

# Improvement of Surface Passivation Homogeneity of Gallium Antimonide by Bromination

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*Etching and sulfuring are equally important process during the surface sulfur passivation of gallium antimonide (GaSb). In this work, we described the effects of etching by certain proportion of bromine methanol solution instead of hydrochloric acid solution (acidification), which could lead to a improvement of surface passivation homogeneity of GaSb. The photoluminescence (PL) spectra and the atomic force microscope (AFM) morphology on GaSb are also indicated a good surface morphology.*

**Keywords** Bromine; methanol; etch; homogeneity

## 1. Introduction

Nowadays, progress in micro- and optoelectronics is closely linked to use of III–V compounds [1]. However, sometimes the full potential of III/V-based devices cannot be realized because of their surface properties. It is well known that many surface states causing high surface recombination velocity are generated upon contact of the surface of III–V semiconductors with air [2, 3]. Many methods of passivation of these surfaces have been investigated. The wet methods of sulphide passivation in sulphide solutions,  $(\text{NH}_4)_2\text{S}$  or  $\text{Na}_2\text{S}$ , have proved to be effective in reducing the density of surface states and correspondingly improving the dark current of mesa diodes [4–6].

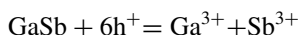
Few studies about the surface passivation homogeneity of GaSb. As our group [7] has previously reported, the peak intensity of passivated surface on GaSb by PL mapping is 0.258 Volt and the standard of deviation of is 178.5%. Previous research shows that surface is etched by hydrochloric acid [8]. On the rough position, two dangling Ga bonds (sometimes even three dangling bonds) and Cl bonds can form highly-charged gallium chloride, so the surface is rich in-antimony, the defect position of the surface start to dissolve. From this position, the Ga layer is gradually being dissolved, exposed Sb layer [9]. The rich-Sb and rich-Cl layer can affect the homogeneity of the surface. In order to avoid this problem and obtain better surface homogeneity, we replaced hydrochloric acid with

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bromine methanol[10]. When GaSb is dipped into the electrolyte, the Fermi level which separated at the interface is leveled, electronic charges transfer from the semiconductor to the electrolyte, the reaction equation is:



$\text{Ga}^{3+}$ ,  $\text{Sb}^{3+}$  reacted with  $(\text{OH})^-$  to form  $\text{Ga}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  in the electrolyte. Oxide is resolved by acid or alkali, as etching solution, can form soluble haloid and compound. In the bromine methanol solution, methanol provided  $(\text{OH})^-$ , while bromine isn't only an oxidant, but also a solvent [11].

In this paper, we discuss the etching with bromine methanol solution in certain proportion in order to improve the surface passivation homogeneity. Meanwhile, the PL spectra and the AFM morphology on surface passivation homogeneity of GaSb are also investigated.

## 2. Experimental Details

Commercial GaSb substrates (tellurium doped to the concentration  $(7-8) \times 10^{17}/\text{cm}^3$ ) were used in this study. All the samples were degreased successively in trichloroethylene, acetone, and methanol for 10 min, and we separated the samples into two groups. The first group named bromination was dipped in the bromine methanol solution in various proportion (concentration of methanol), namely 0%, 25%, 50%, 75% and 100% for 60 s at room temperature for the purpose of obtaining the optimum measuring of PL peak intensity. In order to make comparison, the second group named acidification dipped the samples in the hydrochloric acid solution for 60 s at room temperature [12, 13].

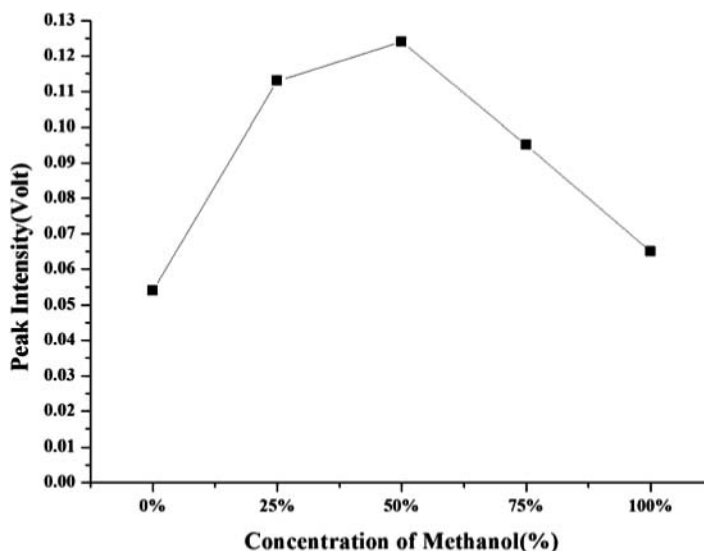
All the samples were treated with ammonium sulphur 8%  $[(\text{NH}_4)_2\text{S}]$  (pH = 9) for various time, namely 60 s, 120 s, 180 s, and 240 s at  $50^\circ$ . After the sulfur treatment, the samples were dried with nitrogen gas.

The PL measurements were performed using a Nanometrics RPM2000 PL spectrometer with a resolution of 0.2mm. The excitation source was the frequency doubled Nd:YAG laser (532 nm) with 100 mW. The AFM measurements were performed using a CSPM5500 AFM with contact mode.

## 3. Result and Discussion

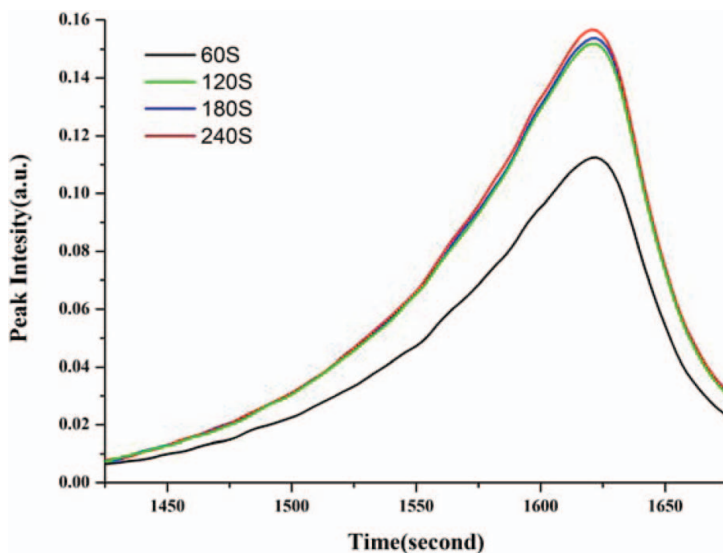
Figure 1 showed that the PL peak intensity of GaSb surfaces etched by bromine methanol is significantly higher about 2–3 times than by pure bromine or methanol solution. Since the pure bromine is lack of  $\text{OH}^-$  which methanol provides, while the pure methanol is lack of bromine as strong oxidizer, so both kinds of the pure solution had few reaction with GaSb. It will be seen from this that bromine methanol played an important role in the etching process. And the best concentration of the highest peak intensity is the 50% methanol solution.

Figure 2 showed the wavelength of PL peaks of all passivated samples were the same as untreated samples (1623 nm). The peak intensities of passivated samples for 120 s, 180 s and 240 s are 0.112 Volt, 0.114 Volt. and 0.116 Volt, much stronger than untreated sample. With the time increased the PL peak intensity increased smoothly. The samples were passivated to be obtained the higher PL peak intensities, while the high PL peak intensities demonstrated that there were complete passivation on the samples surface.

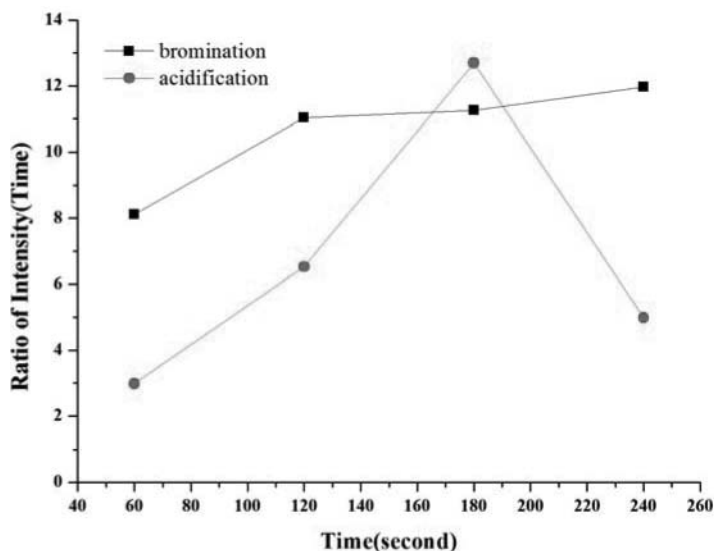


**Figure 1.** PL peak intensities of GaSb surfaces at room temperature for various bromine methanol solution proportion ( $\text{CH}_3\text{OH}\%$ ). The concentration of methanol is 0% (bromine water 3%), 25%, 50%, 75% and 100% (methanol (analytical pure)).

Figure 3 showed the acidified samples reached the highest peak intensity for 180 s, but for 60 s, 120 s, 240 s, the peak intensity is much lower. It suggests that the time control of sulfur passivation for the acidified samples needs more accurately. But the bromide samples reached almost the highest peak intensity for 120 s, and change very little with passivation



**Figure 2.** The PL Spectra of brominated samples after surface passivation for 60 s, 120 s, 180 s and 240 s.



**Figure 3.** The ratio of the peak intensities of bromide samples and acidified samples with the passivated time for 60 s, 120 s, 180 s and 240 s, compared with untreated sample.

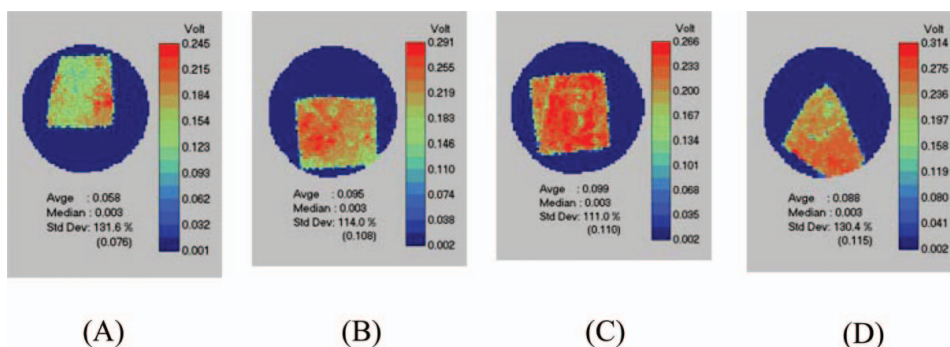
time, the curve became evenness. It suggests that during the time of 120 s–240 s, bromided samples had reached the highest peak intensity.

Respect of the passivation time, reducing the peak intensities of acidified samples is attributed to the scattering by the polycrystalline surface film reconstructed with sulfur due to the over passivation time. It is due to the excess of the sulfur atoms acting as trap centers for the GaSb surface at room temperature [14].

Similarly, we suppose that the bromided samples also have the over passivation time as well as acidified sample. In this study we won't look for the time. The time control of 120 s is enough for the bromide sample in passivation process.

Photoluminescence PL spectra is a carrier-photon process, and is closely related with the surface properties, PL spectral intensity is influenced by the material of the micro-defects, impurities and nonradiativenonradioactive centers of influence, and. The intensity can be measured quantitatively. PL mapping homogeneity is an important parameter. It is a scanning photoluminescence spectroscopy based on the photoluminescence spectrum. PL peak energy homogeneity can accurately display the luminescence peak and impurity luminescence and the luminous intensity distribution around the sample surface in different energy (wavelength) band edge[15]. In this work, The PL intensity homogeneity were used to present the distinguish of PL intensity caused by different density of the surface states at sample surface.

Figure 4 shows that the PL mapping of bromide samples with different passivated time. The average peak intensity can reach 0.245, 0.291, 0.266 and 0.314 Volt, respectively. Figure 4(A) shows that for the time of 60 s, the passivated time bromide samples are go along at the beginning of sulfur passivation process. Most parts of bromide sample are not passivated by sulfur yet, while is too short that only a small part of the bromide sample is being passivated. With the passivated time increased, most parts of Fig. 4(B), 4(C) and 4(D) show that the other three bromide samples have finished sulfur passivation procesprocess. (shown in Fig. 4(B), 4(C) and 4(D))s. As shown in the spectra, most parts of bromide



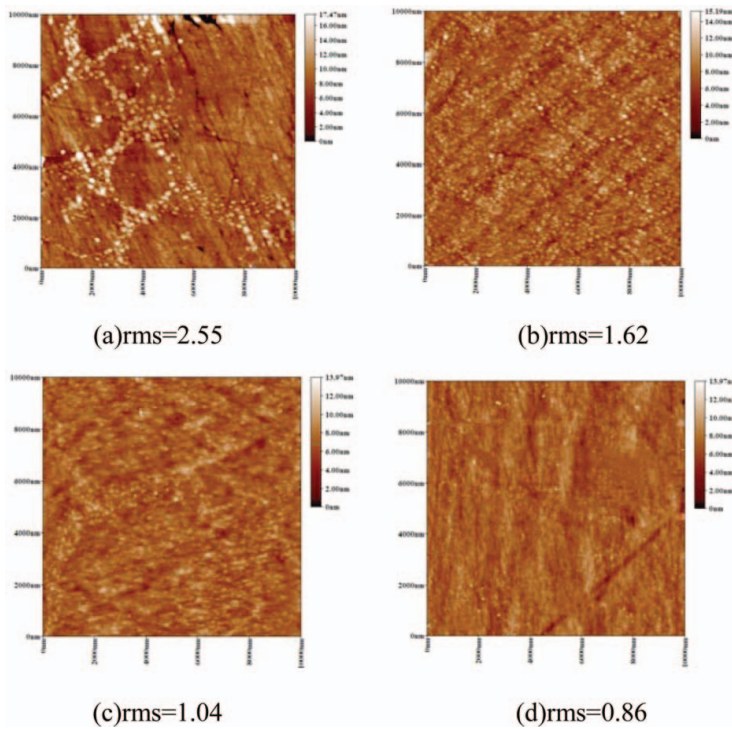
**Figure 4.** PL mapping figure, given the light uniformity of the overall sample cleaned with a Br: methanol = 1:1 solution then etched in ammonium sulfide, the GaSb corrosion time is 60 s(A), 120 s(B), 180 s(c) and 240 s(d).

samples are passivated, except for the edges. Among the three bromide samples, Fig. 4(C) shows the best uniformity. The most part of the samples turned red (from 0.215 Volt to 0.266 Volt), the sample standard deviation of the sample within the whole region reached 111.0%. Figure 4(D) shows the intensity reached the highest voltage (0.314 Volt) at 240 s, but the standard deviation decrease to 130.4%.

For comparison, we used the PL mapping to test the passivated samples with etching by HCl. Two samples showed the best results: one was the PL peak intensity reached 0.258 Volt and the standard deviation reached 178.5%. The other one was the PL peak intensity reached 0.187 Volt and the standard deviation reached 124.8%.

We compared the bromide results with the data in our group's previous report work. The peak intensity is increased by nearly 68% at the same level of the PL intensity homogeneity. The standard deviation decreased about 38% in the same peak intensity level. On the one hand, since during the bromination, the reaction on the etched surface generates only  $\text{Ga}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$ , and both of them dissolved in solution, so we can obtain the pure GaSb surface which improves the efficiency of the passivation. On the other hand, the PL peak intensities are at the same level for the various passivation time. It illustrates that rate of passivation is smooth and easy to control and observe.

Figure 5 shows the AFM morphology of the passivated samples. Figure 5(A) described the sample passivated for 60 s is not homogeneous. In the discussion of Combining with the PL spectra result, due to the lack of short etching time, so the oxide layer on the surface still existed. It intensively affected the increase of PL peak intensity and the reduction of the density of surface states. (B) showed that the surface began to deteriorate with the extension of etching time. The oxide layer on the surface was begun to be removed. (C) showed that the corrosion on the surface was obvious. And the flatness and the homogeneity were both also satisfactory. Figure 5(D) also showed the homogeneous and flatter surface. In order to obtain the ideal surface morphology, each passivated sample was washed with deionized water to remove the sulfide and sulfur crystals on the sample surface. Compared with (A), (B) and (C), (D) sample completely removed the oxide layer and the sulfide and sulfur crystals, so shows the highest PL peak intensity. The removal degree of the oxide layer depends on the corrosion extent of passivated samples. The samples for 180 s and 240 s show the better PL homogeneity due to their better corrosion extent.



**Figure 5.** Measured by the AFM surface roughness of the sample icon, cleaned with a Br: methanol = 1:1 solution then etched in 8% ammonium sulfide, PH = 9 at 55°. (a)Etch time is 60 s. (b)120 s, (c)180 s and (d)240 s selecting a template.

#### 4. Conclusion

In summary, GaSb surfaces are brominated by bromine methanol (Bromine: methanol = 1:1) firstly, then passivated by ammonium sulfide for more than 120 second. The PL intensity is 10.3 times stronger than the untreated GaSb. The standard deviation is 111.0%, and PL peak intensity is 0.266 Volt. Compared with the GaSb surface treated by acidification with HCl, etching with bromine methanol can improve the homogeneity of passivation, which obtain a homogeneous surface morphology (the standard deviation reduced by 38%). Moreover, the passivation time is more controllable in bromination. All the results implied that bromination will open the door to GaSb surface passivation used in optoelectronic devices.

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