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DAMAGE INDUCED ON INP BY ICP PROCESSES IN CH_4 - H_2 CHEMISTRY

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Etching of InP in CH_4 - H_2 chemistry using a high density inductively coupled plasma source is investigated. This study is particularly focused on the characterization of the damage induced by the etching process on the surface by means of quasi *in situ* x-ray photoelectron spectroscopy (XPS). Three main kinds of damage are identified : contamination with carbon species, phosphorus loss, and amorphisation. Sample bias is the major parameter which controls the nature and extent of the damage and three domains can be defined. Below an etching threshold V_e, deposition of carbon inhibits the etching ; between V_e and a damage threshold V_d, damage is limited to a phosphorus loss in a very shallow region ; finally, amorphisation and severe phosphorus loss are observed above V_d. Based on the XPS results, a model is proposed to represent the etched surface and quantify the extent of the damage.

INTRODUCTION

Reactive ion etching (RIE) of InP in CH_4 - H_2 mixtures is known to produce smooth anisotropic pattern transfer and high selectivity with respect to the mask material, but such plasmas induce damage related to amorphisation and loss of P in the surface layers (1, 2). Electron cyclotron resonance (ECR) excited plasma processes have the advantage of offering high etch rates at low sample bias (3, 4). Up to now, RIE and ECR etching have been the most studied processes and most studies were dedicated to optimizing the etch rate (1, 3). However, to meet device fabrication requirements, it is also desirable to estimate or control the damage. Attention is set here on the characterization of the P/In atomic ratio and on the amorphisation of the surface with regard to the etching conditions in high density plasma processes using an inductively coupled plasma (ICP) source.

EXPERIMENT

The experimental set up is shown in figure 1. The ICP source (Alcatel) consists of a quartz hemisphere, 180 mm in diameter, surrounded with a bi-plane circular antenna. This antenna is water cooled and can be powered up to 2 kW *via* a matching box (SAIREM CBA/PL) with a 13.56 MHz rf generator (Alcatel ARF2003). A cylindrical coil coplanar to the horizontal branch of the antenna allows to increase the plasma density by using the

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electron magnetic confining effect. The source is mounted on the upper flange of the etching chamber which dimensions and diagnostics facilities are given elsewhere (5). The distance between the lower plane of the source and sample holder is 173 mm. The sample holder, 150 mm in diameter, is designed to accept 100 mm wafers. It is water cooled and separately biased with an additional 13.56 MHz generator (PlasmaTherm 500E).

Main etching conditions are : pressure 15 mTorr, total flow rate 80 sccm, gas mixture 20%CH_4 - H_2, and etching time 600 s. The source power is varied from 220 to 600 W and sample bias from 0 to 250 V. In some experiments 20 sccm of argon are added to the gas mixture, the total flow rate being brought to 100 sccm. The samples consist of 5.1 cm^2 (100) semi insulating InP. To match with the sample holder the InP sample is pasted with thermal grease onto a SiO_2 (500 nm thick) thermal oxide on Si wafer.

Optical emission spectroscopy (OES) (Jobin Yvon HR640 monochromator and EG&G 1456B multichannel detector) is used to analyse the plasma during the etching, in particular to follow the emission of atomic In (λ = 451.1 nm). After etching the surface chemistry is characterized with quasi *in situ* XPS (Leybold AG LHS 11) using the vacuum transfer facility between the etching chamber and the XPS. This system is equipped with a standard Mg Kα x-ray source, the overall spectral resolution is 1.0 eV when operated at a pass energy of 50 eV. High energy resolution analyses (0.34 eV) are carried out *ex situ* with monochromatised Al Kα radiation. Binding energies are referenced to the Au 4f7/2 core level taken at 84.00±0.02 eV. For spin orbit doublets, the binding energy position and the full width at half-maximum (FWHM) given are those of the component of greater angular momentum. Etch rates are determined by weight loss measurements : considering the etching homogeneous over the sample, the weight loss is converted into thickness loss.

ETCH RATE AND SURFACE COMPOSITION

Figure 2 and 3 report respectively etch rate *versus* source power and bias voltage. The etch rate rises linearly with the source power, a slope of 1.7 Å/min/W is obtained at a sample bias of 100 V. A minimum of sample bias is necessary to obtain etching, below this etching-deposition threshold ($\mathcal{V}e$) an amorphous carbon film grows on InP. Indeed no etching is observed at 0 V, whatever the source power or the gas mixture. Using XPS (see figure 9 below), the etching-deposition frontier is observed at $\mathcal{V}e$ = 25 V for 300 W, whereas no deposition occurs at 25 V for 600 W. At 300 W, addition of argon to the gas causes $\mathcal{V}e$ to reduce to 10 V. So $\mathcal{V}e$ depends on the source power and on the gas mixture. At 300 W, the etch rate (~150 Å/min) is stable from $\mathcal{V}e$ to 50 V, and then increases linearly with a slope of 2.3 Å/min/V. The addition of argon gives very similar results, but the etch rate happens to be always slightly smaller (below 150 V), or much smaller (above 150 V) than without argon. The major reason for this is the decrease of the flux of active species on the surface, in particular CH_x radicals, due to the decrease of the CH_4 partial pressure. However if one corrects the data for this dilution effect (solid line in figure 3), the etch rate for bias below 75 V with addition of argon is alike that without argon, whereas above 75 V it is slightly higher than without argon. In conclusion, addition of argon to the mixture at low bias allows to clean the surface from an excess of carbon, but it has no specific effect on the etch rate. At 600 W two regions are observed. For low bias (below 50 V) the etch rate varies scarcely with bias, whereas above 75 V the etch rate increases linearly with bias with a slope similar to that at 300 W.

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It has been reported previously (2) that the intensity of the In* emission line was a reliable signature of the etching mechanism. Here, the good agreement obtained between the etch rate and the In* line (figure 4) indicates with confidence that biasing the sample has little effect on the plasma characteristics. So, when dealing with plasma-surface interaction, one can consider in a reasonnable approximation, the source power and the sample bias to control respectively and independently the ion flux and the ion energy.

After etching the chemical species observed at the surface are identical to those after RIE (2, 6) : namely (In)P–H (130.4 eV), C–C (285.1 eV), C–In (283.8 eV), <u>In</u>–In–C, or <u>In</u>–In–P (17.0 eV) in addition to the contribution of the InP material located at 129.2 eV (P 2p) and 18.0 eV (In 4d) (figure 5, 6 and 7). The intense C 1s signal in the case of the 300 W - 25 V etching condition is due to the existence of a carbon film at the surface since the bias is close to Ve . Whatever the experimental conditions, one sees from figure 6, 7 and 8 that the In 4d peak intensity remains typically constant. A similar feature is observed for RIE, the In 4d peak intensity being always equivalent to that of an oxide-free MOCVD epitaxial-grown InP. This indicates no significant modification of the In atomic density after etching. On the contrary the P 2p intensity and thus the phosphorus density strongly depends on the etching conditions as observed from the loss of phosphorus and the simultaneous presence of In–In–C, or In–In–P species (figure 8 and 9). The surface concentration in phosphorus is always smaller than in the case of the MOCVD InP, it decreases continuously with bias above Ve . This phosphorus loss increases when using a high source power, or when adding argon to the gas mixture. On the other hand a slight, but significant, decrease in the amount of carbon is observed when increasing bias, this trend becomes more pronounced when using a high source power, or adding argon to the gas mixture. At bias equal to Ve the carbon film on the surface is estimated to be 35 Å thick. Calculation is done assuming the film is of constant thickness and composition, and contains no phosphorus or indium ; an inelastic mean free path of 26 Å has been taken for P 2p or In 4d photoelectrons (7). Since an etch rate of 150 Å/min is measured, at bias equal to Ve etching occurs through this thin carbon film.

Figure 10 and 11 report the mean P/In atomic ratio which is estimated from the overall In 4d and P 2p signals as compared to those for the oxide-free MOCVD epitaxial-grown InP. In every case a phosphorus loss is noticed. Generally speaking, one observes that the higher the bias at a constant source power, or the higher the source power at a constant bias, the more severe the surface degradation. Up to 500 W no significant variation of the surface stoichiometry is noticed when increasing the source power at a constant bias of 100 V. But a severe degradation of the P/In ratio is observed at 600 W. ICP etching using high source powers seems to be very harmful to the surface composition and morphology, this result is very similar to what is observed in ECR processes (3, 4). The P/In ratio is much more sensitive to the sample bias, this suggests the phosphorus loss mechanism to be closely related to the energy flux at the surface. Between the etching-deposition threshold Ve and a bias Vd that we shall call the damage threshold, the sample bias has little effect on the P/In ratio. In figure 11 Vd is located around 75 V and 50 V for 300 W and 600 W respectively. A severe degradation is observed above Vd : in the range investigated, the P/In ratio drops linearly with bias. Increasing the source power causes Vd to decrease. Comparing figure 11 with figure 3, a close relation appears to exist between the sharp increase in the etch rate noticed around 50 V of bias at 600 W and Vd_{600W}. As the ion flux increases linearly with the source power, a reasonable interpretation is that the severe P loss occurs above a particular energy flux threshold. This threshold is of course expected to vary according to the gas mixture, that is according to the intensity and composition of the ion flux and active neutral species flux at the surface.

MODEL FOR THE ETCHED SURFACE

XPS measurements give the following information. Since the In 4d intensity appears to be systematically equivalent to that of a MOCVD InP, an In atomic density equal to that of the bulk is assumed for the surface layers. The P 2p spectra show (In)P–H and P–In species. A simple decomposition of the P 2p spectra with these two contributions then leads to the determination of the FWHM associated to P–In contribution (figure 12). For bias below *Vd* the FWHM does not vary significantly from that of the MOCVD InP ; then it increases continuously between *Vd* and 200 V. These data strongly suggest that in every case the total damaged layer is smaller than the XPS sampled depth, so that bulk InP always contributes to the P 2p spectra. A three-layer model, similar to that proposed for RIE (5, 8), is now taken to be representative of the etched surface. From the surface towards the bulk, the plasma modified sample is described by : i) a superficial layer, amorphous, depleted in phosphorus, containing the various surface species presented above, and in which an exponential gradient of phosphorus is assumed to exist ; ii) a damaged layer, amorphised but stoichiometric in composition ; iii) the bulk InP. The P 2p spectra are thus fitted with three contributions : (In)P–H located at 130.4 eV, amorphous InP, and bulk InP, both situated at 129.2 eV (figure 13). To operate the curve-fitting of the P 2p spectra under the best conditions, the location and the FWHM of the component relative to bulk InP are fixed to the reference values for MOCVD sample, respectively 129.2 eV and 0.93 eV ; in the same manner the location and the FWHM of the component relative to (In)P–H are fixed to the result of the previous decomposition with two components.

The thickness of the phosphorus-depleted layer is estimated from the decomposition of the P 2p spectra with two contributions, using the intensity ratio $P_{InP}/P_{MOCVD\ InP}$. Whereas the total damaged layer is extracted from the intensity ratio $P_{bulk\ InP}/P_{MOCVD\ InP}$ given by the three-layer model. The results obtained (figure 14) are consistent with figure 11 : for low bias, typically below *Vd*, the phosphorus-depleted layer is of similar thickness whatever the bias and source power, whereas for bias above *Vd* the layer increases with ion energy, and strongly depends on the ion flux. On the other hand the thickness of the underlying amorphous InP layer varies linearly with ion energy, and appears independent from the ion flux in a given gas mixture (figure 15). Moreover similar damaged depths have been deduced from photoluminescence measurements (9). The phosphorus profile in the depleted layer is determined assuming the expression of the P 2p peak intensity in function of depth z as,

$$I_P = \int_0^\infty N_P(z)\cdot\exp\left[-\frac{z}{\lambda}\right] \qquad [1]$$

with the following exponential profile for the phosphorus atom density,

$$N_P(z) = N_P\cdot\exp\left[-\frac{(z-z')}{d}\right] \qquad 0 \le z \le z' \qquad [2]$$

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in which $N_P = 5.8\ 10^{14}\ cm^{-2}$ for (100) oriented InP wafer, and z' is the thickness of the superficial phosphorus-depleted layer. The slope of the profile (d) is then determined by comparing the experimental and theoretical P 2p peak intensity. An example is given for extreme bias conditions at : 300 and 600 W in figure 16. The slope of the profile remains roughly constant for all conditions investigated : 0.20±0.05 $Å^{-1}$.

CONCLUSION

Chemical and structural surface modification of InP induced by ICP etching processes have been characterized. Three kinds of damage have been identified : contamination with carbon species, phosphorus loss, and amorphisation. The nature and extent of the damage with regard to source power, gas mixture and sample bias strongly suggest a close relation to the energy flux to the surface brought by the ion bombardment. A description of the influence of these parameters on the etching mechanism in ICP should be proposed shortly (10). ICP processes appear to be flexible enough to offer the possibility to control composition and structural damage. Damage can be limited to phosphorus loss, and to a very shallow region, by using low sample bias, and yet obtain reasonable etch rates. Such a behaviour is of particular interest when the main objective is to obtain a selective etching process. On the other hand, it seems more difficult to obtain anisotropic etching without damage or without the use of a sidewall passivation.

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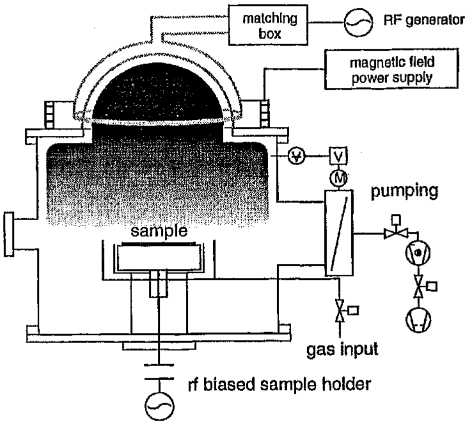

Figure 1 : Inductive Coupled Plasma etching experimental set up.

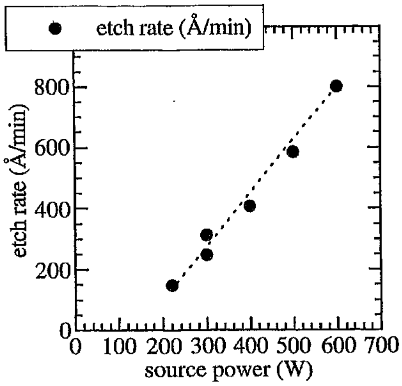

Figure 2 : Etch rate *versus* souce power, for a sample bias of 100 V.

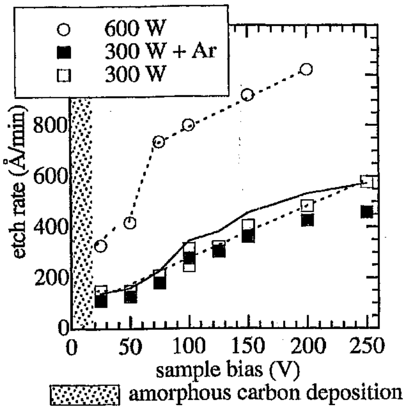

Figure 3 : Etch rate *versus* sample bias, solid line corresponds to 300 W + Ar data corrected from dilution.

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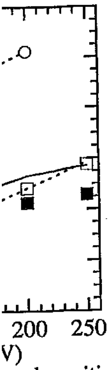

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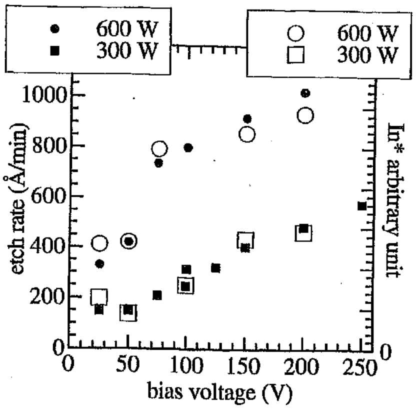


Figure 4 : Etch rate (full pattern) and In* intensity (open pattern) *versus* sample bias.

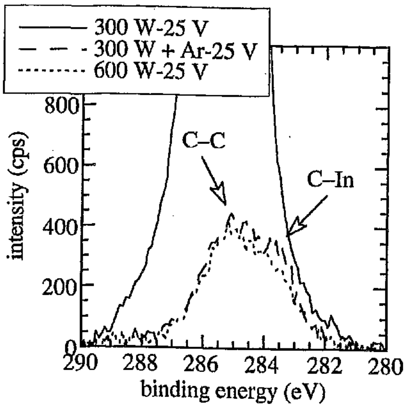


Figure 5 : C 1s spectra at various power and gas mixture for 25 V of bias.

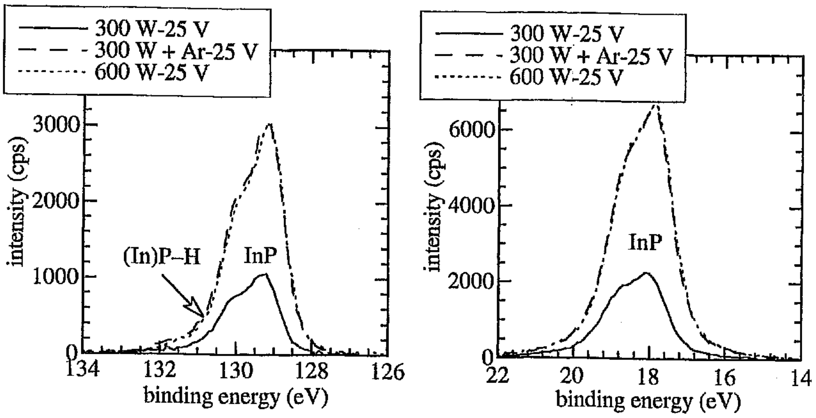


Figure 6 : P 2p and In 4d spectra at various power and gas mixture for 25 V of bias.

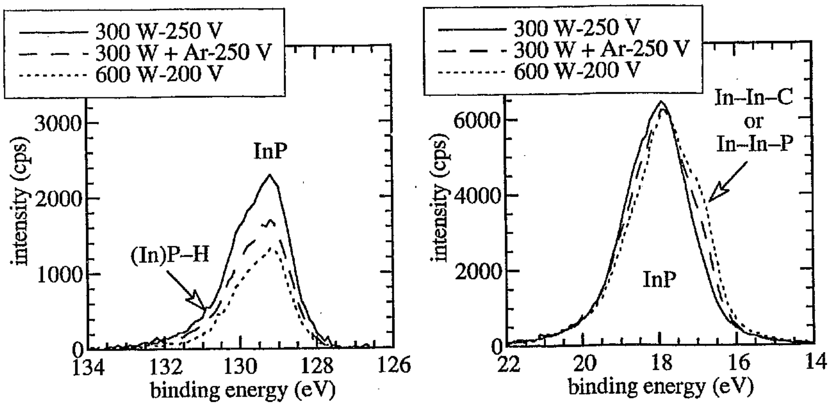


Figure 7 : P 2p and In 4d spectra at various power and gas mixture for high bias.

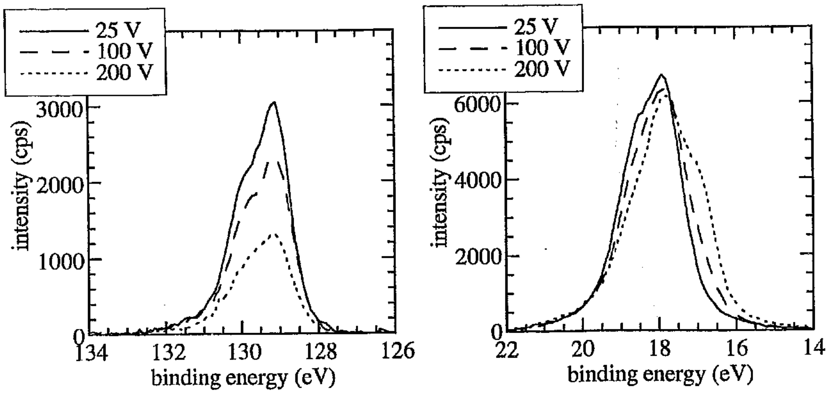
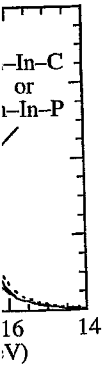


Figure 8 : P 2p and In 4d spectra at various sample bias for 600 W of source power.



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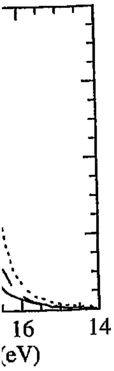

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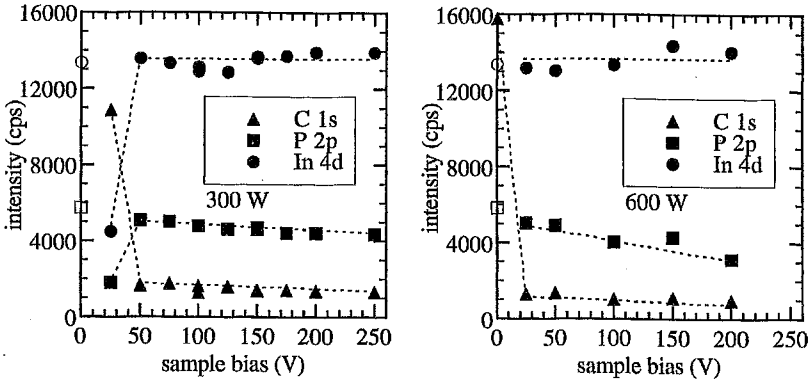


Figure 9 : C 1s, P 2p and In 4d intensity *versus* sample bias for 300 W and 600 W, open patterns at 0 bias represent the contributions for an oxide free MOCVD InP.

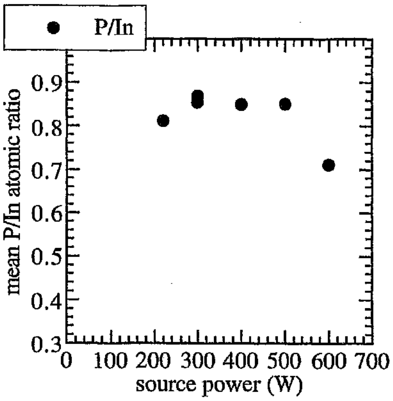


Figure 10 : P/In atomic ratio *versus* source power, for a sample bias of 100 V.

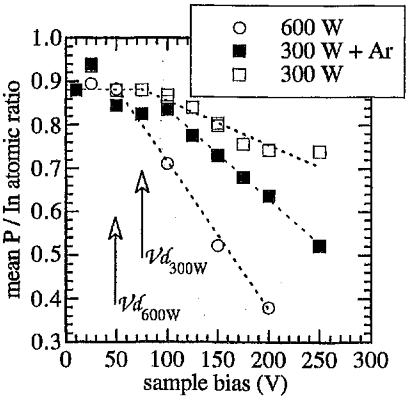


Figure 11 : P/In atomic ratio *versus* sample bias.

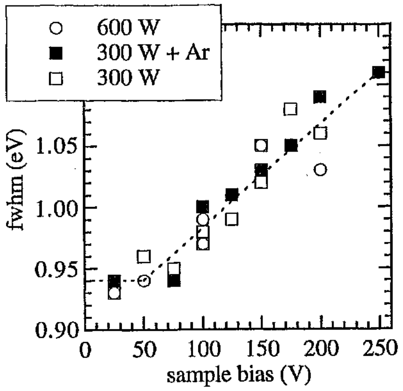


Figure 12 : Full width at half maximum of the P–In contribution to the P 2p spectra.

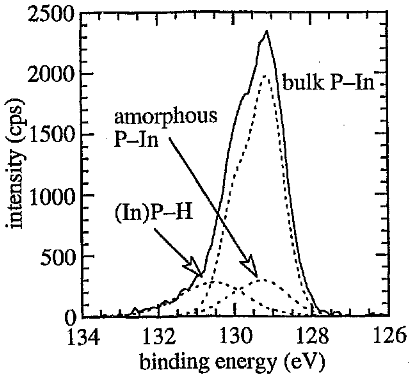


Figure 13 : P 2p spectrum (600 W-100 V) fitted with three components.

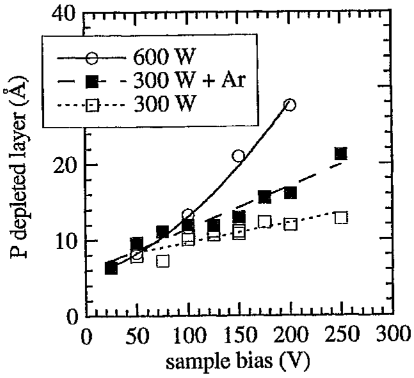


Figure 14 : Thickness of the P-depleted layer *versus* sample bias.

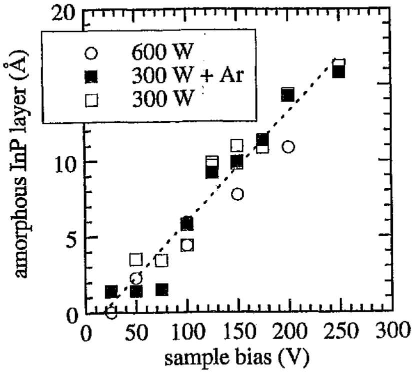
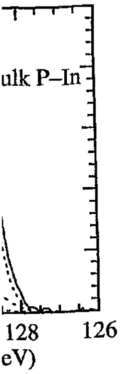


Figure 15 : Thickness of the amorphous InP layer *versus* sample bias.



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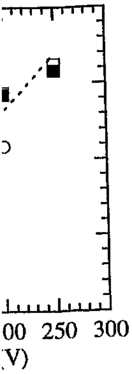

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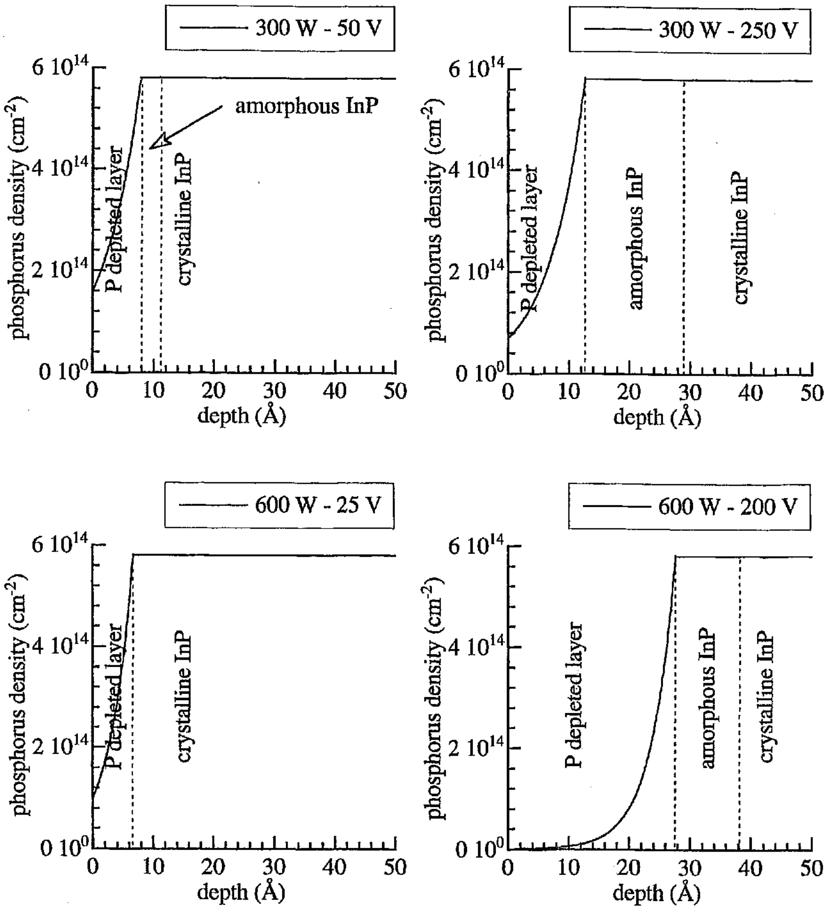

Figure 16 : Schematic representation of the P profile in the etched surface.