Improved photoluminescence from passivated InP Surface by $(NH_4)_2S$ Treatment

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***Abstract*—In this work, ammonium sulfide ((NH4)2S) solution was used to passivated the surfaces of InP substrate. The optical properties were measured by PL (Photoluminescence) measurement, the luminescence intensity increased about 7 times when the passivated time was 15 min. The reasons of enhanced luminescence were also discussed. After passivating, the surface morphology and electrical properties were analyzed by atomic force microscopy (AFM) and Hall effect, respectively.**

Keywords- component: InP, surface states, sulfide passivation, photoluminescence

I. INTRODUCTION

With 1.35eV band gap energy and a direct band structure, InP is an important semiconductor material, which has many applications. In addition， the advantages such as thermal performance, good temperature stability, and high frequency response, InP-based semiconductor is an important material for infrared sensors, aerospace remote sensing applications and high-efficiency solar cells, which can be applied in the field of military, satellite communications and advanced microelectronics. [1], [2], [3]

However, the surface states of InP play an important role in the performance of InP-based devices such as oxide films which were introduced by InP heated in the open air environment. Therefore, the research of semiconductor surface states was important to improve the performance and stability of devices. Many methods to decrease the density of surface states have been investigated, such as acidification and passivation. A common method of passivating III-V semiconductor surfaces is by immersion in $(NH_4)_2Sx$ solutions, as pioneered for GaAs, [4-6] and later extended to other III-V materials, including InP and InAs. [7-10] The wet methods of sulfide passivation in $(NH_4)_2S$ solutions or Na_2S have proved to be effective in reducing the density of surface states and correspondingly improving the dark current of mesa diodes. [11-16] Meanwhile, many methods were used to evaluate the effectiveness of passivation. Due to the luminescence intensity was associated with semiconductor surface states. The intensity of PL was a direct and effective method compared with Schottky contact barrier height[17] and the C-V [18] characteristic curve.

For InP, Malhotra et al used different means of processing for InP surface passivation, the room temperature integrated PL intensity of the passivated InP increased by a factor of 1.8. [19] Zhuang et al reported the improvement of the device properties after the n-type curing InP substrate uing $(NH_4)_2S$ solution then thermal evaporation ZnS film obtained Au/ZnS/InP (100) MIS devices,[14] and the influence of thermal annealing on the performance of $(NH_4)_2S$ passivated InP surface[21]. Chen et al passivated InP(100) surfaces with both gas-phase and solution phase and studied with X-ray photoeletron spectroscopy (XPS) and AFM. [13],[18]

In this paper, 8% of $(NH_4)_2S$ (PH=9) solution was used to passivating the InP surface. PL mapping and Hall measurement were taken in order to study the passivated effectiveness. The PL intensity of samples expected could increase greatly as a very ckear phenomenon, and it would prove the surface state and oxide layer removed. PL measurement could show it directly and clearly and PL mapping indicated the uniform of luminescence.

II. EXPERHIMENTAL DETAILS

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 was 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.

The S doped n-type InP substrate with 500 μm thickness was used in this study. Surface chemistry and etching experiments were done with the samples cleaved into 8mm× 8mm pieces and soaked in acetone for 60s to remove organic contamination and nature oxide layer, rinsed in deionized (DI) water, and finally blown dry with compressed N_2.

The samples were labelled from 1 to 5. Sample 1 as a comparison sample received no treatment. The remaining samples were 1 to 5 soaked in $(NH_4)_2S$ solution corrosive for 3 minutes, 7 minutes, 10 minutes and 15 minutes at 60℃. All

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samples were rinsed in deionized (DI) water to remove S crystal and finally blown dry with compressed N_2 after boiling in the solution.

After testing the samples with the PL, PL mapping and Hall test after treatment to improve the optical and electrical properties, we also used the AFM to observe the surface morphology of the sample. All tests were done at room temperature with no additional in situ processing.

III. RESULT AND DISCUSSION

As demonstrated by our PL result (Figure.1), compared to HCl, $(NH_4)_2S$ passivation was effiecient at removing the oxides and preventing contamination for InP. Figure 1 clearly illustrates the improvement of photoluminescence for being passivated by $(NH_4)_2S$ solution. From the figure we can clearly see that the luminescence intensity of samples treated with $(NH_4)_2S$ solution was stronger than the sample soaked in HCl. Just during 1min passivating the photoluminescence intensity was 1.2 times higher than the HCl treated samples, 1.15 times higher than the untreated samples. Figure 1 could prove that $(NH_4)_2S$ solution can remove oxided layer more effectively than HCl. In addition, it was noteworthy that the halogen reacted with the InP and dissolved Cl_2, Br_2 organic solvents (such as methanol and ethanol). But, for HCl, because InP can react with HCl at room temperature, HCl always used as the etch liquid.[19] As seen in Figure 1, the $(NH_4)_2S$ result is much better than HCl.

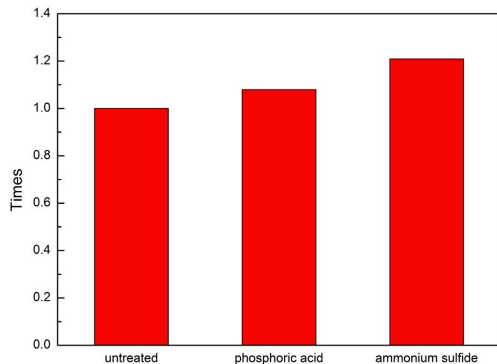


Figure 1. The comparison of thePL intensity charts of the samples that were untreated and passivated for 1 minute at room temperature by HCl and 1 min at 60 ℃ by 8% $(NH_4)_2S$ solution, PH=9 .

Figure 2 shows the influence of the sulfide passivated time on the emission luminescence intensity. As the oxide layer removed, Fermi level pinning and the InP surface non-radiative recombination reduced effectively, so the light intensity significantly increased and FWHM decreased. [6]

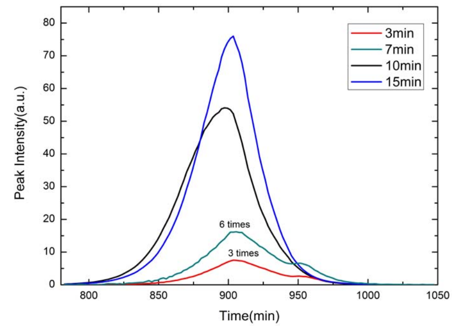


Figure 2. During different sulfide passivated times, the relationship between emission wavelength and light intensity. The temperature of 8% ammonium sulfide is 60℃, when PH=9. Samples are soaked for 3min, 7min, 10min and 15min respectively.

From the Figure 2 we also know that with passivation time becomes longer, the PL intensity increased and FWHM gets smaller too. Figure 3 shows the variation of the PL peak with InP samples changing time passivated in the 8% $(NH_4)_2S$ solution, when PH = 9, and T=60℃. We can get that with the longer soaking time the luminescence intensity of samples increase more significantly. One of the reason is the decline of oxided layer and the other may be the S atom filling the vacation of P, then S-In bond formed[19]. From the obtained experimental results we can clearly see that when the time of passivation less than 7 minutes, the luminescence intensity of the samples does not change a lot. When the soaked time was more than 10 minutes, the change of luminescence intensity was more significantly. It was because the removal of the surface oxide layer was not thorough enough if the etching time was not longer enough. This surface state would affect on the luminescence quality of the samples.

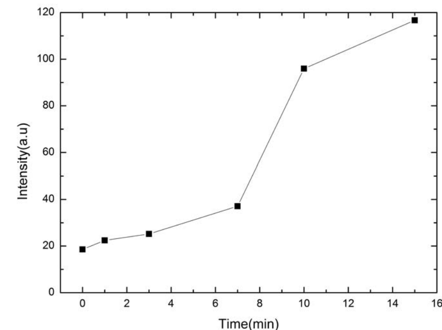


Figure 3. The variation of the PL peak with the changing time for InP samples etched in the 8% $(NH_4)_2S$ solution , when PH = 9 and T=60℃.

In order to prove if the surface was uniform after soaking treatment. PL mapping was also tested to characterize the luminescence intensity uniformity of the samples. Figure 4 shows the PL mapping images of samples dipped in $(NH_4)_2S$ solution for 3min, 7min, 10min and 15min, and labeled a、b、c and d, respectively. It can be seen that with longer time passivated, the better uniformity of the sample is achieved and

the luminescence intensity is increased. Das Linear of the luminescence intensity denotes relative strength that is automatically selected by the device based on the uniformity of the sample. The number showed by Figure 4 is different from that given in Figure 2, but they have the same physical meaning.

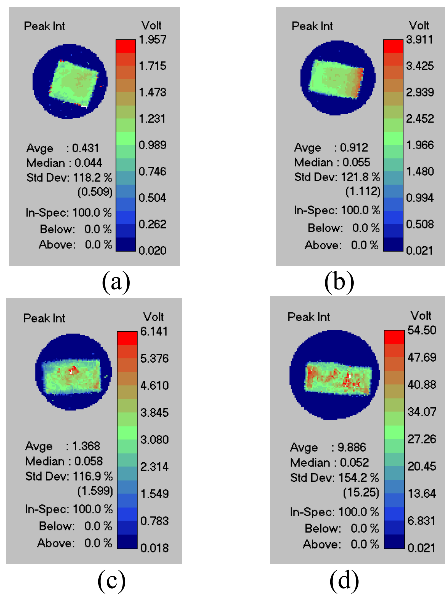


Figure 4. PL mapping of InP samples soaked in 8% ammonium sulfide at 60 ℃, when PH=9.(a), (b), (c) and (d) show etched times for 3min, 7min, 10min and 15min respectivly.

From Figure 4 (a), the most of areas are in the green states, which show that the intensity of luminescence is not strong and also meant the oxide layer covers all the surface of the sample. Figure 4 (b) shows the sample soaked in solution for 7min. At the edge of sample the intensity of luminescence is stronger than sample a, at the same time it meant that part of oxide layer is removed. And sample c also shows the same phenomenon. When the sample was soaked in solution for 15min, the luminescence intensity was the strongest which indicated the local parts of oxide layer were fully removed. And these result were in accordance with the PL measurement.

Figure 5 shows the samples AFM images of the samples. When the samples passivated for 3min, the surface of InP was still smooth and uniformity, which indicated that the oxide layer was not removed enough. With passivated time passed, the surface of InP was still smooth and uniform, and became more and more rough, until oxide layer was fully removed. In addition, comparing the experimental results obtained with AFM to the results obtained with PL mapping, we can clearly explain the reason why the luminescence intensity of passivated samples is non-uniformity. That is consistent with the corrosion degree. The 15-minute-sample to remove the oxide layer is relatively better, so the luminescence intensity uniformity better than the other samples. Through the tested samples with PL, PL mapping and AFM, we get consistent results. Sulfude passivation is an effective means to remove the surface states of semiconductor materials, and it is also effective in reducing the non-radiative recombination centers and the surface resistance of the semiconductor material. This have great practical significance for follow-up formation the ohmic and Schottky contacts. The samples' electrical properties were tested by Hall test, and the hall coefficient and resistance have changed after samples soaked in $(NH_4)_2S$ solution. Hall test are data listed in Table 1, the first column lists sample resistance values of became smaller. The second column lists the carrier concentration, and carrier gets larger. The changing of Hall test data was caused by the changing of sample surface state, such as some chemical bonds, the original existence surface defects and vacancies that were removed or filled.

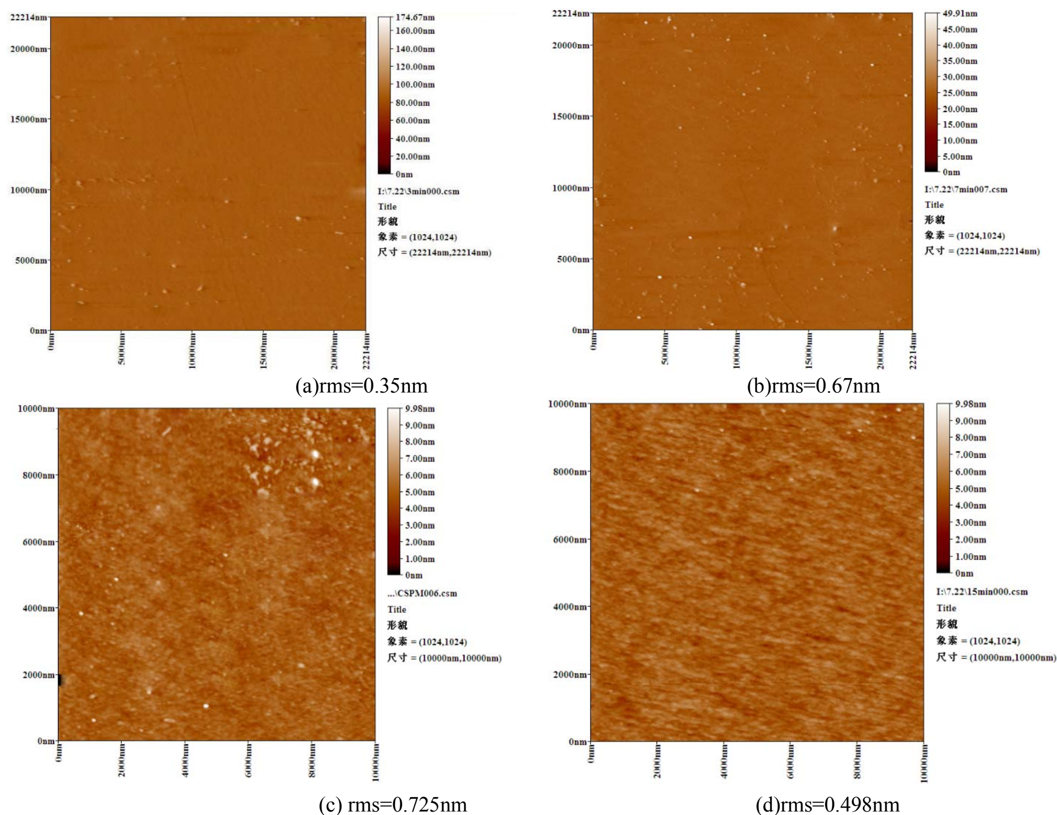
That the carrier concentration becomes smaller could be explained in the following. In this work, n-type InP bulk material was used as a sulfide sample. Then P vacations defects in InP material surface would be filled by S. Because P could gives three electrons, when the S fills the vacancy, S only gives of two electrons, so then the number of carriers would decrease.

TABLE I. HALL MEASUREMENT RESULT

InP	Resistivity	concentration
0min	0.00158ohm-cm	-4.38e+18/cm^2
3min	0.0018ohm-cm	-3.35e+18/cm^2
7min	0.0014ohm-cm	-3.27e+18/cm^2
10min	0.00129ohm-cm	-3.43e+18/cm^2
15min	0.00142ohm-cm	-2.45e+18/cm^2

IV. CONCLUSION

In this paper, 8% (NH4)2S solution was used to passivate the surface of InP. The best passivation time was 15min. Luminescence intensity added 7 times than the samples without sulfide We have established that ammonium sulfide $(NH_4)_2S$ treatment of InP surface produces a model passivated surface with well-defined structure and properties. Today, although the areas of optoelectronic devices and integrated circuits are small, after all it still have a certain area, so the study of luminescence intensity uniformity of semiconductors in a certain area has very great significance to ensure the stability of optoelectronic devices and extend the working life of the device. In order to measure the uniformity of the sample PL mapping is necessary. Although the samples were tested by very different methods, the same results were obtained, The theoretical results can be explained in accordance with the experimental results perfectly. The treatment effectively removed oxides and defects with minimal surface passivation, S filled the P defect, reduced Fermi level pinning effect, and produced a covalently bonded sulfur passivation layer. Given that $(NH_4)_2S$ solution are widely used for III-V semiconductor surface passivation [6], the systematic evaluation of the sample surface in this work establishes a good practical benchmark. In addition, the ammonium sulfide-treated samples the light intensity and Hall coefficient have changed, indicating that the ammonium sulfide treatment on InP removes the oxide layer and surface states effectively.



(a)rms=0.35nm (b)rms=0.67nm

(c) rms=0.725nm (d)rms=0.498nm

Figure 5. AFM map of InP samples passivated in 8% ammonium sulfide solution at 60 ℃, when PH=9 for 3 min (a), 7min(b), 10 min.(c) and 15min(d); The figure show the degree of corrosion on sample surface is increased gradually.

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