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Thermally stimulated luminescence in ion-implanted GaAs

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Abstract

We have studied the temperature dependence of the luminescence of ion implanted GaAs between 10 and 300 K. We found that at certain temperatures the luminescence increases with increasing temperature. We attribute these localised increases in the luminescence intensity to the thermal excitation of carriers out of traps, or in other words, to thermally stimulated luminescence or thermoluminescence. Model calculations which include thermoluminescence produce excellent agreement with the experimental data and allow us to determine the trap parameters. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Defects in semiconductors have been extensively studied in the past because of the important role they play in the performance of devices. Of the wide range of experimental methods which have been used to investigate defects, luminescence techniques have been in the forefront [1]. Photoluminescence (PL) is a well known and frequently applied method to study semiconductors [2]. Thermoluminescence (TL), a technique with major applications in dosimetry and archaeological dating, has also long been used to determine the fundamental properties of localised electronic states in insulators and large band-gap semiconductors [3]. TL involves the generation of metastable charges at localised states typically by illuminating the sample with radiation of energy higher than the band-gap. Information about the localised states can be gained by heating the sample (after illumination) which results in the excitation of the charges out of the traps and their subsequent recombination. Thermoluminescence occurs when this recombination is radiative. Detailed analysis of the TL peak shape can give information on the trap depth, the density of traps, the capture cross-section, etc. [4].

While insulators and large band-gap semiconductors have been extensively studied by both PL and TL in the past, other semiconductors, such as GaAs and related compounds have not been studied by TL in spite of their technological

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importance. The reason however, is clear: when the lifetime of the trapped charge in the localised states is too short to sustain an adequate carrier density after the illumination is discontinued, thermoluminescence cannot be observed. In this report, we shall discuss a method which allowed us to observe TL in GaAs and enabled the determination of some of the characteristic parameters of the traps responsible for the TL emission. The method was tested on a number of GaAs samples that contained controlled amount of defects/traps introduced by ion implantation. To enhance the luminescence efficiency of the samples, each sample also contained an $In_{0.15}Ga_{0.85}As/GaAs$ quantum well (QW) to act as an efficient *collector* of the thermally excited charge carriers. The thermoluminescence and photoluminescence of these samples were studied via emission from the QW.

2. Experimental

Typical TL experiments involve the cooling of the sample to some base temperature, T_0, at which point the sample is illuminated by above band-gap radiation for a period of time [3]. After excitation, the illumination is removed and the sample is heated at a heating rate, β, during which the thermally stimulated luminescence (i.e. TL) is collected and measured. As discussed above, materials which lack an adequate population of metastable states, i.e. materials with short trap lifetimes, do not generate measurable amount of TL, and therefore no *conventional* TL signal can be (or has been) observed from GaAs samples. To be able to study defects in these type of materials using TL, we have slightly modified the conventional TL method so as to *artificially* increase the density of carriers trapped to defects. This was achieved by using above band-gap optical excitation even during the TL measurement (i.e. heating) step. In other words, the sample is continuously illuminated by an appropriate intensity of monochromatic, above-gap radiation. Since the optical excitation is independent of time/temperature its only effect is to produce a background signal (PL) which varies slowly with temperature [1,7]. The overall signal therefore is a combination of photoluminescence created by the optical excitation, and thermoluminescence generated by the thermal excitation of carriers out of the traps. By analysing the temperature dependence of the luminescence *glow-curve* with the help of a suitable model, the defect parameters can be acquired.

The samples used in this study were grown by metal organic vapour phase epitaxy (MOVPE). Each sample contained an $In_{0.15}Ga_{0.85}As/GaAs$ quantum well grown on semi-insulating GaAs. The samples were implanted with either protons or As ions and annealed at 900°C for 30 s. After annealing the PL intensities recovered to approximately the pre-implantation level.

The samples were inserted into a cryostat (He closed cycle refrigerator) the temperature of which could be varied between 10 and 300 K. Samples were excited by a 1 mW HeNe laser operating at $\lambda_{ext} = 543$ nm. Luminescence emission from the sample was collected and dispersed by a 0.25 m spectrometer equipped with a CCD detector and controlled by a personal computer. Since all the samples contained an InGaAs QW, the emission spectrum was dominated by a single, narrow emission line corresponding to the recombination between the lowest energy electron and hole states within the QW (e1 $\rightarrow$ hh1). The temperature of the sample was slowly ramped up at 1 K/min, and the emission spectrum of the QW was measured every 1 K. Since it only took approximately 100 ms to measure the complete QW spectrum at a given temperature, each spectrum could be accurately associated with the given temperature.

3. Results

The *raw* data for an implanted GaAs sample is shown in Fig. 1, where the temperature dependence of the complete QW spectrum is shown between 10 and 100 K. The sample shown on this figure was implanted with H^+ ions (ion dose $1 \times 10^{15}\,cm^{-2}$, ion energy 1 MeV) and annealed at 900°C for 30 s. To be able to compare the experimental data with model calculations, we determined the total luminescence flux (the area under the emission line) and plotted it as a

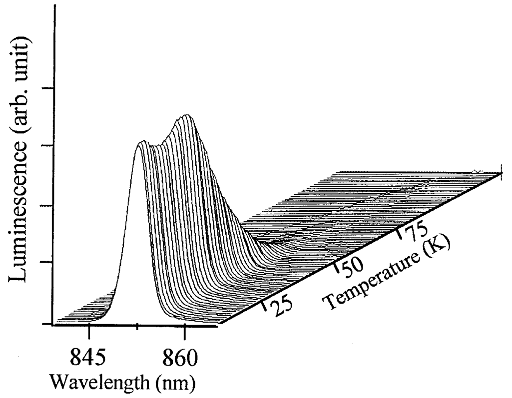

Fig. 1. Luminescence spectra of 1 MeV H implanted GaAs (dose 1×10^{15} ions/cm^2) as a function of temperature and emission wavelength.

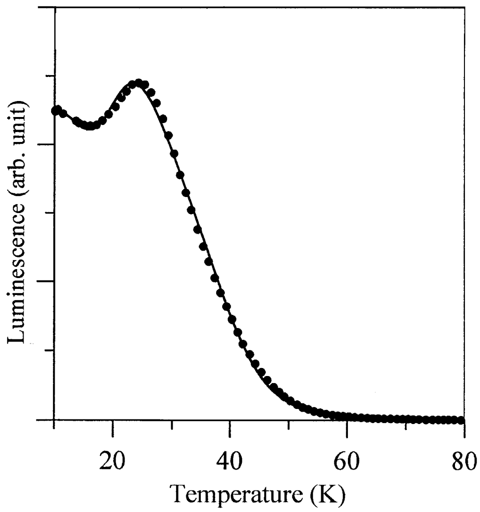

Fig. 2. Integrated luminescence flux as a function of temperature of same sample as shown in Fig. 1.

function of temperature. This quasi *glow-curve* of the same sample is shown in Fig. 2. (The function we refer to as the *glow-curve* is not identical to the *glow curve* used in the conventional thermoluminescence literature because in our experiments the signal also contains a photoluminescence component. However, for the sake of simplicity, we shall often refer to this function as quasi glow-curve or glow-curve for short.) As can be seen in Fig. 2, while the overall luminescence decreases with increasing temperature, there is a temperature range between $T = 20$ and 30 K where the luminescence briefly increases. This *hump* in the luminescence emission is the manifestation of the thermally stimulated excitation of carriers out of the traps into the conduction/valence bands followed by their subsequent recombination via the quantum well (see model calculations below). In other words, this confined increase in the luminescence emission of the QW is the TL component of the overall luminescence signal. The connection between the TL signal and the defects is further underscored by the ion-implantation dose dependence of the signal, an example of which is shown in Fig. 3. In this figure, we compare the *normalised* glow-curves of two similar GaAs samples, one implanted with $1 \times 10^{12}\,\mathrm{cm}^{-2}$ and the other with $5 \times 10^{12}\,\mathrm{cm}^{-2}$ As ions (ion energy 90 keV). Two noteworthy conclusions can be deduced from these results: (a) the characteristic temperature of the TL signal does not shift with ion dose, and (b) the higher defect density results in higher TL signal (i.e. the TL component of the total signal increases relative to the PL component. The overall signal decreases with increasing ion dose due to higher number of non-radiative defects created by the implantation). However, the relationship between the TL signal and the ion dose is not a linear relationship; in samples where

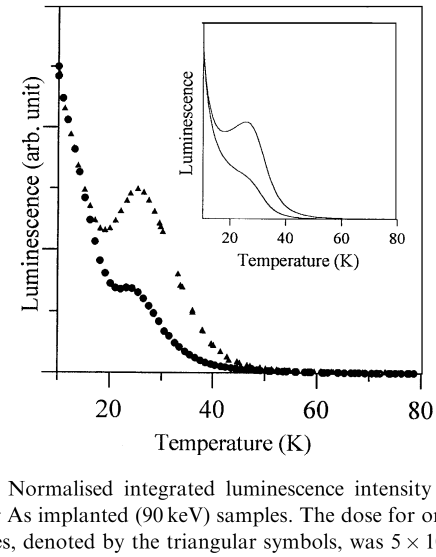

Fig. 3. Normalised integrated luminescence intensity for two similar As implanted (90 keV) samples. The dose for one of the samples, denoted by the triangular symbols, was 5×10^{12} ions/cm^2, while for the other sample, denoted by the circles, the dose was 1×10^{12} ions/cm^2. The inset shows the calculated luminescence spectra, also normalised at $T = 10$ K.

the implantation dose exceeded 10^{14}As ions/cm^2 no TL signal could be observed.

Occasionally, in a very few cases, we have also observed TL signals in *as-grown* (i.e. un-implanted) GaAs samples. In one such sample, the spectrum of which is shown in Fig. 4, two TL peaks were observed, one around $T = 15$ K and another at $T = 55$ K. The interesting aspect of this sample is that the TL peak appearing at $T = 55$ K could be eliminated by annealing the sample to 200°C while the lower energy peak remained unattenuated [5].

4. Theory

We shall now discuss a simple but revealing model to explain the above described temperature dependent luminescence signals, with the aim to understand the basic factors which influence TL emission in materials such as GaAs. The model (and the definition of the various parameters) is shown schematically in Fig. 5. In this model we assume that optical excitation generates free carriers in the GaAs barriers that surround the InGaAs quantum well. Since we do not observe luminescence from the GaAs barriers, we may assume that the free carriers are quickly captured into the quantum well or into a defect state (trapping state), or recombine non-radiatively from the barrier. We also assume that the defect level (E_t), of total density N_0, is near the conduction band of GaAs. Electrons captured into the defect state can be thermally excited out of the trap or can relax from the trap. (It is the short lifetime of the electrons in the defect level which makes conventional TL experiments fruitless in GaAs and similar materials). The experimentally observed luminescence is the result of the recombination between the electrons and holes in the quantum well.

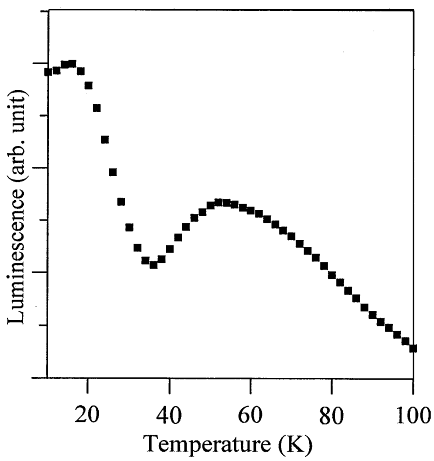

Fig. 4. Integrated luminescence flux as a function of temperature for an as-grown (un-implanted) GaAs sample.

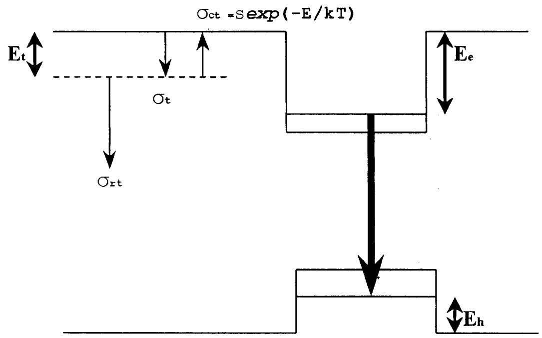

Fig. 5. Schematic illustration of model used in analysing luminescence data.

It is possible to write a set of differential equations (rate equations) that describe the flow of charge between the traps and the QW [6]. However, due to the complexity of the equations and their non-linear coupling, analytical solutions are not possible even assuming the usual approximations, such as quasi-equilibrium and weak retrapping.

To overcome this problem we have used a different approach. We have divided the luminescence emanating from the sample into two parts: luminescence originating from the optically excited carriers (i.e. PL), and luminescence arising from the thermally activated traps (i.e. TL). We assume that the effect of the traps on the *photoluminescence* is small, and can therefore be neglected when calculating the temperature dependence of the PL. In this approximation, the experimentally measured luminescence can be written as:

$$I_{\exp}(T) = \eta(T)[aN_{\text{laser}} + bN_t(T)], \tag{1}$$

where $\eta(T)$ is the quantum efficiency of the material, N_{laser} is the optical excitation rate, N_t

represents the thermal excitation rate out of the traps, and a and b are temperature independent constants. The quantum efficiency, $\eta(T)$, describes the probability that an electron in the conduction band and a hole in the valence band will recombine radiatively via the quantum well. For the GaAs/InGaAs quantum well system, $\eta(T)$ is often approximated by an Arrhenius type temperature dependence and is typically given in the following form [7,8]:

$$\eta(T) = \frac{1}{\left[1 + c_e \exp(-E_e/kT)\right]\left[1 + c_h \exp(-E_h/kT)\right]}, \quad (2)$$

where E_e (E_h) is the confinement energy for electrons (holes) in the quantum well, and c_e (c_h) is the ratio of non-radiative to radiative recombination rate for electrons (holes). This model assumes that the electrons/holes in the conduction/valance band of the barrier region are either captured by the quantum well or are *lost* due to non-radiative recombination. Carriers captured by the quantum well also have two *choices*: they can recombine radiatively (producing the luminescence emission) or can be thermally excited back into the barrier.

The thermal excitation rate, $N_t(T)$, can be calculated if we know the density of electrons in the traps, $n_t(T)$, and the frequency factor, s, since

$$N_t(T) = s n_t(T) \exp(-E_t/kT). \quad (3)$$

To obtain $n_t(T)$ in the given approximation (single defect level, weak retrapping), we can use the following equation:

$$\frac{dn_t}{dt} = \sigma_t \alpha N_{laser}(N_0 - n_t) - s n_t e^{-E_t/kT} - \sigma_{rt} n_t, \quad (4)$$

where the first term represents the capture of carriers into the traps from the conduction band, the second term is the thermal excitation of electrons out of the trap, and the last term represent the non-radiative recombination from the trap. (In Eq. (4) we have approximated the number of electrons in the conduction band by αN_{laser}, where α is a temperature independent factor). Since the optical excitation falling on the sample is constant, we can assume that the density of electrons in the traps does not vary with time, i.e. $dn_t/dt = 0$. Using this quasi-equilibrium approximation, n_t can be calculated and is given by

$$n_t(T) = \frac{\sigma_t \alpha N_{laser} N_0}{(\sigma_t \alpha N_{laser} + s \exp(-E_t/kT) + \sigma_{rt})}. \quad (5)$$

Combining Eqs. (1), (3) and (5), the temperature dependence of the total luminescence is given by

$$I_{exp}(T) = I_0 \eta(T) \left[1 + \frac{B \exp(-E_t/kT)}{1 + C \exp(-E_t/kT)}\right], \quad (6)$$

where I_0 is the luminescence intensity at very low temperatures ($T \ll 10$ K) and depends only on the laser intensity, and B and C are temperature independent functions that depend on the system parameters:

$$B = \frac{s \sigma_t \alpha N_0 b}{a(\sigma_{rt} + \sigma_t \alpha N_{laser})} \quad \text{and} \quad C = \frac{s}{\sigma_{rt} + \sigma_t \alpha N_{laser}}.$$

After substituting the expression for the radiative efficiency (Eq. (2)), the term for the temperature-dependent luminescence becomes

$$I_{exp}(T) = I_0[1 + c_e \exp(-E_e/kT)] \times [1 + c_h \exp(-E_h/kT)] \times \left[1 + \frac{B \exp(-E_t/kT)}{1 + C \exp(-E_t/kT)}\right] \quad (7)$$

5. Discussion

Before we compare the theory with the experimental results, it is important to comment on the model used. We have intentionally kept the model simple in order to concentrate on the fundamental factors that are responsible for the observed remarkable temperature dependence. Some of the assumptions used in developing our model are obviously simplistic. For example, the *single defect* postulate is clearly inaccurate since it is well known that ion implantation generates several defect states in the semiconductor or even a distribution of defect levels [9]. Similarly, the assumption that the recombination rates are temperature independent is not strictly correct [10], and likewise, the chosen quantum efficiency is also known to be a rough approximation [7].

However, our aim was to keep the model simple so as to reduce the number of fitting parameters to a minimum without constraining or distorting the underlying physical picture.

In Fig. 2 we compare the experimentally observed *glow-curve* (closed circles) with that calculated using Eq. (7) (solid line). As can be seen, the fitting is remarkably good especially considering that only a single defect state was assumed. In the calculations we used five fitting parameters, E_t, c_h, c_e, B and C, while the two other parameters (E_e, E_h,) were determined prior to the fitting using the known quantum-well layer thickness and mole fraction. For the given sample, $E_e = 35\,\mathrm{meV}$ and $E_h = 17\,\mathrm{meV}$. Using these values, the trap energy in case of the H implanted sample was determined from the fitting to be $E_t = 9\,\mathrm{meV}$. The value of the trap energy is surprisingly small given that the previously measured defect levels in ion-implanted GaAs range typically between 0.1 and 0.5 eV [9]. However, deep traps ($E_t > 0.1\,\mathrm{eV}$) cannot be detected by TL in ion-implanted GaAs due to the rapid reduction of the luminescence efficiency above approximately 100 K. The shallower traps, also created by implantation, are measurable by TL (as shown above) but are not detectable by some of the other methods, such as DLTS, because the signal from the shallow traps is swamped by that from the donor levels. It is also interesting to note that it is not possible to tell from the TL results alone whether this shallow trap is associated with the barrier or the QW. However, since some of the results were collected on samples implanted with 90 keV ions, ions that could not reach the QW in our samples [8], it is very likely that the defects are created in the barrier and not in the well.

The observed defect dose dependence of the luminescence signal (Fig. 3) can also be accounted for using the expression given in Eq. (7): in the inset of Fig. 3 we display two calculated glow-curves for two different trap densities (normalised at $T = 10\,\mathrm{K}$). The agreement between the experiment and the theory is again outstanding, especially considering that in these calculated spectra only one parameter, the density of traps, has been varied. We did not have a large enough range of ion doses to test the linearity of the observed TL signal; however, we found that while at low doses the signal was monotonic with ion dose, at higher doses the TL signal disappeared altogether. This was most likely due to the generation of unrelated non-radiative traps in the material.

Finally, we would like to comment on the role of the QW in the sample, given that the TL process (i.e. the trap) occurs in the bulk GaAs. It would seem that similar TL could be observed in bulk ion implanted GaAs without having a *built-in* QW. However, in ion implanted (bulk) GaAs the PL efficiency is very low and no luminescence has been observed at the given higher temperatures. The role of the QW is, on one hand, to act as an effective collector of electrons and holes generated in the bulk GaAs, and, on the other hand, be an efficient emitter of luminescence.

6. Conclusion

We have studied the temperature dependence of the luminescence of GaAs containing defects. We found that an important component of the temperature dependence is due to thermally stimulated luminescence. We derived an expression which can be used to analyse thermally stimulated luminescence in GaAs. By fitting the experimental data with model calculations we obtained the trap energy and other trap parameters in ion implanted GaAs.

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