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# Photoluminescence Characterization of $Al/Al_2O_3/InP$ MIS Structures passivated by anodic oxidation

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**Abstract**

Metal-insulator-semiconductor (MIS) structures were produced by electron beam evaporation of $Al_2O_3$ on InP. Polyphosphate thin films of thickness 100–150 Å were used to passivate the interface InP\Insulator. Photoluminescence spectra are reported at low temperature at various stages of the realization process of the MIS-InP structure. Photoluminescence topography at ambient temperature made it possible to characterize the surface state after each technological stage. The interface degradation under the effect of repeated annealing is insignificant up to temperatures of 350 °C. Radiative major defects detected by photoluminescence spectrum with energy 0.95–1.15 eV attributed to the complexes impurities of phosphorus vacancies are substantially reduced by the presence of anodic oxide.

**Key Words:** Indium phosphide; MIS structures; Photoluminescence.

## 1. Introduction

The performance advantages of the compound semiconductor indium phosphide (InP) cannot be fully exploited in microwave and optoelectronic systems until a process is developed to control surface-related instabilities and failure mechanisms. In spite of the promising properties of InP, the problems which slow down the expansion of MISFET-InP are still far to being solved. The passivation of the surface of the III-V compound is necessary and toward this need various chemical treatments have been studied [1–4]. The electrochemical approach used in several previous works [5–7] allows a better control of the treatment and a broad range of oxidation parameters which affect the properties of the obtained oxide. However, in recent years, there have been many reports on the potential passivating properties of anodic oxide for the interface of the MIS-InP structures [8, 9]. The characterization of the interface of the MIS structures is generally based on measurements of high frequency capacitance (Terman analysis) or on quasi-static mode (Berglund technique). These methods require the use of good quality dielectric material deposited by relatively soft methods to preserve the fragile surface of InP [10]. It is thus interesting to develop new characterization methods of the interface to overcome these constraints. Of all the properties that characterize Photoluminescence (PL), the intensity of the PL signal has received the most attention in the analysis of interfaces. This interest is due to the fact that, although several important mechanisms affect the PL response, it is generally found that large

PL signals correlate with good interface properties. PL is a simple, fast, contactless, nondestructive and sensitive method to detect the presence of interface defects [1, 10, 11]. Being a direct gap semiconductor, InP has a very high measured PL signal even at room temperature. A broad ranges of utilization can be made possible for this characterization technique namely, PL spectra at low temperature, PL topography, integrated PL at ambient temperature and PL under electric polarization [10–13]. Even if the setting of this characterization method can be made simple and very flexible, the interpretation of the measurements results are still remaining very delicate. The differences in the PL intensities observed are generally attributed to the interface or surfaces defects and/or to the electric potential of surface.

In this work, we present a simple and useful method for preparing MIS structure on InP with a reduced complexes impurities of phosphorus vacancies. In addition, it is our objective to track the changes of the PL spectra as well as the changes in its topography measured after various technological realization stages of MIS on InP structures subject to electrochemical treatment.

## 2. Experiment

Two standard (100) oriented $n$-InP doped samples ($\sim 10^{16}\,\mathrm{cm}^{-3}$) were used. Samples were cleaned in hot trichloroethylene and rinsed in methanol, and DI water. They were briefly etched in 40% HF solution for 60 s to remove surface defects and oxide layers. Immediately the reference PL spectrum as well as a PL topography are characterized on one of the two samples. The second sample undergoes an electrochemical treatment using a solution of AGW composed of 3% diluted orthophosphoric acid (pH = 2) mixed in glycol propylene in 1:2 ratio. Anodic oxidation of InP is carried out under white light illumination. The first oxidation phase is known as galvanostatic, where the current density remains at $0.2\ \mathrm{mA}\cdot\mathrm{cm}^{-2}$ until the terminal voltage of the oxidation cell reaches 20 V, after which the potentiostatic mode switched to a softer termination of the treatment. The double-layered structure is a characteristic of this type of oxide. The outer Indium-rich thin layer, strongly hydrated, presents poor dielectric properties. At the interface, one finds a thicker layer of condensed phosphates of better quality, similar to $In(PO_3)_3$. The outer layer is dissolved using 0.01% diluted HF solution for 120 s, which allows keeping a phosphorus-rich layer with a thickness of 150 Å. The sample then undergoes annealing at 250°C under $N_2$ atmosphere for 20 min to eliminate any residual water traces.

The next step is the deposition of the insulator (1000 Å of $Al_2O_3$) on the two samples. The deposition is carried out by electron beam heating evaporation within secondary vacuum environment and oxygen partial pressure. This technique is based on the heat produced by high energy electron beam bombardment of the material to be deposited. The electron beam is generated by an thermoionic emission electron gun. Emitted electrons are accelerated towards an anode via a high potential difference (on the order of kV). The crucible is perforated and acts as the anode. A magnetic field is often applied to bend the electron trajectory, allowing the electron gun to be positioned below the evaporation line. An annealing at 300°C under oxygen for 30 minutes helps to compensate the deficit in oxygen, a deficit generally observed in this type of deposit. A final annealing step under forming gas ($H_2$-$N_2$) at 350°C for two hours is performed to cure certain interface defects and to improve the quality of the structure.

To finish the fabrication of the MIS-InP structure, semi-transparent Aluminium contacts are deposited for PL measurements under electrical polarization. Measurements of PL spectra and PL topography were carried out after every technological step and every annealing. Photoluminescence data were collected with samples at liquid nitrogen temperature using an Oriel 7240 monochromator with an argon laser at a wavelength of 514.5 nm and output power of 100 mW. The sample receives only 3 mW distributed on a spot of 2.2 nm of diameter. A silicon detector covers the spectral field 430–1060 nm. The PL topography measurements were performed in air at room temperature. The samples were moved in the X-Y plane under a focused laser beam. The 632.8 nm line of He-Ne laser (power 5 mW) was used for the excitation and the spot diameter of the focused laser beam was ranged from 3 to 80 $\mu$m. A silicon photodiode was used

to receive the excited PL signals. The system is completely controlled by computer. A comparative study between various measurements is made possible and allows presenting conclusions as far as the influence of the treatment used on the quality of the structure is concerned.

# 3. Results and Discussions

## 3.1. Photoluminescence

The reference spectrum reported on naked substrate is typical for an n-InP sample [14–16]. It presents three typical peaks as shown in Figure 1. The highest peak, $I_1$, located at 1.41 eV, shows a luminescence close to the gap which is due to bound excitons related to the surface impurities. A broader peak $I_2$ located at 1.37 eV is attributed to the band-acceptors or donor-acceptors transitions. A broader band $I_3$, having energy in the interval ranged from 0.95 to 1.15 eV, also known as "Band C," is generally attributed to the impurities (Fe, Cu, Mn, Co, Zn) forming complexes and defects with the phosphorus vacancies.

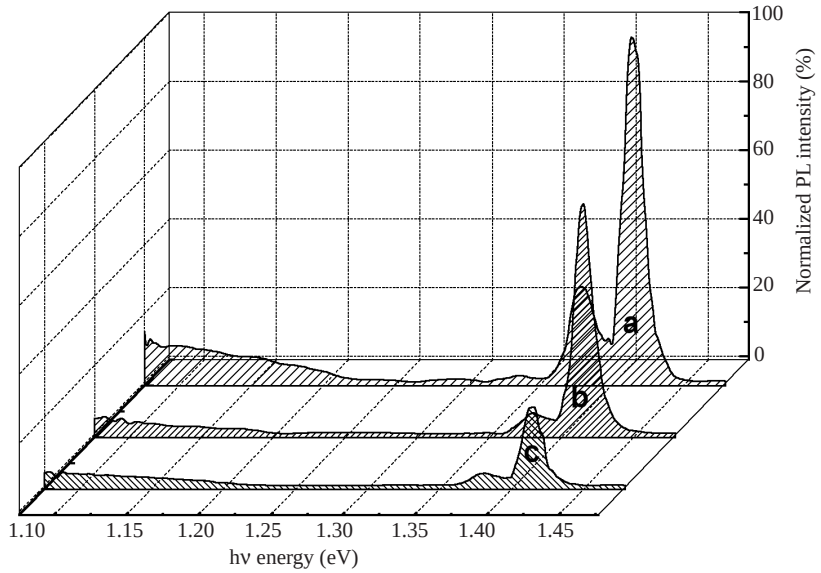


**Figure 1.** The PL spectra of InP surface measured at 77 K after annealing under oxygen ambient at 300 °C: (a) HF pilot sample; (b) passivated InP surface; (c) unpassivated InP surface.

A qualitative indication of passivation is therefore achieved by comparing the PL intensity of the HF pilot sample, passivated InP surface and unpassivated InP surface. Table 1 shows The PL results of the InP surface measured at 77 K according to the conditions of the subsequent processing. The PL spectra reported after anodic oxidation and dry annealing presents a comparable form to proceeding with a considerable reduction of the intensities of all peaks. However, an increase in ratio $I_1/I_2$ is noticed. This behavior can be attributed to a strong curving of energy bands close to the surface [17] due to negative charges existing in the condensed anodic phosphates $In(PO_x)_y$. Indeed, $y$ is generally greater than 3, corresponding to the stoichiometry. In addition to this, measurements of the capacitance-voltage (C-V) characteristics on thicker anodic oxides (around 800 Å) has shown an apparent shift towards positive voltages, which indicates a situation of depletion at rest. However, this observation doesn't completely exclude the presence of defects in InP-Oxide interface involving nonradiative recombinations. After deposition of the insulator on the two samples, we can see clearly (see Table 1) the difference between a surface protected by the anodic oxide and a naked InP surface. The PL increased considerably for the electrochemically treated sample then it strongly falls down for the untreated sample. It is clear that the deposition of$Al_2O_3$ by evaporation using the

electron gun considerably degrades the fragile surface of InP. The increase of luminescence from the treated sample can only be explained by a change in the surface potential due to a global positive charge in the deposited $Al_2O_3$. This positive charge is due to the deficiency in oxygen generally reported for this type of deposit. An annealing under oxygen is generally necessary to improve the quality of $Al_2O_3$ as deposited [9]. After annealing under oxygen at 300°C for 30 min, the $Al_2O_3$ loses its positive charges while approaching the stoichiometry which once reached modifies the curving of energy band at interface. The intensity of the peak $I_1$ (Figure 1) decreases but remains relatively high (66% of reference $I_1$) compared with that of the pilot sample (20%). For the sample treated, the ratio $I_1/I_3$ is comparable with that of the reference spectrum (see Table 1); thus the surface is well preserved during the deposit process. Thermal annealing is generally used in the technological process to cure the interface defects caused by the insulator deposit. An annealing at 350°C under forming gas ($N_2\backslash H_2$) for two hours is recommended [9]. The PL spectra reported on the two samples having undergone the same annealing are presented in Figure 2. We can clearly see the beneficial effect of electrochemical treatment of the InP surface. The ratio $I_1/I_3$ is on the order of 6 for the protected surface (its value for the reference sample lies between 7 and 8) and only 0.1 for non-protected samples. Increase in the $I_3$ peak following annealing at high temperatures is generally attributed to the phosphorus vacancies and/or the complex defects combining impurities and vacancies [14–16]. To explain the beneficial role of anodic oxide one can evoke the following two arguments:

**Table 1.** The PL results of the InP surface measured at 77 K according to the conditions of the subsequent processing.

| PL intensity | First Treatment | | $Al_2O_3$ deposition | | First Annealing $O_2$-30min | | Second Annealing ($H_2$-$N_2$)- 2 h | |
|---|---|---|---|---|---|---|---|---|
| | Sample HF | Anodic Oxidation | Sample HF | Anodic Oxidation | Sample HF | Anodic Oxidation | Sample HF | Anodic Oxidation |
| $I_1$ (%) | 100 | 31 | 22.4 | 168 | 20.5 | 65.9 | 25.8 | 57.4 |
| $I_2$ (%) | 28 | 4.6 | 3.5 | 23.5 | 3.4 | 5.7 | 4.4 | 4.2 |
| $I_3$ (%) | 13 | 4.8 | 3.8 | 4.5 | 34.2 | 7.5 | 274.7 | 9.1 |
| $I_1/I_2$ | 3.6 | 6.7 | 6.4 | 7.1 | 6.0 | 11.6 | 5.9 | 13.7 |
| $I_1/I_3$ | 7.7 | 6.5 | 5.9 | 37.3 | 0.6 | 8.8 | 0.1 | 6.3 |

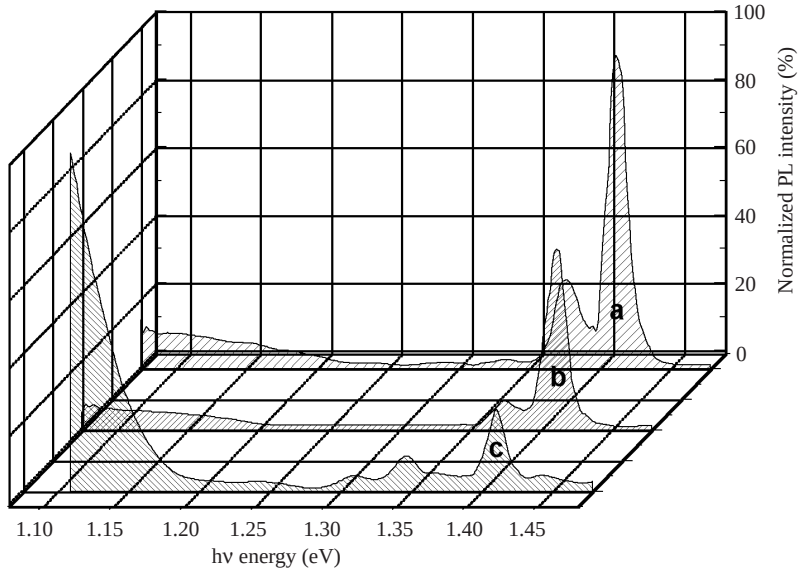


**Figure 2.** The PL spectra of InP surface measured at 77 K after annealing under forming gas ($H_2/N_2$) at 350 °C : (a) HF pilot sample; (b) passivated InP surface; (c) unpassivated InP surface.

(a) The condensed polyphosphates, which are rich in phosphorus, constitute a diffusion barrier thus preventing the decomposition of InP under the effect of temperature.

(b) Being protected, the surface suffers less damage during deposition, thus making it less vulnerable to the effect of repeated annealing.

## 3.2. Photoluminescence mappings

Because PL intensity is an indicator of interface quality, the measurement of PL signal as a function of position will provide information on the spatial uniformity of the interface. Figure 3 shows Photoluminescence topography (PLT) recorded on $1 \times 1$ mm$^2$ surface sections located on two samples. Table 2 shows the average values of integrated PL measured at 300 K on the two samples after each technological step. The PL is standardized and compared to the reference signal recorded from a naked InP surface. It is generally admitted that a strong PL signal indicates a good quality interface [14]. As a strong signal is indeed observed following electrochemical treatment, it confirms the beneficial role of such treatment on the $Al_2O_3$/InP interface. For the protected sample, nearly 30% of the PL signal is preserved, whereas for the non-protected surface, the PL signal decreases to 10% after $Al_2O_3$ deposition and becomes less than 5% following two thermal annealings. The surface of the treated sample is more homogeneous because the anodic oxidation moves the interface towards the volume of the substrate and thus eliminates many surface defects (a buried surface).

**Table 2.** Integrated photoluminescence measured at 300 K after each technological step.

| Samples | Initial Treatment | Deposition of $Al_2O_3$ and annealing $O_2$ | Annealing $H_2$-$N_2$ |
|---|---|---|---|
| Standard HF | 100% | 5 to 10% | $< 5\%$ |
| InP/ anodic Oxide | 10 to 20% | 30 to 40% | 25 to 30% |

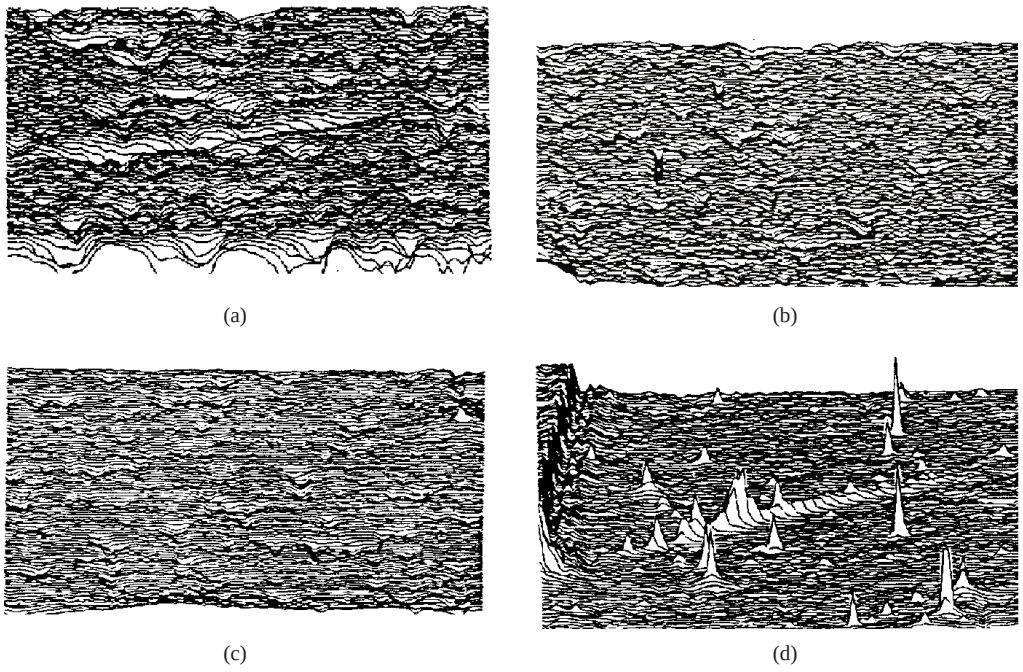


**Figure 3.** PL images measured at 300 K. (a) Pilot sample etched in 40% HF for 60 s, $I_{PL} = 100\%$. (b) Passivated InP surface after deposition of $Al_2O_3$ and annealing under oxygen at 300 °C for 30 min, $I_{PL} = 30$–$40\%$. (c) InP

surface anodically oxidized and annealed under Nitrogen during 30 min at 200 °C , $I_{PL}$ = 10–20%. (d) Naked InP after deposition of $Al_2O_3$ annealed under oxygen at 300 °C for 30 min, $I_{PL}$ = 5–10%.

At the end of the study we proceeded to the scouring of the deposited $Al_2O_3$ on the two samples. The electrochemically treated surface is relatively preserved, whereas the untreated InP surface is characterized by a colored white-silver, which testifies to the presence of the indium metal on the surface and thus an irreversible decomposition of InP at high temperatures.

## 4. Conclusion

The results obtained by spectroscopic measurements of the photoluminescence and PLT confirm the beneficial role of the condensed polyphosphates $In(PO_x)_y$ on the interface quality of MIS-InP structures. Electrochemical oxidation allows moving the interface towards the volume and thus eliminates many surface defects. This greatly improves the homogeneity and the quality of the samples. The Anodic oxide protects the fragile InP substrate during the deposition of $Al_2O_3$. The phosphorus-rich condensed phosphates, obtained by electrochemical deposition, build a diffusion barrier and limit the creation of phosphorus vacancies as well as their complex defects during various annealings. We are expecting that the PL measurements under electrical polarization will allow the determination of surface states density. In addition, to the above, other different chemical treatments will be considered in the future and the previous assessing techniques used.

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