Photoluminescence Analysis of the Ternary Alloy GaAsSb Sulfur Passivation*

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The semiconductor material surface due to dangling bonds reasons, readily combine with oxygen in the air and easily be oxidized. These non-radiative recombination centers are formed in the surface states bring great impact on the electrical properties, optical properties of the photovoltaic device, particularly in the Micro-nano devices. In previous studies, sulfur passivation is a very effective method to remove surface states for semiconductor material, but rarely in the ternary alloy study. In this paper, we utilize the X-ray diffraction (XRD), atomic force microscopy (AFM), photoluminescence (PL) to analyze the properties of sulfur passivation of GaAsSb/GaSb by ammonium sulfide solution, and found that the PL peak intensity of the passivation samples are both higher

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than the untreated sample's. There is also conclusion that passivation time of 360s has a smoother surface than the 60s sample.

Keywords: GaAsSb; Surface state; Sulfur passivation; Photoluminescence.

1. Introduction

GaAsSb ternary compound semiconductor has received increasing interest owing to its potential applications to light sources for communication and microelectronic and optoelectronic applications[1]. It has been reported that GaAsSb as an active layer material for high performance tunnel field effect transistors (TFETs)[2-4], advanced concept solar cells[5] and near infrared lasers[6-7]. However, the growth of ternary alloy semiconductor material GaAsSb have revealed a peculiar miscibility gap by the liquid phase epitaxy (LPE)[8], therefore, the use of non-chemical equilibrium of molecular beam epitaxy (MBE) growth is an important means to solve GaAsSb grown[9-10]. In order to maintain a stable quality epitaxial, in the process of GaAsSb grown, V group elements often above group III element, namely the growth of one group III element, it is necessary growing a group V element[11-12]. Thus, the GaAsSb surface tends to exist in the mixed group V element, the As and Sb element, then the surface states of dangling bonds exist. This feature will bring a fatal flaw to optoelectronic devices, especially the micro-nano optoelectronic devices. Because at the nanoscale, the semiconductor materials will sensitive with optical and electrical properties, in additional these dangling bonds and surface states will bring lots of non-radiative recombination centers, thereby affecting the luminescent, carrier lifetime and carrier velocity of materials.

Surface passivation is one of a highly effective way for light-emitting devices, such as plasma etching, chemical passivation and low energy ion beam sputtering, etc. Among them, the chemical passivation, namely dry and wet chemical treatments, has been the most effectively used to improve the surface related characteristics[13]. Sulphides, such as H_2S, Na_2S and $(NH_4)_2S$, are always be used in experiment[14-16]. However, J. A. Robinson and S. E. Mohney[17] shown that $(NH_4)_2S$ had a slow etching rate, and it is a good choice as sulfur solution.

It is reveal that the photoluminescence (PL) emission arises from band-to-band recombination well away from the surface, the spectral shape and characteristics of the PL emission will not change with passivation treatment, and it is sensitive to surface recombination velocity therefore the PL analysis is widely applied in passivation. Moreover the homogeneity is an important parameter in the use of optical cavity and ohmic contect. In this paper, we will describe the PL of sulfur passivation of GaAsSb, meanwhile the surface

morphology of GaSb is observed from atomic force microscopy (AFM). This work will provide a reference for the ternary alloy semiconductor materials passivation.

2. Experimental

To observe the effects of sulfur passivation of GaAsSb luminescent properties, the sample was grown on an undoped GaSb substrate by DCA P600 molecular beam epitaxy (MBE), and the As/Sb beam ratio is 1/6, then was cleaved into four pieces of 8 mm×6 mm samples，namely a, b, c and d. In order to obtain a clean surface so as to promote the sulfurization process and increase its coverage, we need to remove the residual film and other possible contamination from the surface. All samples were cleaned by standard surface cleaning steps consisting of degreasing in acetone, ethanol and deionized (DI) water, each 60s respectively. After blowing dry with compressed N_2 gas, the sample a was soaked in the DI water at 50°C for comparison, and other three piece of the samples were soaked in a solution of $(NH_4)_2S$ (ph=7) for 60s, 180s, 360s at 50°C respectively.

The structural qulity and composition of the GaSb substrate and GaAsSb/GaSb were examined by X-ray Diffraction (Bruker AXS D8 DAVINCI) with Cu-Ka radiation (λ=1.5406 Å), both reflections were measured with a double-crystal diffractometer. Photoluminescence (PL) intensity measures were performed on a PRM2000 spectrometer in room temperature, using an Nd: YAG (532 nm) laser as source with a resolution of 0.2mm. The atomic force microscopy (AFM, CSPM5500) in the contact mode was used to characterize the surface morphology.

3. Results and discussion

A representative X-ray diffraction spectrum for the GaSb substrate and GaAsSb we used in this experiment is shown in Fig. 1 and Fig. 2.

Figure 1 shows representative X-ray spectra for the GaSb substrate, and the GaSb peak at a Bragg angle is 30.407°. The X-ray diffraction peaks from the grown GaAsSb layer is shown in the neighborhood of the diffraction peak of the GaSb substrate in Fig. 2. The satellite peak of GaAsSb layer is at a Bragg angle of 30.397° and the GaSb substrate is at 30.370°. The peak value of GaSb in the Fig. 2 has a little shift compared to the value of Fig. 1, and it is because stress from the GaAsSb layer on GaSb substrate.

The PL intensity of the samples is shown in Fig. 3, which are untreated and treated with annealing after $(NH_4)_2S$ for 60s, 180s, and 360s.

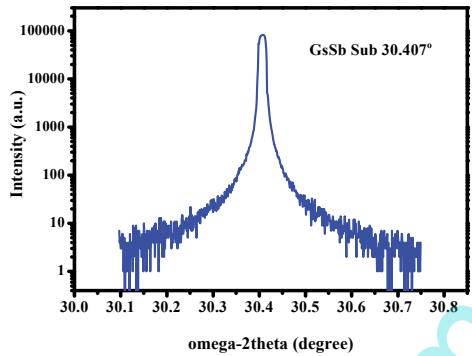

Fig. 1. X-ray diffraction spectrum for GaSb substrate.

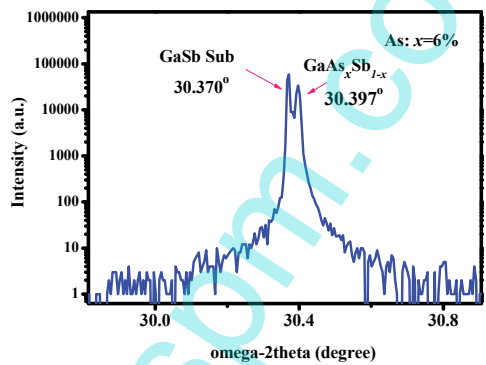

Fig. 2. X-ray diffraction spectrum for GaAsSb/GaSb with the relevant peaks identified.

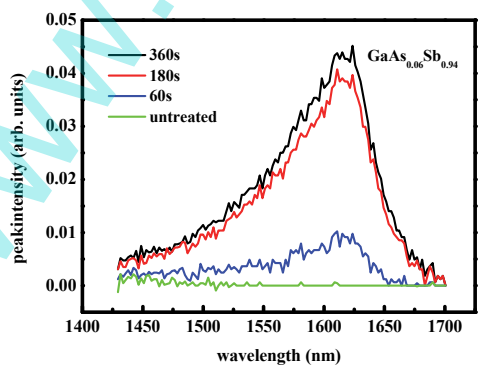

Fig. 3. Spectra of GaAsSb after sulfur passivation for 60s, 180s and 360s compared with untreated.

From the picture, we can see that, the peak intensity of the samples soaked in $(NH_4)_2S$ for 60s, 180s, 360s are both higher than the untreated sample's, and for the 360s is about 100 times larger in comparison with that for the untreated sample. Previous sulfur passivation of binary alloys studies have found that the III-V semiconductor surface has very active chemical properties due to with the dangling bonds, which are the outward of the surface atoms' bands. The presence of O_2 making an oxidation layer is very easy to form on the surface. During sulphur treatment, the sulphur atoms strongly chemisorbed and occupied the active surface sites because of its lower heat of formation, and it will form 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, thereby enhancing the PL intensity. It has been demonstrated in binary alloys such as GaSb, GaAs and other semiconductor materials, but the sulfur passivation of ternary alloy is rarely reported. From this figure we can see, to a certain extent, GaAsSb is in line with a binary alloy sulfur passivated law.

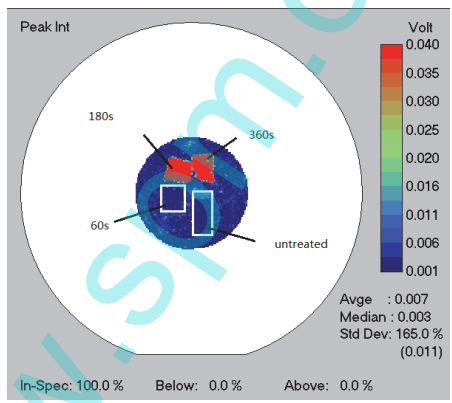

Fig. 4. PL mapping of the samples sulphured for 60s, 180s, 360s is the mainly reason for the improvement in luminescence, we compared samples with and without $(NH_4)_2S$ passivation.

As Fig. 4 shown, the different levels of color indicate the change of the peak intensity, and the position of the untreated sample is labeled by white rectangle. We can clearly see that the treated sample is red, and with the passvatied time longer, the proportion of red got enlarged. 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. The results of sulfur-passivated surfaces suggest that sulfur agent dissolves the native oxide present on the semiconductor surface.

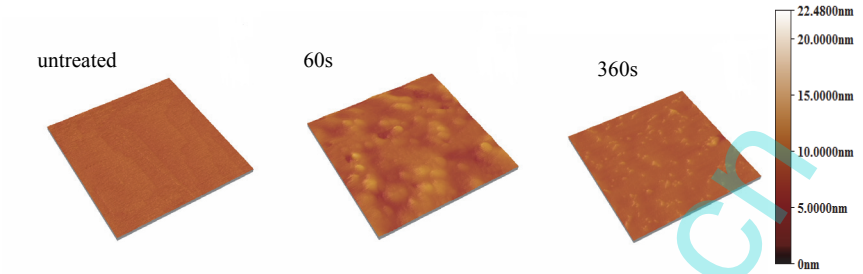

Fig. 5. AFM of the samples passivated for untreated, 60s, 360s.

Figure 5 is the AFM morphology of the samples untreated, 60s, 360s respectively. We can observe that the surface morphologies of GaSb the untreated sample surface is relatively smooth and there is no convex and concave, the surface roughness of root mean square (RMS) is 0.232 nm. It is because GaSb has a thin and uniform oxide. After passivation, the sample surface become rough, the $(NH_4)_2S$ solution slowly etched the residual oxides from the surface. When passivated for 60 s, the numbers of bulges on the surface increased and became large and the surface roughness of RMS became 9.11 nm. However, at passivation time of 360 s, we can observe that the surface of sample is smoother than the 60s ones, and the RMS is 3.21 nm, this is because the most of oxides were removed by $(NH_4)_2S$. 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.

4. Summary

Passivation has become a very effective means of improving the surface state of the semiconductor material. In this article, we used the XRD, PL spectra and AFM to analyze the properties of GaAsSb/GaSb sulfur passivation. As the experiments shown, the best passivation time of GaAsSb/GaSb in this experiment by $(NH_4)_2S$ was 360s, and has a smoother surface than the 60s sample. By sulfur passivation, the non-radiative recombination centers and surface states reduced, and sulphur treatment results in PL intensity increases generally. This conclusion will bring reference for ternary alloys passivation, and conducive to research GaSb-based optoelectronic devices.

Acknowledgments

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