OXYGEN AND MINORITY CARRIER LIFETIMES IN N- AND P-TYPE $AL_{0.2}GA_{0.8}AS$ GROWN BY METALORGANICS VAPOR PHASE EPITAXY

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ABSTRACT

The minority carrier lifetimes in $Al_xGa_{1-x}As$ grown by Metal-Organics Vapor Phase Epitaxy (MOVPE) is generally lower than in GaAs. This is believed to be due to oxygen incorporation in the layers. We describe a study of radiative and non radiative minority carriers lifetimes in n- and p-type $Al_{0.2}Ga_{0.8}As$ as a function of growth parameters, in correlation with oxygen concentration measurements and deep level transient spectroscopy (DLTS) studies. Long non radiative lifetimes and low oxygen contents are achieved using high temperature (780 °C) growth. A main minority hole lifetime killer appears to be a 0.4 eV deep O related electron trap detected by DLTS at concentrations three orders of magnitude lower than the atomic oxygen one. Record lifetimes in MOVPE grown n- and p-type $Al_{0.2}Ga_{0.8}As$ are obtained. An $Al_{0.85}Ga_{0.15}As/Al_{0.2}Ga_{0.8}As$ surface recombination velocity lower than $4.5x10^3$ $cm.s^{-1}$ is measured.

Keywords: Semiconductor, (Al,Ga)As, MOVPE, Minority carrier lifetime, Recombination, Oxygen, Solar cells.

1. INTRODUCTION

Solar cells, as most minority carriers (MC) devices, require for optimum efficiency long MC lifetimes, *i.e.* as near as possible to the radiative limit. Long minority carrier lifetimes ensure good carrier collection, *i.e.* increased short circuit currents, and low dark currents, *i.e.* high open circuit voltages and fill factors. Of course, mostly radiative carrier recombination is also *a fortiori* required in emitting devices as light emitting diodes and lasers. The radiative limit is hard to reach in indirect gap semiconductors, but should not be in direct gap ones, due to the strong near edge radiative transition probability (high absorption coefficient). Indeed, GaAs with a room temperature (RT) unity or near unity internal quantum efficiency η_i have been grown for a long time, whatever the growth method (Alferov *et al.*, 1976; Garbuzov *et al.*, 1977; Nelson & Sobers, 1978; Yablonovitch *et al.*, 1987; Basmaji *et al.*, 1988; Ahrenkiel *et al.*, 1989). However, this is not the case for $Al_xGa_{1-x}As$ alloys: whereas long MC lifetimes and high radiative efficiencies at RT have been obtained in Liquid Phase Epitaxy (LPE) grown $Al_xGa_{1-x}As$ ($x \leq 0.25$) (Alferov *et al.*, 1976; 1976; Abdullaev *et al.*, 1977; Garbuzov *et al.*, 1977), lifetimes much shorter than those measured in GaAs for similar doping levels and growth conditions are often measured in Metalorganics Vapor phase Epitaxy (MOVPE) (Ahrenkiel & Dunlavy, 1989; Zhang *et al.*, 1993) or Molecular Beam Epitaxy (MBE) (Leroux *et al.*, 1987; Sheldon *et al.*, 1993) grown $Al_xGa_{1-x}As$. Rather recently, RT radiatively controlled $Al_xGa_{1-x}As$ samples with $x = 0.1$ were grown by MOVPE, but the situation deteriorates for higher x values (Thomeer *et al.*, 1994). In such large gap semiconductors, the recombination energy cannot be accommodated by bulk excitations (phonon, plasmons...) nor by intrinsic Auger collisions (whose probability is in any case lower in $Al_xGa_{1-x}As$ than in GaAs). The low RT radiative efficiency of $Al_xGa_{1-x}As$ has then to originate from some crystal periodicity perturbation, either bidimensional (surface, interface...), monodimensional (dislocations) or 0-dimensional (defects). Values of $Al_xGa_{1-x}As/Al_yGa_{1-y}As$ interfacial recombination velocities are given in the revue by Pavesi and Guzzi (1994) (see also Thomeer *et al.*, 1994). They are in the 10^3-$10^4 cm.s^{-1}$ range, as in the present work (see below). This is not sufficient to explain low lifetimes in μm thick double heterostructures (DH). AlAs and GaAs are nearly lattice matched, and therefore dislocations should not play a major role in the recombination processes. Henceforth, the origin of poor minority carrier lifetimes in $Al_xGa_{1-x}As$ compared to GaAs has to be found in bulk defects, the so-called Shockley-Read-Hall (SRH) centers.

The main residual impurities in MOVPE and MBE grown $Al_xGa_{1-x}As$ are C and O. Since substitutionnal C gives rise to either shallow acceptors or donors, it should not play a detrimental role in RT recombination. On another hand, O has long been known to bring the dominating recombination center in $Al_xGa_{1-x}As$ whatever the doping (Foxon *et al.*, 1985; Zhang *et al.*, 1993; Thomeer *et al.*, 1994), although a direct correlation between the oxygen concentration and the lifetime has

not been established so far. Another well known recombination center in n-type (Al,Ga)As is the DX center, a strongly lattice-coupled state of substitutionnal donors (Chadi & Chang, 1988). When occupied (*i.e.* only in the dark at low T, but at RT due to thermal equilibrium), it acts as a hole killer center (Brunthaler *et al.*, 1989; Leroux *et al.*, 1989). This is in agreement with its negative U nature (Chadi & Chang, 1988). However, the effect of DX centers at RT should be negligible in p-type and undoped $Al_xGa_{1-x}As$, or in n-type when $x \leq 0.2$. Note that DX centers may be at the origin of the difference between the RT radiative efficiency of p- and n-type LPE grown $Al_{0.25}Ga_{0.75}As$ reported by Abdullaev *et al.* (1977).

In this work are studied the minority carrier recombination parameters in MOVPE grown n- and p-type $Al_{0.2}Ga_{0.8}As$. Following the previous discussion, particular attention is given to the oxygen contamination and the deep level densities in the layers, in order to correlate them to these recombination parameters. This alloy composition of x = 0.2, though less studied than x = 0.3-0.4, corresponds to tandem solar cell applications, in association with Si cells. In particular, high solar conversion efficiencies of 18% (AM = 1.5, concentration = 1 sun) were obtained with this material and the efficiency reaches 21% when stacked with a Si cell (Zahraman *et al.*, 1994).

After a brief revue of the problem of O in (Al,Ga)As (part 2), experimental details are given in part 3. The results are discussed in part 4.

2. OXYGEN IN MOVPE AND MBE GROWN (Al,Ga)As

2.a Oxygen incorporation

For given MOVPE or MBE growth conditions of $Al_xGa_{1-x}As$ alloys, the global oxygen content [O] in the layers increases abruptly as soon as small amounts of Al are introduced, and then increases steadily with x (Hanna Bakraji *et al.*, 1991; Kuech *et al.*, 1992). Under typical MOVPE growth conditions, Secondary Ion Mass Spectroscopy (SIMS) measurements (see also section 4a) show that [O] ranges from a few $10^{17}cm^{-3}$ to over $10^{19}cm^{-3}$ for x ranging between 0.1 and 1 (Kuech *et al.*, 1992). Similar values are obtained by charged particle activation measurements (Hanna Bakraji *et al.*, 1991). The same range of [O] values is also typical for MBE grown $Al_xGa_{1-x}As$ ($0.1 < x < 0.4$) (Foxon *et al.*, 1985; Akimoto *et al.*, 1986; Yamaguchi *et al.*, 1987). Oxygen has a highly detrimental effect on MC lifetime, as evidenced by RT (Terao & Sunakawa, 1984; Foxon *et al.*, 1985; Akimoto *et al.*, 1986) or low temperature (Bhattacharya *et al.*, 1984; Smith *et al.*, 1993; Ryan *et al.*, 1994) photoluminescence (PL) efficiencies and MC diffusion lengths (Yamaguchi *et al.*, 1987). It is also worth mentioning that MBE-grown GaAs doped with Al at levels as low as $5x10^{18}$ cm^{-3} is sufficient to dramatically decrease the MC lifetime (Sheldon *et al.*, 1993) (though a direct correlation with [O] is missing in this case).

In MOVPE, the main sources of oxygen are any traces of O_2 or H_2O in the gas phase, but also the high content of volatile methoxydes ($-OCH_3$) species, principally dimethylaluminiummethoxyde $(CH_3)_2AlOCH_3$ (Terao & Sunakawa, 1984; Hata *et al.*, 1992; Smith *et al.*, 1993), in the trimethylaluminium (TMA) sources. These methovery efficient O precursors, and they can be used to dope intentionally GaAs with oxygen beyond the bulk solubility limit in order to grow semi insulating layers (Park & Skowronski, 1994; Ryan *et al.*, 1994). Reduction of unintentional O contamination can be achieved using other Al precursors such as trimethylaluminium alane, but this is at the expense of increased composition and thickness non-uniformity following exchange reactions with Ga alkyls. In most experiments to date, TMA is purified by distillation

Besides the most perfect purification of the precursors and carrier gases, the reduction of O incorporation in MOVPE grown $Al_xGa_{1-x}As$ also requires:

- high growth temperatures (Hata *et al.*, 1992; Kuech *et al.*, 1992) (higher than 700 °C). It is assumed that at high temperature, the decomposition of arsine produces some subhydrides like AsH or AsH_2 that react with Al methoxydes to remove oxygen. Note that when growing at high temperature, dopant diffusion may have deleterious effects in the design of devices,
- high V/III ratios (~ 100) for basically the same mechanism as the previous one. The O content in the layer decreases as $(V/III)^{-3/2}$ (Hata *et al.*, 1992; Kuech *et al.*, 1992),
- the use of a load-lock system, avoiding moisture chemisorption from the ambient atmosphere in the growth chamber (see section 4a).

In MBE grown $Al_xGa_{1-x}As$, the main source of O contamination is believed to be in the Al sources (Akimoto *et al.*, 1986; Massies). O can be incorporated in the layer through volatile molecules as Al_2O. As in the MOVPE case, the reduction of [O] requires:

- highly purified sources,
- high growth temperatures and V/III ratios (Akimoto *et al.*, 1986),
- good system clean-up and long baking (Foxon *et al.*, 1985).

Besides MOVPE and MBE, the case of oxygen in $Al_xGa_{1-x}As$ grown by metalorganics molecular beam epitaxy has been recently reviewed by Courboulès *et al.* (1994). The oxygen levels obtained using this hybrid technique depend on the Al precursor used, and are again in the 10^{17}-$10^{18}cm^{-3}$ range, as for MOVPE or MBE grown $Al_xGa_{1-x}As$.

2b. Nature of O in $Al_xGa_{1-x}As$

Though present in concentrations of 10^{17}-10^{18} cm^{-3}, O in $Al_xGa_{1-x}As$ rather compensate shallow donors than act as an n type dopant. Actually, it is now known, mainly through local vibration mode (LVM) spectroscopy (Alt , 1989; Skowronski *et al.*, 1990) that O in GaAs is mainly either in an interstitial or in a displaced substitutionnal position. Two different sites have also been deduced by combining charge particle activation studies with channeling experiments (Hanna Bakraji *et al.*, 1991). Interstitial O is electrically inactive. In the displaced substitutionnal site (As site), a Ga-O-Ga center is formed, with a remaining Ga-Ga molecular bond. Analysis of LVM absorption transients have shown that the displaced substitutionnal O can bind two electrons, *i.e.* is a negative U center (Alt , 1989; Skowronski *et al.*, 1990). Recent theoretical calculations confirm this point (Mattila & Nieminen, 1996). It is important in the context of the present work to look at the electronic signatures of O in GaAs and $Al_xGa_{1-x}As$, from DLTS or luminescence.

Huang *et al.* (1994) (see also Huang & Kuech, 1994) have studied by DLTS the deep levels present in MOVPE grown GaAs intentionally O doped using Al-O bonding based precursors. Various electron traps with emission energies between 0.16 and 0.95 eV are reported, the principal ones located 0.95 and 0.75 eV below the conduction band edge. Their density is in the 10^{13}-10^{15} cm^{-3} range, *i.e.* at least one order of magnitude below [O], measured by SIMS. It is worth also mentioning the DLTS study of Qurashi *et al.* (1995) of lightly Al doped GaAs grown by MBE, showing the emergence of new traps (with densities far below the Al one). Though no correlation with oxygen is mentioned, it may be kept in mind in the light of the previous discussion.

Regarding MC recombination, Yamaguchi *et al.* (1987) (see also Ando *et al.*, 1987) relates the oxygen related decrease of MC diffusion length in MBE grown $Al_{0.4}Ga_{0.6}As$ to a 0.86 eV deep electron trap. Similarly, Akimoto *et al*. (1986) show that the room temperature PL efficiency of MBE grown $Al_{0.3}Ga_{0.7}As$ is inversely proportional to the density of a 0.76 eV deep electron trap. Once again, the trap density is in the 10^{14}-10^{15} cm^{-3} range, two orders of magnitude below the oxygen concentration.

A particular attention has to be paid to the study by Zhang *et al.* (1993) of three electron traps labeled A, B and C with emission energies of 0.32, 0.46 and 0.56 eV respectively in $Al_{0.1}Ga_{0.9}As$. These traps are tentatively correlated with O, and are shown to be the main hole recombination centers in the samples studied. The analysis of electron capture transients shows that these centers can trap two electrons successively (Zhang *et al.*, 1993), which is a link with the displaced substitutionnal O center discussed above. The very low first electron capture cross sections of these centers rather suggest charge states of -q, -3q than 0, -2q (Zhang *et al.*, 1993), in good agreement with theoretical predictions (Mattila & Nieminen, 1996). These killer centers in $Al_{0.1}Ga_{0.9}As$ are suppressed by high temperature growth.

The problem of optical signatures of oxygen in GaAs is not clear. The photoluminescence of intentionally O doped GaAs using Al methoxydes and ethoxydes have been studied in references (Huang *et al.*, 1994; Park & Skowronski, 1994; Ryan *et al.*, 1994). Oxygen gives rise to a variety of donor-acceptor pair bands 72 meV to 510 meV below the band edge (Park & Skowronski, 1994). The fact that O doping using these precursors also induces Al doping may be at the origin of such level multiplicity, due to different nearest neighbor Al-O associates (Ryan *et al.*, 1994) (these different nearest neighbor configurations have also to be taken into account in the DLTS studies quoted previously).

Transitions associated to oxygen in the PL of $Al_xGa_{1-x}As$ alloys associates the problem of O luminescence in GaAs and of deep level PL in the alloy (Leroux, 1994; Pavesi & Guzzi, 1994). This is beyond the scope of this paper.

3. EXPERIMENTAL DETAILS

The basic structure used for minority carrier lifetime studies in GaAs-like materials is a double heterostructure (Alferov *et al.*, 1976; Abdullaev *et al.*, 1977; Garbuzov *et al.*, 1977; Nelson & Sobers, 1978; Leroux *et al.*, 1987; Yablonovitch *et al.*, 1987; Basmaji *et al.*, 1988; Ahrenkiel *et al.*, 1989; Ahrenkiel & Dunlavy, 1989; Sheldon *et al.*, 1993; Zhang *et al.*, 1993; Thomeer *et al.*, 1994), in order to minimize surface recombination effects. $Al_{0.85}Ga_{0.15}As/Al_{0.2}Ga_{0.8}As$ DH with an active layer thickness of 2.5 μm were grown by MOVPE under various experimental conditions (temperature, pressure, nature of the growth chamber) in order to assess the relationship between growth conditions, oxygen concentration and MC lifetime in $Al_{0.2}Ga_{0.8}As$. The doping levels and Al concentrations in the active layers and windows correspond to those used in stacked solar cells (Zahraman *et al.*, 1994). In the present study, a laboratory built atmospheric pressure vertical reactor (without load-lock) and a low pressure horizontal one (Aixtron 200, with load-lock) were used. This allows a direct comparison of the electronic quality of $Al_xGa_{1-x}As$ grown in different growth chamber. Si and Zn doped samples were grown in the second reactor (#73, 74), whereas Te doped samples were grown in the first one (#671a-673a). In that case, single heterostructures on n^+ substrates (#671b-673b) were also grown under the same experimental conditions, for deep level transient spectroscopy (DLTS) measurements. The samples were grown at various temperatures, with a V/III ratio of 100 in the vapor phase. The growth rate is 2.5 μm/h. The TMA used in the present study was purified by both distillation and zone melting. The Al content of the active layer was controlled by X ray diffraction and the room temperature PL spectra.

The oxygen concentration in each sample was measured by secondary ion mass spectroscopy (SIMS) using a Cs^+ primary ion beam. Absolute concentrations

were obtained by comparison with an implanted Gstanda. The detection limit is ≈ $2x10^{16}$ cm^{-3} (Figure 1).

Figure 1. Examples of oxygen SIMS concentration profiles obtained in $Al_{0.85}Ga_{0.15}As/Al_{0.2}Ga_{0.8}As$ double heterostructure samples. Sample #671a is grown at 720 °C, and sample #673a at 780 °C

The deep level spectroscopy was performed by a deep level transient spectroscopy (DLTS) technique using a broad band two-phase lock-in amplifier for the signal processing. This set-up apparatus, already described (Pelloie *et al.*, 1986), allows a high sensitivity, such that a deep level concentration resolution better than $5x10^{12}$ cm^{-3} can be obtained with our samples. The DLTS measurements were carried out using a 21.3 s^{-1} - 1950 s^{-1} rate window range in a 77 K - 350 K temperature scale allowing the investigation of a 0.1 eV - 0.8 eV emission energy range.

Minority carrier lifetimes were deduced from photoluminescence decay measurements in the 80-300 K range. PL was excited using a N_2 pumped dye laser (50 Hz, resolution 1 ns) and detected by a Si avalanche photodiode followed by a

boxcar averager. In order to get benefit of variations in the photon recycling factor (defined below), PL decays were also measured in parts of the samples where the substrates were selectively removed following the method given in reference (Zahraman *et al.*, 1994).

The characteristics of the samples discussed here, *i.e.* growth temperature, [O] concentration, deep level concentration and lifetimes, are listed in Tables 1 and 2.

TABLE 1. Properties of the 2.5 μm thick $Al_{0.2}Ga_{0.8}As/Al_{0.85}Ga_{0.15}As$ double heterostructures studied in this work: oxygen content, doping level and room temperature photoluminescence decay time with and without substrate

Sample	**# 671a**	**# 672a**	**# 673a**	**#73**	**#74**
Growth T	720 ^{o}C	750 ^{o}C	780 ^{o}C	780 ^{o}C	780 ^{o}C
[O] (cm^{-3}) -active layer: -window:	 $1.85x10^{17}$ $7x10^{18}$	 $1.5x10^{17}$ $5x10^{18}$	 $1.2x10^{17}$ $5.5x10^{18}$	 $1.0x10^{17}$ $4\text{-}8x10^{17}$	 $1.0x10^{17}$ $4\text{-}6x10^{17}$
n, p (cm^{-3}) Hall effect	$1x10^{17}$ (Te)	$1x10^{17}$ (Te)	$1x10^{17}$ (Te)	$2x10^{17}$ (Zn)	$1x10^{17}$ (Si)
τ (ns) PL decay	2 (with sub.)	3 (with sub.)	13 (with sub.)	15 (with sub.) 25 (without)	17 (with sub.) 29 (without)

4. RESULTS

4a. SIMS data

Typical examples of global oxygen concentration [O] profiles in our DH samples are displayed in figure 1. A flat profile is generally obtained in each individual layer, with a high value in the $Al_{0.85}Ga_{0.15}As$ windows, and a lower value ($1\text{-}2x10^{17}$ cm^{-3}) in the $Al_{0.2}Ga_{0.8}As$ active layer. In the GaAs buffer layer, the oxygen concentration is within or below the detection limit. The range of [O] in the active layer is in agreement with the best literature values (Hanna Bakraji *et al.*, 1991; Kuech *et al.*, 1992) (section 2a). [O] decreases with increasing the growth temperature, as found by Kuech *et al.* (1992).

A salient feature in Table 1 is that the O content in the Al rich window layer is one order of magnitude higher in the samples #671a-#673a than in samples #73 and #74, emphasizing the difference in MOVPE machines. This shows that O contamination does not occur only *via* Al precursors, at least in the laboratory machine. It is also an indication of the beneficial effect of a load-lock chamber for the growth of these Al rich compounds.

Another important conclusion can also be drawn. Table 1 shows that samples #673a and #74, both grown at 780 °C, but in different machines, have roughly equivalent RT PL decay times τ (13 and 17 ns respectively), though there is

an order in magnitude difference in the O content of their windows. This shows that the differences in interface recombination velocities between these samples do not play a major role in τ and justifies the analysis of the lifetimes data (section 4c) in terms of bulk SRH centers.

4b. DLTS data

As the DLTS spectrum of figure 2a shows, 4 electron traps (labeled A1 to A4) are detected in samples #671b, 672b and 673b. Their emission energies range between 0.13 and 0.45 eV relative to the conduction band and their concentrations are around 10^{14} cm^{-3} whatever the sample, *i.e.* 3 orders of magnitude lower than the atomic oxygen one measured in samples #671a-#673a. We recall that such deep level concentrations are typical of those measured in $Al_xGa_{1-x}As$, as mentioned in section 2b (DX centers excluded). As a remark, the concentration of the A4 level could be underestimated if it acts as a recombination center as we shall show hereafter. Indeed, in that case, the hole capture cross section σ_p is not negligible and so on the hole emission rate e_p. This trap could behave as an electron and a hole trap at once, from a DLTS point of view.

The signatures of the traps measured are reported in figure 2b.

Figure 2a. DLTS spectrum measured in sample #673b with a 1060 s^{-1} emission rate window

Figure 2b. Signatures of the traps detected by DLTS in Te doped ($n = 1x10^{17}$ cm^{-3}) $Al_{0.2}Ga_{0.8}As$. The dotted line is the signature of the B killer center in $Al_{0.1}Ga_{0.9}As$ studied by Zhang *et al.* (1993)

Inspection of this figure and of Table 2 shows that the low emission energy traps, labeled A1 and A2, display strong scatter among samples in their signatures and concentrations. They should then not play a major role in hole recombination, whose trends will be reported in section 4c. On the other hand, the high energy ones are common to the three samples and from their signatures can be collected in two groups labeled A3 and A4, with emission energies of ~ 0.45 eV and ~ 0.41 eV respectively. On figure 2b is also given the signature of the B killer level studied by Zhang *et al.* (1993) in $Al_{0.1}Ga_{0.9}As$ (see section 2b). It corresponds rather to that of A3 but is not very different from that of A4. The densities of these two levels decrease with increasing growth temperature, as does [O]. Another salient feature is the one order of magnitude decrease in the concentration of the A4 level between growth at 720 °C and 780 °C. This follows nicely the MC lifetime trends discussed below.

4c. PL decay data

Table 1 gives the PL decay times measured at room temperature in the double heterostructures studied. The increase of effective lifetime with increasing growth temperature is evident and reproducible. It is also in excellent agreement with the trends reported in the literature (Bhattacharya *et al.*, 1984; Terao & Sunakawa, 1984; Foxon *et al.*, 1985; Akimoto *et al.*, 1986; Yamaguchi *et al.*, 1987; Hata *et al.*, 1992; Ryan *et al.*, 1994) (section 2a), showing that it is a general feature in the growth of $Al_xGa_{1-x}As$ by MOVPE or MBE.

A PL decay experiment monitors the global decrease of injected MC density. In a semiconductor slab not too thick relative to the MC diffusion length, and with moderate surface recombination velocity, this decrease can be shown to be exponential whose time constant is an effective lifetime τ expressed by the basic expression (Alferov *et al.*, 1976; 1976; Abdullaev *et al.*, 1977; Asbeck, 1977; Garbuzov *et al.*, 1977; Nelson & Sobers, 1978; Leroux *et al.*, 1987; Yablonovitch *et al.*, 1987; Basmaji *et al.*, 1988; Ahrenkiel *et al.*, 1989; Ahrenkiel & Dunlavy, 1989; Bensaïd *et al.*, 1989; Sheldon *et al.*, 1993; Zhang *et al.*, 1993; Thomeer *et al.*, 1994):

$$1/\tau = 1/\phi\tau_R + 1/\tau_{SRH} + 2S/d = 1/\phi\tau_R + 1/\tau_{NR} \quad [1]$$

In equation [1], τ_R is the band to band radiative lifetime, ϕ is the so-called reabsorption factor (Asbeck, 1977) discussed below, τ_{SRH} is the bulk non radiative lifetime, S is the interface recombination velocity (assumed to be equal for front and back surfaces) and d is the slab thickness. In the context of the present work, we are mainly concerned with the non radiative lifetime τ_{NR} ($1/\tau_{NR} = 1/\tau_{SRH} + 2S/d$), to be extracted from the effective lifetimes measured.

Figure 3 displays a log-log plot of the T dependence of the PL decay time of sample #74. τ decreases slightly with T, starting from room temperature. Below ~ 140 K, it decreases more steeply as $\sim T^{3/2}$. Below 140 K too, the integrated PL intensity, which was increasing with decreasing T, saturates, indicating that the internal efficiency η_i approaches unity.

Figure 3. Temperature dependence of the photoluminescence decay time constant of sample #74 (Si doped, n = 1x10^{17} cm^{-3}). The decay time with the GaAs substrate removed is also shown

The temperature dependence of ϕ can be evaluated as in reference (Leroux *et al.*, 1987). It is very weak and in the present work $\phi(T)$ is assumed to be constant. The $T^{3/2}$ dependence of τ and PL intensity saturation are then strong indications that MC recombination is mainly radiative below 140 K in this sample. Extrapolating this radiative limit to 300 K (dashed line in figure 3) is a first mean of evaluating the RT non radiative lifetime.

An extrapolation is not satisfactory, but a second independent method exists. Figure 3 displays also the RT lifetime measured in parts of the sample where the GaAs substrate was selectively etched. The lifeincreases 17 to 29 ns after substrate removal. Following equation [1], this increase is related to an increase in the reabsorption factor ϕ due to a strong reduction of the escape cone of photons from the back surface. PL reabsorption in time resolved experiments is a rather complicated phenomenon (Bensaïd *et al.*, 1989), but can be simplified in the case of thin slabs as those studied here. The factor ϕ with or without substrate can then be calculated following the approximations of Asbeck (1977), suitably modified to account for the geometry changes. We find that for sample #74, ϕ is equal to 7.3 and 50 for the portions with and without substrates, respectively. From equation [1], one obtains τ_R = 5 ns and τ_{NR} = 33 ns. From the extrapolation of the $T^{3/2}$ dependence, we obtain for the same sample $\phi\tau_R$ = 44.5 ns with substrate and τ_{NR} = 27.5 ns. For sample #73 (see Table 1), the same two independent methods yield $\phi\tau_R$ = 32 ns with substrate, τ_{NR} = 27.5 ns (ϕ dependence), or $\phi\tau_R$ = 39.5 ns, τ_{NR} = 23.5 ns (T dependence). The agreement between the two methods is satisfactory for both samples, and we can thus conclude that a reliable estimate of τ_R and τ_{NR} is obtained.

The radiative lifetime τ_R is equal to 1/Bn (1/Bp) in n-type (p-type) samples. The radiative coefficient B varies as $T^{-3/2}$ and Eg^2 in direct gap semiconductors. In GaAs, B ≈ 2-3x10^{-10} cm^{3}s^{-1} at 300K, though values above 1x10^{-9} cm^{3}s^{-1} have also been reported (Alferov *et al.*, 1976; 1976; Abdullaev *et al.*, 1977; Garbuzov *et al.*, 1977; Nelson & Sobers, 1978; Leroux *et al.*, 1987; Yablonovitch *et al.*, 1987; Basmaji *et al.*, 1988; Ahrenkiel *et al.*, 1989; Ahrenkiel & Dunlavy, 1989; Sheldon *et al.*, 1993; Zhang *et al.*, 1993; Thomeer *et al.*, 1994). From our data, a value of B of ~ 7x10^{-10} cm^{3}s^{-1} at 300K is deduced for $Al_{0.2}Ga_{0.8}As$. This is a reasonable value in view of the gap increase between GaAs and the alloy.

Another conclusion can be drawn: using the τ_{NR} value measured and equation [1], an upper limit to the interface recombination velocity can be obtained

assuming $\tau_{SRH} = \infty$. We get $S \leq 4.5x10^3$ cm.s^{-1} for $Al_{0.2}Ga_{0.8}As/Al_{0.85}Ga_{0.15}As$ interfaces. This particular interface is important for solar cells (Zahraman *et al.*, 1994). This rather low S value compares favorably with those reported in the revue paper of Pavesi and Guzzi (1994) concerning interfaces with a lower Al content in the window layers.

Since thickness and doping levels of the n-type samples studied are the same, *i.e.* ϕ and τ_R are equal, it is possible to extract τ_{NR} in each sample from the above determination. The results are shown in figures 4.

4d. Discussion

Figure 4a displays the inverse non radiative lifetime of our n- type DH samples as a function of the O content in the active layer measured by SIMS. The vertical error bars in figures 4 correspond to the assumption of either maximal ($S = 4.5x10^3$ cm^2) or negligible interface recombination velocities. In a doped sample, the Shockley-Read- Hall lifetime of a given trap can be approximated as:

$$1/\tau_{SRH} = g[N_T]v\sigma \qquad [2]$$

where $[N_T]$ is the trap density, g its degeneracy, v the MC thermal velocity ($v = (3k_BT/m^*)^{1/2}$) and σ the MC capture cross section.

Figure 4a. Room temperature non radiative lifetimes in n-type $Al_{0.2}Ga_{0.8}As$ as a function of the atomic O content in the layer measured by SIMS

A first observation is that the non radiative lifetime is correlated with the oxygen content, *i.e.* the higher [O], the lower τ_{NR}. But figure 4a shows that it is not possible to account for the lifetime data assuming that oxygen, or only one trap related to oxygen are involved. Such attempts are shown as dashed lines and would give an order of magnitude scatter in capture cross section. It is neither possible to account for the data with an expression such as $1/\tau_{NR} = 1/\tau' + \alpha$ [O], which would imply that recombinations are through some unknown level (s) and a second one whose density is proportional to [O]. An immediate conclusion is that an O related lifetime killer is present at low growth temperature, but is significantly suppressed at high growth T (780 °C). This is a confirmation that oxygen can give rise to multiple levels (i.e. configurations) in $Al_xGa_{1-x}As$, in agreement with the LVM spectroscopy (Alt, 1989; Skowronski *et al.*, 1990) and channeled charged particle activation (Hanna Bakraji *et al.*, 1991) studies reported in section 2b.

It is at this stage necessary to compare with our DLTS results. Table 2 and figure 2b show that the low energy traps A1 and A2 detected in our samples do not exhibit clear trends with growth temperature, i.e. also with [O]. They may correspond to equivalents in the alloy of electron traps observed in n-type GaAs. The concentration of A3 decreases slightly with growth T, but less than the global oxygen concentration. We tentatively relate this level to a complex defect involving oxygen. The concentration of A4 decreases by one order of magnitude for a growth temperature increase from 720 to 780 °C (samples #671b, #672b and #673b). This corresponds exactly to a one order of magnitude increase in non radiative lifetimes in samples #671a-#673a. Figure 4b shows that the inverse non radiative lifetime varies linearly with A4 concentration, with the least square fit line going almost through the origin.

Figure 4b. Room temperature non radiative lifetimes in Te doped $Al_{0.2}Ga_{0.8}As$ (samples #671a-673a) as a function of the A4 trap concentration measured by DLTS in layers grown at the same temperatures (samples #671b-673b)

This shows that A4 is the most efficient hole killer center in our (Al,Ga)As samples. A room temperature hole capture cross section $g\sigma_h$ of ~ 2.8 10^{-13} cm^2 is deduced from equation [2]. This is in good agreement with the value reported for the B killer center in $Al_{0.1}Ga_{0.9}As$ by Zhang *et al.* (1993), and attributed to a cascade capture *via* the 3s level of B. The signature of the B (and A) traps referenced by Zhang *et al.* (1993) is nearer to that of A3 than that of A4 (figure 2b), but the alloy composition is also different, which may explain such a discrepancy: in the hypothesis of displaced subsitutionnal O centers, with their negative U nature, the average number of the various Al (Ga) nearest neighbors configurations is of course alloy composition dependent.

Now, the question remains of the nature of the remaining lifetime killers present in the 780 °C grown samples. Indeed, if we define the internal efficiency, as usual as $\eta_i = \tau_{NR}/(\tau_R + \tau_{NR})$, RT efficiencies ranging between 0.8 and 0.9 are obtained for these samples, which is still lower than those obtained in GaAs for similar doping levels. As mentioned in the introduction, Thomeer *et al.* (1994) achieved the MOVPE growth of radiatively controlled unintentionally doped $Al_{0.1}Ga_{0.9}As$ ($\tau > 5\mu s$), but not $Al_{0.23}Ga_{0.77}As$ ($\tau < 17ns$). They tentatively assign this last low value to DX centers. We discard in our case DX centers because first the Al concentration in our samples is too low, second no DX center signature is observed in the DLTS of our Te doped samples, and finally, the lifetimes are similar in p-type and n-type samples (Table 1). In our n-type samples, the lifetime limitation may come from the residual centers (A3, for instance), remaining in spite of the high growth temperature, or from some other unknown O related traps. Similarly, in the p-type sample #73, the lifetime limitation has to originate from some unknown trap (or traps), or, if A4-like centers are involved, in a different charge state than in n-type samples.

It is interesting to compare the present lifetime data with previously published ones in $Al_xGa_{1-x}As$. Inspection of equation [1] shows that this is not straightforward: the PL decay times depend on doping, *via* τ_R and ϕ, heterostructure thickness *via* ϕ and 2S/d, Al content in the window *via* ϕ and S, etc... In some

publications, data are given corrected for surface recombination velocity, in others not. Also, most lifetimes studies are performed on non intentionally doped samples, which is not the case in the present work. A review of mainly non radiative lifetimes in the alloy have been given by Ahrenkiel and Dunlavy (1989), also quoted in the $Al_xGa_{1-x}As$ review paper by Pavesi and Guzzi (1994). Figure 5 show these data together with a survey of SRH lifetimes in GaAs grown by LPE, MOVPE and MBE (Yablonovitch *et al.*, 1987) and the record (Al,Ga)As results of (Thomeer *et al.*, 1994). Our results for x = 0.2 and a growth temperature of 780 °C compare very favorably with others.

Figure 5. Al composition dependence of room temperature non radiative lifetimes in direct gap $Al_xGa_{1-x}As$. Comparison between the best lifetimes measured in this work for x = 0.2 (open squares) with previous measurements

5. CONCLUSION

Using sufficiently high growth temperatures, it is possible to grow $Al_{0.2}Ga_{0.8}As$ alloys by MOVPE exhibiting low residual oxygen content and long

minority carrier lifetime. When grown under these conditions, internal radiative efficiencies higher than 0.8 are achieved, allowing the growth of high efficiency solar cells with this alloy (Zahraman *et al.*, 1994). Combining photoluminescence decay, secondary ion mass spectroscopy and deep level transient spectroscopy, it appears that in this alloy, a major killer center is a 0.4 eV oxygen related electron trap, whose concentration, three orders of magnitude lower than the atomic oxygen one, is significantly reduced by increasing the growth temperature. Our results confirm the multiple configuration of O in this alloy. Non radiative lifetimes higher than 30 ns can be obtained for a growth temperature of 780 °C.

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TABLE 2
Emission energies E_a relative to the conduction band and concentrations N_T of the electron traps detected by DLTS in the Te doped $Al_{0.2}Ga_{0.8}As$ samples studied ($n = 1x10^{17}$ cm^{-3})

es	**#671b**			**#672b**			**#673b**		
th T	720 °C			750 °C			780 °C		
s	E_a (eV)	N_T ($x10^{14}$ cm^{-3})	σ_0 (cm^2)	E_a (eV)	N_T ($x10^{14}$ cm^{-3})	σ_0 (cm^2)	E_a (eV)	N_T ($x10^{14}$ cm^{-3})	σ_0 (cm^2)
	0.13	0.9	$5.8x10^{-17}$	0.19	1	$5.7x10^{-15}$	0.16	1	$2.5x10^{-17}$
	0.23	1.1	$1.5x10^{-16}$	0.34	1	$1.8x10^{-12}$	0.18	0.2	$1.7x10^{-18}$
	0.28	0.5	$7x10^{-17}$	0.45	0.45	$6.5x10^{-14}$	0.45	0.4	$8.5x10^{-14}$
	0.40	1	$3.1x10^{-16}$	0.41	0.47	$8.5x10^{-17}$	0.40	0.1	$1.2x10^{-16}$