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Citation: Journal of Vacuum Science & Technology B **24**, 2726 (2006); doi: 10.1116/1.2366543
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Electron cyclotron plasma etching damage investigated by InGaAs/GaAs quantum well photoluminescence

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(Received 8 November 2005; accepted 26 September 2006; published 22 November 2006)

Photoluminescence (PL) was used to study the damage of (100) GaAs surfaces exposed to BCl_3/Ar plasma generated by an electron cyclotron resonance system. With PL measurement of strained InGaAs/GaAs quantum wells within the etched top GaAs layer, our analysis shows that this technique assesses damages to the structure not detected by atomic force microscopy and photoreflectance. A transport model is used to show a 100 times reduction in the Debye length for a 100 nm layer underneath the etching surface. © *2006 American Vacuum Society.*
[DOI: 10.1116/1.2366543]

I. INTRODUCTION

Dry etching is very adequate for pattern transferring with vertical profile and good morphology in micrometric and submicrometric devices. However, etch-induced damage has to be minimized in order to realize the advantages of these small devices. Particularly, dry etching techniques are frequently used for the fabrication of micro-optical-cavity structures where besides high optical quality of etched mirrors, extremely high electrical quality is required. Given the reduced dimensions of the structures and the proximity of the active region to them to the surface, carrier losses become a fatal problem for device operation.[1] Electron cyclotron resonance (ECR) plasma etching with chlorine based gases is often chosen as the dry etching technique III-V compounds because it provides anisotropic profiles with reduced damage to etching surfaces. Nevertheless, it is important to assess the resulting damages after ECR etching. In fact, it has been reported that ion generation during the etching process may generate nonradiative recombination centers at the surface degrading device performance.[2]

In this work, we investigate surface damages caused by ECR etching by the photoluminescence (PL) spectra of InGaAs/GaAs quantum wells (QWs) after several etching steps of a GaAs top layer. The results are compared to conventional wet etching techniques. A simple carrier transport model is employed to explain qualitatively the PL results. Photoreflectance (PR) spectroscopy was also used to corroborate the values obtained by PL.

II. EXPERIMENT

The samples in this work were grown on semi-insulating (100) GaAs substrates in a Riber 42 chemical beam epitaxy system. The layer structure from the substrate is as follows: *i*-GaAs buffer (150 nm) three *i*-$In_{0.23}Ga_{0.77}As$ quantum wells (15, 10, and 6 nm), separated by 100 nm *i*-GaAs barriers, and *i*-GaAs (400 nm) cap.

A Plasma-Therm SLR 770 ECR chemical vapor deposition system was used for the dry etching. This system employs 100–1000 W microwave power at 2.45 GHz. The ionization and extraction magnet current was set to 180 and 0 A, respectively. The ion energy was controlled with a radio frequency (rf) power supply (0–140 W, 13.56 MHz). Substrate temperature was kept at 20 °C.[3] The etching conditions in our experiment are based on optimized results for high quality GaAs ECR etching reported in the literature (Refs. 4 and 5) Namely, 8 SCCM (SCCM denotes cubic centimeter per minute at STP) BCl_3/12 SCCM Ar/3 mtorr pressure/250 W ECR/100 W rf/20 °C, and ∼−125 V dc bias. The etch rate is 135+/−9 nm/min. The reduced ECR power allows relatively slow etching and good etch depth control.

Wet chemical etch was performed with (H_3PO_4:H_2O_2:40H_2O-DI) with an etch rate of 80 nm/min.

Both dry and wet etches were done in three steps of 100 nm depth each. Therefore the separations between the thinnest (15, 10, and 5 nm QWs) and the GaAs surface are (*A*) 400 nm (unetched), (*B*) 300 nm, (*C*) 200 nm, and (*D*) 100 nm. The inset in Fig. 1(a) shows a schematic drawing indicating the etch depth at each step.

PL was performed at 77 K, with the sample immersed in liquid nitrogen. In all our measurements of PL an Ar^+ laser with emission at 514 nm and a laser spot of 100 μm was used as the pump source. Photoreflectance measurements were performed using a He–Cd laser operating at 441 nm, with 10 nW/cm^2 intensity. The small power density enhances the excitation close to the surface.[6]

III. RESULTS

PL measurements were conducted using different excitation laser powers in the range from 3 to 90 mW measured at

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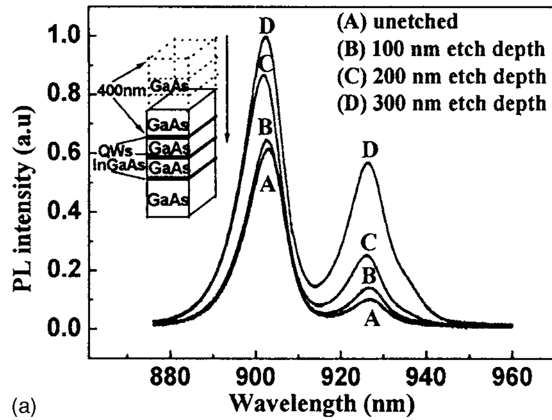

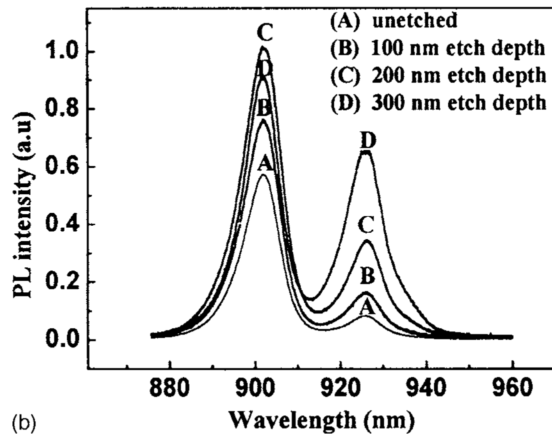

FIG. 1. (a) Photoluminescence spectra of the InGaAs/GaAs QWs before and after the wet chemical etching steps. (b) Photoluminescence spectra of the InGaAs/GaAs QWs after the dry chemical etching steps. The excitation power of the Ar laser was 514 mW.

the sample surface. The observed results are the same for full range of power, then we just report the excitation power of 48 mW in Figs. 1(a) and 1(b), which is an intermediate value of power.

Figure 1(a) shows the typical PL spectra for the samples before etching and after each 100 nm wet etching step. We observe that the PL intensity for both quantum wells increases with etch depth. We will call this behavior *DCBA* sequence, indicating, in descending order, the intensity associated with subsequent etching steps. The emissions at $\lambda_1 \sim 902$ nm and $\lambda_2 \sim 926$ nm correspond to the first (6 nm) and second (10 nm) quantum wells, respectively. The emission of the thicker and deeper quantum well was not observed. In our analysis, it is sufficient to understand the behavior of the two quantum wells closest to the surface.

Figure 1(b) shows the PL spectra for the samples treated with dry etching. In this case, a maximum PL intensity for 200 nm total etching depth (C) is observed for the well closest to the surface. We will call this behavior *CDBA* sequence. The 10 nm well produces the *DCBA* sequence for both dry and wet etches. The reduction in PL intensity for the 300 nm etch depth, for the 6 nm well, while the deeper well maintains the *DCBA* sequence, is an indication of either surface or close to the surface damage reducing carrier injection to the well or damage to the well itself.

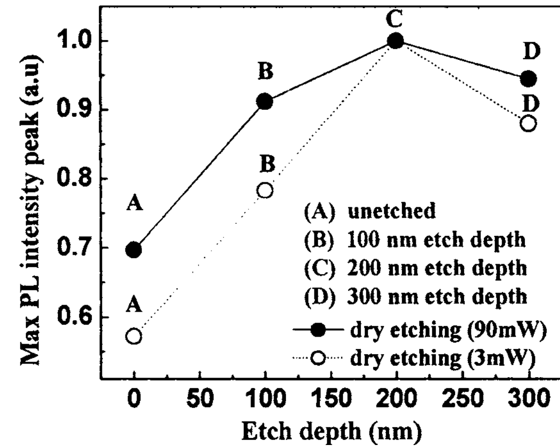

FIG. 2. PL emission peak intensity vs etch depths for the dry etching samples with the pump laser at 3 and 90 mW.

Figure 2 shows the normalized maximum PL intensity for the dry etching samples for the maximum (90 mW) and minimum (3 mW) laser powers. The only pump heating effect observed at 90 mW of excitation is the sublinear behavior of the PL intensity for etching depths smaller than 200 nm. Therefore, the observed sequences are unchanged with excitation power. The spectral line shape and power dependence of the PL indicates that damage to the well is less probable.

Figure 3 shows the atomic force microscopy (AFM) scans after the last etching step (300 nm etching depth) for (a) dry

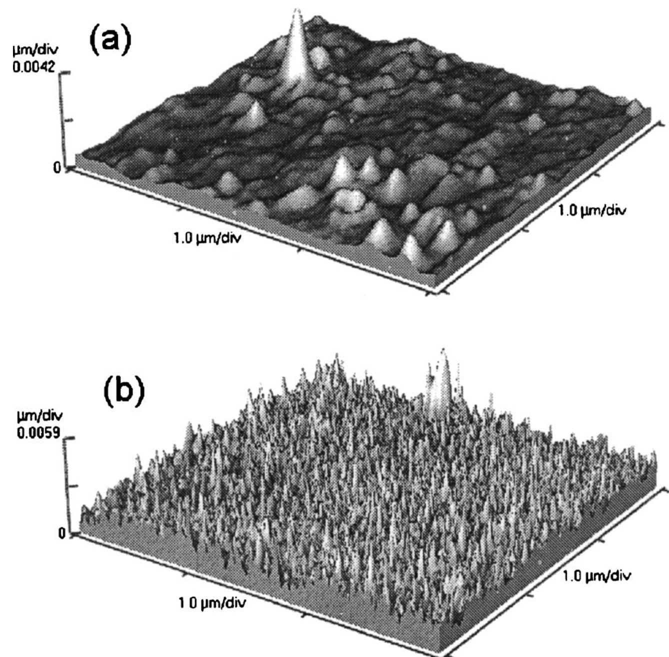

FIG. 3. AFM scans for dry and wet etched surfaces: (a) after 3 min in 8 SCCM BCl_3/12 SCCM Ar mixture, at 3 mtorr with 250 W ECR power/100 W rf power, (b) wet etching solution of $H_3PO_4:H_2O_2:40H_2O$-DI water.

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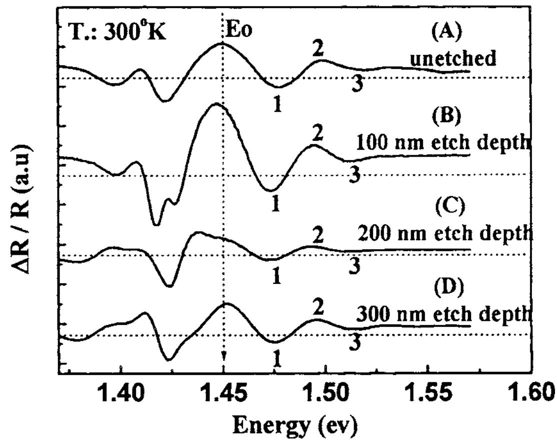

FIG. 4. Photoreflectance (PR) spectra at room temperature of samples etched at 0, 100, 200, and 300 nm by ECR.

and (b) wet processings. rms roughnesses of 0.35 and 0.9 nm are obtained for the dry and wet etchings, respectively. A maximum peak-to-valley height–total etch depth ratios of 0.8% and 3.5% are obtained for the dry and wet etchings, respectively. Therefore, it appears that the surface morphology is not consistent with the PL results since lower roughness is observed for the dry etched sample.

Our goal here is to try to identify the principal surface or close to the surface properties responsible for the PL intensity behavior with the ECR etch such that this technique can be used to assess information on surface damage not available by typical morphological analysis tools.

A first attempt in this direction involves photoreflectance measurements. Figure 4 shows the PR spectra for the samples etched by ECR after the several steps. We observe that the relative reflectance variation $\Delta R/R$ initially increases and after longer etching time it degrades to finally return to its original value. We believe that the initial increase in $\Delta R/R$ is related to the reduction in thickness of the native oxide layer subsequently to the first etch. With the laser excitation more directly at the GaAs, more interband transitions at the Van Hove singularities should increase $\Delta R/R$.[7] On the other hand, after the first step the reduction in $\Delta R/R$ should be related to surface damage caused by sputtering, channeling, or even unintentional Ar ion implantation.[8] Similar behavior has been observed for Ar plasma etching of bulk GaAs.[9]

The surface electric field (E_s) is obtained from the PR spectra using the Franz-Keldysh oscillation (FKO) theory.[10]

$$E_s = \frac{(2\mu)^{1/2}}{(3/4)e\hbar n\pi}[E_n - E_g]^{3/2}, \tag{1}$$

where E_g is the band gap energy, E_n the energy at the oscillation peak, n is an integer, and μ the reduced effective mass of the material along the field direction. Table I presents the results for the electric field and respective surface charge density, obtained by the FKO theory for the sample after the subsequent steps of dry etching. E_s, for etched samples, is ~8% smaller than that obtained for the unetched sample.

TABLE I. Electric field and charge density obtained by photoreflectance.

Sample	Etch depth (nm)	E (±4 kV/cm)	No. of e_s (cm^2)
(*A*)	0	97.3	7.1×10^{11}
(*B*)	100	86.6	6.3×10^{11}
(*C*)	200	90.1	6.5×10^{11}
(*D*)	300	84.6	6.1×10^{11}
($\mathcal{D}$)	300	84.6	6.1×10^{11}

Similar results have been reported for GaAs samples.[11] Also, we note that there is essentially no change in E_s for the different etching depths. An average value of $E_s \sim 90$ kV/cm is obtained.

IV. ANALYSIS

In order to explain the PL results, we have developed a simple transport model based on a Botzmann drift-diffusion model. We assume a steady state condition, low injection, and one dimensional problem.

Given a carrier excess $\delta_i(x)$, the drift-diffusion equation is given by

$$\frac{d^2\delta_i(x)}{dx^2} + \frac{\mu_i E(x)}{D_i}\frac{d\delta_i(x)}{dx} + \left[\frac{\mu_i}{D_i}\frac{dE(x)}{dx} - \frac{1}{D_i\tau_i}\right]\delta_i(x) + \frac{\delta_0\mu_i}{D_i}\frac{dE(x)}{dx} + \frac{TI\alpha}{D_i h\nu}e^{-\alpha x} = 0, \tag{2}$$

where μ_i is the mobility of the carriers, D_i is the diffusion coefficient, $E(x)$ the electric field, τ_i the lifetime of the carrier in the barriers, and the last term represents the *e-h* pair generation assuming a uniform illumination, where T is the transmission coefficient, I is the laser light intensity, α is the optical absorption coefficient in the layer, and $h\nu$ is the photon energy. The electric field caused by surface charges is given by the abrupt junction approximation.[12]

$$E(x) = \frac{qN_D}{\varepsilon_s}(x_o - x_d)\exp\left[\frac{x - x_o}{x_o - x_d}\right], \tag{3}$$

$$0 < x \leqslant x_d, \quad E(x) = 0 \quad x > x_d,$$

where N_D is the donor impurities of concentration, ε_s is the dielectric constant, and x_d is the depletion layer, where $x_d = x_o + 10^{-7}$ nm. The exponential term was added to artificially smooth the depletion layer edge in a spatial extension of $x_o = 10^{-7}$ nm for it improves the convergence of the algorithm employed to solve Eq. (2). The boundary conditions are the following.

(1) The recombination rate at the surface is proportional to the excess carrier density.

$$D_i \left.\frac{\partial\delta_i(x)}{\partial x}\right|_{x=0} = \{s_i + (-\mu E(0))\}\delta_i(0), \tag{4}$$

where the constant S_i is the surface recombination velocity.

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(2) Recombination in the quantum well is much faster than in bulk GaAs. Therefore, if the QW is located at $x=w$ then

$$\delta_i(w)=0. \tag{5}$$

The PL emission of the first QW is estimated by the product of electron and hole fluxes to this QW,

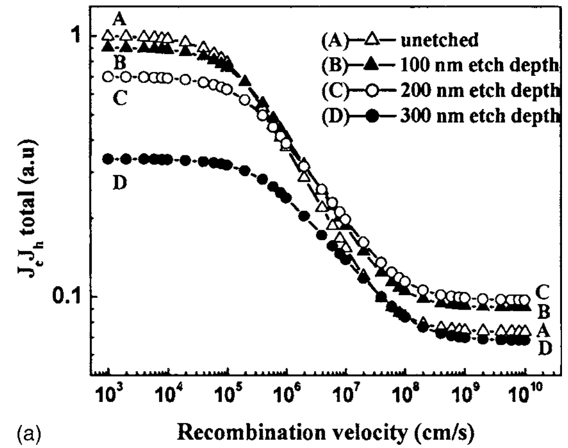
$$\begin{aligned} J_eJ_h \text{ total}_{(\text{one well})} &= (J_eJ_h)_A + (J_eJ_h)_B + (Je_{QW}Jh_{QW})_C \\ &= (-D_n \nabla N_1)(-D_h \nabla P_1) \\ &\quad + (-D_n \nabla N_2)(-D_n \nabla P_2) \\ &\quad + (\alpha_{QW} d_{QW} I/h\nu)^2 e^{-2\alpha \text{GaAsW}}. \end{aligned} \tag{6}$$

$N_1(P_1)$ excess-carrier density, electron(hole), in region 1.
$N_2(P_2)$ excess-carrier density, electron(hole), in region 2.
α_{GaAs} optical absorption coefficient for bulk GaAs.
α_{QW} optical absorption coefficient in quantum well InGaAs.
d_{QW} quantum well thickness.

The first two terms in this equation are obtained by solving Eq. (2) for the region between the top surface and the first quantum well (region 1), and between the first and second wells (region 2), respectively. The last term represents the carriers generated inside the QW by direct absorption.

In order to evaluate whether diffusion could explain the observed difference in PL sequence for dry and wet etchings, we calculated the normalized $J_eJ_h$total versus surface recombination velocity in the absence of the electric field. This result is shown in Fig. 5(a). In Figs. 5(a) and 5(b), we have used $\tau=10^{-8}$ s,[12] at 2.41 eV (514 nm); α for GaAs is 8×10^4 cm^{-1};[13] D_n and D_h of 220 and 10 cm^2/s, respectively; μ_n and μ_h of 8500 and 400 cm^2/V s;[12] S_i ranging from 10^3 to 10^{10} cm/s was used since it is comparable with typical reported values for etched GaAs.[14] Note that a good assumption for the surface recombination velocity is the thermal velocity near 10^7 cm/s.[14] We have chosen a 10^4 factor below and 10^3 above and below this value to perform our simulation. For each etching depth one sees two flat regions where the PL intensity (J_eJ_h) is independent of the surface recombination velocity. For small surface recombination velocities, the carrier flow to the first well is essentially due to diffusion caused by the exponential decaying carrier generation. For very high surface recombination velocities, the flow of carriers from the region between the first well and the surface is totally suppressed, and the entire contribution of carriers to the first well comes from its own absorption and from the region between the first and second wells.

In Fig. 5(a) we see for each curve in this simplified case, only *ABCD* and *CBAD* sequences are predicted. Without the electric field, the only way one can obtain the experimentally observed PL is by assuming the absorption coefficient for the QW (α_{QW}) to be over one order of magnitude greater than for bulk GaAs (α_{GaAs}). A calculated or experimental value for α_{QW} at the Ar$^+$ laser emission wavelength is not straightforward. The absorption process over high photon energies involves detailed properties of high order bands close to the edge of the Brillouin zone. We believe that it is safe to assume that a small energy splitting due to a possible one-dimensional quantization of these bands should not result in any considerable variation in the absorption coefficient. In fact, even different semiconductor materials such as GaAs, Si, and Ge tend to saturate the absorption coefficient at these high photon energies. Therefore, we believe that a good assumption is to assume in our simulation $\alpha_{QW}=\alpha_{GaAs}=8\times10^4$ cm^{-1}.



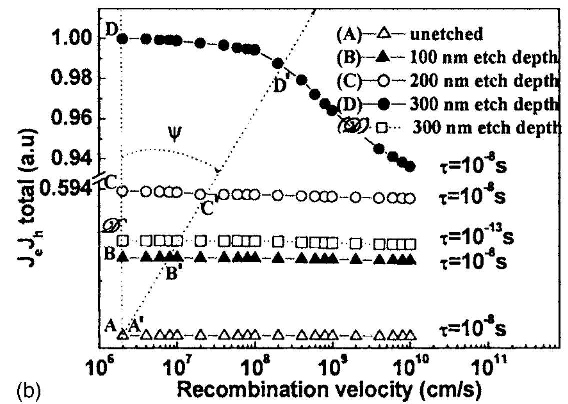


FIG. 5. Total product of electron-hole current densities to the well as a function of the surface recombination velocity for several etch depths: (a) no electric field; (b) electric field as measured by photoreflectance as given in Table I; recombination times $\tau=10^{-8}$ s (A, B, C, D) and $\tau=10^{-13}$ s ($\mathcal{D}$); 500 times reduction in Debye length.

Figure 5(b) shows the $J_eJ_h$total versus surface recombination velocity for the values of surface electric field measurements by photoreflectance $E=(97,87,90,85$ kV/cm), for the depths etched (0, 100, 200, 300 nm) respectively. The *DCBA* sequence, as observed for the wet etched sample, is predicted in a broad range of surface velocities. In fact, even if the surface velocity increases with processing, this sequence will still be observed. This is shown by the dashed line with inclination ψ (the greater ψ, the greater is the increase in surface recombination velocity with etch depth) crossing the points $D'C'B'A'$. We note that our calculation shows that the behavior observed in Fig. 1(a) will only be predicted for

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fields greater than 62 kV/cm. Given the average $E \sim 90$ kV/cm obtained by the FKOs in the PR spectra, this calculation describes well the sequence seen for the wet etched sample. However, there is no single electric field that predicts the *CDBA* sequence observed for the dry etched sample even if large ψ is considered. In fact, based on our simulation and a simple linear extrapolation, which is a conservative estimation, such behavior would be observed only for unphysical surface recombination velocities as high as 10^{20} cm/s.

Three hypotheses could provide an explanation for the observed *CDBA* sequence observed for the dry etched sample. Firstly, channeling or deep ion diffusion can cause damaged to the QW during the last etching step when the well ends 100 nm below the surface. However, given the excellent PL spectrum shape for the top QW in a broad range of excitation powers (3–90 mW), such hypothesis has been disregarded. Second, based on our simulations, we can always obtain the *CDBA* sequence assuming a very artificial increase in field for the last etching step. This hypothesis is not in agreement with the literature where concentration damage tends to saturate with etching depth.[15] Finally, there are reports in the literature where samples etched in high dc bias plasmas, such as ours, may develop an ~100 nm layer below the etched surface (Refs. 15 and 16). This is indicated by scanning electron microscopy and by an increase in contact resistivity with plasma exposure time. Therefore, for the last etching step, the PL spectrum is heavily influenced by the presence of an entirely damaged layer between the well and the surface. In our simulation, a reduction in Debye length within this layer can be implemented. In Fig. 5(b) the open squares are obtained assuming a reduction in Debye length by 500 times, where clearly the *CDBA* sequence is predicted. In fact, we have found that a reduction in Debye length in a range between 100 and 1000 times is necessary for this particular sequence to occur. Considering the values reported of about ten times reduction in mobility with dry etching processes,[17] then we should expect a reduction in carrier lifetime in the range between 10^3 and 10^5. Our results corroborate the literature indicating that high density plasma with high dc bias, besides producing very good surface morphology and even in conditions for which there is no channeling or deep ion diffusion, may still create a damaged layer about 100 nm below the surface that might be very detrimental for the fabrication of small devices. Particularly, the high PL sensitivity to this thin damaged layer is a strong indication that etching technique can deteriorate the performance of active micro-optical devices.

V. CONCLUSIONS

We have studied the use of photoluminescence (PL) of strained InGaAs/GaAs quantum wells (QWs) for the analysis of damages to (100) GaAs surfaces exposed to BCl_3/Ar plasma generated by an electron cyclotron resonance (ECR) system.

A simple transport model was developed and shown to be in good agreement with the PL intensity dependence with wet etching depth. For the PL intensity dependence with dry etching depth, our model indicates that a damaged layer of approximately 100 nm with a 100 times shorter Debye length is needed to match the experimental results. Therefore, it appears that high density plasmas with high dc bias, besides producing very good surface properties, may still create a damaged layer about 100 nm below the surface not easily detected by typical nondestructive analysis tools such as AFM or PR. The effects of this damage layer to the optical properties of active media in optical devices can be very detrimental as shown by the strong PL sensitivity.

ACKNOWLEDGMENTS

The authors would like to thank J. Bettini for the epitaxial growth, E. Laureto for the PR measurements, and H. R. Gutiérrez for the AFM scans. This work was supported by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and the Conselho Nacional de Pesquisa e Desenvolvimento (CNPq).

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