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Defect formation during chlorine-based dry etching and their effects on the electronic and structural properties of InP/InAsP quantum wells

AQ1

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The general objective is the investigation of the defects formed by dry etching tools such as those involved in the fabrication of photonic devices with III–V semiconductors. Emphasis is put on plasma exposures with chlorine-based chemistries. In addition to identifying these defects and describing their effects on the electro-optic and structural properties, the long-term target would be to predict the impact on the parameters of importance for photonic devices, and possibly include these predictions in their design. The work is first centered on explaining the experimental methodology. This methodology starts with the design and growth of a quantum well structure on indium phosphide, including ternary indium arsenide/phosphide quantum wells with graded arsenic/phosphor composition. These samples have then been characterized by luminescence methods (photo- and cathodoluminescence), high-resolution transmission electron microscopy, and secondary ion mass spectrometry. As one of the parameters of importance in this study, the authors have also included the doping level. The samples have been exposed to the etching plasmas for “short” durations that do not remove completely the quantum wells, but change their optical signature. No masking layer with lithographic features was involved as this work is purely oriented to study the interaction between the plasma and the samples. A significant difference in the luminescence spectra of the as-grown undoped and doped samples is observed. A mechanism describing the effect of the built-in electric field appearing as a consequence of the doping profile is proposed. This mechanism involves quantum confined Stark effect and electric-field induced carrier escape from the quantum wells. In the following part, the effects of exposure to various chlorine-based plasmas were explored. Differences are again observed between the undoped and doped samples, especially for chemistries containing silicon tetrachloride. Secondary ion mass spectrometry indicates penetration of chlorine in the structures. Transmission electron microscopy is used to characterize the quantum well structure before and after plasma bombardment. By examining carefully the luminescence spectral properties, the authors could demonstrate the influence of the etching plasmas on the built-in electric field (in the case of doped samples), and relate it to some ionic species penetrating the structures. Etching plasmas involving both chlorine and nitrogen have also been studied. The etching rate for these chemistries is much slower than for some of the silicon tetrachloride based chemistries. Their effects on the samples are also very different, showing much reduced effect on the built-in electric field (for the doped samples), but significant blue-shifts of the luminescence peaks that the authors attributed to the penetration of nitrogen in the structures. Nitrogen, in interstitial locations, induces mechanical compressive stress that accounts for the blue-shifts. Finally, from the comparison between secondary ion mass spectrometry and luminescence spectra, the authors suggest some elements for a general

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53 mechanism involved in the etching by chloride-chemistries, in which a competition takes place
 54 between the species at the surface, active for the etching mechanism, and the species that penetrate
 55 the structure, lost for the etching process, but relevant in terms of impact on the electro-optic and
 56 structural features of the exposed materials. © 2016 American Vacuum Society.
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57 I. INTRODUCTION

58 The semiconductor equipment industry has developed
 59 over the years a number of tools and processes which are
 60 today used at very large scales in fabrication throughout the
 61 world. Dry etching, also designated as reactive ion etching
 62 (RIE) or plasma etching, is one of these tools for the fabrica-
 63 tion of ultralarge scale integrated circuits in the silicon
 64 microelectronics industry as well as in the fabrication of
 65 photonic integrated circuits with compound semiconductors
 66 based on gallium arsenide (GaAs) or indium phosphide
 67 (InP). It is used, in particular, to precisely define features
 68 with submicron dimensions, for example, transistor gates in
 69 the silicon world.¹ Very deep features, such as “through sili-
 70 con vias,” are also realized using different RIE setups.² The
 71 reactive source gases used in plasma etching of silicon are
 72 usually molecules containing fluorine atoms, while chloride
 73 or bromide based plasmas are mainly used for the etching of
 74 III–V semiconductor compounds like GaAs or InP.

75 Plasma etching is considered a mature technology.
 76 Nevertheless, research and development efforts on this
 77 technique are going on in a large number of places, both aca-
 78 demic and industry centers, to adapt the processes and equip-
 79 ment to the challenges occurring constantly on the different
 80 roadmaps, both for silicon devices and III–V compound
 81 semiconductor devices. For example, pushing the limits of
 82 the “more Moore” approach for CMOS technologies requires
 83 plasma etching processes allowing gate design for the next
 84 technology nodes, etching of materials newly introduced
 85 into the gates, better control of the gate dimensions, etc.³ As
 86 far as compound semiconductor device technologies are con-
 87 cerned, the trend to reduce critical dimensions—especially
 88 for plasma etching operations—seems less emphasized, the
 89 efforts being rather focused on developing plasma etching
 90 processes applicable to a wide variety of materials which are
 91 nowadays introduced in the devices. However, some devices
 92 also require plasma etching processes which can generate
 93 features with critical dimensions in the nanometer range
 94 and/or aspect ratios difficult to achieve (good examples of
 95 such devices are the optic or opto-electronic components
 96 based on photonic crystals).

97 Developing plasma etching processes involves research
 98 in different directions:

- 99 (1) plasma physics and chemistry, as well as reactor technol-
 100 ogy (for the part related to design of equipment);
- 101 (2) study of the plasma/surface interaction for each specific
 102 material;
- 103 (3) accurate metrology for the optimization of the expected fea-
 104 tures; this is mainly performed using electron microscopy;
- 105 (4) materials and device physics to check the overall compat-
 106 ibility of the plasma process with device performances.

In this paper, we explore the last direction, with a focus 107
 on plasma etching of InP-based structures. We investigate 108
 the effects of dry etching on the etched materials. We chose 109
 processes commonly used in the photonic device industry 110
 for etching InP and related materials (in our case, the reac- 111
 tive source gases are chlorine-based mixtures with either 112
 SiCl₄ or Cl₂). In the present stage of the study, our goal is to 113
 identify the mechanisms by which the reactive gases interact 114
 with the material. No specific geometric feature is designed 115
 at this stage of the study. We simply expose the material to 116
 the gases, under the conditions typically occurring during 117
 plasma etching, and thereafter, we analyze the changes 118
 induced in the materials using different experimental techni- 119
 ques. Therefore, the issues concerning the etching mask 120
 materials and design are not considered, but will be the 121
 object of forthcoming work. 122

The methodology involves the design of heterostructures 123
 which incorporate specific features [quantum wells (QWs)], 124
 role of which is to provide an in-depth signature of the 125
 effects induced by the etching gases, through changes in 126
 their luminescence spectral parameters. This is an approach 127
 used for a long time by groups trying to understand the 128
 effects of energetic ions or reactive radicals on compound 129
 semiconductors. The first studies on this topic were reported 130
 for GaAs and InP.^{4,5} These pioneer studies dealt with the 131
 effects of ion bombardment (mainly rare gas ions) on sam- 132
 ples with AlGaAs QWs in GaAs or GaInAsP QWs in InP. It 133
 was demonstrated that under the effect of ion bombardment 134
 even at low energy (400–500 eV or even lower), defects are 135
 produced at depths in the order of 100 to a few hundred 136
 nanometers. Channeling was proposed as the mechanism 137
 generating these defects.⁶ Even if the ion bombardment 138
 experiment is not performed along directions where channel- 139
 ing is expected [e.g., etching (100) surfaces of GaAs or InP 140
 does not involve ion bombardment along a major channeling 141
 direction in these crystals], the fact that a very small fraction 142
 of the incident ions end-up travelling the crystal along other 143
 directions such as $\langle 110 \rangle$ can lead to this depth of penetration, 144
 and therefore promote the creation of defects across the 145
 structure. In these early studies, occurrence of defects at a 146
 specific depth below the surface is assumed from the reduc- 147
 tion of photoluminescence (PL) efficiency of the QW located 148
 at such specific depth. From these investigations, the authors 149
 showed that ion bombardment experiments simulating the 150
 conditions occurring during plasma etching affect the mate- 151
 rials on depths much larger than 100 nm, even when the ions 152
 energy lies between 100 and 500 eV. However, studying the 153
 effects of rare gas ions does not allow for the extrapolation 154
 to the case of industrial plasma etching processes. At least 155
 one paper reports on similar studies involving chlorine 156
 atomic and molecular ions derived from the decomposition 157

158 scheme expected for SiCl₄ inside a RIE reactor.⁷ Again, the
 159 decrease in PL yield from the QW is seen to extend deeper
 160 than 100 nm.

161 Similar experiments could not be carried out for the etch-
 162 ing of Si, since there is no simple QW structure (with an effi-
 163 cient PL) that could be grown by epitaxy on Si. However, a
 164 fundamental paper was published by Winters and collabora-
 165 tors,⁸ where the authors demonstrated the penetration of flu-
 166 orine into the Si lattice under conditions that simulate the
 167 exposure to etching plasmas. The measurements, performed
 168 using x-ray photoelectron spectroscopy, demonstrated a pen-
 169 etration depth of at least 20 nm, but the actual depth of pen-
 170 etration could be larger (the technique used in this study does
 171 not allow the probing of larger depths).

172 Our aim in this study is to establish a scheme for the inter-
 173 action of the ions penetrating during the process of exposure
 174 to the RIE plasma and the semiconductor materials under
 175 consideration (InP/InAsP). It is clear from the published
 176 results that this interaction leads to the creation of defects
 177 accounting for the reduction of the PL yield. However, the
 178 detailed mechanisms have not yet been described. The pen-
 179 etrating ions can have an impact on the electronic properties,
 180 both the charge carrier lifetime and the radiative recombina-
 181 tion rate. The approach followed consists in analyzing all the
 182 PL spectral properties affected by the RIE process, and to
 183 use samples with similar design of the QW structure but dif-
 184 ferent doping profiles (in order to see if the presence of inter-
 185 nal built-in electric fields affects the response to the RIE
 186 plasma). Additional characterizations are used to complete
 187 the investigations: secondary ion mass spectrometry (SIMS)
 188 to probe directly the penetration of chlorine and transmission
 189 electron microscopy (TEM) to assess accurately the etch
 190 depths through the QW structure and also to check the crystal
 191 and QW interfaces quality. In a preliminary paper,⁹
 192 reporting our first results for exposure of the InP/InAsP
 193 samples to different chlorine-based plasmas, we have shown
 194 evidence of the chlorine penetration in parallel with signifi-
 195 cant modifications of the PL and cathodoluminescence (CL)
 196 spectra. The present paper describes the extensive study that
 197 we have performed along the general objective stated above.

198 **II. EXPERIMENT**

199 We first describe here the design and growth of the InP/
 200 InAsP heterostructure samples. In a second part, we explain
 201 the conditions for the RIE process. Finally, we give the nec-
 202 essary details on the conditions which have been used for the
 203 examination of the samples before and after exposure to the
 204 RIE plasmas.

205 **A. Sample structure and growth**

206 The QW structures were grown on n-doped (100) InP
 207 substrates (doping level: 10¹⁸ cm⁻³). The whole structure
 208 contains nine QWs. QW thickness is constant for each sam-
 209 ple (7–10 nm). The QWs are made of InAs_xP_{1-x} (with InP
 210 barriers), with As composition “x” graded along the QW
 211 series. In order to avoid reabsorption of the PL, the QW with
 212 the smallest energy bandgap (highest As content) was grown

deepest—i.e., closest to the substrate—while the QW with
 the highest As content was grown closest to the sample sur-
 face. Typical values for x (As composition) are between
 0.35 (QW closest to the surface) and 0.49 (deepest QW). A
 buffer layer (400 nm InP) is first grown prior the QW series.
 The InP barrier thickness is 100 nm. An InP cap (300 nm) is
 finally grown after the last QW. The different QWs will be
 denoted as QW 1 to QW 9 (from surface to bulk). Therefore,
 the bandgap energy decreases from QW 1 to QW 9.

Figure 1 gives a schematic picture of this structure.

The samples were grown by gas source molecular beam
 epitaxy, using AsH₃ and PH₃ precursors, and a solid source
 for In. The layers could be grown either nonintentionally
 doped, or with Si or Be dopants for n-type and p-type,
 respectively. Two different samples will be investigated
 here:

- (1) Sample 1 was grown without intentional doping.
- (2) Sample 2 was doped: n-type (1 × 10¹⁸ cm⁻³) for the InP
 buffer layer, and p-type (7 × 10¹⁷ cm⁻³) for the InP bar-
 rier and cap layers. QWs were not intentionally doped.

B. Reactive ion etching

Commercial inductively coupled plasma RIE systems
 were used. These reactors have two RF power sources: one
 for the plasma excitation, and one for the control of the bias
 at the substrate.¹⁰ For the present study, we focused on dif-
 ferent etching processes available at III–V Lab for the fabri-
 cation of InP-based photonic devices. No specific process
 was designed for the experiments carried here. Three differ-
 ent etching chemistries were investigated, with the param-
 eters described in Table I.

Etching rates differ strongly from one process to the other
 and will be estimated from the SIMS measurements and
 TEM images. The first process (SiCl₄/H₂/Ar) produces an
 etch rate in the order of 500 nm/min. The Cl₂/N₂ process
 with the conditions above was chosen for its very low etch

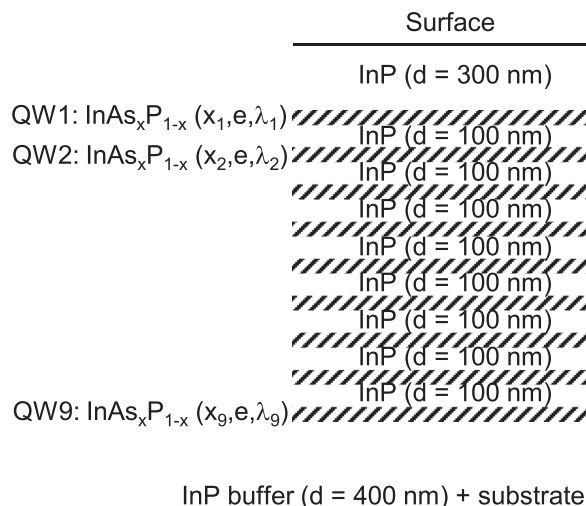


Fig. 1. QW structure used for the study. x denotes the As composition for each QW, e the QW thickness, and λ its corresponding PL wavelength.

TABLE I. Plasma parameters used for the three different etching chemistries investigated.

Etching chemistry	Gas flow rates	Total pressure	RF power plasma excitation	RF power sample stage	Sample bias
SiCl ₄ /H ₂ /Ar	5 sccm SiCl ₄ /2 sccm H ₂ /10 sccm Ar	5 mTorr	1200 W	250 W	60 V
Cl ₂ /N ₂	3 sccm Cl ₂ /20 sccm N ₂	5 mTorr	900 W	25 W	30 V
SiCl ₄ /Ar	4 sccm SiCl ₄ /5 sccm Ar	5–10 mTorr	1000–1200 W	110–350 W	40–90 V

rate. The third process (SiCl₄/Ar) was adjusted to provide different etch rates with the same chemistry.

The temperature at sample surface during etching was estimated using temperature labels. This estimation showed that the surface temperature is always below 200 °C for the conditions of the present study. Care was taken to wait long enough for stationary operation of the reactor during the temperature estimates. Such temperature rise is far from the threshold for atom diffusion in InP-based materials. Therefore, no cooling of the samples was provided.

C. Photoluminescence and cathodoluminescence

The PL experiments were performed at 15 K, with 1064 nm YAG laser excitation. This energy is below the band gap of InP substrate and barriers (thus avoiding excitation in these parts of the structure). Excitation power density was in the range of few hundreds to 1000 W/cm². The standard excitation power density for the spectra presented in this paper is 500 W/cm². This power density is slightly higher than standard PL excitation (~100 W/cm²), but since the barriers are transparent at the pump wavelength, only a small fraction of this power is absorbed by the nine QWs. Furthermore, we checked that all the PL experiments have been conducted in a linear absorption regime and at a low excitation power.

For the CL measurements, we used a Carl Zeiss (LEO 1530) field emission scanning electron microscope, equipped with a Gatan mono-CL2 system with a cooled nitrogen InGaAs array detector. The acceleration voltage for the electrons was set to 20 kV [which gives a penetration depth for InP in the order of 1 μm (Ref. 11)]. The measurement temperature for CL spectra shown in this paper is systematically 80 K.

D. Transmission electron microscopy

TEM observations were made in a field emission gun JEOL 2200FS machine working at 200 keV under different operation modes:

- (1) High resolution TEM (HRTEM). This is the usual mode to get atomic resolution of the sample, allowing, for example, the investigation of the QW interfaces quality.
- (2) High angle annular dark field (HAADF) which, in association with the scanning operation mode of the TEM (STEM), allows getting information on the composition of each layer, thanks to the Z² dependence of the HAADF intensity, with Z the atomic number.¹²
- (3) High resolution scanning TEM, where atomic resolution can in principle be coupled with contrast related to the local chemical composition.

Sample preparation for the TEM observations was done by standard thinning by Ar⁺ ion bombardment of cross sectional samples, whose thickness had been previously reduced by mechanical grinding. To avoid decomposition of the samples as much as possible, these were kept at liquid nitrogen temperature during the Ar⁺ ion thinning process.

E. Secondary ion mass spectrometry

SIMS profiles were produced by Cs⁺ primary ion bombardment at 16 keV. The secondary species detected were Cl (mass 35), P₂ (mass 31), and As (mass 75). We did not perform any kind of calibration to evaluate absolute atomic concentrations. However, quite reproducible signals for P and As were obtained from sample to sample (around 6% reproducibility for the P₂ signal from sample to sample, and 15% for the As signal). Based on the assumption that count rates with a similar magnitude are measured for the As and P profiles in different samples, we took the raw data for the Cl profile as a good indication of the actual Cl concentration profile, without performing any calibration. As for the depth scales and depth resolution of the SIMS profiles, no calibration was required since the samples include their own internal scales consisting in the series of nine InAsP QWs whose depth is known. The SIMS profiles are given as a function of sputter time by Cs⁺ ions. The conditions for ion sputtering (ion energy, ion beam current) were kept constant for all the measured profiles. This ensures the possibility to directly compare the secondary ion signals from the different samples, assuming that the sputter yields for the different elements do not change from each other sample.

III. RESULTS

A. As-grown samples

Figure 2 shows the PL spectra recorded for the as-grown samples. The spectra for the two samples look very different, the PL lines being much broader on the doped sample. This is not related to the crystal quality, e.g., to the more or less abrupt character of the QW interfaces. The crystal quality was checked by the TEM observations, in particular high resolution TEM as illustrated on Fig. 3.

The CL spectra for the two samples are shown on Fig. 4. They display the same trend as the PL spectra, the difference in the shape of the luminescence lines being even more pronounced for the CL. In fact, on the CL spectrum of the doped sample [Fig. 4(b)], one can only distinguish eight peaks. Since the QWs themselves are not doped, we do not have a straightforward explanation for the observed difference. To investigate this, we performed some luminescence measurements on the samples under an electric bias. Our PL setup

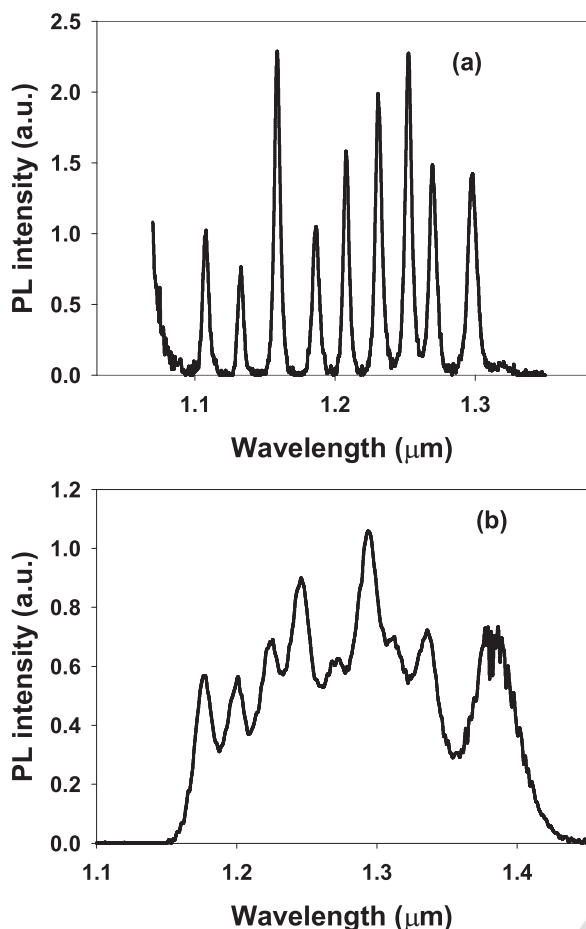


FIG. 2. PL spectra measured at 15 K with 1064 nm laser excitation of the as-grown samples: (a) Undoped sample and (b) doped sample.

342 did not allow biasing the sample; therefore, these measure- 342
 343 ments were performed with the CL setup only. The idea 343
 344 behind this investigation was to check the influence of the 344
 345 built-in electric field present in the samples (due to the dop- 345
 346 ing profile) on the luminescence line shape. The electric field 346
 347 can induce a quantum confined Stark effect (QCSE) and can 347
 348 also move the photogenerated carriers away from the QW 348

where they are generated.¹³ These can strongly affect the PL 349
 line shape. QCSE can produce red-shift to longer wave- 350
 lengths, lowering of the intensity, and spectral broadening.¹³ 351
 Electric field-induced tunneling of the photogenerated carriers 352
 out of the QWs induces quenching of the PL.¹³ 353

In order to probe these two effects (QCSE and lumines- 354
 cence quenching by electric field-induced tunneling), it is 355
 necessary, in principle, to start from the flat-band situation;¹³ 356
 however, the band bending of our samples is complex: 357

- (1) Sample 1 (grown nominally undoped) is nevertheless 358
 grown on a doped substrate (n-type). 359
- (2) Sample 2 involves a p-n junction (at the transition 360
 between the buffer layer and QW 9). Thus, the electric 361
 field reaches its maximum at thermal equilibrium close 362
 to QW 9. 363

The Fermi level is most probably pinned at the surface¹⁴ 364
 for both samples. Since the QW structure is grown very close 365
 to the surface, this Fermi level pinning also affects the distri- 366
 bution of the electric field across the structure. Therefore, it 367
 is quite difficult to assess how the electric field should 368
 change throughout the structure for different applied biases. 369
 For sample 1, we assumed that at thermal equilibrium the 370
 electric field is very low in the QWs region. For sample 2, 371
 we assumed that the maximum of the electric field occurs 372
 close to QW 9 because of the p-n junction. Without being 373
 able to determine the flat band situation, all we did was to 374
 observe the changes in the CL spectra as a function of the 375
 sample biasing, which was applied at the surface through a 376
 contact made of silver paste. The backside of the substrate 377
 was grounded. The CL measurements were made immedi- 378
 ately next to the surface contact. 379

Figure 5 gives the results for the CL measurements under 380
 positive surface bias for both samples. For the undoped sam- 381
 ple, this positive bias induces a red-shift and a quenching of 382
 the luminescence, especially at 3 V. We interpret this as an 383
 increase in the band-bending compared to the situation 384
 where no voltage is applied, and it can be attributed to the 385
 above mentioned QCSE. For the doped sample, there is no 386
 significant change up to 2 V (modifications of the CL 387

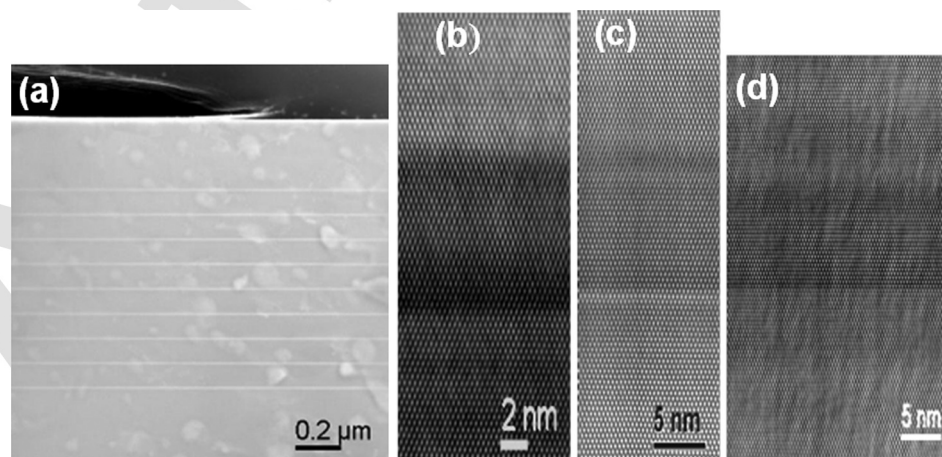


FIG. 3. TEM observations on the as grown doped sample. (a) HAADF image of the whole structure (the substrate is at the bottom). (b)–(d) HRTEM images of QW 9 (a), QW 8 (b), and QW 3 (c). Note that the magnification for these three images is different. The substrate is at the bottom also for the HRTEM images.

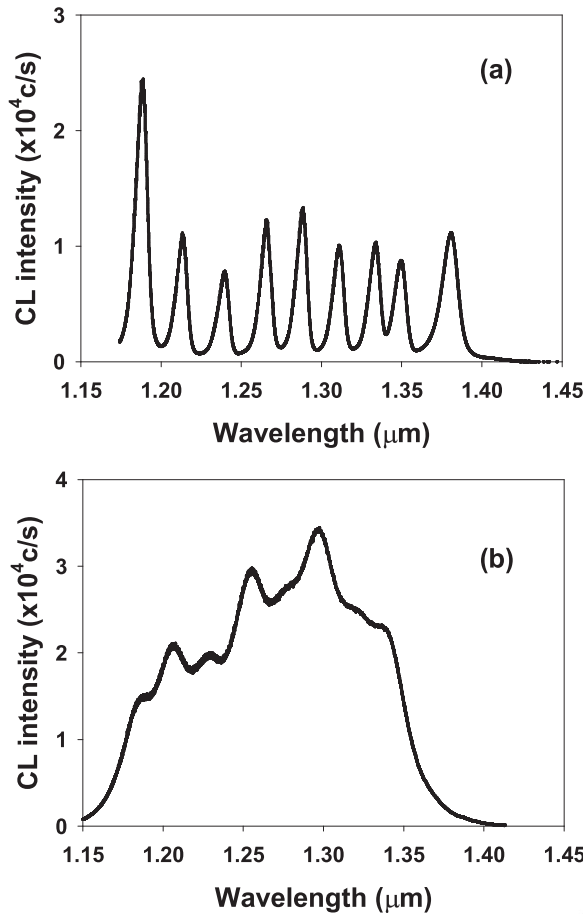


Fig. 4. CL spectra measured at 80 K of the as-grown samples: (a) undoped sample and (b) doped sample.

intensity observed for 0, 1, and 2 V are considered within the reproducibility limits of the CL setup). However, a drastic change starts at 3.2 V: QW 9, which was absent from CL spectra at lower voltage, increases, even dominating the CL emission at 5 V. A sharp line associated with QW 9, possibly made of two contributions, is observed at this voltage. We interpret this observation as evidence that the generated charge carriers were initially (at 0 V) completely driven out of QW 9 by the built-in electric field, resulting in the absence of the CL emission in QW 9. Above 3.2 V, the effective electric field at the p-n junction is reduced so that QW 9 starts being visible on the CL spectra. As for the other QWs, they are probably in a region where the band bending is not significantly modified by the applied bias, due to Fermi level pinning at the surface, and to the fact that the p-n junction absorbs most of the effects of the applied bias.

The difference in the response to surface positive bias of the CL spectra allows us to conclude that these spectra are strongly affected by the doping level through the QCSE and luminescence quenching by electric field-induced tunneling. Band bending in the undoped sample, at thermal equilibrium, is small, and thus, the PL and CL spectra display the intrinsic luminescence line spectra. In the doped sample, the presence of a p-n junction affects the spectra even at thermal equilibrium, in the sense that QW 9 is completely absent in the CL spectrum (although it is seen in the PL with an associated broad line), and all the other QWs produced a broadened luminescence line shape. The different observations for QW 9 on the CL and PL can be attributed to the difference in the excitation processes: due to the limited penetration depth of the electrons at 20 kV, this QW is more difficult to

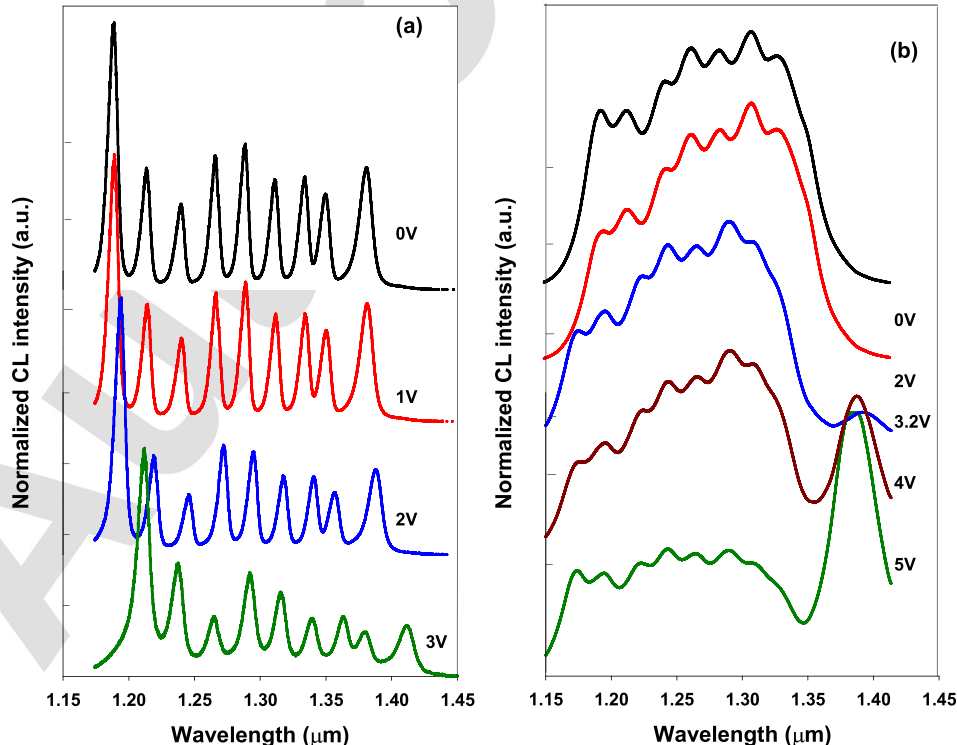


Fig. 5. (Color online) CL spectra as a function of the bias applied: (a) undoped sample and (b) doped sample.

419 excite than in the PL with 1064 nm excitation. From Ref. 11,
 420 it can be estimated that the number of electron-hole pairs
 421 generated by an incident electron with 20 kV kinetic energy
 422 decreases rapidly after a depth of 0.5 μm (although this paper
 423 deals with AlGaAs instead of InP, we can calculate a similar
 424 trend for our samples). On the other hand, 1064 nm corre-
 425 sponds to an energy below the band-gap for photons in InP,
 426 and thus, its penetration is much larger than the depth of the
 427 QW structure in our samples.

428 Finally, we also measured the SIMS profiles for the
 429 as-grown samples. Figure 6 gives an example of such a
 430 profile obtained on the doped sample. The surface peak
 431 observed for Cl is an effect of the very high sensitivity of the
 432 SIMS technique: the sample surface was contaminated by
 433 some Cl compound. However, we can see on Fig. 6 that the
 434 Cl profile drops to the background level after about 10 s sput-
 435 tering. As for the P and As profiles, the QW structure is
 436 clearly identified. Figure 7 displays the As profile alone,
 437 where the qualitative correlation with the As content in the
 438 QW is seen (through an increasing background level
 439 between the deepest QWs).

440 **B. SiCl₄/H₂/Ar process**

441 We now describe the results corresponding to the etching
 442 with the SiCl₄/H₂/Ar plasma, first describing the PL and CL
 443 measurements, and then comparing with TEM and SIMS
 444 observations.

445 The SiCl₄/H₂/Ar process was optimized especially with
 446 respect to the very fast etching rate. In the first set of experi-
 447 ments, the samples were exposed 1 min to this plasma to
 448 avoid the risk of a complete removal of the QW structure.

449 Figure 8 is a superposition of the PL data for the as-
 450 grown samples, and the samples exposed 1 min to the SiCl₄/
 451 H₂/Ar plasma. Note that the two samples were not exposed
 452 in the same run. On the undoped sample, the signal for QW
 453 1 and QW 2 has disappeared after exposure. On the doped-
 454 sample, only the signal for QW 1 disappeared.

455 The plasma takes a fraction of a minute to stabilize; there-
 456 fore, 1 min is the shortest exposure that could be performed
 457 in a stationary regime; thus, we can expect slight differences

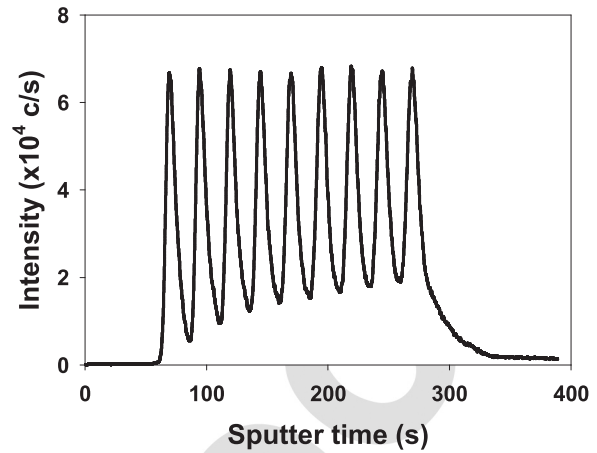


FIG. 7. SIMS profile measured on the as-grown, doped sample, for ⁷⁵As. This isolated profile is the same as that shown for ⁷⁵As in Fig. 6. It is displayed separately for clarity.

in the amount of etched material for two separate exposures, 458
 even if the nominal reactor parameters are the same. 459

Apart from the number of QWs having apparently been 460
 etched, there is another very significant difference. For the 461
 undoped sample, the remaining QWs have similar spectral 462
 characteristics to those of the corresponding QWs on the as- 463
 grown sample, except for a slight shift to shorter wavelength 464
 (“blue-shift”) for QW 4, QW 6, and QW 8. For the doped 465
 sample, a pronounced sharpening of the luminescence peaks 466
 arising from QW 2 to QW 8 is observed; simultaneously, the 467
 peaks present a significant shift to the blue. 468

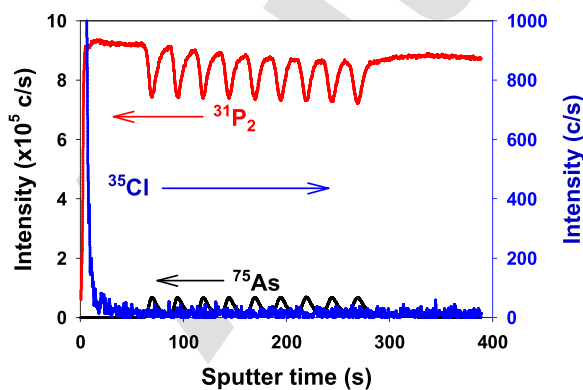


FIG. 6. (Color online) SIMS profiles measured on the as-grown, doped sample: ³¹P₂ (red), ⁷⁵As (black), and ³⁵Cl (blue). The scale on the left is for P and As, and the scale on the right is for Cl.

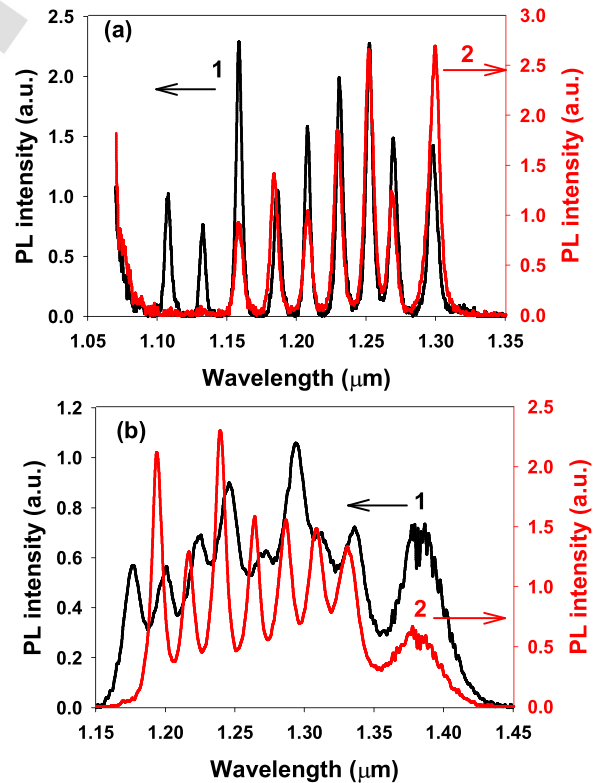


FIG. 8. (Color online) PL spectra of the samples as-grown (line in black) and exposed to the SiCl₄/H₂/Ar plasma for 1 min (line in red): (a) undoped sample and (b) doped sample.

469 In order to specify more precisely the etching depth, we
 470 measured the SIMS profiles. As an example, Fig. 9 displays
 471 the results for the doped sample. The resolution of the pro-
 472 files is disturbed, probably because of the roughening that
 473 occurs at the surface as the etching proceeds faster. Rough
 474 surfaces induce a loss of depth resolution during SIMS
 475 profiling. Anyhow, we can identify in Fig. 9 that the nine
 476 QWs are still present in the sample (there are nine clearly
 477 visible minima in the P profile, with the corresponding nine
 478 maxima on the As profile). To complete the scheme concern-
 479 ing the etch depth, we have performed a TEM observation of
 480 the same sample. This is shown in Fig. 10. From this image,
 481 we can estimate, by comparison with the image in Fig. 3,
 482 that 250 nm of the InP cap have been etched, but all the nine
 483 QWs remain present. Therefore, we can conclude at this
 484 stage that the PL yield of the QWs closest to the surface is
 485 completely reduced after plasma exposure, even if these
 486 QWs have not been etched at all. For the doped samples
 487 (where we have the SIMS and TEM information to compare),
 488 QW 1 is affected by the reduction. For the undoped
 489 sample (for which we have not performed SIMS and TEM),
 490 if we assume a similar etch depth, QW 1 and QW 2 were
 491 affected. It should be noted (for the undoped sample) that for
 492 the QWs remaining visible on the PL the peak intensity is
 493 much higher than the corresponding intensity on the same
 494 sample prior to etching.

495 The other information retrieved from the SIMS has to do
 496 with the Cl profile: after exposure to the SiCl₄/H₂/Ar plasma
 497 for 1 min, it takes more than 50 s sputtering for the Cl signal
 498 to reach a background level slightly higher than for the as-
 499 grown sample. We deduce from this observation that some
 500 Cl has penetrated through the sample. This is best visualized
 501 in Fig. 11 where the Cl profiles for the as-grown sample and
 502 the samples exposed 1 min to the SiCl₄/H₂/Ar plasma are
 503 represented on a log scale (sputtering from 0 to 100 s).

504 To complete this part on the 1 min exposure to the SiCl₄/
 505 H₂/Ar plasma, the corresponding CL spectra measured on
 506 the same samples are shown in Fig. 12. For the undoped
 507 samples, we can notice that the magnitude of the changes is
 508 larger than for the PL measurements on the same samples.
 509 The changes for the CL yield must be related to the smaller

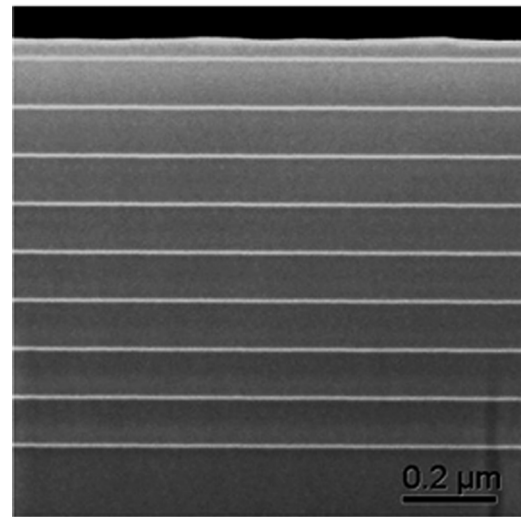


Fig. 10. HAADF image of doped sample after 1 min exposure to the SiCl₄/H₂/Ar plasma.

510 probed depth for the 20 keV electrons than for the 1064 nm
 511 photons: after etching 250 nm of the InP cap layer, the
 512 deeper QWs become more efficiently excited. The blue-shift
 513 observed on the remaining QW transitions is more pro-
 514 nounced than the shift observed on the PL spectrum. This
 515 has to be related to the excitation process, different for PL
 516 and CL. For the doped sample, the most noticeable trends
 517 are the strong increase in QW 9 CL emission after exposure
 518 to the plasma, and the strong blue-shifts for the other QWs,
 519 which is coherent with what is observed on the PL spectra,
 520 although the shift is larger than the one measured by PL. The
 521 spectral sharpening seen especially for QW 2, QW 3, QW 4,
 522 QW 5, and QW 6 on the doped sample after exposure is also
 523 observed on the CL, something similar to the PL. This will
 524 be discussed with regard to the different band bending situa-
 525 tions for the undoped and doped samples, and assumptions
 526 on the nature of the penetrating species.

527 Finally, for the case of the SiCl₄/H₂/Ar plasma, the doped
 528 sample was also exposed for 2 min. We just show in Fig. 13
 529 the PL, TEM, and SIMS data for this sample. Etching has

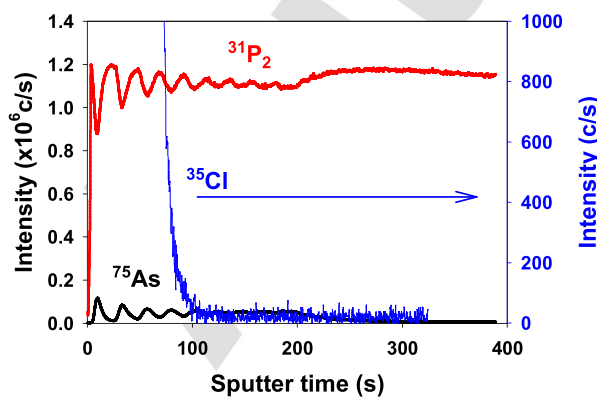


Fig. 9. (Color online) SIMS profiles measured on doped sample after 1 min exposure to the SiCl₄/H₂/Ar plasma: ³¹P₂ (red), ⁷⁵As (black), and ³⁵Cl (blue). The scale on the left is for P and As, and the scale on the right is for Cl.

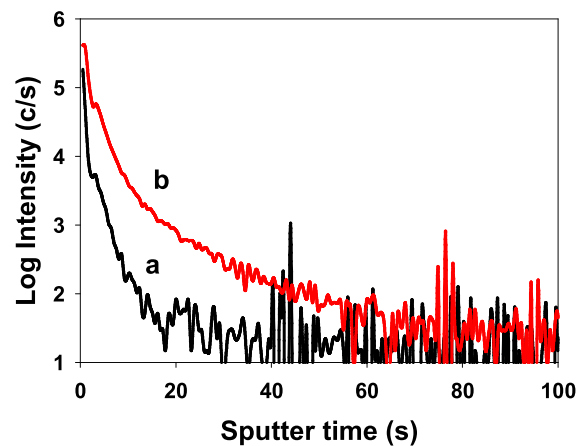


Fig. 11. (Color online) SIMS profiles measured on doped sample before (a) and after 1 min exposure to the SiCl₄/H₂/Ar plasma (b) for ³⁵Cl on a log scale, for the early etching between 0 and 100 s.

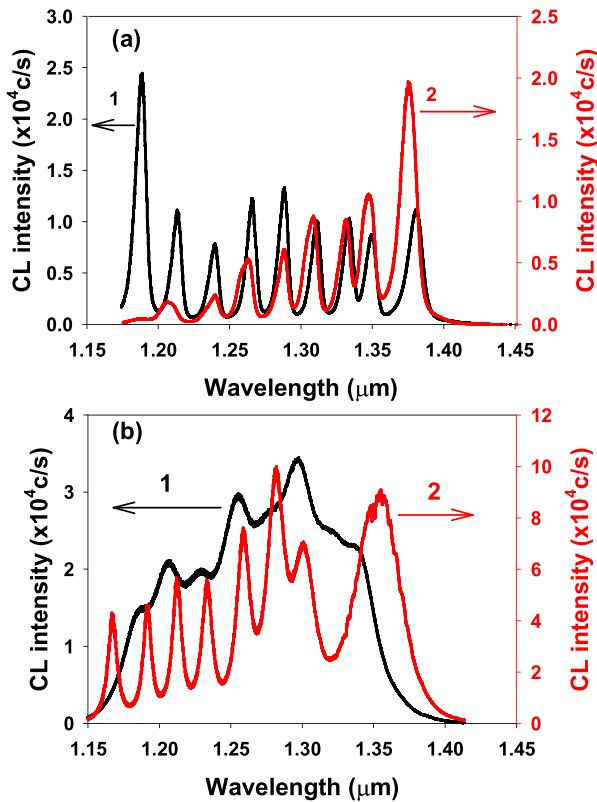


Fig. 12. (Color online) CL spectra of the samples as-grown (1) and exposed to the SiCl₄/H₂/Ar plasma for 1 min (2): (a) undoped sample and (b) doped sample.

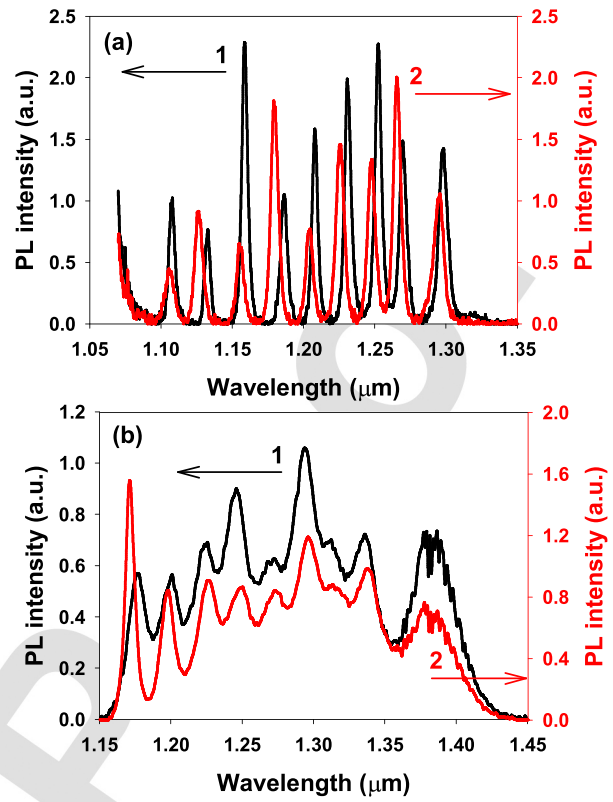


Fig. 14. (Color online) PL spectra of the samples as-grown (1) and exposed to the Cl₂/N₂ plasma (2). (a) Undoped sample, plasma exposure 4 min; (b) doped sample, plasma exposure 3 min.

530 stopped almost exactly at QW 4 (etch depth approximately
 531 600 nm). QW 5, QW 6, QW 7, QW 8, and QW 9 still emit
 532 brightly on the PL spectrum. For these QWs, the transitions
 533 are significantly sharper (in terms of spectral width) than after
 534 1 min exposure to the same plasma and the blue-shift
 535 appears increased.

536 **C. Cl₂/N₂ process**

537 The PL spectra for both the undoped and the doped samples
 538 (unfortunately, the duration of the plasma exposures differ—4 min
 539 in the first case, 3 min in the second case, but this will not block
 540 the discussion) are shown in Fig. 14. The first

point to note is that even after 4 min etching, QW 1 has not
 541 been reached by the etching process, in agreement with the
 542 slower rate of this etching process (as compared to SiCl₄/H₂/
 543 Ar, at least under the conditions used in this work). Indeed,
 544 results from previous studies¹⁵ show that dissociation and
 545 ionization processes of Cl₂ by electron impact are less effi-
 546 cient in Cl₂/N₂ plasmas because of the decrease in electron
 547 density with the percentage of N₂. The precise etch depth
 548 will be examined from the TEM images and SIMS profiles.
 549 The second point is that the PL yield is not at all affected by
 550 the Cl₂/N₂ exposure. This is in strong contrast with what was
 551 observed for SiCl₄/H₂/Ar after 1 min and also with some
 552 published results. The third point, for the doped sample, is
 553

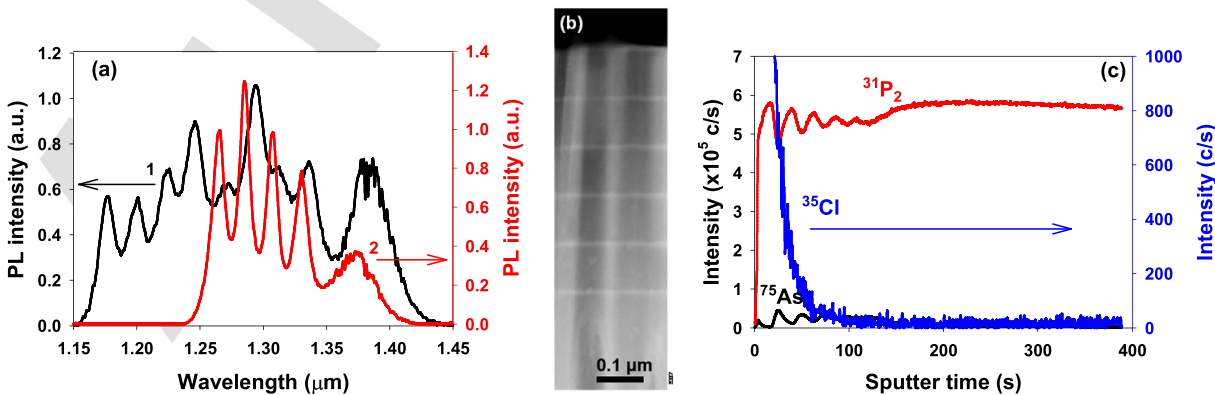


Fig. 13. (Color online) PL spectra (a), HAADF image (b) and SIMS profiles (c) of the doped sample exposed to the SiCl₄/H₂/Ar plasma for 2 min. PL spectra of as-grown sample (1) and exposed sample (2). In the SIMS plot, red is for P, black for As, and blue for Cl.

554 that the Cl_2/N_2 exposure does not seem to affect very signifi-
 555 cantly the spectral shape of the QW transitions, except for
 556 QW 1 and maybe QW 2, whose associated luminescence
 557 bands appear sharper after exposure. The difference appears
 558 very important with the $\text{SiCl}_4/\text{H}_2/\text{Ar}$ exposure [Figs. 8(b)]
 559 where all the luminescence bands, except QW 9, were sharp-
 560 ened. Finally, concerning the undoped sample, we note that
 561 the blue-shifts are now observed for all QW transitions, the
 562 peak shift being larger than for the $\text{SiCl}_4/\text{H}_2/\text{Ar}$ exposure.
 563 Using a standard fitting procedure (using the Voigt profile,
 564 consisting of the convolution of a Lorentzian function by a
 565 Gaussian broadening, for each contribution) for PL experi-
 566 mental spectra, we could determine the following blue-shifts
 567 (Cl_2/N_2 —exposed sample compared to as-grown sample),
 568 indicated on Table II. QWs 2, 4, and 6 have the maximum
 569 shifts. Let us recall that these shifts are much more pro-
 570 nounced than for the $\text{SiCl}_4/\text{H}_2/\text{Ar}$ —1 min exposure [the cor-
 571 responding values were estimated less than 2 nm for QWs
 572 3–9 on Fig. 8(a)]. Fitting the PL spectra for the doped sam-
 573 ple to extract accurate spectral shifts was not fully reliable
 574 because of the overlap between neighboring peaks.

575 A TEM-HAADF image of the doped sample after 3 min
 576 etching with Cl_2/N_2 is displayed in Fig. 15. InP cap layer of
 577 120 nm still remain, while 180 nm were etched.

578 SIMS profiles for the doped samples exposed 1 and 3 min
 579 to the Cl_2/N_2 plasma are shown on Fig. 16. The Cl signal
 580 appears somewhat higher in the bulk part after 1 min than
 581 after 3 min, but this may be due to background contamina-
 582 tion in the SIMS apparatus for this specific measurement.

583 **D. SiCl_4/Ar process**

584 This process was tested with the idea to investigate sam-
 585 ples etched with a single process, but strongly different etch
 586 rates. In order to change the etch rate, the RF power at the
 587 plasma excitation source and at the sample biasing source
 588 were changed, keeping the flow rates for SiCl_4 and Ar con-
 589 stant. The total pressure in the plasma chamber was also
 590 adjusted. Slower etch rate was obtained by reducing the two
 591 RF powers (from 1200 to 1000 W at the plasma excitation
 592 stage and from 350 to 110 W at the sample stage), simultane-
 593 ously increasing the total pressure (from 5 to 10 mTorr) in
 594 the plasma chamber (which helps decreasing the sample
 595 bias).

TABLE II. Spectral shifts estimated from the PL data for the undoped sample in Fig. 14(a).

Quantum well number	Spectral shift (nm)
QW 1	1.7
QW 2	7.2
QW 3	3.3
QW 4	6.2
QW 5	4.1
QW 6	5.6
QW 7	3.9
QW 8	3.9
QW 9	2.8

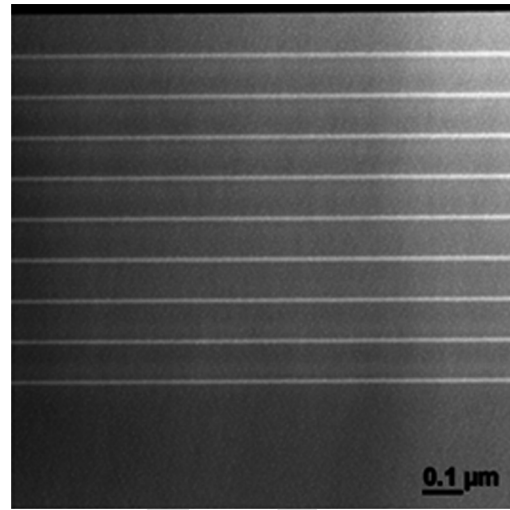


FIG. 15. HAADF image of doped sample after 3 min exposure to the Cl_2/N_2 plasma.

We could perform this part of the study only on the doped sample. We discuss below the CL spectra and SIMS profiles.

(1) SiCl_4/Ar slow etching process:

The results in Fig. 17 were obtained with plasma tuning (RF power, total pressure) to limit the etch rate. The sample bias was 40 V.

The main change on the CL spectra concerns QW 1, which displays a sharp and intense transition after plasma

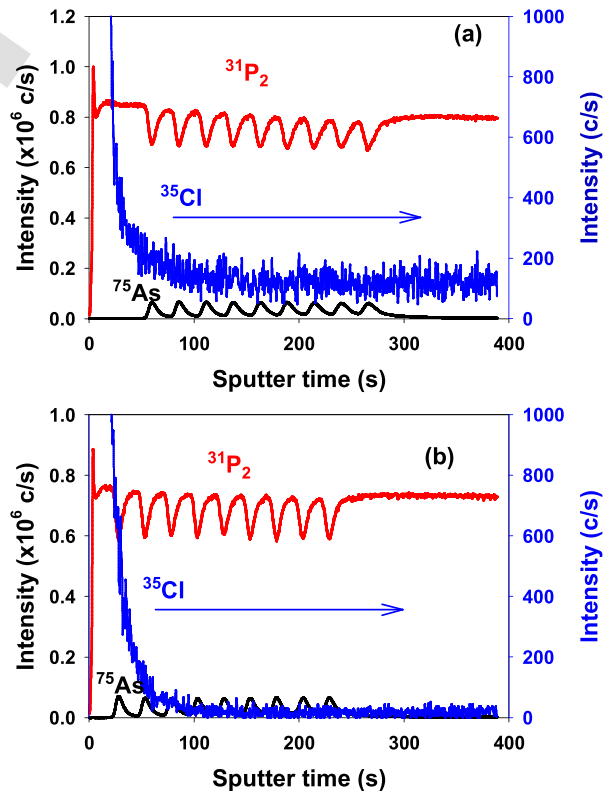


FIG. 16. (Color online) SIMS profiles measured on doped sample after 1 min (a) and 3 min (b) exposure to the Cl_2/N_2 plasma, respectively: $^{31}\text{P}_2$ (red), ^{75}As (black), and ^{35}Cl (blue). The scale on the left is for P and As, and the scale on the right is for Cl.

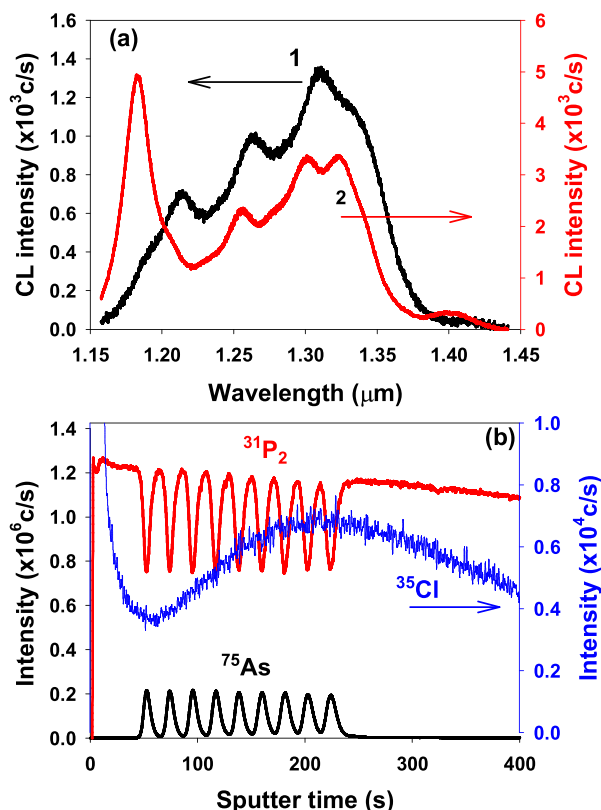


Fig. 17. (Color online) CL spectra (a) and SIMS profiles (b) for the doped-sample as-grown and exposed to the SiCl_4/Ar plasma—slow etching process (1 min). The spectrum (1) corresponds to the as-grown sample, and the spectrum (2) corresponds to the plasma exposed surface.

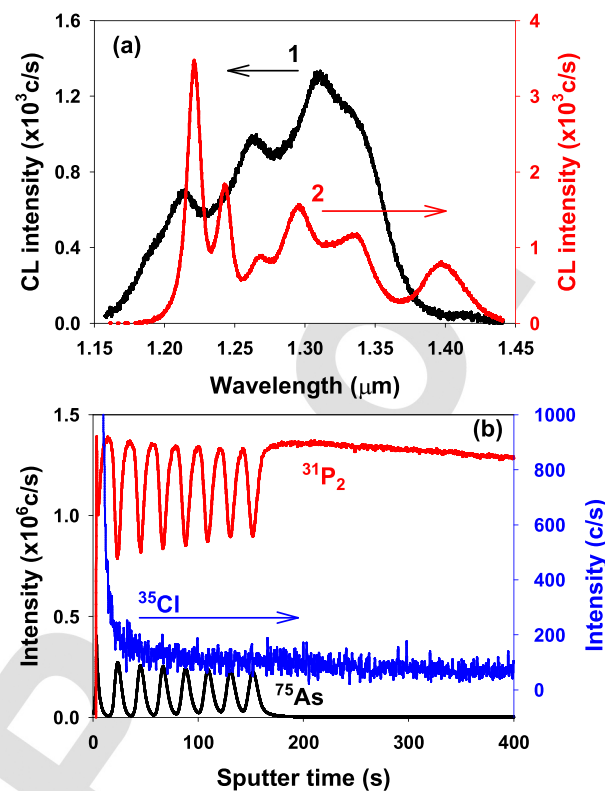


Fig. 18. (Color online) CL spectra (a) and SIMS profiles (b) for the doped-sample as-grown and exposed to the SiCl_4/Ar plasma—fast etching process (1 min). The spectrum (1) corresponds to the as-grown sample, and the spectrum (2) corresponds to the plasma exposed surface.

604 exposure. The other structures did not present relevant
605 changes in the CL spectra. While QW 9 starts to become
606 visible, the SIMS profiles tell us that the sample was almost
607 not etched. They also indicate that the Cl signal has
608 increased to about 7000 counts inside the sample after
609 plasma exposure, compared to about 10–20 counts measured
610 for the as-grown sample (cf Fig. 6). The Cl profile has a clear
611 maximum at about $1\ \mu\text{m}$ below the surface. The distribution
612 of Cl inside the sample presents an implantationlike profile.

613 (2) SiCl_4/Ar fast etching process:

614 To measure the impact of the etch rate (keeping constant
615 the SiCl_4 and Ar flow rates), the RF power for the plasma
616 excitation and at the sample stage was increased. The sample
617 bias reached 90 V. The corresponding results—CL spectra
618 and SIMS profiles—are shown in Fig. 18, for a plasma expo-
619 sure of 1 min.

620 The SIMS profiles show that the etching has reached QW
621 2 (etch depth: 400 nm). From the PL spectra, comparing
622 with the spectra in Fig. 17, we conclude that the lumines-
623 cence bands associated with QW 3 and QW 4 transitions
624 have strongly sharpened, and their intensities have increased.
625 The transitions for deeper QWs also evidence a beginning of
626 sharpening.

627 From the SIMS data, we see that the Cl signal in the bulk
628 is very low, we do not see any more the Cl signal obtained
629 after the slow etching plasma.

IV. DISCUSSION

We suggest in this section a discussion of the results
described in the previous paragraphs. The comparison
between the behaviors of the undoped and doped samples
under the same plasma exposures will be helpful to under-
stand the changes induced by the plasma exposure in the two
samples and the different etching procedures.

The $\text{SiCl}_4/\text{H}_2/\text{Ar}$ plasma was first investigated. The etch
rate with this plasma is 250 nm/min (and 600 nm/2 min; the
deviation from linearity is due to the time necessary for the
plasma to stabilize). After 1 min, we observe the lumines-
cence of QW 1 completely suppressed (and even for QW 2
in the case of the undoped sample). However, only a part of
the InP cap layer has been etched, meaning that the QWs
themselves have not been etched. This suppression of the
luminescence for the QWs closest to the surface is due to the
diffusion of defects, probably Cl-related defects formed
when Cl penetrates the structure below the surface, as shown
by the SIMS profiles. This result keeps resemblances with
some of the published work that we have mentioned in the
introduction.^{5–8}

Apart from this effect, we observe a small blue-shift of
the luminescence peaks (less than 2 nm), in the undoped
sample, in contrast to the very strong change of the lumines-
cence bands observed in the doped sample: their spectral
width is dramatically reduced, and also a noticeable blue-
shift takes place. We noticed in addition that the blue-shift
on the undoped sample is more important when measured

with CL than with PL, due to the different excitation conditions. Taking into account our preliminary study on the as-grown samples, we analyze the observation for the doped sample as evidence that the $\text{SiCl}_4/\text{H}_2/\text{Ar}$ plasma has an effect on the built-in electric field initially present in the sample. The electric field is reduced on the whole thickness of the QW structure, although the etching has affected only 250 nm on the top surface. Reducing the electric field reduces the QCSE which impacts QW 1 to QW 8 in this sample. According to the CL result, the charge carrier escape from QW 9, which is an effect of the strong electric field in the p-n junction, is also suppressed or reduced by the $\text{SiCl}_4/\text{H}_2/\text{Ar}$ plasma etching. This reduction of the internal electric field in the doped sample can only be the consequence of the penetration of charged species during the plasma exposure. We suggest that these charged species could be Cl^- ions, either directly generated in the plasma or resulting from Cl atoms or excited radicals having captured an electron inside the sample. However, the concentration of these ions is not high enough to be detected on the SIMS profiles. Only the higher Cl concentration immediately beneath the surface is observed on the SIMS profiles.

Finally, we also interpret the blue-shifts on the undoped sample as a reduction of the built-in electric field (weak with respect to the doped sample) present in this sample after growth. The fact that this blue-shift is more important when measured with CL is a consequence of the different excitation schemes for CL and PL.

Then we investigated the Cl_2/N_2 plasma. The etch rate for this plasma is very low under the conditions of our experiment. However, its impact on the undoped sample consists in inducing much larger blue-shifts than the $\text{SiCl}_4/\text{H}_2/\text{Ar}$ plasma: a maximum of 7.2 nm is observed for QW 2. On the contrary, on the doped sample, this plasma produces little effect, only a sharpening of the line for QW 1 and, to a lesser extent, QW 2. No blue-shift is observed on the doped sample. The QCSE is still present in the doped sample after this plasma exposure; it is only reduced very close to the surface. Altogether, this plasma has very little effect on the internal built-in electric field. The explanation for the strong blue-shifts observed on the undoped sample cannot be related to suppression of the QCSE, since a similar suppression or reduction does not take place in the doped sample. SIMS profiles for this plasma indicate, as for the previous plasma, only a limited penetration of Cl beneath the surface.

It seems logical to claim that the different effects observed for the two plasmas would be due, at least in part, to the presence of N in the Cl_2/N_2 plasma. We were not able to measure the N profiles in SIMS; however, it is rather probable that N penetrates the sample under such plasma exposure, since N does not contribute to the etching reactions at the surface. Then, considering the possible penetration of N, we could explain the blue-shifts observed on the undoped sample as a consequence of the interaction between the N atoms and the crystal matrix. The blue-shifts of the PL lines measured enter within the margins expected for a compressive stress of the lattice,^{16,17} which would be induced by N interstitials. It is interesting to point the fact that on the PL spectra the QW

lines do not show a conspicuous splitting corresponding to the lh and hh related transitions.¹⁸ Actually, we could have anticipated this seeing two different peaks resolved for each QW transition in the as-grown sample (due to the intrinsic stress of the $\text{InAs}_x\text{P}_{1-x}$ layers). This is not the case, either because the magnitude of the splitting between heavy-hole and light-hole transitions is too small to be resolved experimentally, even for the most strained QW, or because our excitation power density for the PL measurement is not in the adequate range. Even if we do not see the splitting on the as-grown sample, the mechanical stress induced by the N atoms interacting with the structure could create the splitting if this stress occurs in a biaxial geometry. We suggest that the presence of N, in an interstitial position, mainly induces a hydrostatic stress which does not change the symmetry of the PL transitions observed, since hydrostatic stress does not split the lh and hh related bands. The magnitude of the blue-shifts for the different QWs is dependent from their position. A maximum is recorded for QW 2 with a PL peak blue-shifted by 7.2 nm. Then, a decrease of the blue-shift is observed for the deeper QWs. This variable blue-shift could be attributed to the combination of the effect of interstitial N with the native compressive biaxial stress related to As incorporation changing in the different QWs. However, further investigations would be required to confirm this hypothesis.

On the other hand, we did not observe the blue-shifts in the case of the doped sample. This sample is strongly affected by the QCSE, which is not suppressed nor even reduced for most of the structure by the Cl_2/N_2 plasma etching. Actually, we have no exact idea of the scenario resulting from combined QCSE and compressive hydrostatic stress, but certainly, the QCSE might dominate masking the observation of the blue-shifts due to stress.

Finally, let us consider the SiCl_4/Ar plasma experiments, which were designed to test the effects of the etch rate under conditions of constant reactive gas injection. For the very slow etch process, we observed a maximum penetration of the Cl in the structure, with a distribution similar to that resulting from an implantation mechanism. On the other hand, very few changes appeared on the CL spectrum after this slow etching plasma. Only a slight modification of the electric field close to the surface may occur, explaining the alone change of QW 1 related emission, while the emission from the other QWs did not show significant changes. The association of these trends (maximum penetration of Cl, limited change on the CL spectrum) points to the fact that probably the Cl species penetrating the sample is now atomic Cl, contrary to what we claim for the $\text{SiCl}_4/\text{H}_2/\text{Ar}$ plasma. For the fast etching process, we observe a much more limited penetration of Cl than for the slow etching process. The CL spectrum is more strongly affected, suggesting the presence of Cl^- ions, rather than neutral Cl atoms.

From these combined observations, we now try to build up a scheme for the interaction mechanisms of the etching plasma and the QWs structure, at least for the SiCl_4/Ar plasma:

- (1) different forms of Cl play a relevant role in this mechanism, at least Cl^- and atomic Cl;

773 (2) only the Cl present at the surface contributes to the etch-
 774 ing process, while the Cl penetrating across the surface
 775 inside the sample does not contribute to the etching
 776 process;
 777 (3) the etching experiments with SiCl₄/Ar plasmas give a
 778 conspicuous anticorrelation between the amount of Cl
 779 inside the sample and the etching rate.

780 In order to quantify this last point, the SIMS data were
 781 also exploited to identify a possible trend on the concentra-
 782 tion on Cl at the surface at the different steps of the etching
 783 process. The signal measured for ³⁵Cl for the first point
 784 recorded (sputter time 5.4×10^{-1} s/sputter depth approxi-
 785 mately 2.5 nm) was used as an indication of the Cl level at
 786 the surface before performing the sputter profile. This is
 787 shown in Table III (“Surface Cl”). This analysis was carried
 788 out for all the SIMS profiles measured, and Table III indi-
 789 cates also the corresponding etching rate. These data show
 790 that the surface Cl signal is between 1.84 and 6.15×10^5
 791 counts/s for the as-grown surfaces and for the surfaces of
 792 samples exposed to plasmas with a fast etching rate, while
 793 for samples exposed to plasmas with a slow etching rate the
 794 Cl surface signal measured lies between 3.89 and 5.26×10^6
 795 counts/s, i.e., approximately an order of magnitude higher.
 796 Concerning the bulk Cl concentration, one observes that for
 797 the lowest etching rate, especially for the sample exposed to
 798 the SiCl₄/Ar plasma “slow etch rate,” the bulk Cl signal dis-
 799 plays a maximum value.

800 Therefore, the tendency derived from the SIMS data is that
 801 the high etch rates are observed for samples that display the
 802 smaller Cl signal at both the surface and the bulk, while the
 803 slow etch rates are observed when the Cl signal is high at both
 804 the surface and the bulk. This suggests that the Cl species that
 805 are active in the etching process do not penetrate inside the
 806 samples, whereas the forms that penetrate inside the samples
 807 are inefficient for the etching process. Figure 19 illustrates in
 808 more details this tendency observed for the different etch plas-
 809 mas investigated.

810 **V. SUMMARY AND CONCLUSIONS**

811 The experimental work detailed in this paper is based on
 812 the long-established methodology of dedicated QW structure
 813 for the investigation of defect production and consequences
 814 during plasma etching of III–V semiconductor materials.
 815 Using a combination of characterization techniques, includ-
 816 ing PL, CL, SIMS, and TEM, we tried to quantify the effects

TABLE III. SIMS data for Cl at the surface and etch rate. The surface data are taken as the SIMS count for the first point recorded (after 5.4×10^{-1} s sputtering).

No.	Sample description	Surface Cl (counts/s)	Etch rate
1	As-grown sample	1.84×10^5	—
2	SiCl ₄ /H ₂ /Ar—1 min	4.13×10^5	250–300 nm/min
3	Cl ₂ /N ₂ —1 min	3.89×10^6	60 nm/min
4	As-grown sample	6.15×10^5	—
5	SiCl ₄ /Ar plasma—slow (1 min)	5.26×10^6	55 nm/min
6	SiCl ₄ /Ar plasma—fast (1 min)	5.81×10^5	400 nm/min

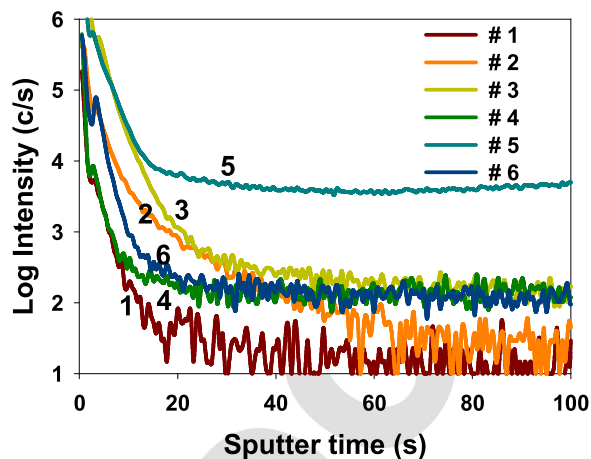


FIG. 19. (Color online) SIMS profiles measured for the different samples displayed in Table III, in log scale, for the early stages of the sputter process between 0 and 100 s.

of different plasma etching chemistries used in the context 817
 of fabrication of InP-based photonic circuits. These chemistries 818
 have in common the fact that they involve chlorine 819
 compounds. 820

821 We first analyzed carefully the properties of the “as-
 822 grown” samples (before any plasma exposure), observing
 823 the importance of taking into account the type and amount
 824 of doping in the samples. Indeed, doping is associated with
 825 the presence of a built-in electric field whose impact on the
 826 luminescence spectra can be very significant, through the
 827 quantum confined Stark effect, and also the fact that gener-
 828 ated carriers can escape from the QWs through tunneling
 829 induced by this built-in electric field. Having understood
 830 why the luminescence spectra differ in samples with differ-
 831 ent doping profiles, we could perform a systematic study of
 832 different etching chemistries. The first chemistry (SiCl₄/H₂/
 833 Ar) yields an etch rate in the order of 250–300 nm/min in
 834 our conditions, which is interesting when trying to etch fea-
 835 tures several micrometers deep. We have limited the expo-
 836 sures to very short durations (1 and 2 min) to avoid etching
 837 the whole QW structure. The luminescence of the QWs clos-
 838 est to the etch front was observed to decrease and disappear,
 839 similar to previous results in the literature; however, this is
 840 the case only for the first and probably second QW, and the
 841 deeper QWs are not affected. The other observation is a very
 842 significant difference between the undoped and the doped
 843 samples: in the case of the undoped sample, no change of the
 844 spectral shape for the remaining luminescence peaks occurs,
 845 while for the doped sample a very pronounced spectral
 846 sharpening is seen. The two types of sample react differently
 847 to the plasma. We tentatively explain this difference suggest-
 848 ing that some of the Cl species from the plasma penetrate
 849 through the QW structure (which is confirmed by the SIMS
 850 profiles), and that part of these species bears an electric
 851 charge (probably Cl⁻ ions). Thus, they modify the built-in
 852 electric field in a way for which the QCSE and associated
 853 carrier escape are reduced.

854 This effect—sharpening of the luminescence peaks—is
 855 much less pronounced in the case of the Cl₂/N₂ plasmas,

856 which anyhow display a reduced etch rate (60 nm/min). The
857 main effect of these plasmas is a blue-shift of the lumines-
858 cence peaks (especially observable on the undoped sample),
859 which we attribute to the penetration of N in the QW struc-
860 ture. N occupies interstitial sites, thus producing a hydro-
861 static compressive stress.

862 Finally, we also investigated a SiCl₄/Ar chemistry, for
863 which we were able to vary the etch rate between 55 and
864 400 nm/min keeping the flow rates constant (i.e., the
865 “chemistry” constant). This last experiment, apart from con-
866 firming the spectral sharpening effect observed with the
867 SiCl₄/H₂/Ar chemistry, leads us to suggest a balance mecha-
868 nism for the interplay between the Cl-species active for the
869 etching process at the surface, and the Cl-species that pene-
870 trate the sample structure and are “lost” for the etching pro-
871 cess, lowering the etching efficiency. From our observations,
872 a tendency appeared for the etch rate to be anticorrelated to
873 the amount of Cl-species present beneath the surface (as
874 detected by the SIMS profiles).

875 All the results described in this paper point to the impor-
876 tance of checking the impact of reactive etching plasmas on
877 the remaining materials structures. Even though our experi-
878 ments were performed in the absence of any mask structure,
879 we can claim that when using similar plasmas for the pro-
880 duction of photonic features with a three-dimensional geom-
881 etry (like a simple rectangular ridge structure), similar
882 effects would occur due to the LATERAL penetration of the
883 etching species through the structures being etched, produc-
884 ing the same artifacts that we have described. Taking into
885 account these possible artifacts in the general design of pho-
886 tonic devices is an issue that cannot be neglected. Thanks to
887 the lateral resolution of the CL technique, which we have
888 not used in the present study, we will be able to extend our
889 general methodology to the case where quantifying etching-
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induced defects within 3D structures (e.g., rectangular wave- 890
guides) is required. This will be the next step of this study. 891

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