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# *Study on Neutral Sulphur Passivation of Gallium Antimonide Surface*

Ning An, Guojun Liu,* Zhipeng Wei,** Rui Deng, Xuan Fang, Xian Gao, Yonggang Zou, Mei Li, Xiaohui Ma

National Key Laboratory of High Power Semiconductor Lasers
Changchun University of Science and Technology
email: *gjliu@cust.edu.cn, **zhipengwei@gmail.com

*Abstract*—**We here report a new passivation method, with neutral sulphur, (NH4)2S, to modify the GaSb surface. The optical and chemical properties of GaSb surface before and after neutral passivation are investigated using x-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) mapping. Neutral (NH4)2S passivation led to 20 times enhancement in photoluminescence (PL) intensity, lower oxide content, and a less amount of elemental Sb than the untreated sample. The passivtion effect results from the significant reduction in surface states due to the formation of Ga and Sb sulfide species. Compared to the regular alkaline (NH4)2S treatment, surface passivation intensity and homogeneity are both improved. Our studies also indicate the neutral sulphur passivation treated surface is much more stable in air for at least 48h.**

***Key word-GaSb surface passivation; neutral (NH4)2S ;XPS ; PL***

## I. INTRODUCTION

GaSb, as an important III–V compound semiconductor material, has been used for the fabrication of a wide variety of electronic and optoelectronic devices, as examples, midinfrared lasers, photodiodes and infrared detectors, etc[1]. During the past decade, much effort has been focused on the epitaxial structure design and growth. However, the procedure of chemical preparation of GaSb surface is still far from satisfaction in terms of surface morphology. Moreover, the chemical processing of GaSb surface is particularly difficult because of its high reactivity, small band gap, and limited solubility of the reaction products, compared to gallium arsenide and indium phosphorus [2, 3].

For many semiconductor device applications, it is important to fabricate surfaces and interfaces with a low level of defect electronic states, located in the band gap of the material [4]. However, E.Papis pointed out that GaSb has a very highly chemical reactive surface, being easily oxidized by atmospheric oxygen with the formation of native surface oxides in several nanometers thickness [5.6]. And the oxides would like to react with GaSb to generate the excess Sb which always acts as non-radiative centers [7]. It always leads to the high surface recombination velocity and large leakage currents that hinder the enhancement of devices' performance. So it is extreamely important to find effective ways to remove the GaSb native oxides and reduce atomic defects.

Based on our previous research [6], we found (NH4)2S is a good choice as passivation agent, as the speed of passivation process can be easily controlled. During (NH4)2S treatment, the sulphur atoms strongly chemisorbed and occupied the active surface sites, because of its lower heat of formation. And after passivation, the amount of defects which act as the recombination centers and scattering centers of carriers will decrease, the properties of oxide/GaSb interface will be improved notably. In our previous research, after (NH4)2S passivation, the relative PL spectrum intensity of the passivated sample can be notably enhanced, and the luminescence homogeneity and surface morphology are also improved [7]. However, the long-term stability of passivation effect is not satisfactory. The effect of passivation could disappear in only a few hours. We supposed the reason for that is the sulfides formed by passivtion is too thin. The Sulfur atoms are not bonded strongly and Oxygen atoms would easily react with GaSb surface again. So how to form thicker sulfides is the key problem.

Usually, (NH4)2S solution is an alkaline agent, with a PH of 9. However, the sulfides of GaSb are soluble in the alkaline solution. We changed the (NH4)2S PH to get the neutral (NH4)2S solution to conduct the passivation of GaSb surface in this work. The properties of passivation are investigated by X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and photoluminescence mapping (PL mapping). Additionally, the long-term stability of passivation is also investigated.

## II. EXPERIMENTAL

Commercial Te doped GaSb substrates, (100) oriented, to the concentration (7-8) E+17 /cm3 were used in this experiment. Prior to sulfur treatment, the untreated GaSb was cleaned by standard surface cleaning steps consisting of degreasing in hot acetone, ethyl alcohol, and DI water. The sulfides we used in surface passivation experiment are neutral ammonium sulfied (8% [(NH4)2S](ph=9) and alkaline ammonium sulfur 8% [(NH4)2S] (PH=7) at 50℃. In order to get neutral solution, HCl was dipped into alkaline ammonium sulfide until the PH turned to 7. X-ray Photoelectron Spectroscopy (XPS) was used to test the effectiveness of neutral passivation. Thermo ESCALAB 250 spectrometer, equipped with Al Kα source at energy of 148606eV. PL measurements were carried out by a Nanometrics RPM2000 photoluminescence spectrometer with a resolution of 0.2mm. AFM test was also performed to characterize the surface morphology. AFM micrographs of the samples were obtained from CSPM5500, in the contact mode.

Previous experimental results show the optimum passivation time for alkaline (NH4)2S is around 180s [6]. So throughout the present experiment, we fixed the passivation time at 180s to compare the passivativion effects of two different solutions.

## III. RESULTS AND DISCUSSION

The possible reactions taking place in the process of (NH4)2S passivation are as follows：

(NH4)2S+H2O→NH4OH+NH4SH (1)

EOx+NH4SH+H2O → ESy+NH4OH+H2 (2)

NH4SH+GaSb+H2O → Gax3Sy3+Sbx4Sy4+NH4OH +H2 (3)

From the above equations, we can conclude that: first, sulfuration breaks the Ga-O and Sb-O bonds. Then it forces these electrons of dangling bonds into the conduction band and surface states. The energy needed can form the chemical bond between sulfur atoms and Ga or Sb. It means the O-bonds on the surface are replaced, at least partly, by S-bonds after sulphur passivation.

However, for the regular alkaline (NH4)2S passivaion, the native oxide layer on the GaSb is first removed , then the S ions bond to Ga and Sb atoms, and finally form sulfides. Simultaneously, the sulfides can also be solved in the alkaline solutions. When the balance of these two reactions is reached, a very thin sulfide layer is formed on the GaSb surface, probably only one monolayer. Sometimes even only a small fraction of the O-bonds on the surface is replaced by S-bonds after sulfur passivation [11]. Although the dangling bonds at the surface decrease the surface recombination center density, we can not achieve the desired results due to the solubility of the sulfides. So how to effectively repress the solubility is a challenge. We decreased the PH value of the alkaline solution until turned to7 by dipping HCl into alkaline (NH4)2S. A thicker sulfides can be formed. And we performed XPS test before and after the neutral passivation to investigate the effectiveness of treatment, as shown in Fig.1 and Fig.2.

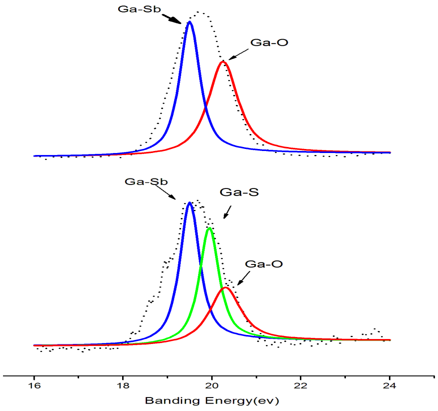

Figure 1. XPS of Ga3d before and after neutral passivation

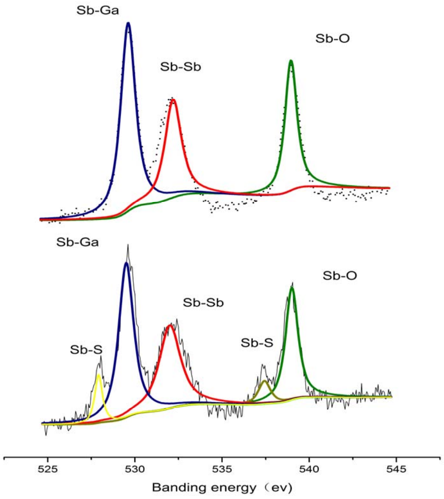

Figure 2. XPS of Sb3d before and after neutral passivation

XPS analysis can indicate the element composing content and chemical conformation through measuring the produced photo energy of samples [12]. Figure 1 and Figure 2 illustrate the XPS of Ga3d and Sb 3d spectra obtained before and after the neutral passivation. The peak components of the spectra after numerically deconvoluted, the Ga–Sb bond in GaSb is at a binding energy of 19.1eV and the Ga–O bond in $Ga_2O_3$ at a binding energy of 20.6 eV [13]. Similar structure appears after neutral $(NH_4)_2S$ treatment, as shown in Fig 1 exhibited, as in the untreated case, with only changes in various peak

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Identify applicable sponsor/s here. If no sponsors, delete this text box. (sponsors) intensities, as noted subsequently. The $Ga_2O_3$ signal after passivation was drastically reduced compared to untreated sample and a new peak at a binding energy of 19.7eV became visible associated with the formation of Ga–S [18]. As Fig.2 clearly shown the Sb 3d spectra were deconvoluted into the Ga–Sb bond in GaSb (528.9 ev), the Sb–O bond in $Sb_2O_5$ (537.1 eV), and the Sb–Sb bond in elemental Sb (532eV) [15]. Due to the neutral passivation, the amount of oxides and excess Sb was decreased. And two new peaks at binding energies of 528.1 eV and 537.8 eV appeared. It can be readily identified to Sb–S species [16]. Both the Ga and Sb peaks shift to lower binding energy as a result of the passivation. This is apparently caused by a shift in the surface Fermi level towards the valence band [17].

From the above results, it is predicted that a sulfide layer has been formed on GaSb surface by the neutral (NH4)2S treatment, which is in good agreement with our previous anticipation. Therefore, the neutral (NH4)2S solution passivation is proved to be an effective method to remove oxidation layer and excess elemental Sb of GaSb surface.

Next, we compared the effect of alkaline and neutral passivation by PL and PL mapping. PL intensity reflects the information about the bandgap surface states. And surface states act as non-radiative recombination centers, thereby reducing the PL intensity [18]. Thus removal of surface states can be observed as an increase in PL yields. According to the previous research, the relative PL spectrum intensity of the sample treated by alkaline (NH4)2S can be approximately 10 times stronger than the as-grown sample [6]. After neutral (NH4)2S passivation, we found the PL intensity was enhanced still further, at roughly two times larger than the alkaline passivation method,as indicated in Fig.3. It means the neutral (NH4)2S solution is more effective than the alkaline solution.

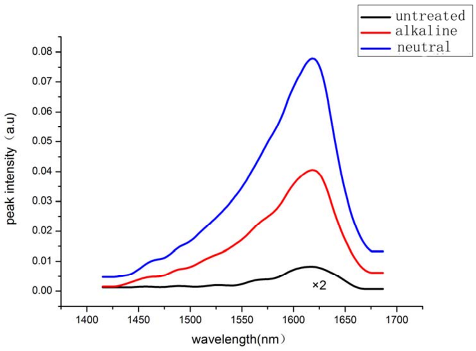
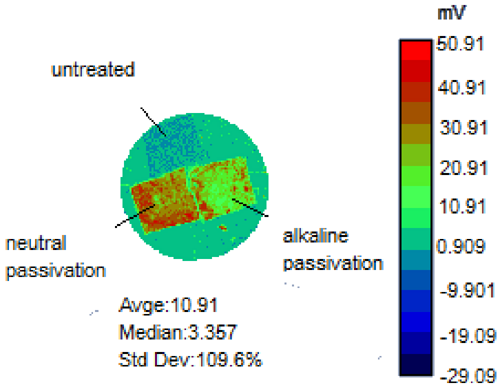


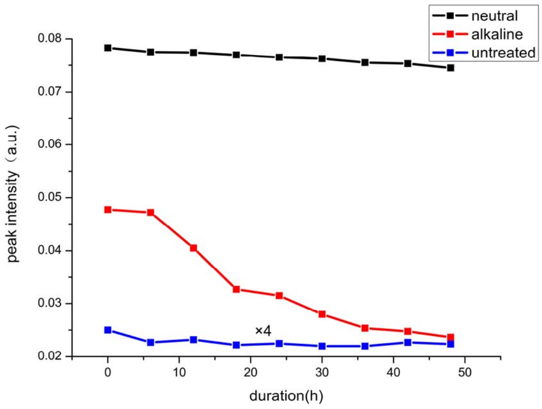
Figure 3. PL intensity spectra of GaSb after alkaline, neutral passivation sampels compaired with untreated case

PL mapping homogeneity is an important means to understand the homogeneity of passivation. It can accurately display the luminescence peak and impurity luminescence peak position of the luminous intensity distribution around the sample surface at different energy (wavelength) band edges. Fig.4 obviously shows that the sample treated by neural (NH4)2S solution has better homogeneity. The different levels of color indicate the change of the peak intensity. The untreated sample is blue in PL mapping photography as the very weak luminesce from GaSb. We can clearly see that the major part of sample passivated by alkaline (NH4)2S solution is a green , the red parts are not fairly well-distributed around surface. In comparison, the sample treated by neutral solution is almost red, only small green dots can be observed. These results agree with the behavior already noticed in XPS measurements and confirmed our previous hypothesis.



PL mapping photography of alkaline and neutral passivation samples compaied with untreated

It has been proved the main factor which causes the failure of passivation is the replacement of sulfur bonds by O-bonds at the GaSb surface during the storage of the sample in air for specific period of time [20]. We investigated the long-term stability of the alkaline and neural passivations. From Fig.5, we can see PL intensity of the sample passivated by alkaline (NH4)2S solution reduced drastically in 18h. And after exposure to atmospheric air for 48h, the PL intensity is just like the untreated sample. It means the effect of passivation has almost disappered. The passivation effect can be maintained for only a few hours. But for the samples treated by neutral (NH4)2S, PL intensity rarely declined in 48h.It can be inferred that during the passivation process, a thicker robust gallium sulfide passivation layer on the GaSb was formed, which prohibits the reoxidation of the Ga-S and Sb-S bonds at the passivation layer/substrate interface.



the variation of peak intensity by alkaline and neutral passivation in 48h at room temperature compared with untreated

## IV. CONCLUSION

This paper presents the first study concerning the effect of neutral (NH4)2S passivation on GaSb surface. The present work indicates the oxides and excess elemental Sb on the surface are mostly removed. The relative PL intensity is approximately 20 times stronger than the untreated, roughly two times larger than the alkaline passivatied sample. Improvement in passivation homogeneity was also observed from PL mapping measurements. The passivation effect results from significant reduction in surface states due to the formation of Ga and Sb sulfide species. However, the sulfides are soluble in the alkaline solution. It could influence the properties of passivatied samples. After neutral passivation, there are sulfur atoms, which are favorably bonded sufficiently strongly to the surface to prevent re-oxidation. Thus the neural passivation has better long-term stability. This conclusion may be useful for application to GaSb-based optoelectronic devices and further research.

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