Optically Active Defects Induced by SiN_x PECVD Deposition on InGaAs-An SRPL Study

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Development of modern optoelectronic integrated circuits (OEICS) for telecommunications widely employs InP and related compounds as a starting material. During OEICS fabrication, surfaces and interfaces are in general exposed to a number of different processing steps, and among them, Silicon Nitride (SiN_x) deposition by Plasma Enhanced Chemical Vapor Deposition (PECVD) technique is widely employed. Spatially Resolved Photoluminescence (SRPL) was used as a tool to study the effect of SiN_x deposition by PECVD in n-type InGaAs layers grown on InP substrates by LPE and MOCVD techniques. With the SiN_x deposition parameters fixed, the "recovery" of the photoluminescence (PL) signal (band edge) was monitored as a function of thermal annealing and incident laser beam power, therefore investigating the optical damage induced by the SiN_x deposition and annealing process influence. We observed a lowering of the order of 10 times on the intensity of the SRPL signal coming from the InGaAs layer after the SiN_x deposition in subsequent dielectric chemical removal. Successive etchings of the InGaAs epilayer followed by PL measurements suggest that the depth of the optical damage as indicated by PL intensity signal recovery s a function of epilayer crystal quality and depends on whether thermal annealing is performed or not. Samples with no thermal annealing showed a fast recovery of the PL signal, ndicating a very shallow damaged layer. Experiments of PL signal recovery as a function of incident light power indicated that thermal annealing of the samples may not only change the optical characteristics of the defects but also extend their action by as much as 1000 Å deeper into the samples. Results indicated that the combination of thermal annealing and poorer crystalographic quality leads to a significant increase on the number of induced defects that behave as non-radiative recombination centers.

I. Introduction

InP and InGaAs have being widely employed by the research and development laboratories to manufacture optoeletronic integrated circuits (OEICS) in the last few years. As the circuits and devices grow in functioning complexity so does the processing steps required to conform the material to the proper design and structure. Among the several processing steps, SiN deposition by Plasma Enhanced Chemical Vapor Deposition (PECVD) stands out as one of the techniques most often used for passivation, as a contamination barrier, and as mechanical protection of semiconductor surfaces. The use of semiconductor dielectric interfaces by the semiconductor industry is limited on how effective the technology employed is in minimizing the electrically and optically active defects at these interfaces. The presence of such defects can strongly limits the device lifetime and lower its reliability. Therefore it is of great interest to characterize these defects and to identify the physical principles that govern their behavior.

Device manufacturing requires mid-process nondestructive probes for bulk and surface characterization. Photoluminescence (PL) has for a long time been recognized as one of such probes. Having a shallow penetration depth, for incident photons with energy bigger than the material's band-gap most of the photogenerated electron hole pairs originate from near the sample surface. Therefore PL can be used as a very sensitive probe for changes of the surface density of states, surface recombination velocity, and to detect the presence of defects at the dielectric semiconductor interface, all of which may affect device performance significantly.

Even though there has been a considerable amount of research on the effect of dielectric deposition and thermal annealing on the electrical and optical properties of InP[1-3] and GaAs[4-6], very little work has being done on InGaAs/SiN_x interfaces[7]. In this paper we report on the use of Spatially Resolved Photoluminescence (SRPL) as a tool to study the effect of SiN_x deposition by PECVD in n-type InGaAs layers grown on InP substrates by LPE and MOCVD techniques. With the SiN_x deposition parameters fixed, the "recovery" of the photoluminescence (PL) signal (band edge) was monitored as a function of thermal annealing, therefore investigating the optical damage induced by the SiN_x deposition and annealing process influence. It is demonstrated that the deposition of SiN by PECVD can introduce non-radiative recombination pathways as deep as 500 Å and that thermal annealing may extend their action by as much as 1000 Å deeper into the samples. Results seem to indicate that crystals with poorer cristalographic quality show a significant increase on the number of deposition induced defects that behave as non-radiative centers, when the samples undergo thermal annealing.

II. Experimental

InGaAs lattice matched epilayers were grown on InP[S] (100) substrates by standard LPE and atmospheric pressure MOCVD techniques. X-Ray measurements indicated a lattice parameter mismatch ($\Delta a/a$) of -1.2×10^{-3} and -3.8×10^{4} for the MOCVD and LPE samples respectively. The samples measured 6 by 8 mm on the side with a 2 to 3 microns of epilayer thickness.

PECVD was used to deposit SiN on the samples in a single batch. Deposition was performed with the substrate kept at 300°C. NH_3/SiH_4 gas ratio of 80/3 and RF power of 50 watts. Ellipsometry measurements indicated an index of refraction of 1.93 and a 3% variation on film thickness of 150 nanometers. Sample thermal annealing after dieletric deposition was perfomed on a standard oven at 530°C during 10 minutes, when needed.

Spatially resolved photoluminescence (SRPL) measurements were conducted with a standard lock-in technique. An Ar^+ laser light beam (λ=514 nanometers) with an incident power of 100mW was focused (off normal incidence) to a spot of with a diameter of 200 micrometers. Laser light of this wavelength is totally absorbed in about 1 micronmeter of InGaAs. Room temperature photoluminescence intensity and wavelength maps with a 200 and 2000 micrometers step resolution respectively, were obtained by placing the samples in a computer controlled S-Y translation stage and having the light detected with a refrigerated Ge detector attached to a 1/4 meter spectrometer. Signal acquisition and processing took about 300 msec for each data point of the SRPL intensity map. SRPL measurements at 77 K were performed in a glass cryostat.

The following procedure was employed in order to evaluate the photoluminescence intensity profile as a function of sample etched depth: first, the samples were cleaved and cleaned in a HF solution and SRPL measurements performed to obtain a reference intensity signal. Next, SiN_x was deposited and annealed when desired. The deposited dielectric was then completely removed from half of the sample and SRPL measutements performed. With the left half covered, the InGaAs epilayer of the sample was etched in H_3PO_4:H_2O_2:H_2O (1:1:50) and the SRPL measurement performed. These last two steps were then sistematically repeated so as to study how the photoluminescence intensity changes as the InGaAs epilayer is etched away. Etched depth measurements were performed on a Tencor Alpha Step 100, indicating a chemical etch rate of 1000 Å/min.

Particular attention was given to the III-V surface condition since it is known[1] that the PL intensity is highly sensitive to the surface density of states. Each repeated step was followed by a final cleaning in HF for 30 seconds, rinsing in DI water and N_2 blow dried to ensure the same initial conditions just prior to every PL measurement. Photoluminescence measurements after successive sample cleanings with HF showed no influence of such cleaning on the observed results.

III. Discussion

Photoluminescence wavelength maps at 77 K were performed on each sample to verify the stoichiometry uniformity. An average of twelve spectra on different positions were taken from each sample having the peak position and the FWHM of the band edge luminescence transition recorded. The obtained results indicated a 0.05 percent variation on the Ga concentration throughout the InGaAs epilayer in all samples. The same maps were taken at room temperature to find out the energy position of the radiative transistion peak associated to the band edge, determining in this way the wavelength for the acquisition of the photoluminescence intensity maps. PL intensity maps were taken next by fixing the spectrometer to this wavelength and having the sample scanned in the X and Y directions as described above. Figure 1 shows a typical result. The lower intensity region corresponds to the area of the sample where the SiN_x was removed. The average of the intensity signal in this region was taken as the corresponding PL intensity signal associated to the epilayer after SiN_x removal.

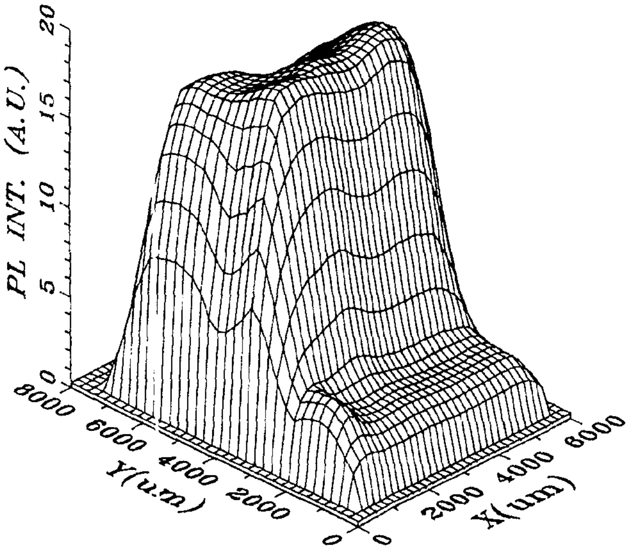

Figure 1: Typical result of a SRPL measurement of SiN_xInGaAs sample after partial silicon nitride film removal. The higher intensity region corresponds to the area where the dielectric film remains.

The SRPL intensity signal acquired as described above was monitored as a function of the etched depth of the InGaAs layer for both sets of samples. Figure 2 shows the obtained results. We observed a lowering of the order of 10 times on the intensity of the ÇRPL signal coming from the InGaAs layer after the SiN_x deposition and subsequent dielectric removal, followed by a partial or almost total recovery of the PL intensity signal as the sample is etched away.

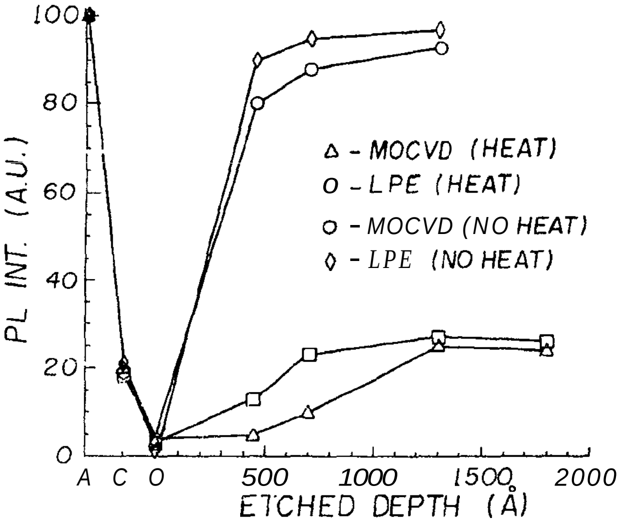

Figure 2: SRPL intensity signal as a function of etched depth of the InGaAs epilayer measured as described in the text. Position A, C and 0 indicate the result of PL measurements for the sample as received, after dielectric deposition, and immediately after dielectric film removal, respectively.

Two distinct behaviors were observed. For samples with no thermal annealing after the SiN_x deposition, the SRPL intensity has established to its original value within less than 500 Å of epilayer chemical etch. For samples with thermal annealing, on the other hand, it takes about 1000 Å of etched depth to have the SRPL intensity to increase and saturate, although it never recovers its starting magnitude.

MOCVD samples present a systematically lower PL efficiency than LPE samples. This may be related to the larger lattice mismatch of the MOCVD samples as compared to the LPE samples.

From Fig. 2 we can see that thermal annealing also reduces the PL intensity, meaning that heating enhances the nonradiative transitions deep into the In-

GaAs epilayer, unabling the PLintensity to rise back to its starting magnitude even after 2000 Å of etched depth. Comparing the results from the LPE and MOCVD samples we see that the combination of thermal annealing and poorer crystal quality somewhat enhances the optical damage induced by the PECVD process in the sample.

The observed results can hardly be explained with a single physical process or mechanism. The deposition of a dielectric thin film on top of a III-V semiconductor significantly reduces the reflectance of the semiconductor surface. This antireflecting property should enhance the PL intensity signal[7]. Nevertheless the experimental results show exactly the opposite, since the PL signal is quite reduced after dielectric deposition and remains so after chemical removal of the dielectric film. This behavior is observed in all samples, regardless of thermal annealing. This can be accounted for by an increase in the native oxide thickness, through the introduction of traps that would work as non radiative recombination centers. The existence of such superficial defects increases the surface recombination velocity, lowering the PL intensity. With InGaAs the most common native oxides that can lower the intensity of the PL signal are In_2O_3, and Ga_2O_3, and As_2O_3[8]. This hypothesis can explain the lowering of the PL intensity after dielectric deposition. Nevertheless the low PL intensity persists even after dielectric removal and surface cleaning with HF solution. Sample deeping into DI water and the air exposure between cleaning and data acquisition would allow for an oxide layer formation about 15 Å thick. This is not enough to account for the no recovery of the PL intensity immediatelly after HF cleaning. Hence the most likely explanation for the suppression of the PL intensity at the surface layer is the damage induced by heavy ions impinging on the surface leading to the formation of non radiative recombination centers.

The persisting low PL efficiency deep into the thermally annealed samples needs some additional explanatory mechanism. It is known that low temperature deposition plasma processes using NH_3 and SiH_4 gases occur in an very Hydrogen rich atmosphere leading to dielectric films with 15 to 30% concentration of Hydrogen and producing a significant concentration of Hydrogen atoms at the InGaAs surface. These Hydrogen atoms can combine primarily with As dangling bonds leading to the formation of gas at the surface while the dielectric film is being deposited. Similarly to the InP case, where Hydrogen atoms can lead to P vacancy formation[9], PECVD in InGaAs can lead to the formation of In vacancies, In/Ga vacancies complexes, and other structural defects due to the Ga leftover. The creation of such crystallographic defects caused by the reduction of InGaAs by Hydrogen atoms and damage induced by energetic ions takes place at the surface or within a few atomic layers of the surface. Thermal annealing can trigger the diffusion of the defects created in this way deep into the bulk forming non radiative recombination centers that could explain the observed behavior of the PL intensity as a function of etched depth. Preliminary results[10] of the optical damage induced by H_2 plasma on InGaAs support this hypothesis.

Studies of the influence of the light power on the changes of the PL intensity signal seem to indicate that for samples with thermal annealing the PL signal is independent of the incident light power; this means that whatever defects are present, they are insensitive to changes on the incident light power. For samples that have undergone thermal annealing, on the other hand, the PL intensities are strongly dependent on the incident light power, showing that the induced defects originate non-radiative transition paths that are not saturated for up to 100 mW of incident light power at least up to 750 Å, and for more than 1000 Å of etched depth for samples grown by LPE and MOCVD respectively. These results will be discussed in detail elsewhere[11].

IV. Conclusion

We have shown that SRPL can be used as a tool to study the deposition of SiN_x on InGaAs epilayers by PECVD, and that such deposition produces optical damage inducing the formation of non-radiative pathways that can reach up to 1000 Å deep into the sample when thermal annealing is performed.

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