LOW TEMPERATURE CLEANING OF InP SUBSTRATES USING H-ATOMS. IN-SITU OPTICAL METHODS FOR H_2 PLASMA AND SURFACE CHARACTERIZATION

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ABSTRACT. Optical emission spectroscopy (OES), phase modulated spectroscopic ellipsometry (PMSE) and laser reflectance interferometry (LRI) techniques have been used for the in situ diagnostics of the H_2 r.f. plasma and of the cleaning process of InP substrates by H-atoms. A very high H-atom density ($[H]\sim 1\text{-}\ 7\cdot 10^{15}$ cm^{-3}) in the H_2 plasma downstream flow has been evaluated by the etching rate (r_E) measurements of a phosphorus film, since the relationship $r_E = k\cdot[H]$ can be applied. The effectiveness of the cleaning process by H-atoms has been evaluated by PMSE measurements, which indicate that the complete removal of InP native oxide can occur in few minutes without surface damage. The end point of the cleaning is well detected by kinetic ellipsometry.

INTRODUCTION

Recently, hydrogen plasma processing of III-V semiconductors and, in particular, of InP has been developed for the removal of surface contamination and native oxide top-layer, so leaving a clean and well ordered surface for the epitaxil growth [1-4]. In addition, hydrogenation of InP by H_2 plasma exposure can induce passivation of shallow acceptor impurities [5,6] and, hence, the possibility of improving the performance of the optoelectronic devices.

However, if the plasma conditions and the H-atom flux interacting with the InP surface are not appropriately controlled, the InP substrates can lose their stoichiometry and mirror-like aspect, as a consequence of the preferential etching of phosphorus [3,7] Moreover, radiative and ion induced damage of crystal lattice produce electrically active states in the forbidden gap.

Hence, in order to achieve high cleanliness and passivation, while minimizing the damage of the crystal structure, it is becoming important to establish diagnostic methods to control the plasma, the H-atom flux onto the surface and the surface modifications. With respect to this, optical diagnostics are particularly attractive as they are in-situ non intrusive techniques.

In the following, we present the results of optical emission spectroscopy (OES), phase modulated ellipsometry (PMSE) and laser reflectance interferometry (LRI) for the cleaning and passivation of InP surfaces by a controlled atomic hydrogen flux present in the downstream region of a low pressure H_2 r.f. plasma. These in situ diagnostic methods have been employed for describing the plasma production of H-atoms, their recombination kinetics in the downstream region, and their interaction with InP surface to be cleaned.

EXPERIMENTAL

H_2 plasma treatments are performed in the home made apparatus schematized in fig. 1.

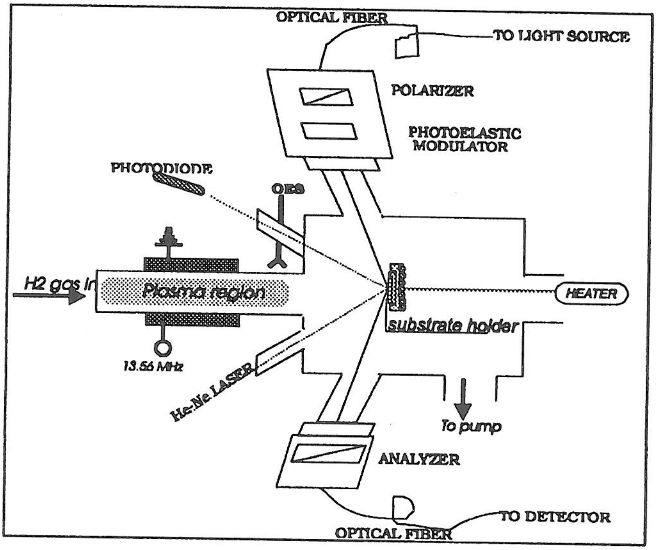


Fig. 1. *Scheme of the experimental apparatus*

The H_2 r.f. discharge is ignited between two semicircular electrodes by applying a 13.56 MHz voltage in a 4 cm i.d. quartz tube. This plasma source is assembled on a stainless steel chamber in which both processes of phosphorus etching and of InP substrate cleaning are performed. In this configuration it is assumed that the plasma region end coincides with the end of the quartz tube. Thus, effects related to plasma radiative damage of InP substrates can be minimized.

The efficiency of the H-atom plasma source is investigated by varying the pressure in the range 0.1 - 2 torr, the r.f. power level from 1 to 80 watt and the H_2 gas flow rate from 100 sccm to 1000 sccm. The monitoring of the plasma phase is performed by optical emission spectroscopy (OES); the light emission is collected by an optical fiber at the plasma tube end. Ar actinometry [8] (addition of 2% Ar to the gas feed) is used to estimate relative changes in H atom density in the plasma through the intensity ratio of H* emission at 654.6 nm and Ar* emission at 756.5 nm. Whereas, the evaluation of the H-atom density in the afterglow region is performed by using LRI (He-Ne laser) to measure the etching rate of a phosphorus film target positioned 10 cm away from the plasma end.

The H_2 plasma cleaning experiments are performed on SI (100) InP substrates, positioned in the afterglow region, at the pressure of 1 torr, at the r.f. power of 60 watt, and at the flow rate of 800 sccm. The effect of substrate temperature (25 - 300°C), in situ annealing (300 - 640°C) and hydrogen exposure time (5 - 60 min) is investigated by in situ spectroscopic ellipsometry (SE) operating in the range 200 - 800 nm. Single wavelenght ellipsometry (SWE) ($\lambda = 269$ nm) is used for the kinetic study of the InP cleaning and for the end point detection of the native oxide reduction process.

RESULTS AND DISCUSSION

H_2 plasma characterization

The actinometric OES can be helpful in determining the H-atom density level in the glow discharge, once the origin of the H* emitting specie is established. For the H* generation, two mechanisms can be formulated:

(a) one-electron excitation process

$$H_2 + e \rightarrow H^* + H + e \qquad (1)$$

(b) two-electron excitation process

$$H_2 + e \rightarrow H + H + e \qquad (2)$$

$$H + e \rightarrow H^* + e \qquad (3)$$

On the basis of these processes, and under the approximation that the H* decay is only radiative, the following equation can be derived [9]:

$$[H] \propto (I_{H^*}/I_{Ar^*} - k_e\,[H_2]) \qquad (4)$$

Therefore, from the quantitative point of view, the ratio I_{H^*}/I_{Ar^*} is, subtracted by the constant contribute k_e $[H_2]$, a measure of the H-atom density in the plasma volume.

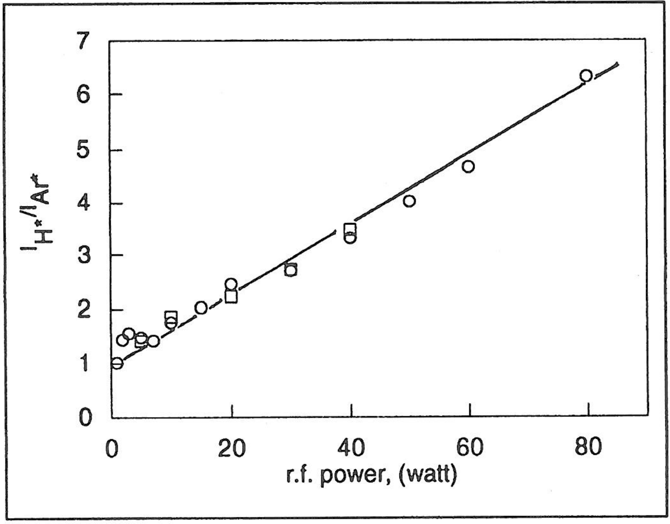


Fig. 2. *Intensity ratio, I_{H^*}/I_{Ar^*}, vs r.f. power in H_2 (○) and H_2-phosphorus (□) plasmas.*

In fig.2 the intensity ratio I_{H^*}/I_{Ar^*} is plotted as a function of r.f. power for H_2 plasmas also during phosphorus etching. The observed linear dependence is read in terms of equation (4), in that the intercept is the constant contribute k_e $[H_2]$ of the process (1), and the increasing trend is related, according to the process (3), to the linear increasing contribute of H atoms.

OES measurements at different H_2 gas flow rate show the constancy of I_{H^*}/I_{Ar^*} ratio, and, hence, of H-atom density. This result indicates that the H atom formation kinetics is very fast and that the plasma equilibrium condition, i.e. the balance between H_2 dissociation and H atom recombination, is reached even at flow rate as high as 1000 sccm (residence time = 20 msec). The existence of this plasma steady state condition assures that the H-atom density at the beginning of the downstream region assumes the same value at each investigated gas flow rate.

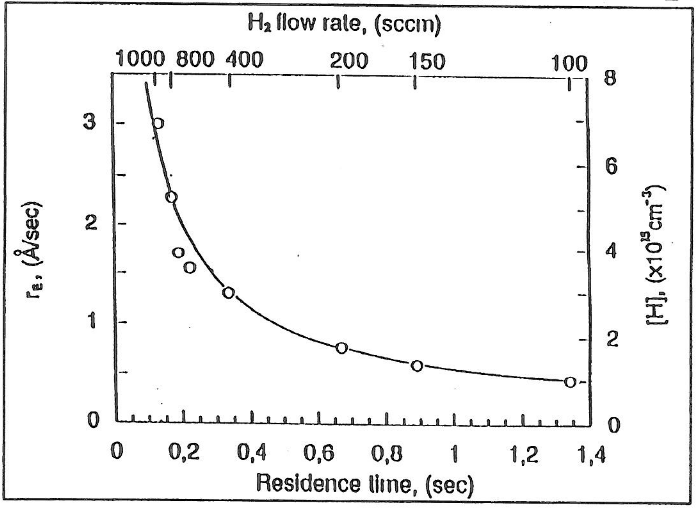
In the downstream region, the H-atom density can not be derived from OES measurements, as the excitation processes (eq. 1-3) are not effective. In this region, the H-atom density and decay kinetics are controlled by the following processes:

$$H + H + H_2 \rightarrow H_2 + H_2 \qquad (5)$$

$$H \xrightarrow{\text{wall}} 1/2\, H_2 \qquad (6)$$

The evaluation of H-atom density is based on the etching process of a phosphorus film whose etching rate, r_E, has been reported to be linearly correlated to H-atom density ($r_E = k\cdot[H]$) [10]. Measurements of r_E at different gas flow rate are shown in fig.3. This r_E profile is fitted by a kinetic model which includes only the homogeneous recombination process (eq.5); the following relationship is derived [10]:

$$[H]\ (cm^{-3}) = (2.1\pm0.4)\cdot 10^{15}\cdot r_E\ (\text{Å/sec}) \qquad (7)$$



The very high efficiency of our H-atom source ([H] = 1 - 7·10^{15} cm^{-3} in fig.3) is direct consequence of the low residence time (<1 sec) in the afterglow region, and of the above cited steady state condition for H-atom production.

Fig. 3. Phosphorus etching rate, r_E, and the corresponding H-atom density, [H], vs H_2 residence time in theplasma downstream region (1torr, 60 watt).

H_2 plasma cleaning: in situ characterization of InP surfaces

Plasma cleaning process of InP surface by H-atoms is used as an alternative to the widely utilized wet etching procedure [11]. The pecularity of the *in situ* plasma cleaning treatment is that the indium oxide In_2O_3 is completely reduced by H-atoms, while it is still present on a InP surface cleaned by ex situ wet etching, since the reoxidation process is very fast. However, previous studies [12,13] have demonstrated that a direct and prolonged exposure of InP surface to H-atom flux as high as 10^{17} - 10^{18} atoms/cm^{2}sec induces a decomposition of the InP substrate forming PH_3 and leaving metallic indium droplets on it. In the present experiments, the selective phosphorus etching by H atoms is avoided by operating the cleaning in presence of small amount of PH_3. The PH_3 comes from the etching of the red phosphorus charged in the plasma tube. The presence of PH_3 and the remote plasma configuration, which avoids lattice desruption by ion bombardment, allow to obtained a cleaned, well-ordered and mirror-like InP surface even at H-atom flux as high as $5\cdot 10^{20}$ atoms/cm^{2}sec.

The surface modification during the hydrogen treatment is monitored by SWE (λ = 270 nm), whereas the most significant surface states are identified by SE spectra. These spectra are interpretated by using three-layers BEMA models [14]. Fig. 4 shows the typical time evolution of the imaginary part, ε_i, of InP surface during the H_2 plasma treatment and annealing.

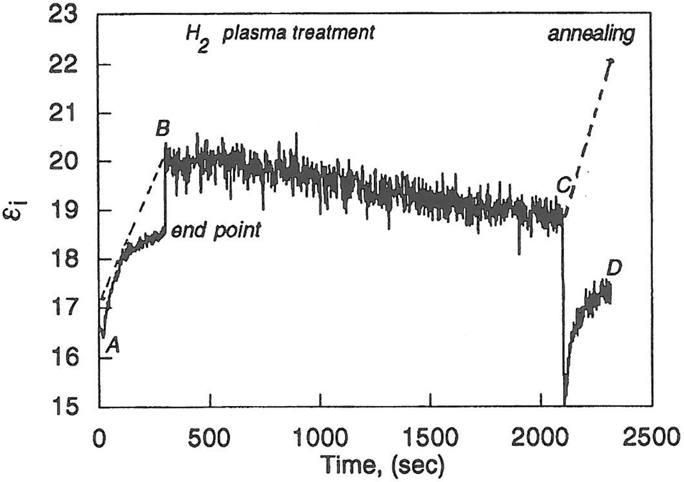


Fig. 4. Time evolution of ε_i (4.6 eV) during: (A-B) H_2 plasma cleaning at T=270°C, (B-C) H_2 plasma exposure at T_{room}, and (C-D) annealing at T=430°C in presence of PH_3. Dashed line is for the ε_i values as measured at T_{room}.

Starting from the InP substrate, covered with a 25Å thick oxide layer, it is observed an increase of ε_i value, which is indicative of the reduction of the oxide layer thickness. At the point B, the cleaning process can be considered complete (end-point), and the correspondent SE spectrum is representative of a c-InP surface covered with a 20Å InP layer which includes 15% of voids (v). The overall reduction process can be schematized as follow:

$$(InP)\text{-}O_x + 2\,H \rightarrow InP(v) + x\,H_2O \qquad (8)$$

in which hydrogen atoms selectively remove oxygen so producing H_2O and leaving a less dense InP outmost layer. The effectiveness of the oxygen removal strongly depends on surface temperature. In fact, H_2 plasma processing of InP surfaces at T<230°C (temperature used for the experiment of fig.4) does not show any significant decrease of the oxyde layer thickness. This strong temperature dependence of the cleaning process could be interpreted on the basis of a kinetic model in which the out-diffusion of H_2O is the rate limiting step. Further exposure of the cleaned InP surface to H-atoms implies phosphorus etching and, hence, the InP surface degradation as observed by the decrease of ε_i in fig. 4 (B-C curve). The created phosphorus vacancies can be resaturated by annealing a T = 430°C in presence of PH_3 (C-D curve) as confirmed by the high value of ε_i (D point) and by the SE spectrum whose BEMA model gives an InP surface characterized by microroughness.

CONCLUSION

The remote H_2 plasma treatment of InP substrates is a valid procedure for removal of surface native oxide. The main features of this cleaning procedure are:

- the possibility to be *in situ* applied just before running epilayer growth;
- the complete removal of native oxides and other contaminations as well;
- the possibility of surface damage (loss of phosphorus) when under prolonged H-atom exposure.

The last inconvenient can, however, be avoided by monitoring the end point of the cleaning (e.g. by ellipsometry) or by performing an annealing procedure (T = 430°C) in presence of PH_3.

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