Photoluminescence of n-InP (100) surface passivated with aqueous Na$_2$S solution

Y M Serov$^1$, M V Lebedev$^1$, O V Rakhimova$^2$, T V Lvova$^1$, I V Sedova$^1$

$^1$Ioffe Institute, St. Petersburg, Russia
$^2$St. Petersburg Electrotechnical University LETI, St. Petersburg, Russia

Abstract. Passivation of the n-InP(100) surface with an aqueous solution of sodium sulphide (Na$_2$S) has been investigated by spectroscopic photoluminescence (PL). After sulphide treatment the PL signal intensity of InP increased significantly and this increase is dependent on duration of sulphide passivation. The correlation of the increase in the PL intensity after sulphide treatment with the variation of the solution pH in contact with InP(100) surface has been established, that expect the possibility for optimization of the passivation process by monitoring the change of the solution pH value in the course of sulphide treatment of the semiconductor.

1. Introduction

Indium phosphide (InP) is a III–V direct gap semiconductor used in high frequency electronics and optoelectronics. However, its applications, especially the ones based on InP nanostructures, are suffering from the surface instability, inducing detrimental effects on the surface electronic and optical properties. Sulphur-based surface passivation intended to mitigate these effects has been investigated since late 1980s and is proved to improve device properties, such as Schottky barrier temperature stability [1] and field-effect transistor parameters [2]. Nevertheless, early works show no impact of sulphur passivation on the InP photoluminescence (PL) intensity [3]. More recent results [4] demonstrate that InP PL signal might be enhanced essentially by sulphide treatment, though the dependence of the PL intensity on the time of sulphide treatment is non-monotonic, and thus the optimization of the sulphide passivation process should be performed. In the major part of the literature on sulphur passivation of InP the treatment with ammonium sulphide [(NH$_4$)$_2$S] solutions is considered as a rule. At the same time, the impact of InP treatment with aqueous solutions of sodium sulphide (Na$_2$S) on the PL intensity have not been investigated so far, even though aqueous Na$_2$S solutions demonstrates higher efficiency of GaAs surface passivation than the aqueous (NH$_4$)$_2$S solutions [5]. On the other hand, for the GaSb surface passivation with an aqueous Na$_2$S solution it was shown that the PL intensity correlates with the variation of the solution pH during the surface treatment [6]. Here we adopt this approach for optimization of the InP passivation process and study the effect of the surface treatment with aqueous Na$_2$S solution on the PL of n-InP (100) surface.

2. Experimental procedure

Two sets of samples have been prepared from the Te-doped n-type InP (100) wafers with the doping density of about $2 \cdot 10^{17}$ cm$^{-3}$ and $1 \cdot 10^{18}$ cm$^{-3}$. The wafers were cleaned by boiling in toluene and twice in acetone for 5–7 min each and then rinsed with stream of bidistilled water for 5 min.
At first, the variation of the solution hydrogen potential (pH) during interaction with InP surface was monitored using the sample cleaved from the cleaned wafer with the doping density of $2 \cdot 10^{17}$ cm$^{-3}$. The pH dependence on time was measured with a glass-electrode pH meter (Sartorius PP-15, Germany) with an accuracy of ±0.002. The glass electrode was fixed on a stand rod. The 20 mL of the freshly prepared 1M Na$_2$S aqueous solution was put into a standard beaker with a total volume of 50 mL heated by a hot plate. Prior to recording the pH variation, the solution was heated to the temperature of about 40°C, and then stored in contact with the glass electrode of the pH-meter approximately for 5 min before stabilization of the pH-value signal. After signal stabilization, the InP sample with the area of about 1 cm$^2$ was placed into the solution on the bottom of the beaker beneath the glass electrode and the dependence of the solution pH on time of the contact with semiconductor was recorded. The distance from the sample surface to the glass electrode tip was about 1 mm.

Other cleaved samples, except the reference ones, were treated with a 1M aqueous solution of sodium sulphide (Na$_2$S·9H$_2$O, Aldrich) at a temperature of about 40°C for different periods of time from 1 to 15 min. The times of treatment were chosen in accordance with the previously measured pH-time dependence in order to check the hypothesis on the correlation between the solution pH value and the obtained effect of passivation on the sample PL.

For the PL measurements the samples were fixed in the cryostat and studied either at room temperature (300 K) or at liquid nitrogen temperature (77 K). The photoluminescence was excited with a diode laser with the wavelength of 377 nm in continuous mode or 405 nm in pulsed mode. The laser beam was focused on the sample surface into the spot with the diameter of about 50 μm by the lens with the focal length of 79 mm. The photoluminescence signal was collected with the apochromatic triplet and focused on the spectrometer entrance slit. PL spectra were obtained with a Princeton Instruments SP-2500 spectrometer ($L = 0.5$ m, grating – 300 lines/mm) and detected with a CCD-camera. In order to compensate possible surface inhomogeneity, the PL spectra for the each sample were averaged over the surface after the measuring in a few points. Also during the measurement it was discovered for the samples under investigation that the PL signal from any point on a sample rises over a time of laser irradiation. We associate such a behaviour with the saturation of deep traps near the irradiated point and mitigate the impact of the phenomena by fixing the 1 min duration of surface irradiation before measurement.

**Figure 1.** Na$_2$S solution pH variation during the treatment of the InP(100) surface. The stages of the process are labeled under the plot as I, II and III (see the text). The black line represents the smoothed pH curves, while the gray dots correspond to the raw data.

### 3. Results and discussion

The measured dependence of the solution pH on the time of InP exposure to the solution is presented in figure 1. Since the measured values of pH after 1.5 min of treatment look fluctuating, the smoothed black line is presented in figure 1 along with the original data. The small peak on the pH curve, appearing at the beginning of the measurement process, might be associated with the establishing of the equilibrium in the solution after the disturbance induced by immersing the sample. Thus, the treatment process can be divided into three stages, denoted in figure 1 with Roman numerals. At the first stage, within the first minute of InP surface exposure to the Na$_2$S solution, the pH value remains
constant. Approximately after 1 min of exposure to the solution, the pH value increases sharply and then does not change significantly up to 3.5 minutes. Indeed, even though the smoothed line in figure 1 starts rising before 3 minutes, but its rise does not exceed the fluctuations level shown in figure 1 by the dashed horizontal lines until 3.5 min. And at the third stage of the process, the pH goes up monotonically. Such a behavior draws our attention to the treatment time periods at the border-lines between stages, specifically to the times of 1 min and 3.5 min. The corresponding samples allow us to distinguish the effects of different stages of the passivation process.

Figure 2 shows the measured average PL spectra of the InP reference sample with the doping density of $1 \cdot 10^{18}$ cm$^{-3}$ and the 3.5 min sulphide passivated sample from the same wafer. The spectra obtained for these samples at 77 K and 300 K are shown in figure 2 (a) and (b) respectively. All measured spectra of the InP PL at room temperature exhibit peaks approximately at 920 nm, corresponding to the band edge emission. At the 77 K the band gap becomes wider and the maximum of band edge emission shifts to the 873 nm. The shapes of the band edge PL spectra measured both at 300K and 77K are clearly unaffected by the sulphide treatment, while the PL intensity rises after passivation. Similar results were obtained for others samples with the same doping level with the small variation of the PL intensities between samples with different passivation time (1 min, 3.5 min, 10 min). However, there is the clear distinction in PL intensity between the reference and 3.5 min-treated samples. One can see the moderate 1.5-fold and 1.9-fold PL enhancement at 77 K and 300 K, respectively.

![Figure 2](image_url)

**Figure 2.** Average PL spectra of the InP samples set with the doping density of $1 \cdot 10^{18}$ cm$^{-3}$ at 77 K (a) and 300 K (b). The PL was excited with the 405 nm pulsed laser with the excitation density of 50 W cm$^{-2}$. Reference spectra are shown in dashed lines, while the solid lines represent typical PL spectra of the sulphide treated sample.

The similar results obtained for the samples with the doping density of $2 \cdot 10^{17}$ cm$^{-3}$ at 77 K and 300 K are shown in figure 3 (a) and (b), respectively. But in this case we observe much more pronounced PL enhancement in the spectra measured at 300 K. On the other hand, the PL increase at 77 K remains almost the same as in the highly-doped samples. So we can conclude that the effect of surface passivation on InP PL intensity is more essential at room temperature than at 77 K. It may be associated with the suppression of the surface recombination at low temperature, in which case the surface initially exerts less influence upon the PL intensity.
Figure 3. Average PL spectra of the InP samples set with the doping density of $2 \cdot 10^{17}$ cm$^{-3}$ at 77 K (a) and 300 K (b). The PL was excited with the 377 nm continuous wave laser with the excitation density of 250 $\text{W} \cdot \text{cm}^{-2}$. Reference spectra are shown in dashed lines, while the solid lines represent typical PL spectra after passivation.

The outstanding PL enhancement observed for the sample with $2 \cdot 10^{17}$ cm$^{-3}$ doping density at 300 K provides us a possibility of the meaningful comparison between the samples subjected to exposure to the sulphide solution for different time. In order to perform the comparison, the values of the PL intensity enhancement achieved after passivation were considered as ratios of the sample PL integral intensities to the integral intensity of the corresponding reference sample. The dependence of the PL enhancement on the treatment time is shown in figure 4 and exhibits clear non-monotonic behavior. The aforementioned choice of treatment durations based on the pH measurements allow us to conclude, that the passivation efficiency rises over time at the first stage of the passivation process, yielding the increase of the surface PL intensity, while at the second stage the PL intensity even slightly decreases, and then at the third stage remains almost constant. This behavior indicates that the major part of changes of the surface condition occurs at the initial 3.5 min of the passivation process, while the most important chemical processes probably are finished within the first minute. The x-ray photoemission spectroscopy (XPS) measurements were conducted in order to determine the chemical state of the surface and identify the specific mechanism of the InP surface passivation. The detailed XPS study is going to be published later, but the preliminary results testify good agreement with the aforementioned hypothesis, featuring essential reduction in the O/In ratio and appearance of the sulphur photoemission after sulphide treatment for the first minute of InP exposure to the solution indicating removal of the native oxide layer at this stage of the treatment. Longer treatment does not affect essentially the S/In ratio on the surface, while the O/In ratio stops to change when the treatment time exceeds 3.5 min.

It is also interesting to compare the observed impact of the InP passivation with aqueous Na$_2$S solution on the PL of the low-doped samples ($2 \cdot 10^{17}$ cm$^{-3}$) with the similar results reported by Tian et al for the passivation with the aqueous (NH$_4$)$_2$S solutions of the InP samples with a similar doping level [4]. In [4] the 3.2-fold PL enhancement was reported after 10 minutes of treatment with smaller values of enhancement for shorter or longer treatment. Comparing it with the results obtained in the present study we can assume, that the passivation by aqueous sodium sulphide solution might be more effective approach, yielding better results in a shorter time. On the other hand, the difference between the results for the two sets of samples under investigation (figures 2 and 3) suggests that there might be a number of subtle parameters beside the doping density, prohibiting such direct comparison of PL
enhancement without performing an experiment with different sulphide solutions in standardized conditions.

![Figure 4](image.png)

**Figure 4.** Dependence of the PL intensity enhancement on the time of the InP surface treatment with the aqueous Na$_2$S solution. The stages of the passivation process determined from the pH variation data are labeled under the plot as I, II and III.

4. Conclusion
The passivation of n-InP(100) surface with an aqueous Na$_2$S solution can improve essentially the PL properties of the semiconductor without any significant changes in spectral shape. The PL enhancement by a factor of 6.7 was observed for the low-doped (2 · $10^{17}$ cm$^{-3}$) sample treated with aqueous Na$_2$S solution for 1 min at room temperature, while smaller PL enhancement values were obtained for other conditions of sulfur treatment. The comparison of the PL enhancement with the solution pH exhibits clear correlation and proves that the optimization of the InP sulphide passivation process with the Na$_2$S solution can be based on the control of the solution pH value during sulphide treatment and should use the sharp increase of pH as a reference point. It also indicates that the core modification of the InP surface during the treatment takes place in an initial few minutes of exposure to the solution. During this short period of time the passivation efficiency rises in the first minute and slightly decreases afterward, implying the necessity of the process optimization.

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