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CATHODOLUMINESCENCE AND ELECTRON BEAM INDUCED CURRENT STUDY OF HYDROGEN TREATMENT OF p-n GaAs JUNCTION

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Abstract - The effects of hydrogen diffusion on p-n GaAs junctions have been studied by electron beam induced current (EBIC) and cathodoluminescence (CL) at room temperature. Hydrogen passivates both the acceptors in the p-side of the junction and the donors in the n-side of the junction. As a consequence the diffusion lengths increase, the surface recombination velocities decrease, and, finally, the CL intensity increases after the hydrogen treatment. The observation of hydrogen effects on both sides of the junction indicates that hydrogen diffuses at least in the neutral charge state. We also observe an electron-beam induced reactivation of the passivated centers after exposition of the sample for some minutes to the electron-beam.

1.- Introduction

The modern technology of semiconductor devices demands different post-growth techniques for changing the optoelectronics properties of grown samples. Among them, the diffusion of hydrogen could be a very important tool for fabrication of devices, because it is a planar process convenient to realize an arbitrary pattern of diffused regions. Hydrogen diffusion passivates shallow impurities as well as deep traps [1]. Consequently it changes the physical properties of the samples. However, only a few papers have been published on the use of hydrogen diffusion to improve device performances [2]. This is attributed to the problem of long term stability of the hydrogen effects, and to the fact that hydrogen not only passivates deep traps but also shallow dopants [3-5].

Photoluminescence (PL) measurements on undoped GaAs showed an enhancement of the luminescence after hydrogen treatment [6]. This motivates the present study of p-n junctions as a first step to exploit the beneficial effect of H diffusion. In fact p-n junctions are the fundamental blocks of devices as solar cell, photodetectors and light emitting diodes which could benefit of the enhancement in the luminescence intensity. To investigate their opto-electronic properties we have used the different imaging modes of the scanning electron microscopy (SEM), such as cathodoluminescence (CL) and electron beam induced current (EBIC).

Hydrogen diffusion in p and n doped GaAs was studied by Secondary Ion Mass Spectroscopy (SIMS) a few years ago [7]. Hydrogen is a very highly diffusing element which in a relatively short time can diffuse over several μm (for example $\approx 35 \mu\text{m}$ for a diffusion at 300°C lasting 30 minutes in p-doped sample). A shallow n^+ layer inhibits the in-diffusion of hydrogen in p-type material whereas a shallow p^+ layer has no effect on n-type material. This fact raises the question about the charge state of the hydrogen diffusing specie. Theoretical calculations suggests that in p- and n-doped GaAs, the stable charge state is

positively or negatively charged hydrogen, respectively [8]. A.J. Tavendale *et al* [9] and M.H. Yuan *et al* [10] demonstrated by Reverse Bias Annealing (RBA) that hydrogen indeed drifts as positive and negative charge species in p-doped and n-doped GaAs, respectively.

2.- Experimental technique

The p-n junctions have been obtained by Zn diffusion in Si-doped samples (nominal donor concentration $N_D \approx 2 \times 10^{18} \text{ cm}^{-3}$). The Zinc diffusion was carried out in closed tubes, using ZnAs_2 as diffusion source at a temperature of 575°C [11]. Resistivity measurements yields a mean Zn concentration of $N_A \approx 6 \times 10^{19} \text{ cm}^{-3}$ in the diffused region. The diffusion front position measured by SIMS and secondary electrons (SE) gives a diffusion depth of about $1.6 \mu\text{m}$.

For the diffusion of hydrogen we have used a rf plasma (13.56 MHz) produced in an Alcatel GIR300 reactor. The samples were exposed to the plasma at 300°C for 45 minutes, at a pressure of 120 mTorr and a power density of 0.74 Wcm^{-2} . The samples were exposed prior to the deposition of the contacts. For the contact deposition we used a low temperature technique to prevent the out-diffusion of H.

Cleaved faces of the samples were examined with a Cambridge 360 SEM. The CL luminescence radiation was focused at the entrance slit of a 32 cm focal length monochromator by an elliptical mirror system. The luminescence was detected with a Si photodiode, or a cooled Si avalanche photodetector. The sample holder also permits simultaneous EBIC and CL measurements.

3.- Experimental results

Capacitance-Voltage (C-V) measurements were performed on all the samples. The data shows a strong increase in the depletion layer and a strong reduction of the dopant density after the H treatment. S.J. Pearton *et al* [7] studied by SIMS a sample with a structure very similar to the one used in this work: a thin ($0.5 \mu\text{m}$ thick) p^+ layer with $[\text{Zn}] \approx 10^{19} \text{ cm}^{-3}$ grown on a Si doped GaAs sample ($[\text{Si}] \approx 10^{17} \text{ cm}^{-3}$). The measured hydrogen concentration passes from $2 \times 10^{19} \text{ cm}^{-3}$ in the p^+ top layer to $1 \times 10^{18} \text{ cm}^{-3}$ in the adjacent n type GaAs material. The same measured H concentration profile was observed in a sample without the p^+ surface layer. Hence we can assume that in our samples hydrogen diffuses through the junction and passivates the acceptors in the p-side as well as the donors in the n-side. From the C-V data, we found $N_{AH} \approx 1 \times 10^{17} \text{ cm}^{-3}$, the electrically active acceptor concentration decreased by two orders of magnitude, and $N_{DH} \approx 1 \times 10^{17} \text{ cm}^{-3}$. Indeed an increase in the series resistance was measured: 15Ω for the non-hydrogenated sample, named PN0, and 500Ω for sample PNH (both with a sample surface of 6 mm^2). In the p-side of the junction the compensation ratio $(N_A + N_D)/N_A$ passes from ≈ 1 in sample PN0 to >10 in sample PNH.

By measuring the EBIC current, J , under steady state condition it is possible to correlate the EBIC signal decay with the diffusion length L of the minority carrier [13]. For one dimensional diffusion and for weak injection, we have $J \approx J_0 \exp\{-x/L\}$ where x is the distance from the junction and J_0 the current at the junction. We have measured J for different acceleration voltages in order to change the excitation depth [12]. All the EBIC profiles have been fitted with an exponential function and the so obtained diffusion lengths are reported in Table I.

Considering the boundary condition at the surface (here is the cleavage surface), it is possible to extract the surface contribution from the total minority carrier lifetime τ_{tot} :

$$\frac{D}{L^2} = \frac{1}{\tau_{\text{tot}}} = \frac{1}{\tau} + \frac{2S_{[110]}}{d} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} + \frac{2S_{[110]}}{d} \quad (1)$$

where D is the diffusion constant, τ_r is the radiative lifetime, τ_{nr} is the non radiative bulk lifetime, $\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$ is the bulk total lifetime, $S_{[110]}$ the surface recombination velocity on the $[110]$ surface and d

the excitation depth. Using eq. (1), we extract $2S_{[110]}/D$ and $(\tau D)^{-1}$ from Table I.

Tension [keV]	Excitation depth maximum [μm]	untreated sample PNO		hydrogen diffused sample PNH	
		diffusion length (n side) [μm]	diffusion length (p side) [μm]	diffusion length (n side) [μm]	diffusion length (p side) [μm]
5	0.08	0.26	0.23	0.89	0.40
10	0.26	0.33	0.25	1.10	0.35
15	0.5	0.48	0.38	1.00	0.45
20	0.83	0.68	0.51	1.10	0.60

TABLE I: Results from the EBIC measurements for the untreated PNO and hydrogen diffused PNH samples. The maximum excitation depth from the cleavage surface is deduced by the acceleration voltage using the results of Ref. [16].

The diffusion constant is related to the mobility μ of the minority carriers by the Einstein relation $D = \mu kT/q$, where q is the electronic charge and T the temperature. The mobility of holes in a n-region with a dopant density N_D is approximated by the mobility of holes as majority carrier in a p-region with a density $N_A \approx N_D$. A Similar assumption can be made for electrons in the p-region. Using the data reported in Ref. [13] and the Einstein relation, we deduce the diffusion constant (see Table II) and via the data of Table I, the surface velocity $S_{[110]}$ and the minority carrier lifetime τ . The radiative lifetime for band-to-band recombinations is $\tau_r = 1/(BN_I)$ where B is the radiative recombination coefficient ($B \approx 2 \times 10^{-10} \text{ cm}^3/\text{sec}$ for GaAs [14]) and N_I is the dopant concentration (where $I = A$ for the p-side of the junction and $I = D$ for the n-side) [15]. Hence from the knowledge of τ and τ_r , the non radiative lifetime τ_{nr} and the internal quantum efficiency $\eta = \tau_{nr}/(\tau_{nr} + \tau_r)$ are obtained (see Table II).

	untreated sample PNO		hydrogen diffused sample PNH	
	n-side	p-side	n-side	p-side
dopant density [cm^{-3}]	2×10^{18}	6×10^{19}	1×10^{17}	1×10^{17}
mobility [$\text{cm}^2/\text{Volt sec}$]	120	1550	250	1500
D [cm^2/sec]	3	40	6	40
S [cm/sec]	150×10^6	2329×10^6	104×10^6	370×10^6
τ [sec]	1.32×10^{-9}	4.4×10^{-11}	1.6×10^{-9}	5.3×10^{-11}
τ_r [sec]	4×10^{-9}	8.3×10^{-11}	5×10^{-8}	7×10^{-10}
τ_{nr} [sec]	1.97×10^{-9}	9.46×10^{-11}	1.7×10^{-9}	5.8×10^{-11}
η	0.32	0.53	0.52	0.08

TABLE II: Minority carrier parameters deduced from Table I for the untreated PNO and hydrogen diffused PNH samples.

A relative error of about 50 % is estimated on the value of η quoted, due to the errors on the data reported in Table I and the imprecision on the mobility and on the coefficient B .

We show in Figure 1a, the CL intensity profile of PN0 and PNH recorded with an acceleration voltage of 10keV (excitation depth $\approx 0.26 \mu\text{m}$). The band at the (b) mark is due to the recombination of e-h pairs in the p-side of the junction. As the junction is located $1.6 \mu\text{m}$ below the [001] surface ((c) mark) and as the diffusion length is $L \approx 0.3 \mu\text{m}$, the CL intensity profile is strongly affected by the presence of the junction. A meaningful discussion of the influence of H on η and S is not possible on this side of the junction. However an increase by a factor of ≈ 2 in the total intensity is visible, in agreement with previous results for undoped GaAs [6].

FIGURE 1: Cathodoluminescence (CL) integrated profiles on [110] surface at room temperature. The [001] surface is located at the mark (a). 1a at beam energy of $V = 10\text{keV}$ and probe current of 2nA , the full line is the non-hydrogenated PN0 sample and the dashed line the hydrogenated PNH sample. 1b at $V = 20\text{keV}$ and $I = 2\text{nA}$, the full line after an exposition of 1min. to the e-beam and the dashed line after an exposition of 13min.

We observe a strong contribution from the n-side of the junction. The peak at the mark (d), is due to the sum of two contributions. For e-h excitation in the depletion layer, the e-h pair are separated by the electric field present at the junction and no luminescence is visible (this explains the minimum at the junction). As the e-beam goes away from the junction, we have the injections of holes from the p-side. These holes have been generated by reabsorption of the luminescence emitted in the n-side [17]. This effect is relevant as long as we excite at a diffusion length away from the junction. Increasing further the distance, we observe a decrease in the CL intensity because the contribution from the reabsorption on the p-side decreases. The CL intensity increases after the H treatment in agreement with the EBIC findings (Table II). This increase is observed up to $\sim 20 \mu\text{m}$ from the surface. The CL intensity becomes equal to that of sample PN0 for depths of $\approx 40 \mu\text{m}$.

An interesting behaviour is observed if we report the CL intensity ratio between the samples PNH and PN0 at the marks (d) and (e) of Fig. 1 versus the acceleration voltage (Table III). The ratios decrease as the penetration depth increases.

In Figure 1b, we present the integrated CL profiles after exposing the sample PNH for 1min. and 13min. to the e-beam (20keV and 1nA). We observe a reduction of the CL intensity for the longest exposure time.

Beam Tension [keV]	Maximum excitation depth [μm]	$I_{\text{CLH}}/I_{\text{CL}}(\text{d})$	$I_{\text{CLH}}/I_{\text{CL}}(\text{e})$
10	0.26	2.5	2.2
15	0.5	1.1	1.4
20	0.83	0.3	0.4

TABLE III: Integrated CL intensity ratio $I_{\text{CLH}}/I_{\text{CL}}$ between the hydrogenated PNH sample and the non-hydrogenated PN0 sample. $I_{\text{CLH}}/I_{\text{CL}}(\text{d})$ and $I_{\text{CLH}}/I_{\text{CL}}(\text{e})$ refer to the CL intensity recorded at the mark reported in Fig. 1.

4.- Discussion

The values obtained in Table II show a strong variation of the electronic properties after hydrogen treatment. The surface recombination velocity $S_{[110]}$ decreases by a factor ≈ 1.5 (≈ 6) in the n-side (p-side). The total lifetime increases in the n and p region. Consequently, the internal quantum efficiency is affected by the hydrogen diffusion. It augments by a factor ~ 2 in the n-side and decrease by a factor ~ 7 on the p-side. The quantum efficiency reduction on the p-side is due to the radiative lifetime increase caused by the reduction of N_A [18] and to the drop of the non-radiative lifetime.

We interpret the variation of the CL intensity ratio $I_{\text{CLH}}/I_{\text{CL}}$ with beam energy by the differences in the influence of the surface recombination velocity on the radiative recombinations. The [110] surface traps more carriers in PN0 than in PNH. Then $I_{\text{CLH}}/I_{\text{CL}}$ become higher lowering the beam voltage. The CL ratio is not dominated only by the surface recombination velocity. Another effect is also present. The augmentation of the diffusion length after hydrogen treatment (see Table I) produces a higher collection of carriers at the junction. This induce a decrease of the CL signal and then it explains the value below 1 of the CL ratio at 20keV. The integrated EBIC signal on the n-side of the junction increases indeed by a factor ≈ 2 after the hydrogen treatment. And this ratio is approximatively constant with the beam energy.

In Figure 1b, we have shown an increase of the CL intensity after a relatively long exposure time of the sample PNH to the e-beam. This is due to a e-beam induced reactivation of the impurities. Thus the diffusion length of the carrier decreases and, as argued above, the CL intensity signal increases. The Si-H neutral complex formed during the passivation is dissociated during the minority carrier injection:

A similar phenomenon in p-doped GaAs has been reported in Ref. [9].

5.- Conclusion

Our observations imply that H diffuses relatively rapidly in p-type GaAs, and that the electric field due to the p-n junction has a minor influence on the motion of the diffusing specie. In fact relevant H induced variations of the physical properties have been observed on both sides of the junction. This fact suggest that H diffuses at least in the neutral charge state. H passivates the impurities accordingly to the following model [1]. As H enters in the p-side of the junction, it looses one electron which cancels a free hole and then the positively charged H is attracted by the negatively charged acceptor forming a neutral complex (passivation of dopant). The H bound in the complex is no longer able to move. The neutral H diffuses

and passes the junction. In the n-side, the neutral H loses a hole which recombines with an electron. Then a complex is formed between the positively charged donor and the negatively charged H. The e-beam induced reactivation confirms this scheme. However, our study does not exclude the possibility that H diffuses also in other charge states.

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