PHOTOLUMINESCENCE CHARACTERIZATION OF $Al/Al_2O_3/InP$ MIS STRUCTURES PASSIVATED BY ANODIC OXIDATION

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Metal-insulator-semiconductor (MIS) structures were produced by electron beam heating evaporation of Al_2O_3 on InP. Thin films of polyphosphates of 100—150 Å in thickness were used to passivate the interface InP/insulator. Photoluminescence spectra were reported at low temperatures at various stages of the realization of a MIS-InP structure. The photoluminescence topography (PLT) 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, which are detected by the photoluminescence spectrum with energy ranged from 0.95 to 1.15 eV and attributed to the complex impurities of phosphorus vacancies, are substantially reduced by the presence of anodic oxide.

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. Various chemical treatments were studied in [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 the anodic oxide for the interface of MIS-InP structures [8, 9]. The characterization of the interface of MIS structures is generally based on the measurements of high-frequency capacitance (Terman analysis) or on a quasi-static mode (Berglund technique). These methods require the use of a 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 for the interface to overcome these constraints. Of all the properties that characterize photoluminescence (PL), the intensity of a 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. A broad range of utilization can be made possible for this characterization technique, namely PL spectra at low temperature, 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 results of measurements are still remaining very delicate. The differences in the PL intensities observed are generally attributed to the interface or surface defects and/or to the electric potential of the surface.

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

2. Experiment

Two standard samples of (100) oriented n-InP doped ($\sim 10^{16} cm^{-3}$) were used. Samples were cleaned in hot trichloroethylene and rinsed in methanol, and DI water.

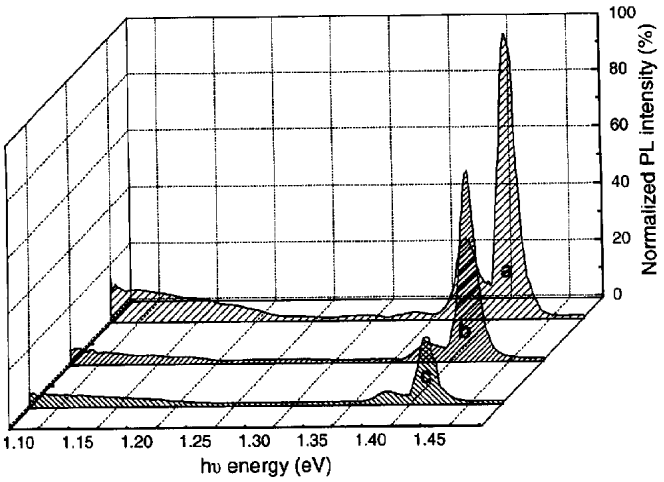

Fig. 1. The PL spectra of InP surface measured at 77 K after annealing under oxygen ambient at 300 °C: (*a*) HF pilot sample; (*b*) passivated InP surface; (*c*) unpassivated InP surface

They were briefly etched in a 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 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 the 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 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 a better quality similar to $In(PO_3)_3$. The outer layer is dissolved using a 0.01 % diluted HF solution for 120 s which allows keeping a phosphorus-rich layer with a thickness of 150 Å. The sample undergoes then an annealing at 250 °C under 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 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 the 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 potential (kV). The crucible is a perforated disc and can 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 under oxygen during 30 min helps to compensate the deficit in oxygen which is generally observed in this deposit type. The last annealing under the forming gas (H_2-N_2) at 350 °C for 2 h is performed to cure certain interface defects and to improve the structure quality. To finish the fabrication of the MIS-InP structure, some semitransparent aluminum contacts can be deposited for PL measurements under electrical polarization. The measurements of PL spectra and a PLT were carried out after every technological step and every annealing. Liquid nitrogen photoluminescence data were collected by an Oriel 7240 monochromator with an argon laser at a wavelength of 514.5 nm and an output power of 100 mW. The sample received 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 room temperature. The sample put on the X-Y plane was moved under a focused laser beam so that the data on PLT were obtained. The 632.8 nm line of a He-Ne laser (a power of 5 mW) was used for the 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 a computer. A comparative study between various measurements is made possible and allows presenting the conclusions about the influence of the treatment used on the structure quality.

3. Results and Discussions

3.1. Photoluminescence

The reference spectrum reported on a naked substrate is typical of 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 the bound excitons related to 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 and known under the name of "band C" is generally attributed to the impurities (Fe, Cu, Mn, Co, Zn) forming complex defects with phosphorus vacancies.

A qualitative indication of passivation is therefore achieved by comparing the PL intensities of the HF pilot sample, passivated InP surface, and unpassivated InP surface. Table 1 shows the PL of the InP surface measured at 77 K according to the conditions of the subsequent processing. The PL spectrum reported after anodic oxidation and dry annealing presents a comparable form by proceeding with a considerable reduction of the intensities of all peaks. However, an increase in the I_1/I_2 ratio 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 higher than 3, corresponding to the stoichiometry. In addition, the measurements of the capacitance-voltage (C—V) characteristics on thicker anodic oxides (around 800 Å) have 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 on the InP-oxide interface involving nonradiative recombinations. After the deposition of the insulator on two samples, we can clearly notice (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, but it strongly fell down for an 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 deposit type. An annealing under oxygen is generally necessary to improve the quality of Al_2O_3 so deposited [9]. After the annealing under oxygen at 300 °C during 30 min, the Al_2O_3 loses its positive charges while approaching the stoichiometry which once reached modifies a curving of the energy band at the interface. The intensity of peak

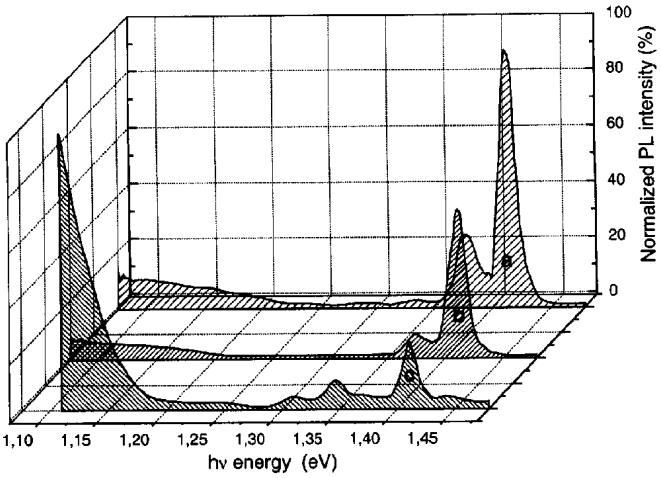

Fig. 2. The PL spectra of InP surface measured at 77 K after annealing under forming gas (H_2-N_2) at 350 °C: (*a*) HF pilot sample; (*b*) passivated InP surface; (*c*) unpassivated InP surface

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 deposition. Thermal annealing is generally used in the technological process to cure the interface defects caused by the insulator deposition. An annealing at 350 °C under the forming gas (H_2-N_2) during 2 h is recommended [9]. The PL spectra reported on two samples having undergone the same annealing are presented in Fig. 2. We can clearly notice the beneficial effect of electrochemical treatment on the surface of InP. The ratio I_1/I_3 is of 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. An increase of peak I_3 after the annealing at high temperatures is generally attributed to 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:

T a b l e 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 in O_2, 30 min		Second annealing in (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

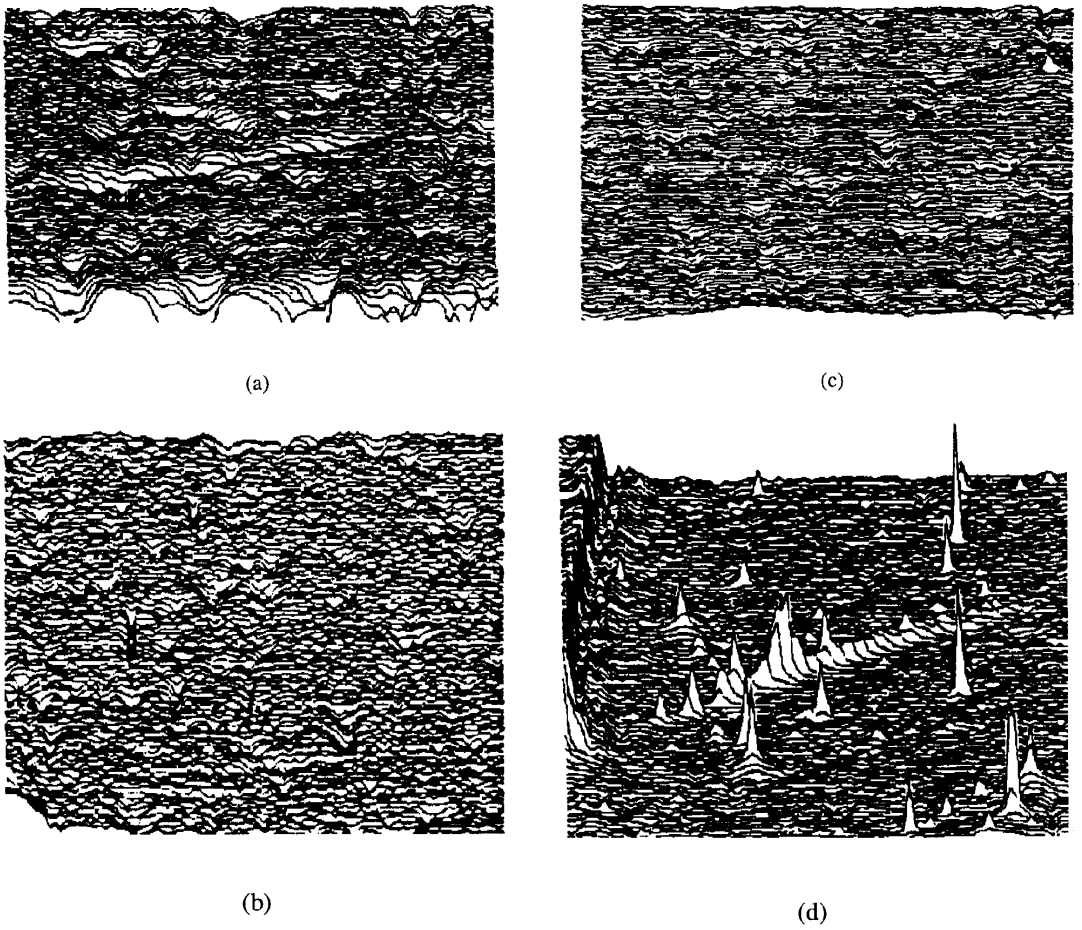

Fig. 3. PL images measured at 300K. (*a*) Pilot sample etched in 40 % HF for 60 s, I_{PL}=100 %. (*b*) Passivated InP surface after deposition of Al_2O_3 and annealing under oxygen at 300 °C during 30 min, $I_{PL} = 30 \div 40$ %. (c) InP surface anodically oxidized and annealed under nitrogen during 30 min at 200 °C, $I_{PL} = 10 \div 20$ %. (d) Naked InP after deposition of Al_2O_3 annealed under oxygen at 300 °C, during 30 min, $I_{PL} = 5 \div 10$ %

(a) Condensed polyphosphates which are rich in phosphorus constitute a diffusion barrier and prevent the decomposition of InP under the effect of temperature.

(b) The protected surface during a deposition is less damaged, and hence it is becoming less vulnerable to the effect of repeated annealing.

3.2. Photoluminescence mappings

Because the 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. Figure 3 shows some PLT taken on a 1×1 mm^2 surface located on targeted regions on the surface of two samples. Table 2 shows the average values of integrated PL measured at 300 K on two samples after each technological step. The PL is standardized and compared to the reference signal reported on naked InP. It is generally admitted that a high PL signal is the indication of a good quality of the interface [14]. This fact confirms once again the beneficial role of electrochemical treatment on the Al_2O_3/InP interface. For the protected sample, nearly 30 % of the PL signal is preserved, whereas the PL signal for the nonprotected surface falls down to 10 % after the Al_2O_3 deposition and becomes less than 5 % after two thermal annealings. The surface of the treated sample is more homogeneous because the

T a b l e 2. Integrated photoluminescence measured at 300 K after each technological step

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

anodic oxidation moves the interface inward the substrate volume and thus eliminates many surface defects (buried surface).

Finally, we have proceeded to the scouring of the deposited Al_2O_3 on 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 the spectroscopic measurements of PL and PLT confirm the beneficial role of the condensed polyphosphates $In(PO_x)_y$ for the interface quality of MIS-InP structures. Electrochemical oxidation allows moving the interface inward the volume and thus eliminates many surface defects. This highly improves the homogeneity and 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 complex defects during various annealings. We expect that the PL measurements under electrical polarization will allow the determination of the density of surface states. In addition to the above, other different chemical treatments will be considered in the future.

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ФОТОЛЮМІНЕСЦЕНТНІ ХАРАКТЕРИСТИКИ МІН-СТРУКТУР $Al/Al_2O_3/InP$, ПАСИВОВАНИХ АНОДНИМ ОКИСЛЕННЯМ

А. Махджуб, Г. Боурдусен, А. Джеллул

Р е з ю м е

Стуктури метал—ізолятор—напівпровідник було отримано шляхом нагрівання електронним пучком та випаровування Al_2O_3 на InP. Поліфосфатні тонкі плівки завтовшки 100—150 Åвикористовувались для пасивування межі поділу InP—ізолятор. Спектри фотолюмінесценції реєстрували на різних стадіях процесу отримання МІН—InP-структури. Топографія фотолюмінесценції при температурі оточуючого середовища дала можливість характеризувати стан поверхні на кожній технологічній стадії. Руйнування поверхні поділу внаслідок декількох відпалів не є суттєвими до температур 350 °C. Кількість радіаційних дефектів, що проявляються у спектрі фотолюмінесценції в інтервалі енергій 0,95—1,15 еВ і пов'язані з комплексними домішками вакансій фосфату, суттєво зменшувалася при анодному окисленні.