Effect of passivation on the n-InP optical and electronic properties

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Abstract. The effect of sulphur surface passivation on the optical and electronic properties of InP was investigated. In the work, the approach of simultaneous measurement of the dynamics of the absorbed current and cathodoluminescence under continuous electron beam irradiation is used. This approach allows us to study the trapping of charge by traps and their influence on the luminescent properties. It was shown that hole traps are observed in the samples; moreover, the localization of a positive charge leads to an increase in the luminescence intensity. Passivation was found to significantly reduce the number of hole traps.

1. Introduction
Indium phosphide (InP) is a very prospective III–V semiconductor material used in various high-speed electronic and optoelectronic applications [1–3] due to its direct band gap and high electron mobility. The continuous downscaling of semiconductor devices towards nanosize range increases impact of surface and interface properties on the device performance. As a rule, the III–V surfaces contain high density of surface states within the band gap that causes non-radiative surface recombination. These surface states are caused by defects introduced by formation of the native oxide layer. To reduce the detrimental effects of surface states on the optical and electronic properties of semiconductor these surface states should be passivated. The prospective method for III–V surface passivation is wet chemical passivation that enables removal of the native oxide layer and simultaneous formation of the thin layer consisting of chemically inert material. One of such methods for chemical passivation is the sulfur passivation [4], which is the treatment of the semiconductor surface with sulfide solutions.

2. Samples and experimental methods
The samples were cut from a Te-doped n-InP(100) wafer with the doping density of about 10^{18} cm^{-3}. Three samples were studied – initial, sulfur-treated for 10 min and sulfur-treated for 15 min. The treatment was performed with a 1M aqueous solution of sodium sulfide (Na_2S) at 40 °C. The treatment time was chosen by analogy with the results obtained on the related material GaP [5].

The surface morphology of the samples before and after passivation was analyzed by the atomic force microscopy (AFM) method using an NTegra Aura (NT-MDT, Zelenograd, Russia) setup in room conditions. The standard NSG-01 probes with a tip curvature of less than 10 nm were employed. The surface morphology was characterized by the root-mean-square (RMS) roughness of the sample surface averaged over 3×3 μm² area with 11 nm resolution.

The cathodoluminescent properties of the films and the dynamics of the absorbed electron beam current were studied on a CAMEBAX electron probe microanalyzer (Cameca, France) equipped with an original optical spectrometer for recording cathodoluminescence spectra [6]. The CL intensity and
absorbed current dynamics were studied at 77 K. The electron beam energy of 2.5 keV was used, which corresponds to the penetration depth of about 40 nm. The electron beam current was 5 nA, while the electron beam diameter was 8 μm. Each spectrum was recorded for 1 minute. CL spectra were obtained using a filter that cut off the spectral bands in the visible range up to 1.7 eV. The simultaneous measurement of the absorbed current dynamics and CL intensity allowed checking the presence of the traps in the samples under the study, as well as to reveal the influence of these traps on the luminescent properties [5]. In addition, such an approach enabled determination of the type and concentration of the traps, as well as the probability of the charge localization.

If the electron traps occur in the sample, then they can capture electrons after starting the electron beam irradiation. Therefore, in the beginning, the absorbed current measured by a nano-ampere meter can be much lower than in the sample without electron traps. On further irradiation of the sample with electron beam, the number of unoccupied electron traps is reduced and thus the absorbed current increases to the steady-state value corresponding with the equilibrium between electron capture and release processes. Once the hole traps occur in the sample, the initial absorbed current will be higher than in the similar sample without the hole traps due to generation of additional free electrons. On further irradiation, the hole traps will be filled and the current will decrease to the steady value at which the hole capture and release will compensate each other. The characteristic time of the change in the absorbed current depends on the probability of carrier capture by traps. In general, the time dependence of the absorbed current $J(t)$ for the sample with one type of electron and hole traps can be described as follows [7]:

$$J(t) = J_0 - A_e \exp\left(-\frac{t}{\tau_e}\right) + A_h \exp\left(-\frac{t}{\tau_h}\right),$$

(1)

where the term $A_e \exp\left(-\frac{t}{\tau_e}\right)$ represents the contribution of the electron traps, whereas the term $A_h \exp\left(-\frac{t}{\tau_h}\right)$ represents the contribution of the hole traps. The coefficients $A_e$ and $A_h$ are proportional to the trap densities in the sample; $\tau_e$ and $\tau_h$ are characteristic times of electron and holes capture processes and, correspondingly, $1/\tau_e$ and $1/\tau_h$ are the probabilities of the electrons and holes capture by traps. It should be noted that several types of traps for one kind of carriers can occur in a real sample and thus the experimental dependencies can be even more complex. In this approximation, the traps density can be estimated as the area under the corresponding curve, or $S=A*\tau$, equivalent to the value of the localized charge.

3. Results and discussion

3.1. Atomic Force Microscopy

The topography of the sample surface before passivation (figure 1a, 1d) and after sulfide treatment for 10 (figure 1b, 1e) and 15 minutes (figure 1c, 1f) clearly specifies that the treatment with 1M aqueous Na$_2$S solution for 10 or 15 min improves surface morphology in similar extents. The RMS value decreases twice from 0.28 nm for the initial sample to 0.14–0.16 nm for sulfur-treated samples. On the other hand, the increase in the time of treatment can result in formation of the thicker passivating layer, which may hamper the CL intensity. Therefore, we have chosen the sample exposed during 10 minutes for the further studies of the influence of wet sulfur treatment on the CL output.
Figure 1. Surface topography and the corresponding depth profiles along white horizontal lines for InP(100) samples before (a, d) and after passivation for 10 (b, e) or 15 min (c, f).

3.2. Cathodoluminescence and absorbed current

The CL spectra of initial and passivated samples measured at two distinct locations on both samples are shown in figure 2. The spectra consist of two bands. The band with the maximum at 1.41 eV corresponds with the band edge luminescence whereas the band with the maximum at 1.17 eV is caused by the point defects luminescence. The CL intensity distribution of initial sample is less homogeneous than that of the passivated sample. The dynamics of the CL intensity and absorbed current under continuous electron beam irradiation was obtained for 1.41 eV band.

Figure 2. The CL spectra of initial (a) and passivated (b) InP. Lighter and darker curves of the same color correspond to different places of the same sample.

The dynamics of the CL intensity in all cases demonstrate two competing processes (figure 3). One process is the CL enhancement with the time constant $\tau_{\text{CL}}$ similar to the time constant $\tau$ of the absorbed current decay. The other process is the decay of the CL intensity with much longer time constant. We assume that the CL enhancement is related to charge localization, whereas the decay is caused by the growth of the contamination film at the surface [8]. The enhancement of the CL intensity is also observed for 1.17 eV band testifying that the holes capture by the surface traps results in the decrease of the non-radiative recombination.
Figure 3. Dynamics of the absorbed current and CL intensity under continuous electron beam irradiation for initial (a, c) and passivated (b, d) InP. Lighter and darker curves of the same color correspond to different places of the same sample.

The absorption current dynamics demonstrates only the exponent describing positive charge localization on the traps. The dynamics of absorbed current and CL intensity were approximated on the basis of (1) and the results are shown in Table 1. As was mentioned above, the CL intensity varies from point to point, but the characteristic time $\tau_{CL}$ remains constant. The absorbed current and CL intensity dynamics have similar time constants, which enables us to testify that the localization of the solely positive charge causes increase in the CL intensity.

| Sample     | CL (1.4 eV band) $\tau_{CL}$ | Absorbed current |
|------------|-------------------------------|------------------|
| Initial    | 0.9 s                         | 1.2 s, 3.1 nA, 3.7 nC |
| Passivated | 0.4 s                         | 0.3 s, 0.98 nA, 0.3 nC |

Table 1. The approximation parameters for the dynamics of CL intensity and absorbed current.

Obviously, the localized charge decreases by a factor of 12 after sulfur passivation indicating the considerable decrease in the traps density.

4. Summary

The n-InP(100) samples were investigated before and after passivation with 1M aqueous Na$_2$S solution. It was shown that the passivation results in essential smoothening of the InP(100) surface. The CL properties became more uniform after the sulfur passivation. Under electron beam irradiation the positive charges localize at the traps and this localization results in the increase of the CL intensity. We
suggest that the charge localization occurs at the non-radiative recombination centers. The charge capture by these centers causes reduction in the non-radiative recombination probability. To conclude, the wet sulfur passivation of the n-InP(100) surface reduces the amount of the surface traps and improves the properties of the semiconductor.

Acknowledgements
The reported study was funded in part by RFBR, project number 20-03-00523.

References
[1] Rouvalis E, Renaud C C, Moodie D G, Robertson M J, Seeds A J 2012 IEEE Trans. Microw. Theory Tech. 60 509
[2] Smit M, Williams K, van der Tol J 2019 APL Photonics 4 050901
[3] Liu L, Alt A R, Benedickter H, Bolognesi C R 2012 IEEE Electron Device Lett. 33 209
[4] Lebedev M V, Lvova T V, Shakmin A L, Rakhimova O V, Dementev P A, Sedova I V 2019 Semiconductors 53 892
[5] Lebedev M V, Dementev P A, Lvova T V and Berkovits V L 2019 J. Mater. Chem. C 7 7327
[6] Zamoryanskaya M V, Konnikov S G, Zamoryanskii A N 2004 Instrum. Exp. Tech. 47 477
[7] Dement’ev P A, Ivanova E V, Zamoryanskaya M V 2019 Phys. Solid State 61 1394
[8] Orekhova K N, Serov Yu M, Dement’ev P A, Ivanova E V, Kravets V A, Usacheva V P and Zamoryanskaya M V 2019 Technical Physics 64 1336