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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 heating evaporation of Al_2O_3 on InP. Polyphosphate thin films with the thickness of 100 to 150 Å were used to passivate the interface InP/Insulator. Photoluminescence spectra were obtained at low temperatures at the various stages of MIS-InP structure formation. At ambient temperature, photoluminescence topography 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 the temperatures close to 350 °C. Major radiative defects detected using photoluminescence spectrum with energies ranged from 0.95 to 1.15 eV were attributed to the impurity complexes of phosphorus vacancies, concentration of which is substantially reduced in the presence of anodic oxide.

Keywords : indium phosphide, MIS structures, photoluminescence.

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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 be solved. The passivation of the surface of the III-V compound is necessary. Various chemical treatments were studied [1-4]. The electrochemical approach used in several previous works [5-7] allows to better control 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]. Thus, it is 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 method, fast, contactless, nondestructive and sensitive to 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. Broad ranges of utilization can be made possible for this characterization technique, namely: PL spectra at low temperature, PL topography (PLT), integrated PL at ambient temperature, and PL under electric polarization [10-13]. If the setting of this characterization method can be made simple and very flexible to use, 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 structures on InP with a reduced complexes impurities of phosphorus vacancies. In addition, the objective is 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 subjected to electrochemical treatment.

2. Experiment

Two standard samples of (100) oriented *n*-InP doped (~10^{16} cm^{-3}) were used. Samples were cleaned in hot

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trichloroethylene and rinsed in methanol, and deionized 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 PLT are reported on one of these two samples. The second sample undergoes an electrochemical treatment using the 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 0.2 mA·cm^{-2} until the terminal voltage of the oxidation cell reaches 20 V, and then the potentiostatic mode switched to a softer termination of the treatment. The double-layered structure is a typical to this kind of oxide. The outer indium-rich thin layer strongly hydrated exhibits 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 of 150 Å thickness. Then the sample undergoes annealing at 250 °C in N_2 atmosphere during 20 min to eliminate any residual water traces. The following technological step consists of depositing the insulator (1000 Å of Al_2O_3) on these two samples. The deposition is carried out by electron beam heating evaporation within secondary vacuum environment and under 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 electron gun, which uses the thermoionic emission of electrons produced by an incandescent filament (cathode). Emitted electrons are accelerated towards an anode by a high difference of potentials (kV). The crucible is perforated disc able to act 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 in oxygen atmosphere during 30 min allows to compensate the deficiency of oxygen, which is generally observed in this type of deposit. The final annealing in 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, some semitransparent aluminium contacts can be deposited for PL measurements under electrical polarization. Measurements of PL spectra and PLT were carried out after every technological step and every annealing. Liquid nitrogen photoluminescence data were collected by Oriel 7240 monochromator with an argon laser at the 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 in diameter. A silicon detector covers a spectral field extending from 430 to 1060 nm. The PLT measurements were performed in air at the room temperature. The sample put on the X-Y plane was moved under a focused laser beam in a such a manner that the data of PLT measurements were obtained. 632.8 nm line of He-Ne laser (power 5 mW) was used for excitation, and the spot diameter of the focused laser beam was ranged from 3 to 80 µm. A silicon photodiode was used to receive the excited PL signals. The device is completely controlled by computer. A comparative study of 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 obtained on uncovered substrate is typical for an *n*-InP sample [14-16]. It presents three essential typical peaks as shown in Fig. 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. The broader peak I_2 located at 1.37 eV is attributed to the band-acceptor or donor-acceptor transitions. The broader band I_3 having the energy in the interval ranged from 0.95 to 1.15 eV also known as the “band C” is generally attributed to the impurities (Fe, Cu, Mn, Co, Zn) forming complex defects with the phosphorus vacancies.

A qualitative indication of passivation is therefore achieved by comparing the PL intensity of the HF pilot sample passivated InP surface with that unpassivated InP surface. Table 1 shows the PL results for the InP surface measured at 77 K according to the conditions of the subsequent processing. The PL spectra obtained after anodic oxidation and dry annealing presents a comparable shape to proceeding with a considerable reduction of the intensities of all peaks. However, an increase in I_1/I_2 ratio is noticable. This behavior can be attributed to a strong curving the energy bands close to the surface due to negative charges existing in the condensed anodic phosphates $In(PO_x)_y$. Indeed, y is generally higher than 3, corresponding to the stoichiometry. In addition to this, the 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 the rest. However, this observation does not completely exclude the presence of defects in InP-oxide interface involving nonradiative recombination. After deposition of the insulator onto these two samples, we can clearly notice (see Table 1) the difference between a surface protected by the anodic oxide and an uncovered InP surface. The PL increased considerably for the electrochemically treated sample, then it strongly decreased 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

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Table 1. 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_2-30 min		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

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

Samples	Initial ereatment	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 %

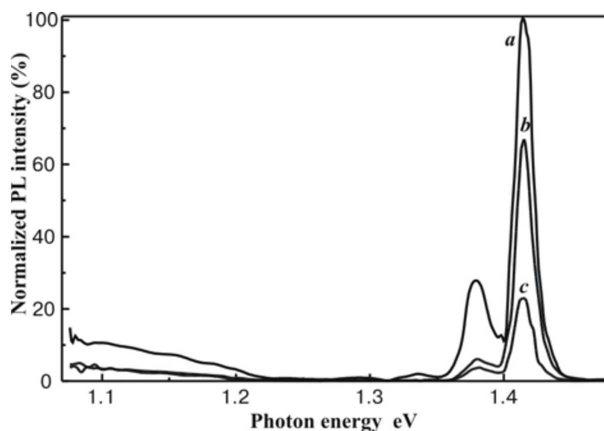

Fig. 1. PL spectra of InP surface measured at 77 K after annealing in oxygen ambient at 300 °C: (a) HF pilot sample; (b) passivated InP surface; (c) unpassivated InP surface.

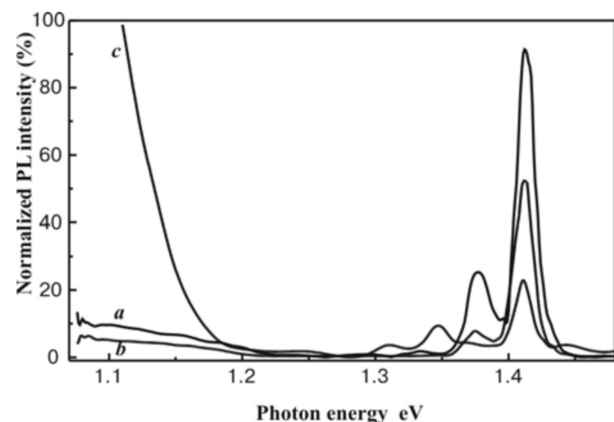

Fig. 2. PL spectra of InP surface measured at 77 K after annealing in forming gas (H_2-N_2) at 350 °C: (a) HF pilot sample; (b) passivated InP surface; (c) unpassivated InP surface.

treated sample can only be explained by a change in the potential of surface due to a total positive charge in the deposited Al_2O_3. This positive charge is caused by the oxygen deficiency generally reported for this type of deposits. An annealing in oxygen atmosphere is generally necessary to improve the quality of Al_2O_3 deposited in this way [9]. After annealing in oxygen at 300 °C for 30 min, Al_2O_3 loses its positive charge while approaching the stoichiometry which once reached modifies curving the energy band at the interface. The intensity of the peak I_1 (Fig. 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 (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 in forming gas (H_2-N_2) during two hours is recommended [9]. The PL spectra obtained for these two samples having undergone the same annealing are presented in Fig. 2. We can clearly notice the profound effect of electrochemical treatment on the surface of InP. The ratio I_1/I_3 is by the order of 6 for the protected surface (its value for the reference sample lies between 7 and 8) and only 0.1 for nonprotected samples. The increase of the peak I_3 after 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 important role of anodic oxide, one can evoke the following two arguments:

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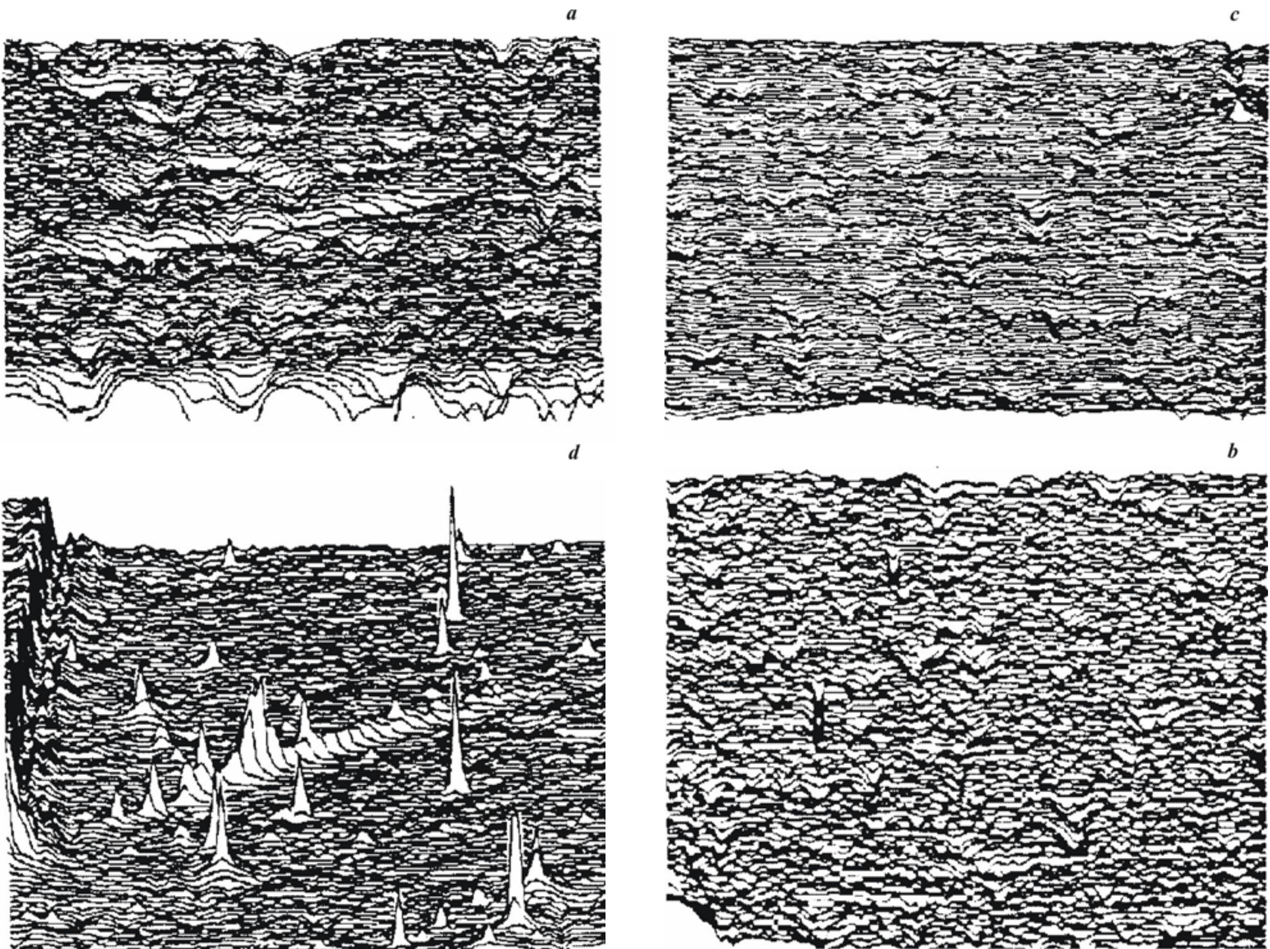

Fig. 3. PL images measured at 300 K: (a) pilot sample etched in 40 % HF for 60 s, I_{PL}=100 %; (b) passivated InP surface after deposition of Al_2O_3 and annealing in oxygen at 300 °C for 30 min, I_{PL} = 30…40 %; (c) InP surface anodically oxidized and annealed in nitrogen for 30 min at 200 °C, I_{PL} = 10…20 %; (d) uncovered InP after deposition of Al_2O_3 and annealed in oxygen at 300 °C for 30 min, I_{PL} = 5…10 %.

a) the condensed polyphosphates which are rich with phosphorus create a diffusion barrier and prevent the decomposition of InP on exposure to temperatures;
b) the protected surface during deposition is less damaged, and hence, it is becoming less vulnerable to the effect of repeated annealing.

3.2. Photoluminescence mappings

Because PL intensity is an indicator of interface quality, the measurements of the PL signal vs position provide information on the spatial uniformity of interface properties. Fig. 3 shows some PLT taken on 1×1 mm^2 surface located on targeted regions at the surface of these two samples. Table 2 shows the average values of integrated PL measured at 300 K on these two samples after each technological step. The PL is standardized and compared to the reference signal reported on the uncovered InP. It is generally admitted that a high PL signal is an indication of a good quality of the interface [14]. This fact confirms once again the dominant role of the electrochemical treatment on the Al_2O_3/InP interface. For the protected sample, about 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 % after two thermal annealing. 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 (buried surface).

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

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4. Conclusion

The results obtained by our spectroscopic measurements of PL and PLT confirm the profound effect 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. It highly 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 from a diffusion barrier and limit the creation of phosphorus vacancies as well as their complex defects during various annealing. 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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References

1. M. Schvartzman, V. Sidorov, D. Ritter, and Y. Paz, Surface passivation of (100) InP by organic thiols and polyimide as characterized by steady-state photoluminescence // *Semicond. Sci. Technol.* **16**, p. L68-L71 (2001).
2. D. Kikuchi, Y. Matsu, and S. Adachi, Chemically treated InP(100) surfaces in aqueous HCl solutions // *J. Electrochem. Soc.* **147**, p. 1973-1978 (2000).
3. N. Shibata and H. Ikoma, X-Ray photoelectron spectroscopic study of oxidation of InP // *Jpn J. Appl. Phys.* **31**, p. 3976-3980 (1992).
4. M. P. Besland, S. Jourba, M. Lambrinos, P. Louis, P. Viktorovitch, and G. Hollinger, Optimized SiO_2/InP structures prepared by electron cyclotron resonance plasma // *J. Appl. Phys.* **80** (5), p. 3100-3109 (1996).
5. T. Djenizian, G. I. Sproule, S. Moisa, D. Landheer, X. Wu, L. Santinacci, P. Schmuki, and M.J. Graham, Composition and growth of thin anodic oxides formed on InP (100) // *Electrochimica Acta* **47**, p. 2733-2740 (2002).
6. M. P. Besland,Y. Robach, and J. Joseph, In-situ studies of the anodic oxidation of indium phosphide // *J. Electrochem. Soc.* **140**, p.104 (1993).
7. P. Schmuki, G. I. Sproule, J. A. Bardwell, Z. H. Lu, and M. J. Graham, Thin anodic oxides formed on GaAs in aqueous solutions // *J. Appl. Phys.* **79** (9), p. 7303-7311 (1996).
8. R.R. Sumathi, N. Dharmarasu, S. Arulkumaran, P. Jayavel, and J. Kumar, Improved electrical properties on the anodic oxide/InP interface for MOS structures // *J. Electron. Mater.* **27** (12), p. 1358-1361 (1998).
9. J. Joseph, A. Mahdjoub, Y. Robach, Propriétés électriques des structures MIS/InP passivées par un oxyde // *Revue Phys. Appl.* **24**, p. 189-195 (1989).
10. A. Ahaitouf, A. Bath, P. Thevenin, and E. Abarkan, Analysis of interface states of n-InP MIS structures based on dependence of capacitance and photoluminescence intensity // *Mater. Sci. Engineering B.* **77**, p. 67-72 (2000).
11. W.D. Chen, X.Q. Li, L.H. Duan, X.L. Xie and Y.D. Cui, Photoluminescence enhancement of $(NH_4)_2S_x$ passivated InP surface by rapid thermal annealing // *Appl. Surf. Sci.* **100-101**, p. 592-595 (1996).
12. Y. Zhao, N. Sun, H. Dong, J. Jiao, J. Zhao, T. Sun, and L. Lin, Characterization of defects and whole wafer uniformity of annealed undoped semi-insulating InP wafers // *Mater. Sci. Engineering B.* **91-92**, p. 521-524 (2002).
13. H.W. Dong, Y.W. Zhao, H.P. Lu, J.H. Jiao, J.Q. Zhao, and L.Y. Lin, Photoluminescence assessment of undoped semi-insulating InP wafers obtained by annealing in iron phosphide vapour // *Semicond. Sci. Technol.* **17**, p. 570-574 (2002).
14. S.K. Krawczyk, M. Garrigues, and H. Bouredoucen, Study of InP surface treatments by scanning photoluminescence microscopy // *J. Appl. Phys.* **60** (1), p. 392-395 (1986).
15. E.V.K. Rao, N. Duhamel, and M. Gauneau, Surface accumulation of manganese in Si^+ – implanted and annealed semi-insulating indium phosphide // *Ibid.* **56** (12), p. 3413-3417 (1984).
16. M. Gauneau, R. Chaplain, A. Rupert, E.V.K. Rao, and N. Duhamel, Further evidence of chromium, manganese, iron, and zinc redistribution in indium phosphide after annealing // *Ibid.* **57**(4), p. 1029-1035 (1985).

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