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Study on Surface Passivation Homogeneity of Gallium Antimonide using Photoluminescences

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Improvement in optical and surface morphology were observed after sulphur passivation of gallium antimonide surface. The effect of surface passivation of Te-doped n-GaSb by $(NH4)_2S$ treatment was investigated by using photoluminescence (PL), Atomic Force Microscope (AFM). The optimum passivation time is around 180 s. Under this condition, the relative PL spectrum intensity of passivated sample can be approximately 10 times stronger than as-grown sample. Meanwhile, the best luminescence homogeneity and suface morphology could be obtained.

Keywords GaSb surface passivation; photoluminescence; homogeneity

I. Introduction

GaSb is an important III–V compound semiconductor material for optoelectronic device applications [1]. With high quantum efficiency, high hole mobility, wide range of band gaps, superlattices with tailored optical and transport characteristics, the GaSb-based devices are promising candidates for a variety of applications in the mid-infrared (2–5 and 8–14 um wavelength) regimes, including infrared imaging sensors for surveillance systems, fire detection, and environmental pollution monitors [2].

Many characteristics of semiconductor devices is linked tightly with semiconductor surface properties [3]. Previous studies reveal that GaSb has a very highly chemical reactive surface [4]. being easily oxidized by atmospheric oxygen with the formation of native surface oxides in several nanometers thickness. An additional consequence of surface oxidation is the formation of elemental antimony at the oxide–GaSb interface, which creates a conduction channel parallel to the interface that leads to high surface leakage current. Such high surface state densities, high surface recombination can cause the catastrophic optical damage (COD), which deeply hindered the development of GaSb-based devices [5].

Surface passivation, an important form of surface modification, has been recognized as one of the most advanced and intriguing methods to build tailored nanomaterials. Such methods include plasma etching, chemical passivation and low energy ion beam sputtering, etc [5, 6]. Research shown that chemical passsivation, namely dry and wet chemical treatments, has been the most effectively used to improve the surface related characteristics [7]. Lee *et al*. [8] shown sulfur passivation lead to obvious reduction of leakage current. S. H. Wang *et al*. [9] obtained a shallower, low resistance Ohmic contact under $(NH_4)_2S$ passivation. X.Y. Gong *et al*. [10] shown proved reduction of dark current and remarkable increase of photoresponse due to the sulfer treatment.

There are many testing methods for assessing the effect of the passivation. Dutta *et al*. [11] attributed a reduction of the surface state density following passivation, evident from an increase in photoluminescence intensity. Papis *et al*. [12] detected and characterized a superficial film after passivation by ellipsometer. Liu *et al*. [13] used photoluminescence and x-ray photoelectron spectroscopy (XPS) to examine the effect of treating GaSb with a saturated aqueous Na_2S solutions 0.186 g/mld. Robinson and S. E. Mohneya [14] reported on the structure, thickness, and composition of surface layers formed during passivation with 8% $(NH_4)_2S$ by transmission electron microscope (TEM).

In recent yeas, PL has been widely applied in passivation analysis. PL intensity is sensitive to surface recombination velocity S. This velocity S is proportional to the trap density and also depends on the capture cross sections of electron and hole traps. The relationship between the PL intensity and S is nonlinear and is a function of various other parameters (minority-carrier diffusion length) [17]. band bending due to the presence of a charge space field near the surface. When $S < 10^4$ cm s-1, the surface recombination is generally less important than bulk recombination. Thus, an order of magnitude increase in PL intensity can correspond to decrease of several orders of magnitude in S. Surface states can act as non-radiative recombination centres, thereby reducing the PL intensity. Thus removal of surface states can be inferred confirmed from the increase in PL yield.

With respect to the passivation, the homogeneity is an important parameter in the use of optical cavity and ohmic contect. To our knowledge, the reports about the passivation homogeneity is limited. In this paper, we focus on the homogeneity of sulphur passivation via the analysis of the PL spectra, meanwhile the surface morphology of GaSb is observed from AFM.

II. Experimental

Commercial GaSb substrates, (100) oriented, tellurium doped to the concentration (7, 8) E+17/cm^3 were used in the experiments. Prior to sulphur treatment, the samples were cleaned by standard surface cleaning steps consisting of degreasing in hot acetone, ethyl alcohol, and DI water. Sulphides, such as H_2S, Na_2S and $(NH_4)_2S$, are always be used in experiment [10]. However, J. A. Robinson and S. E. Mohney [2] shown that$(NH_4)_2S$ had a slow etching rate, it is a good choice as sulfur solution. So in our surface passivation experiment, the GaSb substrate was treated using ammonium sulphur 8% [$(NH_4)_2S$] (ph = 9) at 50°C. PL spectra was used to characterize the optical properties before and after passivation. The PL measurements were carried out using a Nanometrics RPM2000 photoluminescence spectrometer with a resolution of 0.2mm. The frequency doubled Nd:YAG laser (532 nm) with 100 mW is used as the excitation source. In order to characterize the surface morphology, we performed the AFM test. AFM micrographs of the samples were obtained from CSPM5500, in the contact mode.
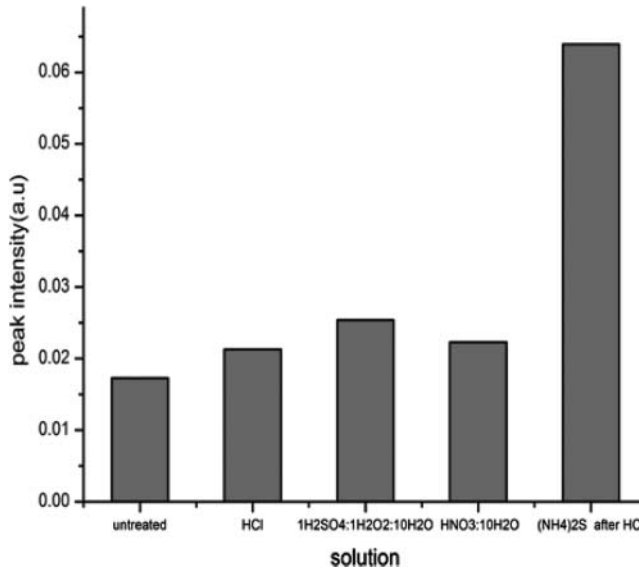
Figure 1. Relative peak intensity height of the samples in different etchants, including HCl and $1H_2SO_4{:}1H_2O_2{:}10H_2O$, $HNO_3{:}10H_2O$ and HCl, $(NH_4)_2S$ for 1min compaired with untreated.

The first investigation is the effect of the native surface oxides on luminescence of GaSb. In order to confirm the removal of surface oxidation is not the main reason for the improvement in PL intensity, we conduct this experiment as followed. The wafers were etched using different etchants, namely HCl, $1H_2SO_4{:}1H_2O_2{:}10H_2O$, $1HNO_3{:}10H_2O$, for 60 s for each etching. Another special sequence is HCl treatment for 60 s, followed by $(NH_4)_2S$ for another 60 s. All the above processes were ended by blowing dry in N2. The PL spectra of these samples at room-temperature is shown in Fig. 1.

Next, the sulphur treatments were carried out for different lengths of time. The GaSb wafers were immersed in $(NH_4)_2S$ for 30 s, 60 s, 120 s, 160 s, 180 s, 200 s, 220 s, 240 s at 50°C. The variations in PL intensity, PL mapping, AFM micrographs were obtained after passivated for different times are shown as Figs. 2–6.

III. Results and Discussion

The surface has very active chemical properties, with the "dangling bonds", which are the outward of the surface atoms' bands. Surface states are the electronic energy state of the surface [14]. Sulfuration is an effective passivation way for reducing surface states density of III-V compounds [11]. It can improve the nature of the device. Due to the presence of O_2, an oxidation layer is very easy to form on the surface [17]. During sulphur treatment, the sulphur atoms strongly chemisorbed and occupied the active surface sites because of its lower heat of formation. In fact, the O-bonds on the surface of the devices seem to be replaced, at least partly, by S-bonds after sulphur passivation [13].

A widely accepted model to describe the curing of the chemical reaction is as follows:

First, sulfuration breaks the bond between atoms. Then it forces these electrons of dangling bonds into the conduction band and surface states. The energy needed can form the chemical bond between S with Ga or Sb. Z. Y. Liu *et al*. [18] used XPS to confirm this
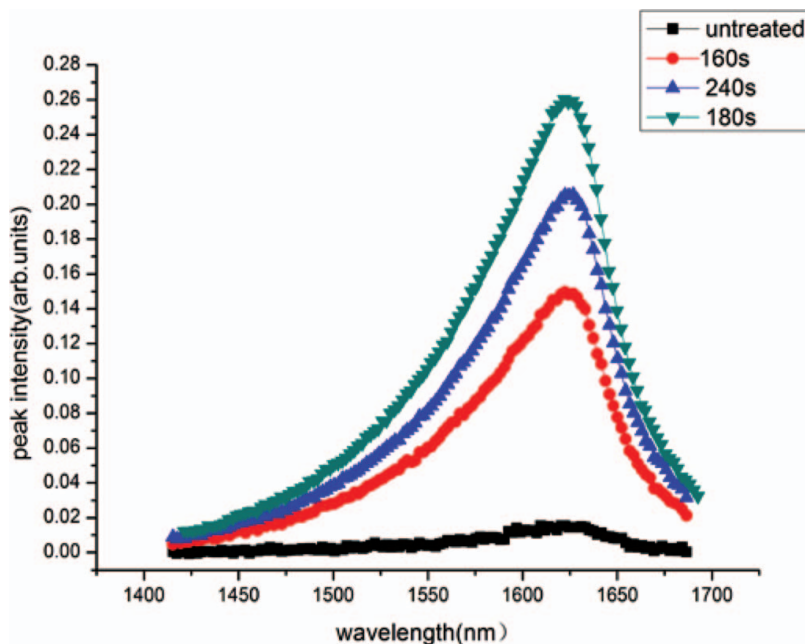
Figure 2. Spectra of GaSb after surface passivation for 160 s,180 s and 200 s compaired with untreated.

hypothesis. All in all, the dangling bonds at the surface decrease the surface recombination center density. This phenomenon was confirmed by increases of PL intensity.

Figure 1 shows PL peak intensity measured at room temperature for the Te-doped n-GaSb before and after acidification. In order to find whether the removal of oxidation
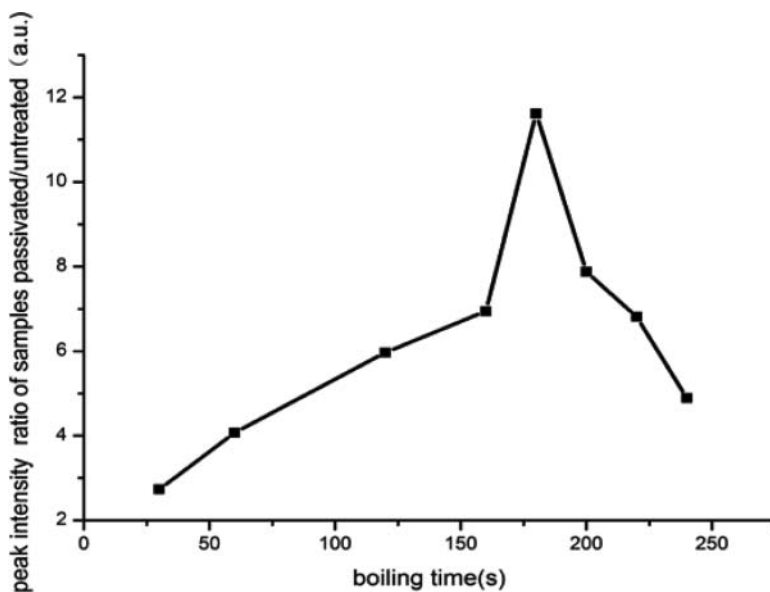

Figure 3. Peak intensity ratio of samples with/without passivation treatment vs passivation time.
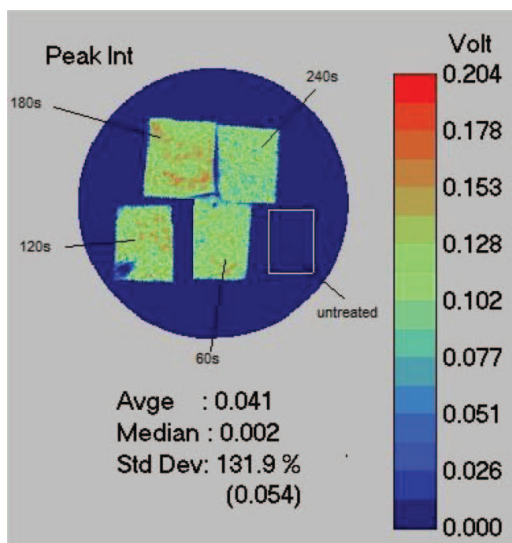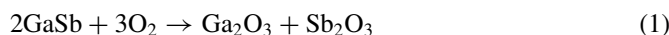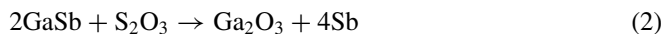
Figure 4. PL mapping of the samples sulphured for 0 s, 60 s, 120 s, 180 s, 240 s.

(namely GaO, SbO) is the mainly reason for the improvement in luminescence, we compared samples with and without $(NH_4)_2S$ passivation.

As we known at the interface, the oxidation takes places as follow:

$$2GaSb + 3O_2 \rightarrow Ga_2O_3 + Sb_2O_3 \tag{1}$$

and Sb_2O_3 would react with GaSb like this:

$$2GaSb + S_2O_3 \rightarrow Ga_2O_3 + 4Sb \tag{2}$$

From the above equations, we know there are more Sb atoms exist at the interface. The excess Sb is the non-radiative center. From Fig. 1, we can clearly see that peak intensity of samples treated with HCl, $1H_2SO_4:1H_2O_2:10H_2O$ and $1HNO_3:10H_2O$ are nearly 0.02 ev, just the same as the untreated. However, the samples soaked in $(NH_4)_2S$ solution for another 60 s, followed by HCl treatment, presents the highest peak intensity, about 0.06 ev,
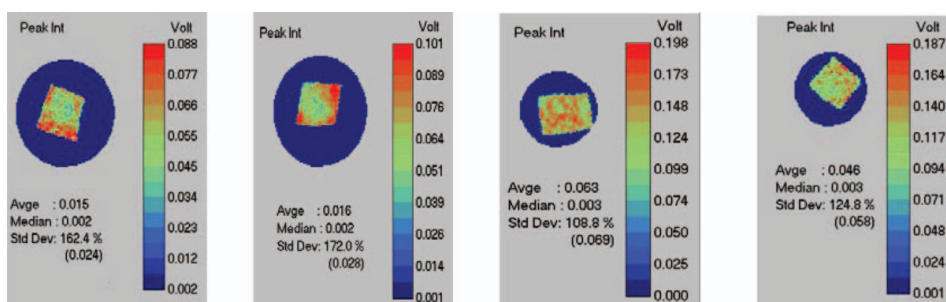
(a)passivation time=60s (b)passivation time-120s (c) passivation time=180s (d) passivation time=240s

Figure 5. The PL mapping map of GaSb samples etched in 8% ammonium sulfide at 50°C, PH = 9.(a), (b), (c), and (d) demonstrated etched for 60 s,120 s,180 s, and 240 s respectivly.
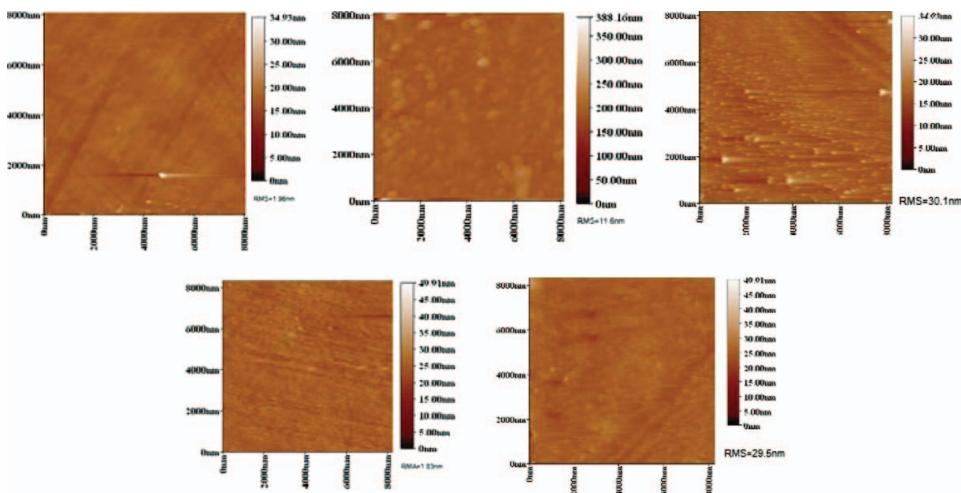
Figure 6. AFM of the samples passivated for 0 s, 60 s, 120 s, 180 s, 240 s.

roughly three times larger than other four cases. The results of sulfur-passivated surfaces suggests that sulfur agent dissolves the native oxide present on the semiconductor surface and forms the S–S, S–III, and S–V bonds in the surface layer. The formation of these bonds causes a reduction in the density of surface state density.

The change in the barrier height can be understood due to the following: (1) the influence of work function (as a result of decrease in the surface state density), (2) changes in the fixed charge density in the surface layer, and (3) minimization of reactions at the interface [9]. So we can conclude that only remove oxide layer can not reduce the surface states, non-radiative centers, and can not improve the GaSb optical propierty.

Next, sulphur treatments were carried out for various times. The variations in PL intensity after $(NH_4)_2S$ treatments for different times are supposed from the gradation in passivated surface film quality. Figure 2 shows PL spectra measured for the samples treated by $(NH_4)_2S$. The notations denoted by 0 s, 160 s, 180 s, and 220 s in Fig. 2 correspond to as-grown, 160 s, 180 s, and 220 s sulfur treatment time at 50°C, respectively. In all cases, since the PL emission arises from band-to-band recombination well away from the sample surface, the spectral shape and characteristics of the PL emission in all samples did not change with passivation treatment, justifying the use of the PL peak intensity as a metric of passivation [18]. It is seen that the emission peaks for the four samples before or after passivation appeared at almost the same energy position. The PL spectra for the sample showed one peak, corresponding to the wavelength of 1623 nm. It is clearly illustrated that after passivation, the luminescence improved, and reached the highest peak intensity at the 180 s.

In order to understand the relation between the peak intensity and the passivation time, the as-grown samples were soaked in $(NH_4)_2S$ for 30 s, 60 s, 120 s, 160 s, 180 s, 220 s, 240 s at 50°C,respectively. Figure 3 shows that the peak intensity rises monotonously with time before 180 s. The peak intensity for the sulfur-treated GaSb for 180 s was about 10 times larger in comparison with that for the untreated sample. And after 180 s, the peak intensity began to decrease. When the passivation time is 240 s, the peak intensity became only 0.075 ev. So it is clear that the PL intensity depends critically on the passivation time. For our samples, the optimum sulfur treatment time was 180 s.

In order to study the homogeneity of passivation, we conducted sulfur treatments for 60 s, 120 s, 180 s, and 240 s using the PL mapping measurement respectively.

We know that photoluminescence (PL) is a carrier-photon process, and closely related with the surface characteristics. PL spectral intensity will be influenced by micro-defects, impurities and non-radiative centers. PL mapping homogeneity is an important means to understand the homogeneity of passivation. PL mapping is a scanning photoluminescence spectroscopy. 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 edge [21].

Figure 4 obviously shows that the longer the passivation, the higher the peak intensity, and the much better homogeneity of passivated surface were observed. The as-grown sample is blue in PL mapping photography as the very weak luminesce from GaSb. The different levels of color indicate the change of the peak intensity (the position of the untreated sample is labeled by white rectangle). We can clearly see that the treated sample are green, and with the passvatied time longer, the proportion of red got enlarged.

Figure 5 shows the PL mapping photography of the samples dipped in ammonium sulfide solution for 60 s, 120 s, 180 s and 240 s, respectively. It can be seen that the non-homogeneities of passivated samples for 60 s, 120 s, 180 s, 240 s are 162.4%, 172.4%, 108.8%, 124.8%. In comparison, when the passivation time is 180 s, the sample has the best homogeneity, which is in coincidence with our experiment results.

This behavior suggests that the number of dangling bonds existing at the surface is diminished due to sulfur treatment, which leads to the reduction in the number of exciton non-radiative recombination centers. After sulfur treatment for 240 s, the peak intensity decreases in comparison with the treated sample for 180 s. Reduction in the PL intensity due to the over passivation time is attributed to the scattering by the polycrystalline surface film reconstructed with sulfur. This phenomenon is attributed to the excess of the sulfur atoms acting as trap centers on the surface of GaSb at the room temperature [4].

We also conducted AFM measurements to verify the optimize passivation time. As Fig. 6 shows, the untreated sample surface is relatively smooth, the surface roughness of RMS is 1.96 nm. This is because GaSb has a thin and uniform oxides. After passivation, the sample surface got worse. Ammonium sulfide solution slowly etched the residual oxides from the surface. When passivated for 60 s and 120 s, the surface roughness of RMS became 11.6 nm, 30.1 nm, respectively. However, at passivation time of 180 s, we got a very smooth surface with the RMS only 1.83 nm, this is because the whole oxides were removed by $(NH_4)_2S$. As the passivation time was longer, 240 s, the surface got wores again, the roughness of RMS became 29.5 nm. We suppose $(NH_4)_2S$ etched the suface of GaSb at this moment.

IV. Conclusions

This paper presents the first study, to our knowledge, on the homogeneity of sulfuration on GaSb. The optical properties and structure morphology of sulphur treated GaSb samples in $(NH_4)_2S$ have been analysised It has been shown that sulphur treatment results in PL intensity increases generally. Passivation has a significant effect on the reduction of the surface states. The optimum passivation time is 180 s, the PL intensity was enhanced 10 times larger than as-grown samples, with the most homogeneous and smooth surface at the same time. This conclusion may be conducive to GaSb-based optoelectronic devices research.

Acknowledgments

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