Minority Carrier Recombination of Ordered Ga$_{0.51}$In$_{0.49}$P at High Temperatures

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Abstract

The minority carrier lifetime of high-quality ordered GaInP lattice matched to GaAs and the surface recombination velocity at its interface to AlInP were measured using time-resolved photo-luminescence (TRPL) in the temperature range of 77 – 500 K. The surface recombination velocity was found to be relatively low (under 500 cm/s) over the measured temperature range. The effective lifetime increased with temperature up to around 300 K, and then decreased in the 300 – 500 K range. The variations in the effective lifetime, caused by the variations in the bulk lifetime, are explained by considering the separate contributions of radiative and non-radiative recombination and their respective temperature dependencies.

GaInP lattice matched to GaAs is an important material of the III-V semiconductor family that is used in high performance photovoltaic cells in light-emitting diodes (LED's)$^2$, heterojunction-bipolar-transistors (HBT's)$^{3,4}$, and high-electron-mobility-transistors (HEMT's)$^5$. It can also be considered for photon enhanced thermionic emission (PETE), which is a type of solar converter based on electron emission from semiconductors operating at high temperature. PETE converters may theoretically reach very high efficiencies of over 50% with the right combination of high-quality semiconductor materials and optimized operating conditions$^{6,7}$. Knowledge of the material electronic properties at high temperatures is thus crucial for the design and analysis of these devices and an important input parameter for performance simulations. In particular, photovoltaic cells in concentrator systems operate at temperatures above ambient and possibly up to 100°C$^{8,9}$, whereas PETE cathodes are designed to operate at temperatures of several hundred degrees$^7$. Therefore, the electronic properties of the material and its interfaces should be characterized in the corresponding temperature range.

The bulk minority carrier lifetime and the surface recombination velocity (SRV) are typically extracted using time resolved photo-luminescence (TRPL) measurements of samples with different thicknesses. PL measurements are widely used to characterize other materials such as GaAs$^{10-13}$. However, limited information is available for Ga$_{0.51}$In$_{0.49}$P which can be grown lattice-matched to GaAs with bandgap energies between 1.8 and 1.9 eV at room temperature. The bandgap is controlled by...
the degree of CuPt-type ordering which has been intensively studied in the past\textsuperscript{14-16} and showed improved physical properties such as carrier diffusion and mobility\textsuperscript{17,18}. Disordered Ga\textsubscript{0.51}In\textsubscript{0.49}P has a bandgap energy of approximately 1.9 eV at room temperature whereas ordering reduces this value to nearly 1.8 eV. The lifetime of minority carriers in GaInP has been previously characterized\textsuperscript{19-21}, while ordered Ga\textsubscript{0.51}In\textsubscript{0.49}P\textsuperscript{19,22} has shown longer lifetimes compared to the disordered material. Most of these studies were performed only at room temperature, with the exception of Ref.\textsuperscript{23} where disordered GaInP was investigated in a temperature range of 12-300 K and Schultes et al.\textsuperscript{22} who have measured an ordered GaInP effective lifetime, but only up to room temperature and with no separating analysis for SRV and the different bulk lifetimes. Here we present TRPL measurements of ordered Ga\textsubscript{0.51}In\textsubscript{0.49}P with different thicknesses at temperatures up to 500 K. This enables us to extract the bulk recombination parameters for this high quality material\textsuperscript{24}.

Double-heterostructures of ordered Ga\textsubscript{0.51}In\textsubscript{0.49}P have been grown by metal-organic-vapor-phase epitaxy in an AIX2800-G4 reactor with an 8\times4-inch configuration. Trimethylgallium, trimethylindium, trimethylaluminium, dimethylzinc, arsine and phosphine were used as precursors for the growth. Substrates were (100) \textit{p}-GaAs with 6° off-orientation towards <111>B. Growth temperature was 640°C with pressure of 50 mbar in H\textsubscript{2} atmosphere, leading to partially ordered GaInP with a bandgap energy of 1.82 eV at 300 K. The V/III ratio was 42 for the GaInP and 85 for the AlInP barrier layers, and the GaInP was grown at a growth rate of 0.85 nm/s. The epitaxy layers were \textit{p}-type with a target doping level of \(N_A = 2.1\times10^{16} \text{ cm}^{-3}\) for the GaInP absorber and \(N_A = 5\times10^{16} \text{ cm}^{-3}\) for the AlInP cladding layers.

The structure was protected with a thin cap layer of \textit{p}-GaAs. Samples were measured with three values of the active layer thickness: 300, 600 and 1200 nm. The cladding thickness was 50 nm and the cap layer was 10 nm thick, as can be seen in Figure 1. X-ray diffraction revealed an 80° offset between the GaInP peak and the GaAs substrate peak specifically for the 600 nm sample, resulting in an elastic inplane strain of 0.038%. All other sample layers had lower strain.

The TRPL setup was described in details before\textsuperscript{25}. The wavelength of the laser is 404 nm, the beam power was adjusted to 0.7 mW and the spot size is approximately 50 \(\mu\text{m}\), which corresponds to an initial photon flux of \(1.8\times10^{13} \text{ cm}^{-2}\) incident on the sample. This resulted in an initial excess carrier concentration in the active layer of approximately \(\Delta n = 2.2\times10^{16} \text{ cm}^{-3}\), calculated for an average lifetime of 100 ns (which is reasonable based on the results reported here). The lifetime analysis was performed a few dozen nano-seconds after each laser pulse, and therefore in the low injection regime, where \(\Delta p \ll p_0\). The sample is installed in a high vacuum cryostat chamber (VPF-800, Janis Research Co.) on a sample holder that can be temperature controlled between 77 and 800 K. The photo-luminescencence (PL) emitted from GaInP is collected by a combination of a subtractive double monochromator (Triax 190, Jobin Yvon Inc.), an avalanche photo
A photodiode (APD) single photon detector (ID-100, IDQ, Inc.) and a Time-Correlated Single Photon Counter (T900, Edinburgh Instruments Ltd). The overall instrument response (full width at half maximum) is about 40 ps.

The effective lifetime is extracted for each sample at a specific temperature using an exponential fit to the measurement in the slow decay regime, as seen in Figure 2(a). The bandgap of the active GaInP layer was measured by detection of the wavelength of maximum emission, and it follows closely the theoretical values shown as a function of temperature in the inset of Figure 2(b). The variation of effective lifetime as a function of temperature is shown in Figure 2(b) for the three different samples.

![Figure 2](image)

**FIG. 2.** (a) Exponential fit for the extraction of the effective lifetime, for the 600 nm thick GaInP. (b) Measured effective lifetime of three samples for three absorber thicknesses, as a function of temperature between 77 – 500 K. Inset graph shows measured band-gaps of the GaInP layer, compared to calculated band-gap.

Two different recombination regimes are observed for each sample. The first is dominated by bulk radiative recombination at low temperatures. This is observed as an increase in effective lifetime, which is expected for radiative recombination. We find a temperature dependence very close to $T^2$ based on our calculations including photon recycling (see Equation (2)). At temperatures above 300 K, the dominant recombination is non-radiative since the effective lifetime decreases with increasing temperature.

The 300 nm thick GaInP sample demonstrates a significantly lower effective lifetime than the thicker samples. This is probably primarily due to the CuPt-ordering which has been reported in several works to occur gradually during growth\cite{26,27}, thus resulting in a potentially significant fraction of the 300 nm thick GaInP DH being disordered. Since a previous set of studied samples demonstrated a significantly shorter effective lifetime in disordered GaInP compared to ordered material, this 300 nm thick sample suffers from shorter non-radiative lifetimes originating from the partially disordered system. The results of this 300 nm thick sample are nevertheless presented here to demonstrate this effect. Another effect that becomes important when comparing samples of different thicknesses is that thinner samples have a shorter radiative lifetime due to less photon recycling effects\cite{28}. The effects of photon recycling can be quantified using a photon recycling factor $f$\cite{28,29}, which influences the effective radiative lifetime $\tau_{\text{Rad}}^{\text{eff}}$ as

$$\frac{1}{\tau_{\text{Rad}}^{\text{eff}}} = \frac{1-f}{\tau_{\text{Rad}}}$$

where $\tau_{\text{Rad}} = 1/B_{\text{Rad}}N_A$ is the radiative lifetime without photon recycling based on the Einstein coefficient $B_{\text{Rad}}$ which dictates the isotropic emission. This
The coefficient is computed using the van Roosbroeck relation:

\[ B_{\text{rad}} = \frac{1}{n_i^2} \frac{2\pi}{\hbar^2 c^2} \int_0^\infty n_s^2 \alpha(E) \frac{E^2}{e^{(E/\kappa B)}-1} dE \]  

(2)

where \( \alpha \) is the temperature dependent absorption coefficient, based on a simple bandgap shift model that ignores excitonic effects at low temperature\(^3\), \( n_s \) and \( n_i \) are the temperature dependent real part of the refractive index and intrinsic carrier concentration respectively, and the remaining parameters retain their usual meaning. The value of \( B_{\text{rad}} \) is evaluated to be \( 1.6 \times 10^{10} \text{ cm}^3 \text{s}^{-1} \) for ordered GaInP, based on spectroscopic ellipsometry data measured at room temperature\(^2\). The photon recycling factor, computed similarly to Ref.\(^{29}\), is given in Figure 3 as a function of thickness for various temperatures to demonstrate its importance in Equation (1). When accounting for the influence of thickness, it thus becomes relevant to account for the effects of photon recycling.

The effective photo-luminescence lifetime \( \tau_{\text{PL}} \) of a symmetric double heterostructure can therefore be approximated as\(^{29}\):

\[ \frac{1}{\tau_{\text{PL}}} = \frac{1-f}{\tau_{\text{Rad}}} + \frac{1}{\tau_{\text{SRH}}} + \frac{2S}{d} \]  

(3)

where \( \tau_{\text{SRH}} \) is the bulk SRH lifetime, \( d \) is the active layer thickness, and \( S \) is the interface recombination velocity. The influence of photon recycling is therefore critical to account for in this calculation, otherwise its effects will be mimicked by a higher interface recombination velocity.

Measurement of two or more identical samples, which differ only by the active layer thickness, thus allows for the extraction of the minority carrier SRH lifetime, and the corresponding interface recombination velocity, if the radiative lifetime is removed from Equation (1). The results, extracted at each temperature using Equation (3), are shown in Figure 4 only for the thicker two samples to remove the influence of partial disordered growth from the bulk lifetime. At high temperatures, the dominant recombination mechanism is the bulk non-radiative process, which causes the decrease of the overall effective lifetime, as can be seen in Figure 4(a). For temperatures close to 150 K and below, the theoretical calculations of the radiative lifetime result in shorter values than the measured effective lifetimes. This is most likely because the active dopant concentration is reduced due to incomplete ionization at such low temperatures, which leads to a reduced majority carrier concentration which in turn leads to longer radiative lifetimes. This effect has negligible influence close to and above room temperature. Additional reason for underestimating the calculated radiative lifetime, can be due to the decrease in the density of states (DOS) at low temperatures, which leads to a lower absorption coefficient, thus lower \( B_{\text{rad}} \) coefficient and higher radiative lifetime. Figure 4(b) shows that the interface recombination velocity is relatively low over the whole measured temperature range. This indicates the high quality interfaces of these heterostructures. We note that there is an increase in \( S \) with temperature above 250 K, and we attribute it to the multiphonon emission carrier capture process described in details below. It should be mentioned that...
The heterostructure barriers are adjusted to be high in order to confine the free charge carriers within the GaInP active layer. Lower barriers would result in carrier leakage out of the active layer at high temperatures, which could be mistakenly interpreted as increasing SRV with temperature\textsuperscript{33}. This effect may have small contribution at high temperatures to the rising SRV on Fig 4(b).

The reproducibility in each measurement is within 5\%.

The decrease of the non-radiative lifetime above room temperature, depicted in Figure 4(a), can be explained based on the multiphonon emission carrier capture reported by Henry and Lang\textsuperscript{34,35}. The non-radiative minority carrier lifetime in the framework of the Shockley-Read-Hall statistics\textsuperscript{36,37} can be approximated as:  

\[ \tau_{NR} = \frac{1}{\Sigma N_{T} \nu_{th}} \]  

where \( \sigma \) is the carrier capture cross section, \( N_{T} \) is the traps density and \( \nu_{th} \) is the carrier thermal velocity. Using \( \nu_{th} = \sqrt{\frac{3kT}{m^{*}}} \), where \( m^{*} \) is the effective mass, given as\textsuperscript{38} \( m^{*} = 0.051m_{0} \) and the multi phonon capture cross section \( \sigma \) proposed by Henry and Lang\textsuperscript{34}:  

\[ \sigma = \sigma_{\infty} \exp\left(-\frac{E_{\infty}}{kT}\right) \]  

where \( \sigma_{\infty}, E_{\infty} \) are the capture cross section and the thermal activation energy at high temperatures, the lifetime takes the form:  

\[ \tau_{NR} = \frac{C_{1}}{\sqrt{T \exp\left(-\frac{C_{2}}{T}\right)}} \]  

where \( C_{1} = \frac{1}{\sigma_{\infty} \sqrt{\frac{3kT}{m^{*}N_{t}}}} \) and \( C_{2} = \frac{E_{\infty}}{k} \) which agrees reasonably with the results as can be seen in the inset of Figure 4(b).

Using the parameters obtained from an optimization algorithm to obtain the best fit, and the range\textsuperscript{34,35} \( 4 \times 10^{-16} \text{ cm}^{2} < \sigma_{\infty} < 10^{-14} \text{ cm}^{2} \), we can estimate: \( E_{\infty} = 0.202 \text{ eV} \) and \( 10^{7} \text{ cm}^{-3} < N_{t} < 10^{9} \text{ cm}^{-3} \).\textsuperscript{38} The value of \( E_{\infty} \) falls in the range being reported for III-V semiconductors: \( 0 \text{ eV} < E_{\infty} < 0.56 \text{ eV} \). The values for \( N_{t} \) are small, which indicates the high material quality of GaInP.

For applications that require operation at high temperatures, such as some photovoltaic converters, the results indicate that further research should be done in order to avoid the decreasing overall bulk lifetime above room temperature. This requires

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**Figure 4** (a) Bulk SRH lifetime of the Ordered GaInP layer extracted between 300-500 K. Effective measured lifetimes and the calculated radiative lifetimes as a function of temperature between 77 – 500 K. The thinnest sample is not worth studying due to the disordering effects, thus not shown in the graph. (b) Low interface recombination velocity at all temperature range. Inset graph shows theoretical fit based on multiphonon emission carrier capture to the non-radiative lifetime behavior at high temperatures extracted from the measurements.
lowering non-radiative recombination processes in the material, which can be accomplished by minimizing the concentration of traps which act as efficient recombination centers.

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SRV [cm/s] vs Temperature [K]

Bulk SRH lifetime [ns] vs Temperature [K]

Inset: SRV vs Temperature [K]

Error bars indicate the variability in the data.