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BCl_3/Ar ICP Etching of GaSb and Related Materials for Quaternary Antimonide Laser Diodes

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Inductively coupled plasma (ICP) etching of GaSb, AlGaAsSb, and InGaAsSb using BCl_3/Ar plasma discharges was investigated for the fabrication of GaInAsSb/AlGaAsSb/GaSb laser diodes. Etching rates and selectivity were characterized as functions of gas flow ratio, accelerating voltage, and ICP source power, and the etching mechanism was discussed in detail. It is observed that the etch rate of GaSb and AlGaAsSb is much higher than that of InGaAsSb. The etched surfaces of GaSb, AlGaAsSb all have comparable root-mean-square roughness to the unetched samples over a wide range of plasma conditions; however, it is much rougher in etching of InGaAsSb. The selectivity between GaSb and AlGaAsSb was close to unity over the entire range of plasma conditions investigated, which is desirable for the fabrication of quaternary antimonide laser diodes.
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Antimonide-based semiconductor diode lasers emitting in the spectral range 2-5 μm are of considerable interest for a variety of applications, such as molecular spectroscopy, infrared countermeasures, and trace gas sensing. Quantum well structures with InGaAsSb wells and AlGaAsSb barriers are commonly used in most GaSb-based laser diodes.[1-4]

Compared to wet chemical etching, dry etch schemes are more attractive for device manufacturing due to the anisotropic profiles, increased etch uniformity, and reproducibility. Additionally, dry etching is especially important for patterning group III antimonides with high Al concentration, for wet etching of these materials yields slow etch rates and rough surfaces.[5] Pearton *et al.* have reported both reactive ion etching (RIE) and inductively coupled (ICP) plasma etching of GaSb in various chemistries, and obtained controllable etch rate of GaSb varying from hundreds of angstroms per minute to a few micrometers per minute.[6-12] However, there has been surprisingly little in the literature concerning dry etching of the quaternary antimonides. Recently, Peake *et al.* have reported the ICP-RIE etching of GaInAsSb and AlGaAsSb using pure BCl_3 gas for the fabrication of thermophotovoltaic (TPV) devices.[13] Etch rates of 2700 and 3000 Å/min were demonstrated for InGaAsSb and AlGaAsSb, respectively.

The structure of ridge-type InGaAsSb/AlGaAsSb multiquantum well laser diodes commonly contains the following layers: a p^+-GaSb cap layer, p^+-AlGaAsSb cladding, the undoped active region consisting of three or more InGaAsSb quantum wells, and AlGaAsSb quantum barriers incorporated in the undoped AlGaAsSb waveguide layers. In etching, we are supposed to etch away the cap and cladding layer, which is totally about 2 μm thick; therefore, it is critical to determine the etch conditions for appropriate etch rates and nonselective etching of GaSb and AlGaAsSb. Compared to other sources, ICP plasmas are easier to scale up, more economical, and allow a better control of energy and reactive species density. In addition, it is believed that ICP sources have more mature and convenient automatic tuning technology. In this paper, we report on ICP etching of GaSb, AlGaAsSb, and InGaAsSb in BCl_3/Ar plasma discharges. We only investigated the etching at relatively low ICP power ($\leqslant 400$ W) so that the etch rates were relatively slow and controllable for the fabrication of laser diodes. The research was aimed to understand the etch mechanism of the ICP etching process in BCl_3/Ar plasmas as well as provide reliable processing data for the fabrication of laser diodes. Optimum etching conditions are provided after analyzing the results.

Experimental

All the structures used in the experiments were grown by using a homemade type VI molecular beam epitaxy (MBE) machine. Elemental Al, Ga, In, As, and Sb are used as grown sources. The InGaAsSb and AlGaAsSb epitaxy layers were grown lattice-matched to GaSb substrates and nominally undoped. The samples were patterned with conventional AZ6809 photoresist. A loadlocked homemade ICP-98C dry etching system with the ICP source operating at 2 MHz was employed for the experiments. The flux of BCl_3 and Ar gases was monitored using a mass flow controller. A 13.56 MHz radio frequency (rf) power was supplied to the sample chuck, which is correlative with the dc self-bias. The samples were placed on a 4 in. silicon wafer, which was in thermal proximity contact with the lower water-cooled cathode with 200 mm diam.

Etching was performed with an ICP source power varied from 150 to 400 W and dc biases from −70 to −200 V (corresponding to rf power of approximately 30-100 W). The BCl_3 percentage in the gas flow was changed from 0 to 80% with the total gas flow rate of BCl_3 and Ar held constant at 20 sccm. The process pressure was held constant at 4 mTorr. Etch depth was measured by stylus profilometry, while atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to examine surface roughness and etch profile.

Results and Discussion

Figure 1 shows ICP etch rates for GaSb, AlGaAsSb, and InGaAsSb as a function of BCl_3 percentage (by flow) in BCl_3/Ar chemistry at fixed ICP source power (120 W), pressure (4 mTorr), and rf chuck power (40 W). The selectivity between GaSb and AlGaAsSb was also calculated and plotted in the figure. For each material the etch rate initially increases as more BCl_3 is added to Ar due to the increase in available atomic chlorine. The etch rates of GaSb show a relatively small variation when BCl_3 addition is greater than 30%, indicating that the effect of a higher concentration of reactive Cl on the GaSb etch is compensated by the effect of a lower Ar ion sputtering rate. Compared to GaSb, the AlGaAsSb etch rate shows a more significant increase when the BCl_3 concentration is raised from 10 to 40%, indicating that BCl_3 removes Al more efficiently than Ar due to the high volatility of the $AlCl_3$ etch product (boiling point 183°C). The decrease in etch rates of AlGaAsSb at higher percentage of BCl_3 is believed because the etching process may be limited by mass transfer of ions from the plasma bulk to the substrate surface. The etch selectivity between GaSb and AlGaAsSb is relatively constant, approximately 0.92 ± 0.10. The etch rates for InGaAsSb were much lower compared to the other two materials, mainly due to the relative low volatility of indium chlorides (with boiling points higher than 560°C). Etching for III-V compound semiconductors in high plasma densities is predominantly controlled by ion-assisted desorption of somewhat volatile products,[14] which means desorption of the etch products occurs prior to coverage of the etch surface. While the addition of BCl_3 increases, sputter desorption could be improved due to higher mass ions. In our experi-

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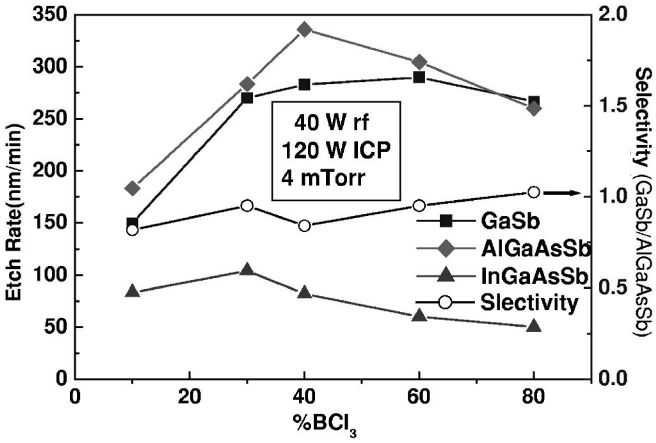

Figure 1. Etch rates of GaSb, InGaAsSb, and AlGaAsSb and selectivity between GaSb and AlGaAsSb as a function of BCl_3 concentration in BCl_3/Ar discharges (4 mTorr, 120 W source power, 40 W chuck power).

ments, the etch rates for InGaAsSb were quite insensitive to the change of BCl_3 concentration and decreased slightly at high BCl_3 concentration, indicating that the buildup of $InCl_3$ outweighs the ion-assisted desorption of the etch product at high BCl_3 addition so that the physical sputtering desorption of the etch products played a dominant role in the etching.

The effect of dc self bias (which controls ion energy) on the etch rates and the selectivity between GaSb and AlGaAsSb is shown in Fig. 2a. Because the bias controls the energy of ions impacting the sample surface, there should be a general tendency for increased etch rates due to the increasing dc bias voltage. However, in Fig. 2 we note that under all conditions examined the etch rates of both GaSb and AlGaAsSb showed small variation. The weak dependence of etch rate on dc bias indicates that the physical sputtering is not a dominant factor in etching under such conditions. It is also believed that in etching of GaSb and AlGaAsSb, the formation of the etch products is controlled to a greater extent by the initial bond breaking, and thus the etch rates are less a function of the efficiency of etch product desorption. The slight decrease in etch rates of GaSb and AlGaAsSb when the bias increased may be related to sputtering desorption of reactive species before they have time to react with samples. The etch rates for GaSb and AlGaAsSb are also close due to the high volatility of the etch products. The selectivity between GaSb and AlGaAsSb is also relatively constant of unity. Once again, the etch rates were much lower for InGaAsSb, due to the relative involatility of indium chlorides.

The etch rates and selectivity in BCl_3/Ar as a function of ICP source power are displayed in Fig. 2b. In our experiments, to avoid too high sample temperature in etching, which would probably deteriorate the photoresist mask and make it unachievable to measure the etch depth accurately, the ICP source power investigated didn't exceed 400 W. As the figure shows, the etch rates for all the materials increase monotonically with increasing the source power, mainly due to the higher concentration of chlorine radicals and higher ion flux to the substrate surface created by the increasing ICP power, which can enhance both the chemical and physical etch components of the process. The simultaneous increase in the etch rates of GaSb and AlGaAsSb also yields a relatively constant etch selectivity between the two materials of approximately 1.04 ± 0.08. The etch rates for InGaAsSb increased from 1600 to 7100 Å/min as the ICP power was increased from 150 to 400 W. It was observed that the surface morphology of the etched InGaAsSb could be improved by increasing the ICP power, mainly due to the more uniform evacuation of $InCl_3$ in higher ICP power; however, it is still relatively rough compared to the other two materials over the conditions we investigated.

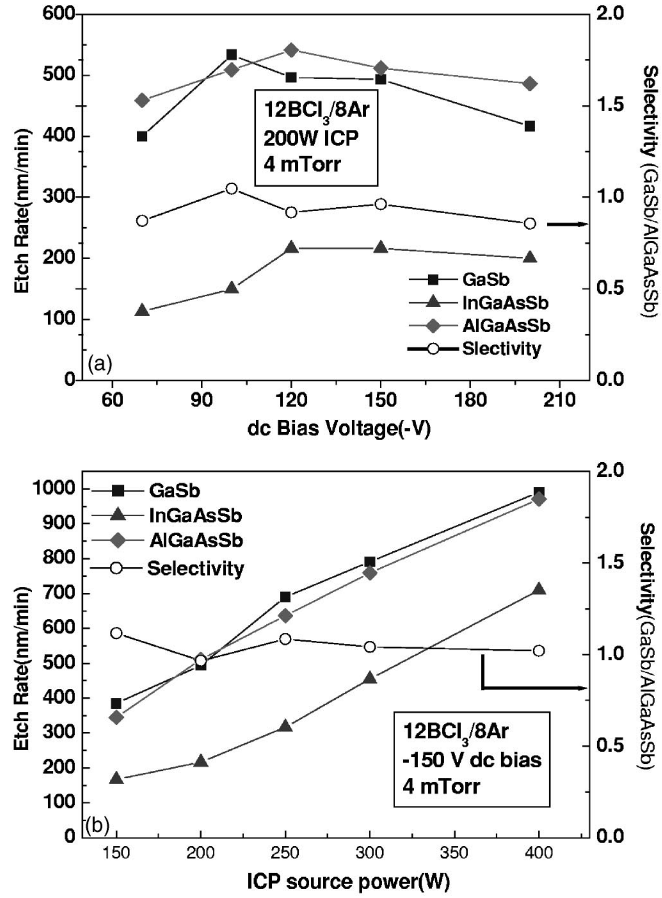

Figure 2. In 4 mTorr, 60% BCl_3 addition BCl_3/Ar discharges, etch rates of GaSb, InGaAsSb, and AlGaAsSb and selectivity between GaSb and AlGaAsSb (a) at different dc bias (200 W ICP power) and (b) at different ICP source power (−150 V dc bias).

Figure 3b-d shows the AFM scans results of the surfaces of GaSb, AlGaAsSb, and InGaAsSb etched with $12BCl_3/8Ar$ chemistries at 200 W ICP source power, −150 V dc bias, and 4 mTorr pressure. The AFM scan of the unetched GaSb sample was also shown in Fig. 4a for comparison. The lowest root-mean-square

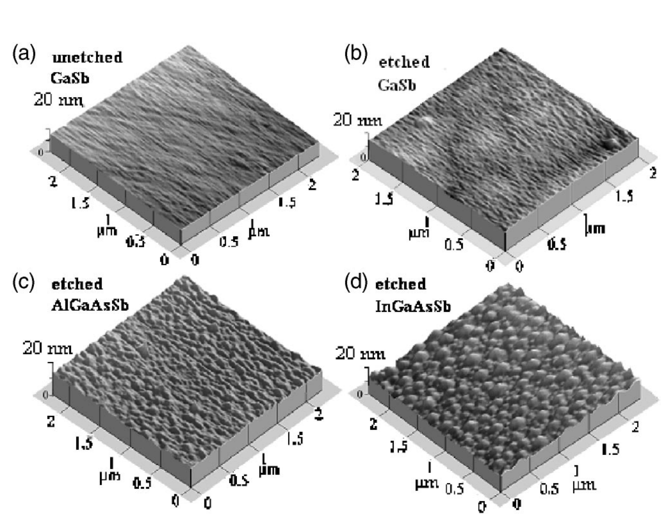

Figure 3. AFM scans for (a) unetched GaSb and (b) etched GaSb, (c) AlGaAsSb and (d) InGaAsSb after etching in $12BCl_3/8Ar$, 4 mTorr, 200 W source power, and −150 V dc bias ICP plasma.

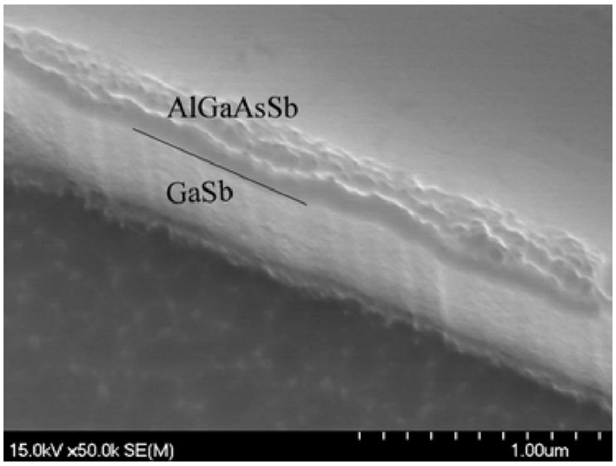

Figure 4. The SEM cross section of AlGaAsSb/GaSb heterojunction (top: AlGaAsSb layer, bottom: GaSb substrate) etched in BCl_3/Ar discharges (4 mTorr, 60% BCl_3 concentration, −150 V dc bias voltage, 150 W source power).

(rms) roughness of 0.72 nm was observed in etching of GaSb, fairly similar to the unetched sample (rms roughness 0.41 nm). The etching surface was also quite smooth for AlGaAsSb, with rms roughness of 1.27 nm. By contrast to the results for GaSb and AlGaAsSb, the surface of the InGaAsSb was much rougher with a resultant rms value of 4.53 nm for etch depth of only 1.1 μm. Note that the surface is full of little hillocks, presumably due to the low volatility of $InCl_x$ etch products and preferential loss of Sb. Additionally, it is assumed that a combination of In and Ga oxides on the initial surface could deteriorate the surface morphology after the etching.

The etch yields anisotropic profiles and relatively smooth surfaces for all the materials over a wide range of conditions. Because the etching rates of GaSb and AlGaAsSb are close, a nonselective etching of these two materials can be achieved. Figure 4 shows a SEM cross-sectional picture of a AlGaAsSb/GaSb heterojunction structure etched with 150 W ICP source power, −150 V dc bias voltage, 4 mTorr pressure, and 60% BCl_3 concentration. It is clearly shown that the surface is smooth and the sidewalls are vertical.

Conclusions

We have investigated ICP etching characteristics of GaSb, AlGaAsSb, and InGaAsSb in BCl_3/Ar plasmas for the fabrication of quaternary antimonide laser diodes. A relatively low ICP source power was applied in the experiments to obtain appropriate etch rates for the device fabrication. Etch rates of 4900 Å/min with rms roughness of 0.72 nm, 5100 Å/min with rms roughness of 1.27 nm, and 2100 Å/min with rms roughness of 4.53 nm were demonstrated for GaSb, AlGaAsSb, and InGaAsSb, respectively. Because the selectivity between GaSb and AlGaAsSb was close to unity over the entire range examined, we can use the same condition in etching of both materials, which is desirable for device processing. The rms surface roughness of AlGaAsSb and InGaAsSb is greater than that of the unetched samples but acceptable for our purposes.

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