Surface state and optical property of sulfur passivated InP

Shanshan Tian [a], Zhipeng Wei [a,*], Yongfeng Li [b,*], Haifeng Zhao [d], Xuan Fang [a], Jilong Tang [a], Dan Fang [a], Lijuan Sun [c], Guojun Liu [a], Bin Yao [b], Xiaohui Ma [a]

[a] Changchun University of Science and Technology, 7186 Wei-Xing Road, Changchun 130022, China
[b] Key Laboratory of Physics and Technology for Advanced Batteries, Ministry of Education, College of Physics, Jilin University, Changchun 130012, China
[c] Yunnan forestry Technological College, No.1 Jindian, Panlong District, Kunming 650224, Yunnan Province, China
[d] State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

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ABSTRACT

We report photoluminescence (PL) of indium phosphide (InP) surface passivated by sulfur (S). A three-fold enhancement of band edge emission from the bulk InP was observed after the InP was passivated by ammonium sulfide ($(NH_4)_2S$) solution for 10 min. X-ray photoelectron spectroscopy measurements indicate that the oxide at InP surface is removed after being sulfurized in $(NH_4)_2S$ solution. However, the enhancement significantly decreases for a longer treatment time, which is maybe due to a thick S layer deposited at the InP surface resulting in low light transmission.

1. Introduction

III–V semiconductors are widely used in the fields of high speed electronic devices, micro- and optoelectronic devices [1,5]. In recent years, indium phosphide (InP) has also attracted much attention as a potential application material in the field of long-wavelength laser, detector and the advanced microelectronics for military and satellite communication because of its good temperature stability, good heat dissipation and high frequency response [2–5]. However, instability of its surface hinders its further development greatly. For example, up to now, no metal–insulator–semiconductor field-effect transistor (MISFET) using III–V material has ever been developed commercially because of surface Schottky barrier formation. To eliminate the effect of the surface states, some researchers have been making efforts to passivate surface of InP through various methods, especially sulfur treatments.

Recent research indicates that the S (sulfur) treatments can reduce the surface Fermi-level pinning [6], interface-state density in metal–insulator–semiconductor (MIS) [3], the surface recombination velocity (SRV) [7,8] and increase the intensity of photoluminescence. S treatment using ammonium sulfide ($(NH_4)_2S$) has been reported to be effective in surface passivation of InP [9,10]. Li et al. have reported that there exists a thick S overlayer on GaAs using an anodic S passivation technique, and thus the PL intensity of GaAs is significantly decreased [11]. Chen et al. also reported that the barrier height of n-GaAs Schottky diodes treated by $(NH_4)_2S$ solution was not stable [12]. These results indicate that the thick S overlayer can affect the surface of S-treated GaAs greatly. An S layer with a suitable thickness can protect the surface from the wet environment and being oxidized. However, a thicker sulfur layer can prevent the light output because of the scattering of light by the polycrystalline sulfur film [13]. Therefore, it is necessary to further study the effect of sulfur layer thickness on luminescence properties of III–V materials.

In this paper, we present a photoluminescence (PL) investigation on the S-treated InP surface. A 3.2-fold PL

* Corresponding authors.
E-mail addresses: zhipengwei@gmail.com (Z. Wei), liyongfeng@jlu.edu.cn (Y. Li).

enhancement was observed after the InP was passivated by the $(NH_4)_2S$ for 10 min. Luminescence properties of InP are significantly dependent on treatment time. The possible origin of the related surface states is also discussed.

2. Experimental

An S doped n-type InP ($Nd \sim 2 \times 10^{17}$ cm^{-3}) substrate with a thickness of 0.5 mm was cleaved into 8 mm × 8 mm specimens, and 6 pieces of them were used in this experiment. All the specimens were cleaned by a standard process, soaked in acetone for 60 s to remove the organic contamination of the surface and then rinsed in de-ionized (DI) water. To remove the native oxides, all the specimens were soaked in the 5% HF solution for 1 min. The specimens were rinsed again in DI water and finally blown dry with compressed N_2 gas.

The samples were denoted from a to f. Sample a is a reference sample without S treatment. The remaining samples were soaked in 8% $(NH_4)_2S$ solution for 5 min, 10 min, 15 min, 20 min, and 25 min at 60 °C, corresponding to samples b, c, d, e and f, respectively. Then the samples were rinsed using DI water and finally blown dry with compressed N_2 gas.

Low-temperature PL measurement was used to characterize the luminescence properties before and after passivation. PL measurements are done by PL9000 Fourier transform spectrometer with the samples mounted in a He cryostat at 10–300 Kusing 447 nm emission line from an Arion laser and a liquid nitrogen cooled Ge detector. The laser power density is 6 Wcm^{-2}. The power density at the PL sample surface is 3 mm × 5 mm. The temperature-dependent PL measurements were also performed for some samples to confirm the transition mechanism. Thermo ESCALAB 250 spectrometer with Al K_α source at energy of 1486.06 eV was used to perform the x-ray photoelectron spectroscopy (XPS) measurement. All XPS spectra were calibrated by the C 1s peak located at 284.6 eV.

3. Results and discussion

Fig. 1(a) shows the room temperature (RT) PL spectra of the InP samples without and with S treatment for 5, 10, 15,

20 min and marked as b, c, d e, respectively. We marked the untreated sample as a. All PL peaks have almost the same position at 1.341 eV, which is due to band edge (BE) emission. However, the PL intensity is strongly dependent on S passivation time. The PL intensity increases by a factor of 3.2 after $(NH_4)_2S$ passivation for 10 min. This result indicates that the dangling bonds at the surface are terminated by sulfur, which leads to the reduction of nonradiative recombination centers [14]. For longer passivation time, the PL intensity starts to decrease. To illustrate clearly the change trend of the PL intensity, the PL intensity as a function of passivation time is plotted in Fig. 1(b). Iyer and Lile argued that a thicker S overlayer can scatter light and results in weaker PL intensity [13].

To clearly illustrate the variation of the luminescence properties of the InP after passivated by S, low temperature PL measurements were carried out at 77 K. Fig. 2 shows the 77 K PL spectra of the InP samples without and with S treatment for 10 min and 20 min. The peaks centered at 1.417 eV are due to the transition from the conduction band minimum (CBM) to the acceptor levels, as denoted by e-A. The shoulders at 1.442 eV near the main peaks are attributed to the transition from conduction to valence band emission, as denoted by BE [16].
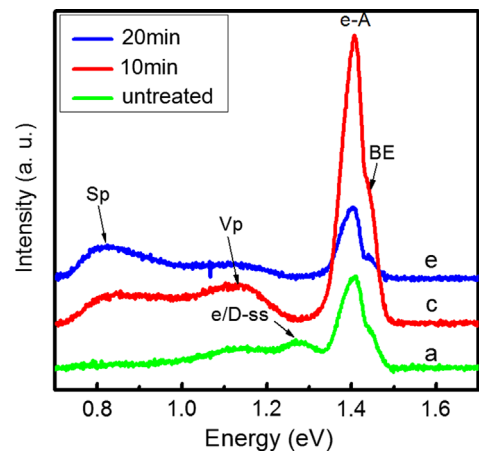

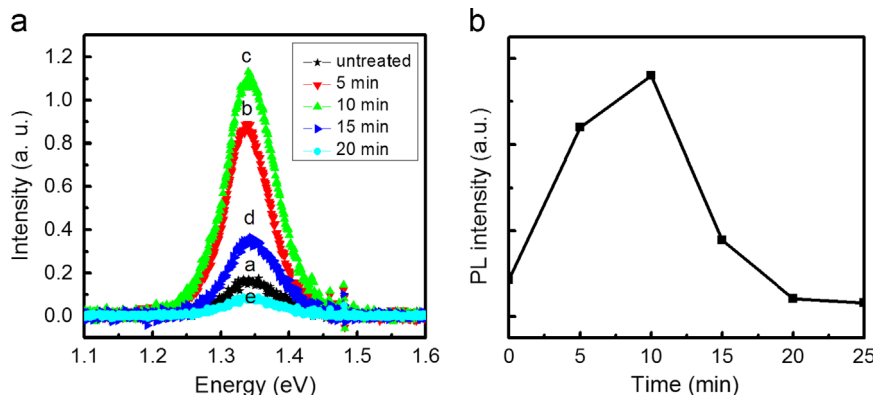**Fig. 2.** The 77 K spectra of the InP samples with various passivation time.

Fig. 1. (a) Room temperature PL spectra of the InP samples soaked for 5 min, 10 min, 15 min, and 25 min, respectively. (b) Sulfide passivated time dependnet PL intensity of the InP smaples.

The PL band centered at 1.277 eV denoted by e/D-ss, originates from the recombination via surface states [15,16]. Such a luminescence band has the following properties: (i) it disappears (or is reduced) after S treatment, (ii) it appears at different photon energies for samples with different doping levels and doping types. As can be seen in Fig. 2, the surface-state-related PL band is relatively broad appearing at widely different energies with a comparable intensity to the peaks attributed to the bulk recombination [2]. It is known to be due to the radiative recombination from the conduction band and/or shallow donors to the surface states and disappeared after S treatment [15,16].

The increase of luminescence intensity after S treatments is clearly attributed to the reduction of surface nonradiative recombination velocity due to the reduction of surface states. In Fig. 2, there are also two PL bands centered at 1.14 eV and at a range of 0.72–0.95 eV. Leonelli suggested that the broad peaks are related to the phosphorous vacancy (V_p) and the sulfur at phosphorous site (S_p) [17]. We can observe that there is only Vp-related peak in the sample without sulfur passivation, then significant Sp-related peaks were observed after passivation for 10 min. After passivation for 20 min, the intensity of V_p-related peak reduced, which is due to the process of passivation, sulfur occupies the position of the V_p. Thus, the density of V_p decreases, the peak of V_p-related weakens. Rao et al. had reported that the 1.14 eV band was tentatively attributed to a V_p related complex [18]. Our results also support this point.

Fig. 3 shows the normalized temperature-dependent PL spectra of the InP sample with passivated in 8% $(NH_4)_2$S. It is observed that the BE peak redshifts with increasing temperature, originating from the band gap of the bulk InP decreases primarily due to electron–phonon interaction and partially due to thermal expansion [19]. It can be fitted by Varshni's empirical formula $E_g(T)$ [19]:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \tag{1}$$

We obtained the parameters according to Fig. 4 as: $E_g(0) = 1.464$ eV, $\alpha = 6.5 \times 10^{-4}$ eV/K, $\beta = 150$ K. With the temperature increasing, the bandgap of the bulk InP becomes narrower (the energy of radiative recombination released becomes lower), So the peak position shows redshift. At 30 K, the PL peak located at about 1.418 eV is due to the transition from the conduction band to acceptors (e-A). When the temperature is up to 77 K, there exist two peaks which are located at 1.417 and 1.442 eV and are attributed to the e-A and BE emission, respectively. At 150 K, the two peaks are more apparently. The origin of the 1.368 eV peak at 150 K is the same with the 1.417 eV peak at 77 K. And the origin of the 1.409 eV at 150 K is also the same with the 1.442 eV peak at 77 K. As the temperature reaches up to 200 K, the BE peak located at 1.383 eV dominates. At room temperature, the main peak is the BE peak which centered at about 1.342 eV.

To further investigate the influence of passivation on luminescence properties of InP, we analyzed the PL spectra measured at 77 K. Fig. 5 shows the normalized PL spectra of the samples a–e. The band centered at about 1.278 eV in the PL spectrum of un-treated sample is due to the e/D-ss transition peak discussed above, which disappeared after S-treatments. The band centered at about 1.403 eV are the e-A transition peaks, and the band centered at about 1.45 eV are the BE peaks. It can be observed that the BE peaks are apparent in the untreated, S-treated for 5 min, 10 min and 15 min samples, when the S-etching time is more than 20 min, the BE peak becomes weak, and even when disappeared as the etching time reached 25 min. The reduction of the density of surface states caused by S passivation decreases the surface recombination velocity and improves the PL intensity of the InP. SRV is proportional to the trap density and also depends on the capture cross sections of electron and hole traps. It should be noted that the PL intensity is not only sensitive to SRV, but also depends on other parameters, such as minority-carrier diffusion length and band bending due to the field of charge space near the surface [20–22].
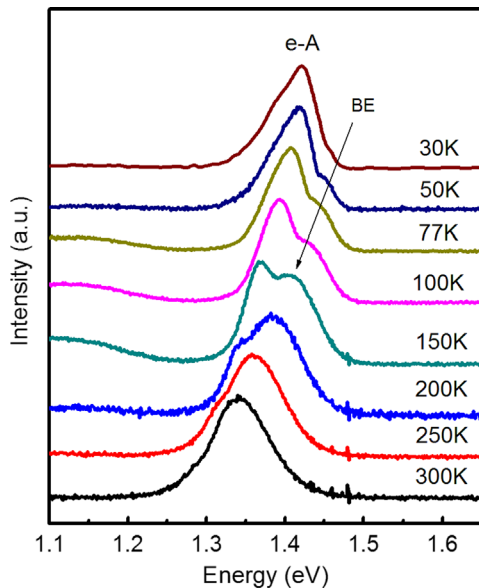

Fig. 3. The normalized temperature-dependent spectra of the InP sample with passivated time of 10 min.
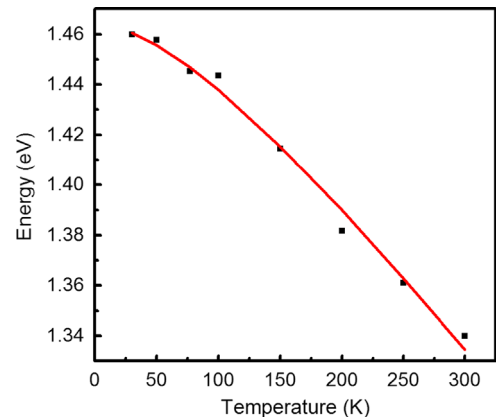

Fig. 4. The band gap energy of the bulk InP with various temperature.

In order to investigate the chemical state at the InP surface, we performed the XPS measurment. Fig. 6 shows the XPS spectra of P 2p and S 2p core levels for the InP samples with and without S-treatment. The peak ranging from 127.5 eV to 131 eV originates from the peak of P–In bonds. It can be fitted into two peaks, which is attributed to the P $2p_{1/2}$ and P $2p_{3/2}$, respectively. Han et al. have reported similar results [23]. The bands ranging from 132 eV to 135 eV are attributed to $InPO_3$ and $InPO_4$ [23]. It can be observed that, for the InP without S-treatment, the $InPO_4/InPO_3$-related peak is apparent, however, for the ones with S-treatment, the $InPO_4/InPO_3$-related peaks disappeared and the In–P bonds peaks are dominant. This result suggests that the oxidation layer of the surface is removed after 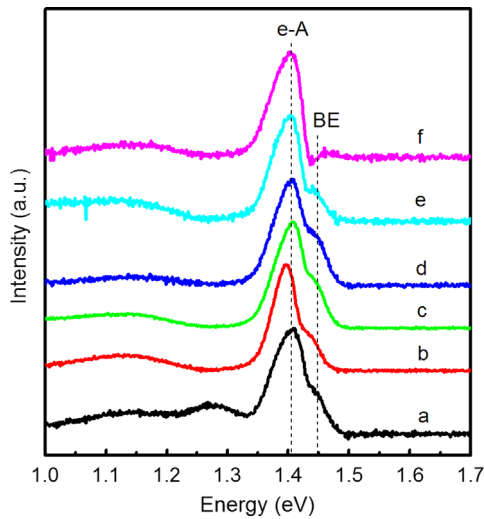S-passivation. Fig. 6b shows the XPS spectra of S 2p core level of the two S-treated samples for 10 and 20 min. The peak ranging from 160 eV to 162.7 eV is attribute to the monosufile which contains only the S $2p_{3/2}$-In bonds and S $2p_{1/2}$-In bonds [23]. Because the peaks of P–S bonds are not observed in the spectra of P 2p. The peaks located at 163 eV are related to elemental sulfur [23]. It can be seen that the peak of elemental sulfur becomes stronger after S-treatment for 20 min than S-treatment for 10 min. The relative atom concentration ratio of Sulfur element and In-S bonds is calculated by the following formula [24]:

$$\frac{n_i}{n_j} = \frac{\sum_i I_i / S_i}{\sum_j I_j / S_j} \qquad (2)$$

where $S = 0.54$, is the XPS atomic sensitivity factor of S. We calculated that the relative atom concentration ratios of Sulfur element and In–S bonds were 1/32.4 and 1/9.55, for the samples c and e, respectively. It shows that the surface of InP was covered with a thick S overlayer after S-treatment for 20 min. From the XPS results, we can draw conclusions as follows: (i) dangling bonds at the surface are terminated by S–In bonds without oxide and S–P bonds; (ii) the oxide of InP surface is removed by the sulfide passivation; (iii) the surface of InP is covered with a thick S overlayer after long-time S-treatment and the thick S overlayer would decrease the PL output.

Fig. 7 is the AFM morphology of the samples a, b, c, and e. We can observe that the surface morphologies of InP become more and more rough with the passivation time extending. The surface of sample A is very smooth and there is no convex and concave. With the increase of passivation time, the numbers of bulges on the surface increased and became larger. We can observe that the surface of sample E is very rough, it is due to the etch of the alkaline solution and the deposition of polycrystalline sulfur on the surface.
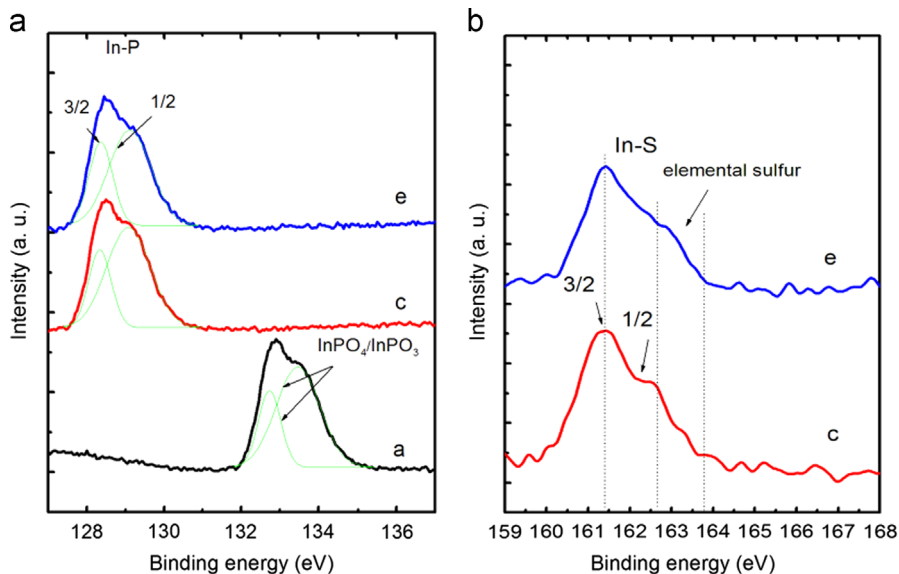

Fig. 5. Normalized 77 K spectra of the InP samples with various passivation time.

Fig. 6. (a) The P 2p and (b) S 2p XPS spectra of the InP with and without S-treatment.
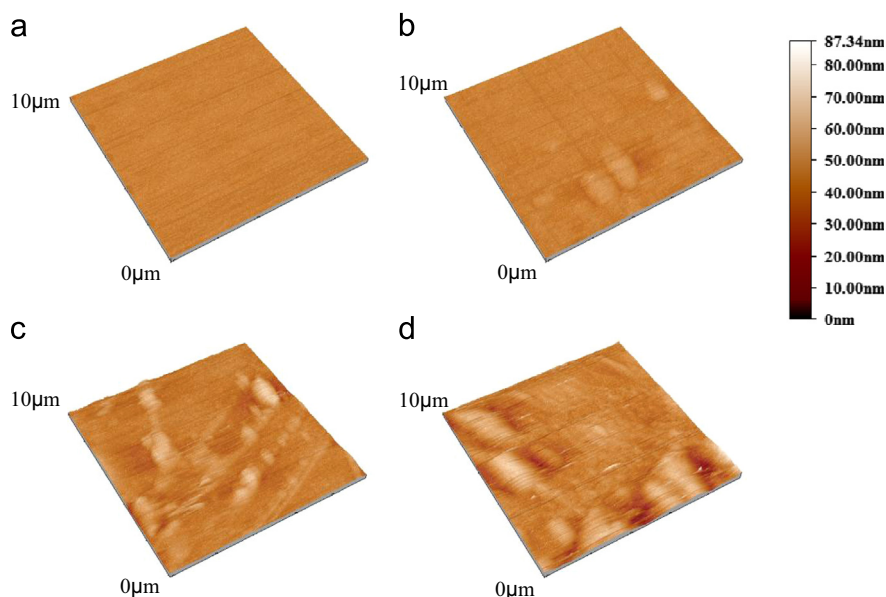
Fig. 7. The AFM morphology of the samples a, b, c, and e.

4. Conclusions

The luminescence properties of the S-treated InP surfaces were investigated by PL measurement. The PL intensity of InP after sulfuration for 10 min increased by a factor of 3.2 compared to the untreated one. After S passivation, the oxide of InP surface is removed, the dangling bonds at the surface are terminated by S–In bonds. The reduction of the surface states and low surface nonradiative recombination velocity lead to the enhancement of the PL intensity. After S-treated for 10 min, the PL intensity begins to decrease and even weaker than the untreated one when treated time reached 25 min. The surface of the InP is covered with a thick S overlayer after long-time S-treatment and the decrease of the PL output should be caused by the thick S overlayer. Our investigation indicates that the luminescence properties are strongly dependent on the process of sulfurization treatment.

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