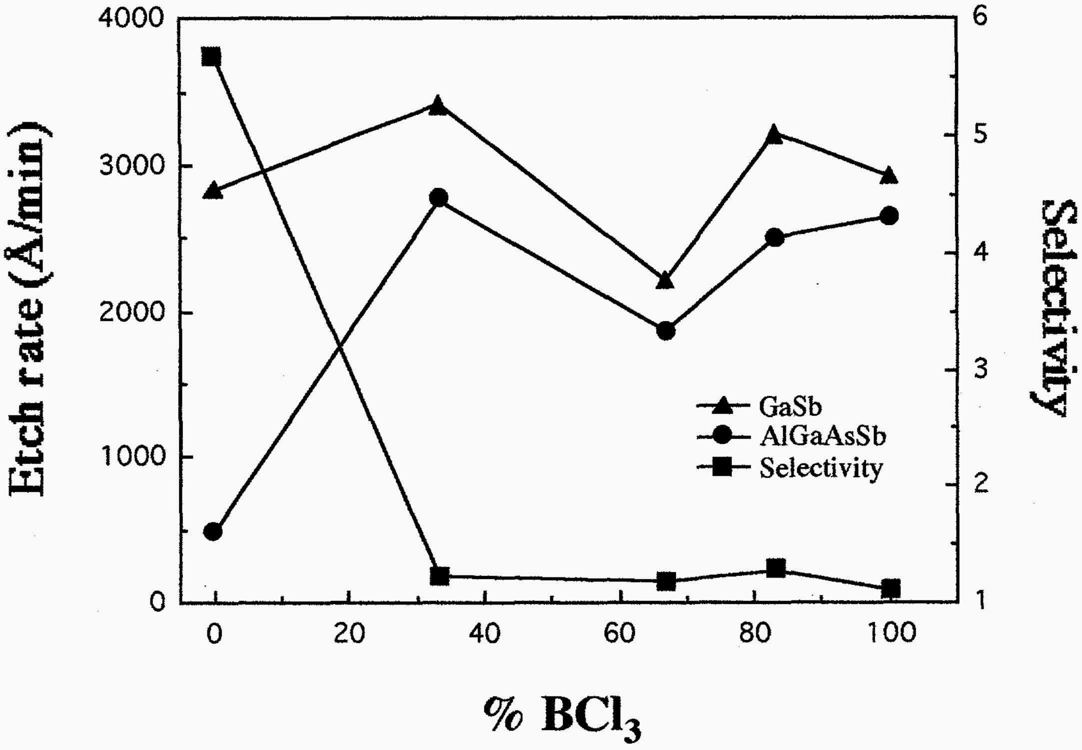
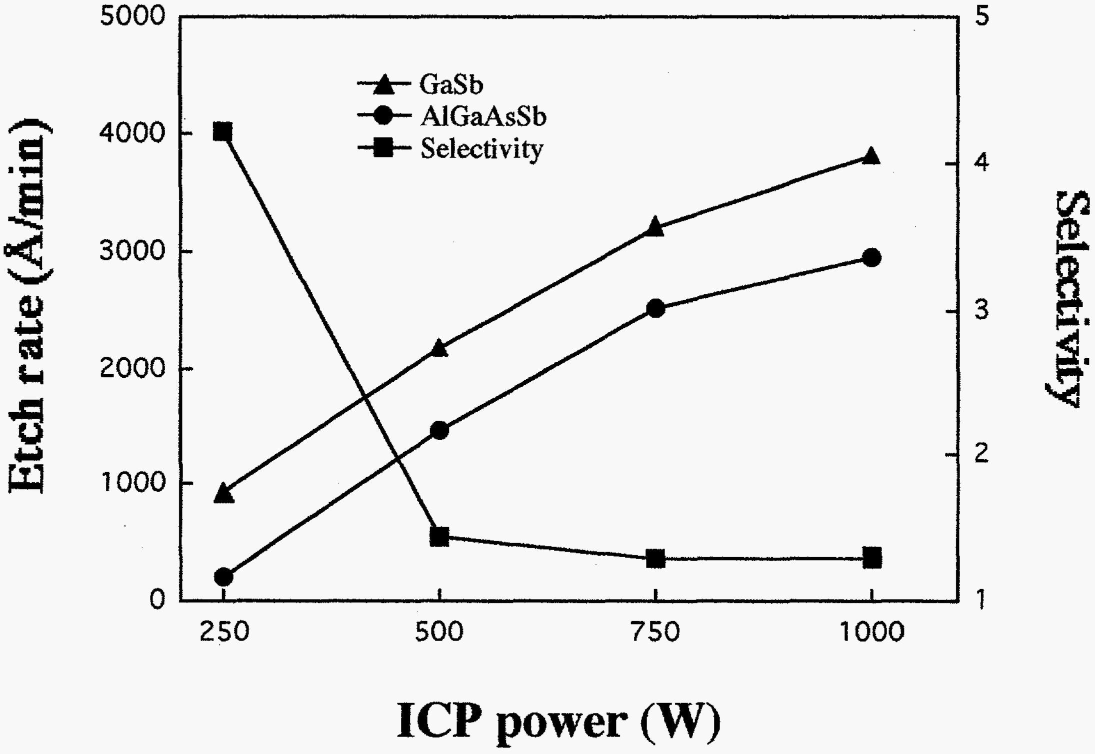
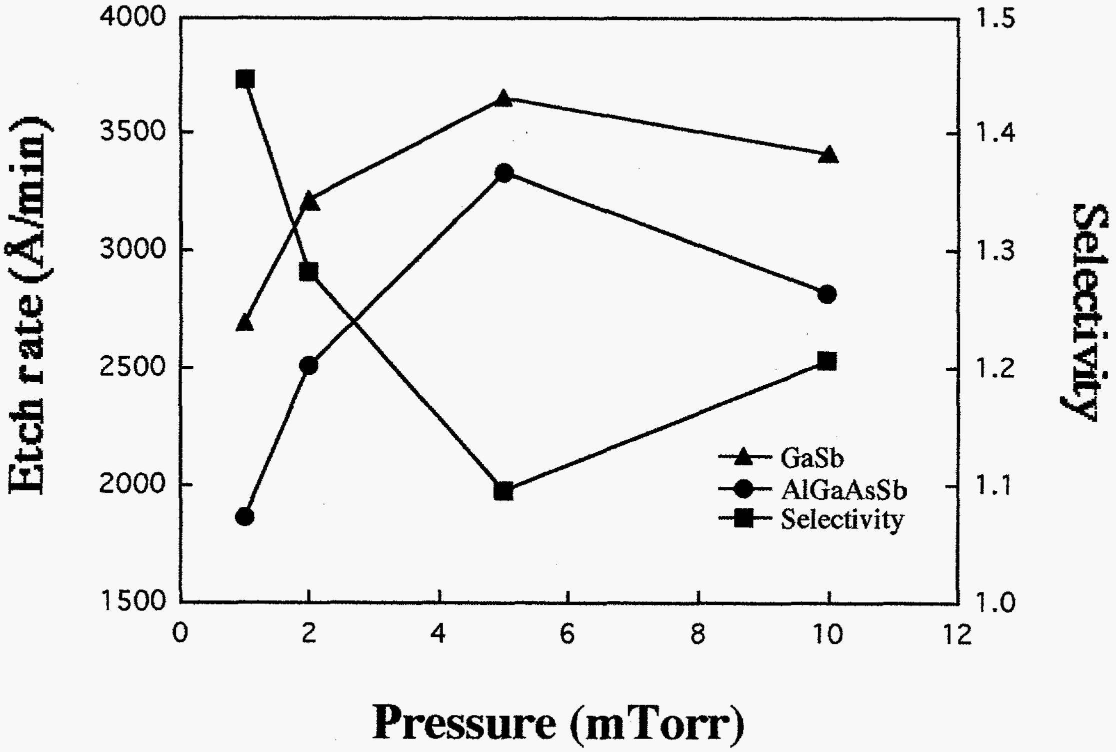

5500
4500
3500
2500
1500
Etch rate (Å/min)
1.5
1.4
1.3
1.2
1.1
1.0
Selectivity
0
50
100
150
200
250
300
350
DC bias (V)
GaSb
AlGaAsSb
Selectivity

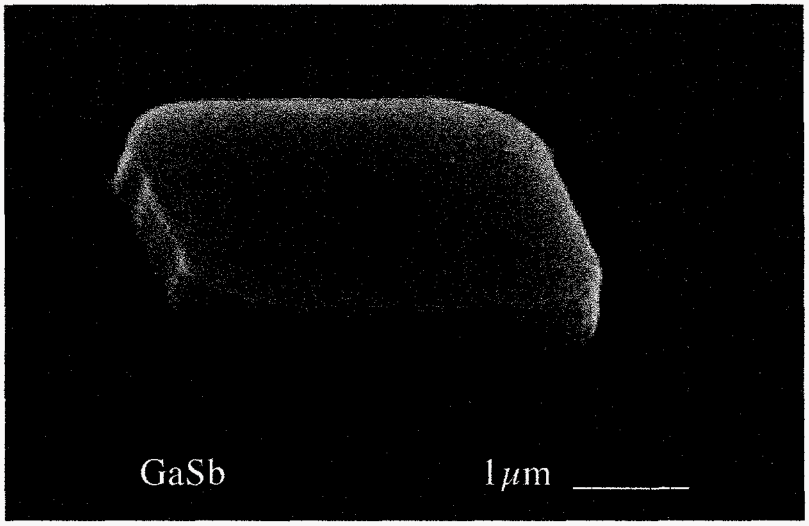

4000
3000
2000
1000
0
Etch rate (Å/min)
6
5
4
3
2
1
Selectivity
0
20
40
60
80
100
% BCl3
GaSb
AlGaAsSb
Selectivity



5000
4000
3000
2000
1000
0
Etch rate (Å/min)
GaSb
AlGaAsSb
Selectivity
5
4
3
2
1
Selectivity
250
500
750
1000
ICP power (W)



4000
3500
3000
2500
2000
1500
Etch rate (Å/min)
1.5
1.4
1.3
1.2
1.1
1.0
Selectivity
0
2
4
6
8
10
12
Pressure (mTorr)
GaSb
AlGaAsSb
Selectivity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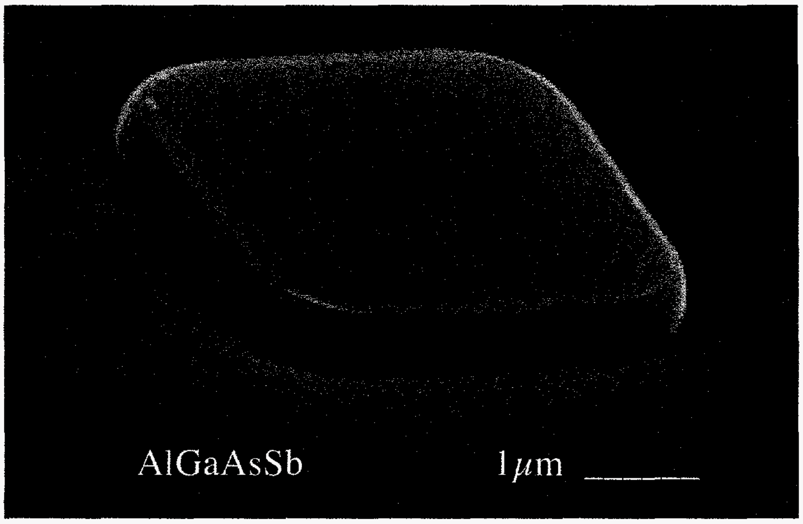
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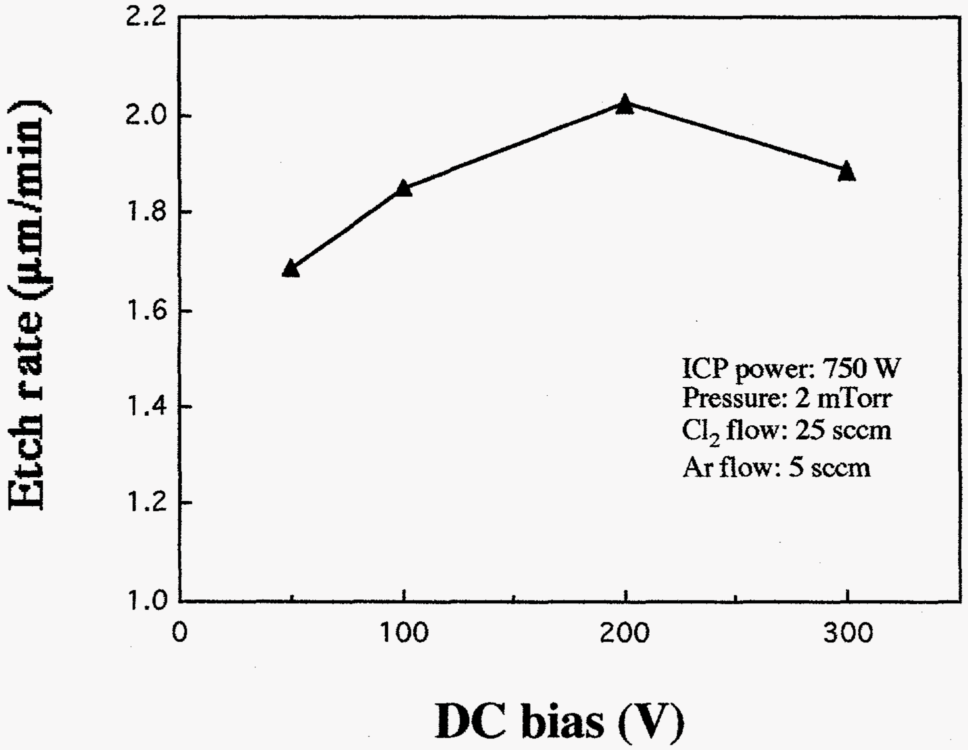
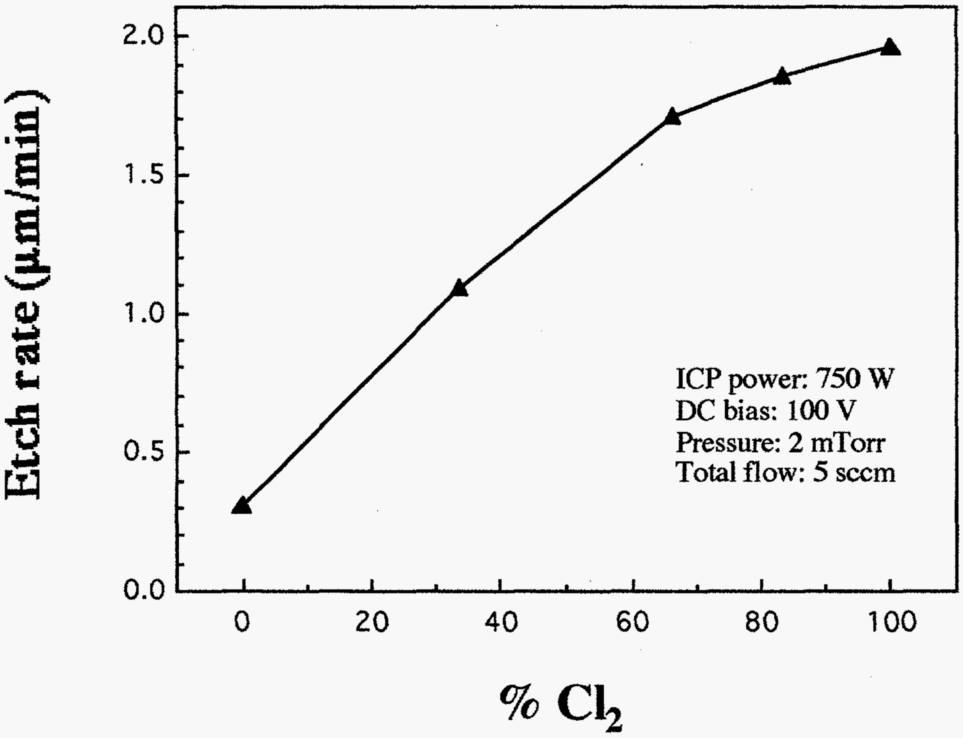


2.2
2.0
1.8
1.6
1.4
1.2
1.0
0
100
200
300
Etch rate (µm/min)
DC bias (V)
ICP power: 750 W
Pressure: 2 mTorr
Cl$_2$ flow: 25 sccm
Ar flow: 5 sccm


Etch rate (µm/min)
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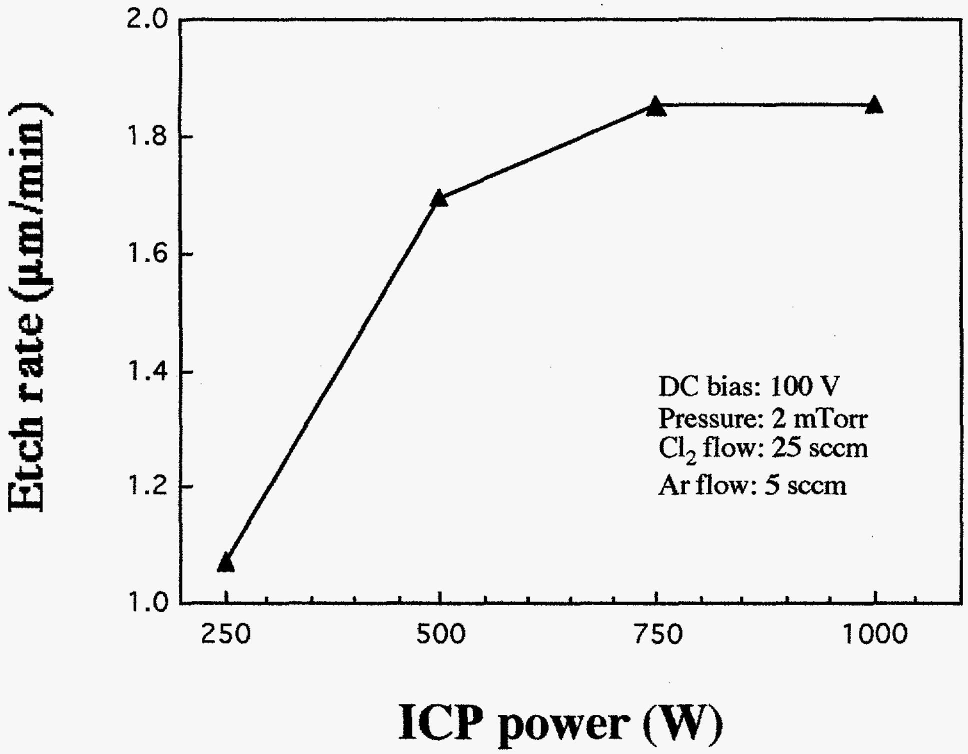
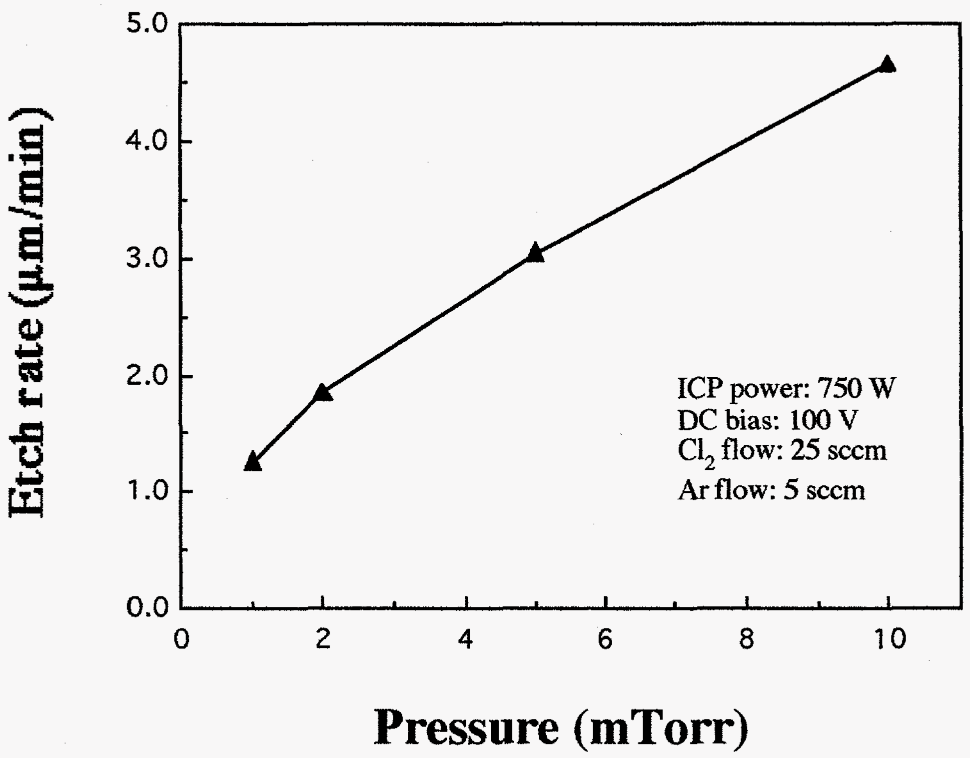
1.0
0.5
0.0
0
20
40
60
80
100
% Cl_2
ICP power: 750 W
DC bias: 100 V
Pressure: 2 mTorr
Total flow: 5 sccm


2.0
1.8
1.6
1.4
1.2
1.0
Etch rate (µm/min)
250
500
750
1000
ICP power (W)
DC bias: 100 V
Pressure: 2 mTorr
Cl_2 flow: 25 sccm
Ar flow: 5 sccm


Etch rate (µm/min)
Pressure (mTorr)
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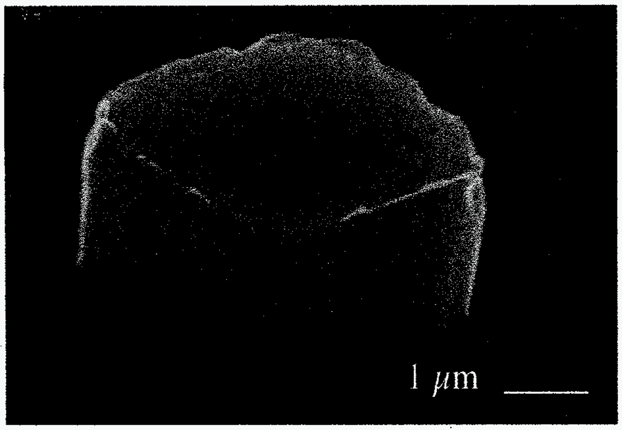
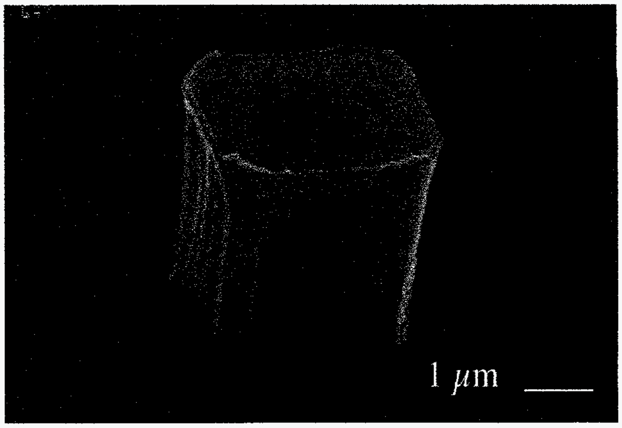
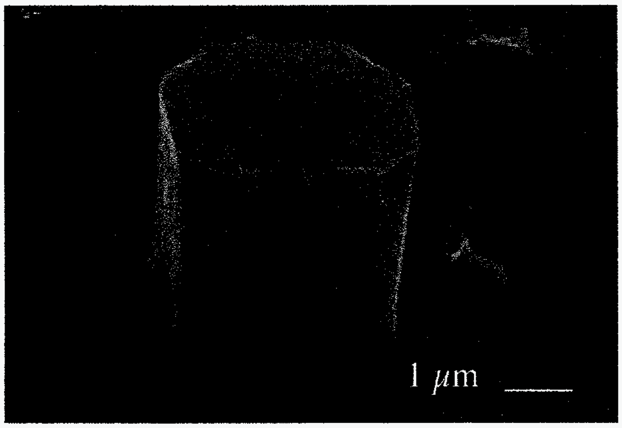
3.0
2.0
1.0
0.0
0
2
4
6
8
10
ICP power: 750 W
DC bias: 100 V
Cl$_2$ flow: 25 sccm
Ar flow: 5 sccm



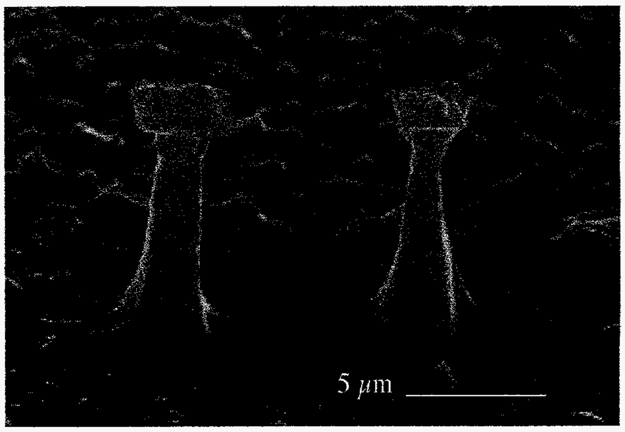
(a)



(c)



(b)



(d)