

# Investigation of the In<sub>2</sub>O<sub>3</sub> oxied grown by electron beam on the In metal and on the InP

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## ABSTRACT

Recently, the development of indium oxide such as In<sub>2</sub>O<sub>3</sub> on the semiconductor InP has known successful applications in the gas sensor technology, the emission devices, the biotechnology etc... The indium oxide In<sub>2</sub>O<sub>3</sub> attracted considerable research according to many ways to synthesize it at the reduced dimensional scale. In our study; we interest to develop on In metal InP surface the indium oxide owing to the stimulated oxidation by the electron beam. The oxidation process on InP is advantaged by a previous treatment due to the sputtering of the compound surface by the argon ions at low energy 300eV with a current density 2μA/cm<sup>2</sup> and heating in UHV. Our results are based on the use of the analysis techniques such as the Auger Electron Spectroscopy (AES) and the Electron Energy Loss Spectroscopy (EELS) which are well appropriated to study the surface of point of view physical structure and chemical environment. The shape of AES and EELS spectra display the development of In<sub>2</sub>O<sub>3</sub> oxide of small size on the irradiated area of InP semiconductor. Our experimental results related to the interaction process electrons-matter are associated to the simulation method TRIM to show the interaction process ions-matter.

**Keywords:** AES, EELS, TRIM, oxide In<sub>2</sub>O<sub>3</sub>, structure, morphology, surface

## 1 INTRODUCTION

The oxide In<sub>2</sub>O<sub>3</sub> is of great importance in the technological applications. It is used for instance as source/drain electrodes on the semiconductor InP. It also has a wide range of applications for obtaining the appropriated optoelectronic devices because of its gap 2.9eV. It is even used as gas sensors because of its great interaction of its surface with some poisonous gas molecules. The In<sub>2</sub>O<sub>3</sub> oxide is used as a good and transparent electrode in the solar cells. [1-2]. The In<sub>2</sub>O<sub>3</sub> films are susceptible to grow on substrates by various deposition methods, such as sputtering, spraying chemical vapour deposition ion plating, vacuum evaporation; reactive evaporation [3]. In this work, we use the stimulated oxidation of In and InP by the electron beam in situ for obtaining In<sub>2</sub>O<sub>3</sub>. The effect of the

interaction of the incident electrons with the target InP is monitored by the Auger Electron Spectroscopy (AES), the Electron Energy Loss Spectroscopy (EELS), associated to the simulation method TRIM (Transport and Range of ions in Matter)

## 2 EXPERIMENTAL

We use the analysis methods as the Auger Electron Spectroscopy (AES) and the Electron Energy Loss Spectroscopy (EELS) which are well appropriated to characterize the surfaces of materials using a hemispherical spectrometer operating in direct mode N(E).

The In and InP samples were chemically cleaned by diluted solution of H<sub>2</sub>SO<sub>4</sub>, then rinsed in methanol and finally washed in de-ionised water. Finally both samples were characterized by AES (electron beam of energy 4keV with a current density of 10<sup>-3</sup> A/cm<sup>2</sup>). The incident electron beam was focused onto an area of 1mm diameter on each target. The characterization by EELS was achieved at low and high energy to distinguish the energy losses due to surface plasmons to those due to bulk plasmons. The experimental parameters were chosen in order to reduce the effect of the electron beam on the material surface [4]. We studied at room temperature and after heating the physical structure and the chemical composition of compound surface InP previously submitted to argon ions bombardment at appropriated energy (300eV) with a current density of 2μA/cm<sup>2</sup> in normal incidence on the target. The argon gas was introduced owing to leak gauge to reach a pressure of 10<sup>-5</sup> Torr. Both spectroscopy techniques (AES and EELS) are complementary to display the physical structure and the chemical environment of the material surface. The AES and EELS spectra were recorded in UHV of 10<sup>-9</sup>Torr.

## 2. Results and discussions

### 2-1 AES and EELS of InP submitted to Ar<sup>+</sup>

After just the introduction of the InP sample in the spectrometer chamber, the first recorded AES spectra C-KLL and O-KLL revealed that the surface of these compounds involved a contamination layer composed of

carbon and oxygen, confirmed by the EELS. However the surface was subjected to the cleaning operation at low energy 300eV by the argon ion bombardment during 10 minutes. After such a bombardment followed by a moderate heating in UHV at 250°C, the Auger signals C-KLL and O-KLL vanished completely. As shown on figure 1 (I), we recorded the EELS spectra of InP at low primary energy  $E_p=250\text{eV}$ . The energy loss peak located at 15.4eV is due to bulk plasmons of InP. We even show on figures 1 (II) the Auger transitions (In- $M_5N_{45}N_{45}$ , P-LMM) of InP. The structures of these AES spectra correspond to stoichiometric InP.

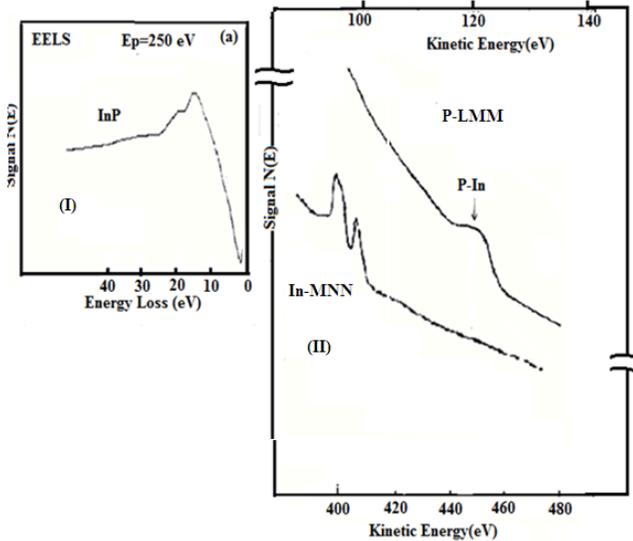


Fig1: EELS (I) and AES (II) spectra of stoichiometric InP

After the cleaning step, we submitted the InP surface to a further argon ions bombardment in the same experimental conditions as previously but we increased the irradiation time to 20min, 45min and 90min. The recording of EELS spectra at the primary energy  $E_p=1000\text{ eV}$  of InP previously submitted to  $\text{Ar}^+$  are shown on fig.2.

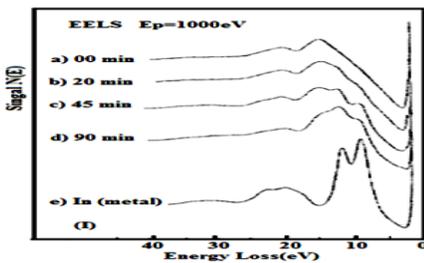


Fig 2: EELS spectra of InP bombarded by  $\text{Ar}^+$  during different times. The spectrum e/ In(metal) is taken for comparison

We note that the  $\text{Ar}^+$  ions lead to break chemical bonds between indium and phosphorus to form the In metal distributed on InP to constitute the (In; InP) system. We clearly see on the spectra (b); (c) and (d) the energy loss peaks related to surface and bulk plasmons located at 8.6eV and 11.6eV in good agreement with those of the pure In metal shown on spectrum (e). The recording of the Auger transition In- $M_5N_{45}N_{45}$  of InP previously submitted to  $\text{Ar}^+$  bombardment is shown on figure 3.

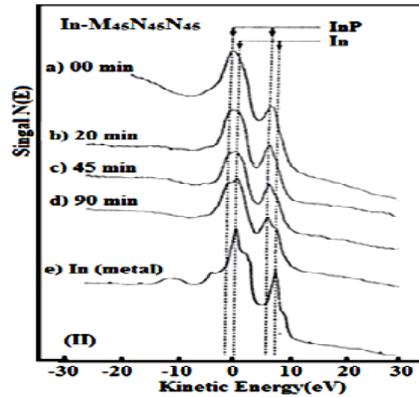


Fig 3: AES spectra of InP bombarded by argon during different times. The spectrum e/ In (metal) is taken for comparison.

Its shape changes during the bombardment process. There is appearance of peak located at 2 eV relatively to the main peak In- $M_5N_{45}N_{45}$  related to the chemical bound In-In.

## 2-2 TRIM Simulation method of interaction $\text{Ar}^+$ -InP

The interaction of ions with matter plays an important role in the treatment of material surface. The argon ion bombardment might be a useful means to clean the surface of materials. As shown previously a careful cleaning of InP compound is achieved by the ions  $\text{Ar}^+$  accelerated at low energy (300eV). Afterwards, the ionic irradiation of InP leads to form the diphased (In;InP) system. Although, the used methods such as AES and EELS are very sensitive to characterize the surface, but it is difficult to determine the affected depth of the surface by  $\text{Ar}^+$  ions. Thus, we combine to these analysis techniques the simulation method TRIM (Transport and Range of ions in Matter) to show the interaction mode between the  $\text{Ar}^+$  ion and the target in order to relate the disturbed depth as a function of  $\text{Ar}^+$  energy [5]. The  $\text{Ar}^+$  ions bombardment is achieved according to the normal incidence with the surface. the effect of  $\text{Ar}^+$  ions induces a displacement of atoms of the target with the possibility to form vacancies on irradiated area. Our aim is to know the depth affected by  $\text{Ar}^+$ . We recorded the TRIM spectra for the  $\text{Ar}^+$  ions as for different energies shown on figure 4.

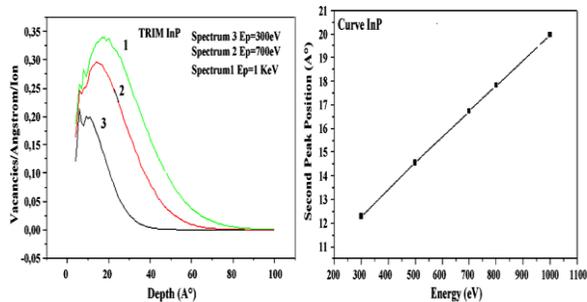


Fig 4: TRIM spectra of InP bombarded by Ar<sup>+</sup>, recorded at different energies. The picture at the right indicates the variation of the location of TRIM second peak as function of the energy.

The TRIM spectrum is constituted of two main peaks located at different depths. The interaction process between Ar<sup>+</sup> and the surface occurs first with the outmost layer of the target. This leads to the appearance of the first peak on the TRIM spectrum. However, the location of this peak remains practically independent on the Ar<sup>+</sup> ions energy. We suggest on the physical basis that the first layer of the surface undergoes the violent interaction with the Ar<sup>+</sup> ions. There is creation of vacancies in that disturbed layer. Besides, the appearance of first peak is also related to parameters related to the TRIM simulation method. Our point of view is particularly focused on the second peak of the TRIM spectrum in order to understand the behaviour of material in bulk when subjected to ions irradiation. The importance of damage due Ar<sup>+</sup> ions on the target is related to the location of TRIM second peak. The study of the interaction phenomenon ions-matter is complex. It depends on the cross-section as was reported by other authors and the physical parameters related to the physical and chemical structure of the target [6]. We record on figure 4 the variation of the depth at which the TRIM second peak appeared as a function of the Ar<sup>+</sup> energy. This constitutes the possibility to understand the effect of the ion irradiation on the bulk of material. Its linear variation is a good means for indicating the homogeneity of the physical and chemical structure of clean InP compound. On the other hand, the linearity of the curve is due to non-reactive character between the argon ion and the target. The argon ion bombardment induces a physical damage but without chemical reactivity [7-9]. However; the association of the TRIM simulation method with the AES and EELS results display that the effect of argon ions bombardment although achieved at low energy, causes a pronounced disturbance in bulk of depth 20 Å of the target with breaking of chemical bonds (In-P) to form the (In; InP) system.

### 2-3. Stimulated oxidation by the electron beam of (In, InP) system.

The system (In; InP) obtained after the argon bombardment of InP as described before; was irradiated by the electron beam in UHV. The effect of the electron beam on such a system was monitored by the analysis methods AES and

EELS. The effect of the electron beam led to modify the structure of the AES spectra In-M<sub>45</sub>N<sub>45</sub>N<sub>45</sub> of indium and P-LMM of phosphorus with displacement in energy of these peaks during the irradiation process of the sample. The monitoring of spectral features In-M<sub>45</sub>N<sub>45</sub>N<sub>45</sub> and P-LMM in conjunction with the oxygen signal O-KLL as a function of irradiation time displayed an oxidation phenomenon on the InP surface as shown on figure 5.

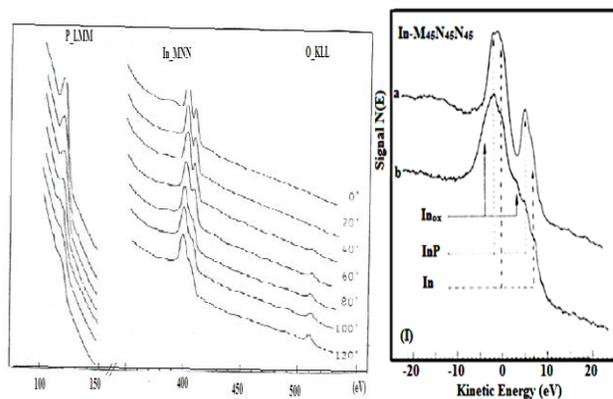


Fig 5: AES spectra of InP irradiated by the electron beam during increasing times. The picture at the right indicates the AES spectra In-M<sub>45</sub>N<sub>45</sub>N<sub>45</sub> of InP a/ bombarded by Ar<sup>+</sup>; b/ irradiated by the electron beam.

The collective displacement of these features to the lower kinetic energy indicates the occurring of charge phenomenon on the InP surface. Such a charge effect is related to the modification of the chemical environment, the presence of defects induced by the Ar<sup>+</sup> ions. It is considered due to trapped charges susceptible to accumulate at the surface to create an electrical potential which induces the decrease of the kinetic energy of the Auger signals. The charge phenomenon occurred in association with the electron stimulated oxidation of the surface. The structural defects advantaged the ability of electron beam to break the chemical bonds In-P. The decrease of Auger signal P-LMM and the modification of the shape of In-M<sub>45</sub>N<sub>45</sub>N<sub>45</sub> in conjunction with the O-KLL signal constitute the means to justify the indium oxidation. As shown on figure 5; the appearance of peak to the lower energy at 4 eV to main peak In-M<sub>45</sub>N<sub>45</sub>N<sub>45</sub> is attributed to the chemical bond In<sub>ox</sub> of In<sub>2</sub>O<sub>3</sub> in agreement with the results previously described about the In metal oxidation. The decrease of the P-LMM Auger signal is due to a phenomenon of phosphorus depletion. We justify the ability of the chemical reactivity between indium and oxygen through the AES spectra of pure In metal irradiated by the electron beam as shown on figure 6.

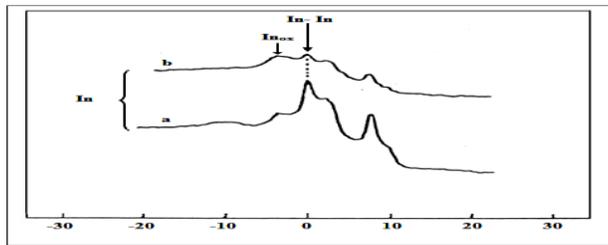


Fig.9

Fig 6 : In- $M_{45}N_{45}N_{45}$  AES transition of In metal at the state a/ pure; b/ oxidized by the electron beam

The analysis according to the EELS clearly displays the discrimination between the energy loss peaks characterizing  $In_{ox}$  and InP, so located at (6eV; 23eV) and (15.4eV) respectively; as shown on figure 7.

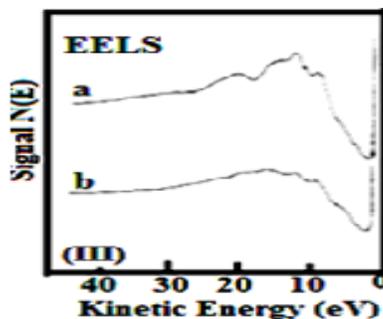


Fig 7: EELS spectra of InP a/ bombarded by  $Ar^+$ ; b/irradiated by the electron beam.

The energy loss peaks located at 6eV and 23eV are due to interband transition and plasmons of  $In_2O_3$ . Whereas, the energy loss peak located at 15.4eV concerns the bulk plasmons of InP.

We note that the heated (In;InP) system at 300°C submitted again to the electron beam in the same experimental conditions is of great stability of point of view location in energy of Auger signals In- $M_{45}N_{45}N_{45}$ , P-LMM and O-KLL. There is increase of O-KLL signal and decrease of P-LMM signal with modification of the shape of In- $M_{45}N_{45}N_{45}$  involving the Auger transition characteristic to  $In_2O_3$ . The electron beam played the role to just oxide the indium islands of (In;InP) system. The electron beam did not induce new breaking of chemical bonds (In-P). The structural homogeneity assumed by the heating at 300°C allowed the growth of  $In_2O_3$  on well distinguished areas of dimensions estimated to several nanometres on the InP surface. The oxidation process achieved with no appearance of charge phenomenon. So, the temperature played the role to eliminate the structural defects which were at the origin to activate the development of charge effect. The temperature of 300°C seems to be well appropriated to

allow the development of indium oxides of small areas on the InP surface by the electron beam.

## 4. Conclusion

The spectroscopy methods AES and EELS were really useful to characterize the InP submitted to the argon ions bombardment. They revealed the formation of metallic indium distributed randomly on the surface of these compounds to form the system (In; InP). The  $Ar^+$  bombardment of 300eV energy led to break too much the chemical bonds In-P with desorption of phosphorus from the surface in agreement with the results of the TRIM simulation method. The association of the simulation method TRIM to EELS and AES displays the interaction process of  $Ar^+$  with InP target. Through; the TRIM spectra we can reveal the disturbed depth of InP by the  $Ar^+$  reaching 60Å with a pronounced maximum at 20Å. The disturbed depth depends of the  $Ar^+$  energy. The combination of AES, EELS and TRIM constitutes a reliable tool to study the morphology and the composition surface of InP irradiated by the  $Ar^+$  ions. The heating in UHV of (In;InP) system at 300°C led to coalesce the In metal to form the droplets of In on InP of small size. That aspect was favoured because of the low melting point of metal indium (123°C). The temperature played an important role in the elimination of structural defects for obtaining a good reconstruction of the surface. After the heating at 300°C, a further electron irradiation of (In; InP) system led to a stimulated oxidation of indium areas to form the oxide  $In_2O_3$  small areas of the InP compound. The great sensitivity of AES and EELS revealed the growth of  $In_2O_3$  with great stability without any appearance of charge effect during the electron irradiation of the target.

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