Evidence of chlorine ion penetration in InP/InAsP quantum well structures during dry etching processes and effects of induced-defects on the electronic and structural behaviour

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A B S T R A C T

In this work, the overall point of interest is the occurrence of artefacts associated with dry etching processes on InP-based structures. By artefacts we mean creation of defects in the remaining material after etching, defects which might be deleterious to both performance of the photonic devices being fabricated, and reliability/lifetime of these devices. A specific sample structure was defined on InP with InAs0.5P0.5 quantum wells (QWs). These QWs are buried within 1 μm from the surface, for maximum sensitivity to reactive species produced in the etch plasma, and are designed with a gradual As/P composition, such that the luminescence peak produced by each QW is clearly identified. These samples thus possess a “built-in” marker including its own scale. We focused on chemistries with chlorine (SiCl4/H2/Ar and Cl2/N2), implemented in an inductively coupled plasma reactor. With such chemistries, etch rates of 0.5 μm/min can be reached.

The samples are not really etched, but just exposed shortly to the plasma for the interaction to take place. Actually, we just etch at most a few tens of nanometers. Characterisation was carried out by spectrally-resolved cathodo-luminescence and photo-luminescence. We also measured secondary ion mass spectrometry profiles, which revealed the penetration of chlorine into the samples. High resolution transmission electron microscopy was used, to probe the crystal quality. By comparing doped and undoped samples, we show that the chlorine observed after exposure consists at least partly in Cl− ions. The other important observation is some mechanical compressive stress, which is also a consequence of the local concentration of Cl impurities after exposure to the plasma.

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1. Introduction

Dry etching is ubiquitous for the fabrication of an increasing variety of photonic devices. For example, ridge-waveguide passive devices or semiconductor laser sources, but also photonic crystal-based components as well as many types of photo-detector arrays rely on this kind of process. In order to reach the desired specifications (in terms of the accuracy of the orientation and roughness of surfaces revealed by the dry etching, the aspect ratio, the depth of etching, ...) the dry etching process is often realised under harsh conditions, where the etch rate can reach microns/min. However, there are only a limited number of papers investigating the effect of such processes (which involve in particular ion bombardment and exposure to reactive plasma radicals) on the remaining material. Berrier et al. [1] studied the effect of dry etching conditions on carrier lifetime reduction in InAsGaP quantum wells (QWs) in InP-based photonic crystal structures. In early studies, using cathodo-luminescence (CL) spectral imaging, we have looked at the effects of dry etching on the spectroscopic properties of rectangular ridge waveguides etched in InP or QW structures on InP (I23). It was shown that mechanical stress is induced in such structures following the dry etching.

In this paper, we develop a methodology for the investigation of effects induced on the material exposed to the plasma in the dry etching reactor. A QW structure is designed with the objective to associate each line on the luminescence spectra to a specific depth inside the material. Thus, by looking at the evolution of the spectra before and after the plasma etching, we hope to learn about the effects induced at
different depths. The samples are characterised with photo-luminescence (PL) at low temperature, CL, secondary ion mass spectrometry (SIMS), and high resolution transmission electron microscopy.

2. Sample structure

The samples were grown on an n-doped InP(100) substrate, with a series of InAs$_x$P$_{1-x}$ QWs located close to the surface. The barrier material is InP. A 400 nm buffer is first grown, and then a series of 9 QW/barrier is grown with fixed thickness “e” (between 7 and 8 nm for the QW, and 100 nm for the barrier). A 300 nm InP layer is finally grown at the surface. The energy gap of the QWs is adjusted by decreasing the As/P ratio during the growth of the successive QW, thus increasing the energy gap from substrate to surface (which prevents reabsorption effects on the PL and CL spectra). The samples were grown by gas phase molecular beam epitaxy. Fig. 1 shows the sample structure. A similar approach for the investigation of ion bombardment effects on InP and GaAs-based structures was already used (see e.g. [4]).

In this study, 2 different samples were used:
Sample 1 without intentional doping and sample 2 with a pn junction, where the InP buffer layer is doped n-type with Si ($10^{18}$ cm$^{-3}$), while the barrier and surface InP layers are doped p-type with Be ($7.10^{17}$ cm$^{-3}$). The InAs$_x$P$_{1-x}$ QWs remain undoped.

3. Dry etching conditions

The samples were exposed to the plasma in an inductively-coupled plasma dry etch reactor, using either SiCl$_4$/H$_2$/Ar or Cl$_2$/N$_2$ gas mixtures. The adjustable parameters are the flow rates of each gas component, the total pressure inside the reactor, the RF power used for plasma excitation and the RF power applied to the sample holder to control the self-bias. The sample temperature was not controlled for these experiments.

For the SiCl$_4$/H$_2$/Ar chemistry, the etch rate with the conditions chosen for the present study was in the order of 500 nm/min, therefore only very short exposures (typically 1 min) of the samples to the plasma were investigated to avoid etching the whole structure. For Cl$_2$/N$_2$ chemistry, the etching was much slower allowing longer exposures without any risk of complete etch of the structure.

4. Photo-luminescence

Fig. 2 shows the PL measured on the as-grown undoped sample (sample 1) at 15 K. 1064 nm YAG laser excitation was used for all the PL results discussed. The contribution of each of the 9 QWs is clearly identified in the spectrum.

Also shown on Fig. 2 are the PL spectra measured on sample 1 after exposure to the SiCl$_4$/H$_2$/Ar plasma (1 min) and to the Cl$_2$/N$_2$ plasma (4 min.). The main observations are:

- the signal of the first 2 QWs, the closest ones to the surface, disappears for the SiCl$_4$/H$_2$/Ar plasma (red curve), indicating that these QWs have been etched, or at least that their luminescence has been destroyed
- meanwhile the Cl$_2$/N$_2$ plasma has not etched any of the QWs (blue curve)
- all the PL lines display a blue-shift upon exposure to the plasma. The magnitude of the blue-shift is higher for Cl$_2$/N$_2$ than for SiCl$_4$/H$_2$/Ar
- the blue-shift seems to vary continuously depending on the depth of the QW. The maximum shift is observed for some of the QWs in the centre of the whole structure, reaching 8 nm approximately (6 meV).

Similarly, Fig. 3 shows the PL spectra measured in the same conditions as in Fig. 2 for the doped sample (sample 2), immediately after growth, after 1 min exposure to the SiCl$_4$/H$_2$/Ar plasma, and after 3 min. exposure to the Cl$_2$/N$_2$ plasma.

The PL spectra differ significantly from those on sample 1. Comparing the black curves, one sees that the PL lines appear much broader on the doped sample. This is due to the presence of the electric field...
induced by the pn junction. The spectral broadening of the PL line evidences some quantum confined Stark effect (QSCE) on this sample. QSCE tends to shift the PL lines to lower energy, to broaden them and to reduce their maximum amplitude [5].

One can see on Fig. 3 that the Cl-based plasma exposure strongly sharpens the PL lines of sample 2, also increasing significantly their maximum amplitude, and inducing some blue shift. This is evidence that the plasma exposure reduces the QCSE.

We have also measured the PL spectra as a function of the excitation laser power density. These measurements indicated a linear dependence of the PL signal, at least in the range of laser powers investigated.

5. Secondary ion mass spectrometry

In order to assess the possible penetration of Cl inside the sample structures, SIMS profiles were measured for all the samples, using Cs\(^+\) as the primary ions. Fig. 4 shows 2 examples of such profiles, obtained for sample 2 on the as-grown surface and after exposure to the Cl\(_2/N_2\) plasma (2 min.). The different masses analysed are indicated.

Due to the sensitivity of this technique, Cl is always observed when profiling the samples. However, on the as-grown sample, the Cl signal drops to the background level after a few seconds sputtering. On the opposite, on the exposed sample, the Cl signal remains much higher than the background level throughout the structure (in the case of Fig. 4, the Cl signal is about 10 times the background level for the exposed samples — note that for Cl a logarithmic scale is used). We have not performed the necessary steps to produce calibrated signals on our SIMS data, however all the samples exposed to the etching plasmas displayed Cl penetration, with different amounts and distributions.

6. Cathodo-luminescence on biased samples

In order to better understand the luminescence behaviour, CL spectra were measured at 80 K, with an acceleration voltage of 20 kV for the electron beam, and with the possibility to bias the sample surface during the measurements. We just show here 2 series of spectra obtained on sample 2.

Fig. 5 shows the CL measured on the as-grown sample as a function of the positive bias applied to the surface. In principle, positive bias on the p-side of a pn junction should reduce the strength of the internal electric field (and hence the QCSE). This is the case for the deepest QW, which lies very close to the pn junction where the electric field is maximum due to the doping profile used for sample 2. For the other QWs, little effect is observed on Fig. 5. We think that this is due to the complex band profile induced by the combination of pn junction and pinning of the Fermi level at the surface.

Finally, in order to probe the structural quality of the samples at the different stages, high resolution transmission electron microscopy was also performed on thin slabs obtained by thinning under the Ar\(^+\) ion beam, with the samples cooled in liquid nitrogen to avoid decomposition as much as possible. As an example, we show on Fig. 7 a scanning transmission electron microscopy on the region of the deepest QW of sample 2 after exposure to the plasma. This figure, as well as all the results that we have obtained on the different samples and the different areas investigated, indicates the very high crystal quality of the samples, even after exposure.

8. Discussion

From the different observations, and the use of both doped and undoped samples, we can assess that the first very important issue that we face during these experiments of exposure of the test sample to the Cl-based etching plasmas is the penetration of Cl across the whole QW structure. As indicated, all the SIMS profiles display this tendency. It should be emphasised that even if we cannot measure accurately the temperature at the surface of our samples during etching, we were able to estimate the local heating to be certainly less than 200 °C.
Therefore, the Cl profiles cannot be simple diffusion profiles. A realistic hypothesis at this stage is that the Cl penetration is related to some channelling effects. Rutherford backscattering experiments would be required to check this.

On the other hand, the PL and CL data on sample 2 show that the plasma exposure affects the electric field present initially in the sample, in a direction where this field is reduced, at least close to the pn junction. We assume that this demonstrates the presence of Cl ions (most probably Cl\(^{-}\)) after plasma exposure. These negative ions interact with the dopants, compensating the n-doped region. Similar ion “diffusion” has already been reported for experiments where a Si surface was exposed to different fluor-based plasmas (with F\(^{-}\) ions penetrating deeply into the sample) [6].

The PL and CL spectra also show that plasma exposure induces a blue shift, whose amplitude depends on the plasma conditions, duration, and location of the QW within the structure. We assume that this is also a manifestation of the penetration of Cl across the QW structure, where the presence of Cl (most probably in interstitial position in the lattice) induces a local hydrostatic compressive stress, which is known to produce blue shifts of the PL [7].

The effects which we have identified in this study reveal the existence of defects introduced during the dry etching process, whose distribution extends well below the surface exposed to the plasma. We speculate that such defects will have an impact on the performance of the photonic devices being fabricated, through their interaction with either – or both – electronic or optical properties. These defects may also affect to long-term reliability of the devices. Anyhow, this still has to be demonstrated and can be seen as a new direction of investigation on the optimisation of such processes as dry etching.

9. Conclusion

The methodology that we proposed for the investigation of side-effects of plasma exposure in dry etching of InP-based materials is based on two ideas. First the design of a dedicated quantum well structure to be used as a marker of the effect of the plasma exposure. Second the combination of experimental techniques like SIMS, luminescence and TEM to retrieve information on the effects of plasma exposure. But additional techniques like Rutherford Backscattering Spectrometry should also be considered at the light of the unexpected results demonstrated in this work. With this methodology, we have highlighted effects of the plasma exposure related to the deep penetration of some of the etching species in the sample, thereby affecting the properties of the material. These effects should be taken into account in the design of photonic structures such as optical waveguides which rely on the dry etching process for their fabrication.

References


Fig. 7. High resolution STEM image of QW n°9 on the doped sample, after 2 min. etching in SICl4/H2/Ar.