Carrier recombination dynamics in Ga$_{0.51}$In$_{0.49}$P double-heterostructures up to 500 K

Alexandre W. Walker$^{1*,a}$, Amit Shaked$^{2*}$, Ronen Dagan$^{2}$, Abraham Kribus$^{3}$, Yossi Rosenwaks$^{3}$, Jens Ohlmann$^{1}$, David Lackner$^{1}$, Frank Dimroth$^{1}$

$^{1}$Fraunhofer Institute of Solar Energy, Freiburg, 79110, Germany
$^{2}$School of Electrical Engineering, Tel Aviv University, Tel Aviv 69978, Israel
$^{3}$School of Mechanical Engineering, Tel Aviv University, Tel Aviv 69978, Israel

*authors contributed equally to this work

E-mail: alexandre.walker@nrc-cnrc.gc.ca

Abstract

The bulk minority carrier lifetime and interface recombination velocity in GaInP double-heterostructures (DHs) lattice matched to GaAs are extracted using time-resolved photoluminescence (PL) measured between 300 and 500 K. Effective lifetimes show a strong dependence on temperature for samples with insufficiently strong confinement potentials due to significant thermionic emission losses out of the DHs. An increased PL signal from the underlying GaAs layer relative to GaInP’s PL at high temperatures supports this hypothesis. The impact is a shorter recombination lifetime which can be wrongly interpreted as a high interface recombination velocity of up to 4500 cm/s at 500 K. These effects are investigated experimentally using samples of different barrier heights based on the Al-content in (Al$_x$Ga$_{1-x}$)$_{0.51}$In$_{0.49}$P. A larger barrier height is shown to inhibit thermionic emission out of the DH, thus revealing a more accurate interface recombination velocity of 300 cm/s at 500 K. The results are then used to develop a correction procedure to extract a more accurate interface recombination velocity at the barriers of the DH. Optoelectronic device simulations are used to gain insight into carrier dynamics as a function of temperature and the DH’s barrier height, and confirm a strong inhibition of the thermionic emission losses as the Al-content is maximized in the barrier.

Keywords: III-V semiconductors, double-heterostructures, photoluminescence, minority carrier recombination lifetime, interface recombination velocity

1. Introduction

The state-of-the-art in photovoltaic device research and development for both terrestrial and space applications is multi-junction solar cells composed of III-V semiconductors [1-5]. The ternary semiconductor Ga$_{0.51}$In$_{0.49}$P (hereafter GaInP), which is lattice matched to GaAs, is critical in this development due to its optimal bandgap in sharing the incident solar photon flux. Furthermore, its material quality is sufficiently good to observe strong photon recycling and luminescence coupling effects [6-8]. It is also being used for other optoelectronic applications such as red laser diodes [9-10], and in novel devices such as cathodes for photon-enhanced thermionic emission devices [11-12]. The design of such devices using TCAD presently relies on a material property database that is extensive but limited to temperatures
the radiative recombination coefficient [8,20-21]. A lack of these properties exists in the literature for temperatures above 300 K, most notably the minority carrier transport properties (i.e. diffusion length, lifetime and mobility), which have only been reported recently up to room temperature but without separate bulk and interface contributions [18]. For high temperature applications such as lasers, high concentration photovoltaics and photon-enhanced thermionic emission devices, knowledge of the minority carrier lifetime becomes critical, along with contributions from interface recombination. However, measuring lifetimes at high temperature using time-resolved photoluminescence of double-heterostructures (DHs) can result in strong carrier leakage out of the confines of the DH via thermionic emission, which complicates the interpretation of the results. This study focuses on the analysis of bulk and interface recombination in preferentially ordered GaInP (with Eg(T=300 K)~1.8 eV) DHs at temperatures up to 500 K using time-resolved photoluminescence (TRPL), coupled to optoelectronic modeling for insight into carrier dynamics. The barriers of the DHs are composed of (AlxGa1-x)0.51In0.49P, hereafter referred to as AlxGaInP, including lattice matched Al0.52In0.48P, hereafter referred to as AlInP.

The difficulty in accurately extracting minority carrier lifetimes in TRPL experiments above room temperature was recently reported for GaInP and AlxGaInP due to the limited choice of barrier materials [22]. The strong carrier leakage observed due to thermionic emission resulted in an appreciable deterioration in the observed lifetime, which was not observed in the GaAs/AlGaAs material system due to the larger barrier provided by AlGaAs for high Al contents; this is in agreement with previous work conducted up to temperatures of 670 K [23]. The typical method of extracting an effective interface recombination velocity at the DH interfaces actually mimics both thermionic emission losses and interface recombination. The true interface contribution to the lifetime is difficult to decouple accurately. A method for quantifying the thermionic emission losses to reveal the true interface recombination velocity (IRV) is therefore of interest.

This paper is structured as follows. In section 2, the structural details of the samples are described along with a description of the modeling environment. Section 3a discusses the experimental results in terms of lifetimes and interface contributions. Section 3b investigates the carrier dynamics in the DHs via numerical modeling. Section 3c then focuses on an analytical correction to the TRPL analysis to account for thermionic emission losses within the lifetime and interface extraction procedure. Finally, section 4 gives the conclusions.

2. Experimental and Theoretical Methods

2.1 Structural Details

All DHs are grown on <100> GaAs substrates using an AIX2800-G4 metal-organic vapor phase epitaxy reactor. The growth temperature was 640°C and the V/III ratio was 41, 75 and 85 for the GaInP, AlGaInP and AlInP respectively. Further details on the growth are reported elsewhere [21]. The details of each GaInP DH are summarized in Table 1 where dimethylzinc is used to dope all epitaxially grown layers. Three variations of the structure are explored (samples A-C), where variations include the composition of the barriers (using the Al content in AlxGaInP) to investigate the impact of the barrier heights of the DH on the carrier dynamics of GaInP; note that this is done in conjunction with the doping of said barrier layers due to Zn solubility and dopant activation limitations in AlxGaInP [24]. In order to extract bulk and interface recombination contributions, a set of three GaInP thicknesses is explored for AlInP barriers (sample C). For low Al-containing barriers composed of Al0.33GaInP (sample A), a different set of three thicknesses is characterized, albeit with a GaInP test layer doped to 1E17 cm-3; this set of samples is referred to as samples D. The Zn doping was subsequently revised to 6E16 cm-3 for samples A-C which primarily impacts the bulk radiative lifetime in the GaInP. However, it also impacts the barrier height due to band alignment. This is estimated to be <30 meV at 300 K from device simulations, and is assumed to be insignificant compared to the total potential barriers; in other words, this change should not impact overall carrier dynamics at the barrier. Although this forbids a direct comparison of bulk lifetimes between samples D and samples A-C, a comparison of the extracted interface recombination velocities is assumed to be reasonable. The samples are characterized using TRPL between 300 K and 500 K using a 404 nm

Table 1. Epitaxial details of the p-Ga0.51In0.49P DHs with various barriers composed of AlxGaInP. Doping concentrations are extracted from electrochemical capacitance-voltage profiling, and are limited by the Al-content of the barrier material. *Note that only samples A and D were characterized for different thicknesses. **Samples D have 30 nm thick barriers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Thickness (nm)</th>
<th>Doping (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cap</td>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>1E18</td>
</tr>
<tr>
<td>Barrier</td>
<td>x=0.35</td>
<td>x=0.7</td>
<td>x=1</td>
<td>x=0.35</td>
<td>50&quot;</td>
<td>7E17</td>
</tr>
<tr>
<td>Al,GaInP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300, 600, 1200</td>
<td>6E16</td>
</tr>
<tr>
<td>Test</td>
<td>GaInP</td>
<td></td>
<td></td>
<td></td>
<td>50&quot;</td>
<td>7E17</td>
</tr>
<tr>
<td>Buffer</td>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>1E18</td>
</tr>
<tr>
<td>Substrate</td>
<td>GaAs</td>
<td></td>
<td></td>
<td></td>
<td>450000</td>
<td>1E18</td>
</tr>
</tbody>
</table>
2.2 Numerical Modeling

The DH is simulated as a one-dimensional structure in COMSOL Multiphysics V5.0, wherein the Poisson, electron and hole current-continuity equations are solved self-consistently throughout a dynamic mesh with sub-nanometer resolution close to the interfaces. Heterojunction transport is modeled using thermionic emission with an associated interface recombination velocity (IRV). Finally, the upper boundary of the structure (GaAs/air) is modeled using a value of surface recombination velocity of 107 cm/s which is comparable to the thermal velocity of carriers [25]. Below the DH, a 2 μm GaAs buffer layer is assumed to mimic a substrate.

The Beer-Lambert law is used to model the generation of carriers in the DH assuming a 30% reflection from the semiconductor/air surface (using GaInP’s measured refractive index at 404 nm [16]; Fabry-Perot interference is assumed to be negligible. Solving the coupled set of semiconductor equations with a generation term thus sheds light on the carrier dynamics in the system, accounting for thermionic emission, Shockley-Read-Hall, radiative, Auger and interface recombination and using Fermi statistics for carrier distributions. Material properties for this system including bandgaps, density of states effective masses and electron affinities for band alignment, carrier mobilities, including bandgaps, density of states effective masses and carrier distributions. Material properties for this system and interface recombination and using Fermi statistics for carrier trapping via shallow defects [27]. The TRPL decay is fitted after said injection regime to probe the low injection range representative of GaInP recombination after shallow trap populations are assumed to be filled [27]. At this wavelength, the barriers absorb between 18-40% of the laser light depending on the composition of the barrier according to transfer matrix method simulations using a model based spectroscopic ellipsometry measurements of the AlxGaP [16]. The measured TRPL decays for this sample for a thickness of 600 nm are illustrated in Figure 1a. Nearly mono-exponential decays are observed across the entire temperature range after the initial high injection, which gives confidence that the extracted lifetimes are dominated by recombination via deep-level defects and not limited by carrier trapping via shallow defects [27]. The TRPL decay times decrease from 65 ns to 10 ns as the temperature increases to 500 K. Note that an increase in lifetime would be expected as a function of temperature if the system was dominated by radiative recombination [19,21,28]. This implies that nonradiative recombination is increasing significantly, either due to enhanced Shockley-Read-Hall recombination in the bulk or at interfaces, or that thermionic emission is increasingly dominant.

Figures 1b & c illustrate the measured TRPL decays for the medium and high barrier samples composed of Al0.35GaInP/GaInP/Al0.35GaInP and AlInP/GaInP/AlInP respectively (samples B & C in Table 1). Increasing the Al-
content to 70% (sample B) illustrates similar effective lifetimes compared to sample A at 300 K and 350 K. However, at 400 K & 450 K, lifetimes from sample B are as much as 20-40% shorter than sample A. Assuming the bulk GaInP material quality is similar between these samples, which is reasonable due to consecutive growth runs, this indicates that the increased Al-content of the barrier results in a shorter non-radiative recombination within the barrier; this is expected based on shorter TRPL lifetimes of Al$_x$GaInP DHs compared to GaInP DHs for the same doping and thickness of the inner layer [22]. As thermionic emission becomes increasingly important for increasing temperature, the TRPL lifetime is impacted by the shorter lifetime in the Al$_x$GaInP barrier. This is assumed to be a Shockley-Read-Hall mechanism in the barrier material itself for carriers that escape the DH, although it could be a trap-assisted tunneling of carriers through the barrier to the open surface. Sample B also shows an overall lower integrated PL intensity compared to sample A at temperatures above 450 K, which supports the interpretation that an additional recombination channel is activated, whereas the integrated PL intensity at 350 K and 400 K are identical for both samples A and B. Finally, at 500 K, the lifetimes suggest that thermionic emission dominates, since both samples A & B show similar lifetimes despite a significantly reduced PL intensity in sample B.

Increasing the Al-content to 100% (sample C) results in an increase in effective lifetime of 12% at room temperature and 550% at 500 K. Overall, an increase in lifetime is observed across the entire temperature range studied. This is in parallel with a significantly increased PL signal observed for all temperatures investigated. Assuming the bulk material and interfaces do not improve for the high Al-content sample, this implies that the thermionic emission is strongly inhibited. It is important to note that the interface recombination velocity shows a dependence on the doping concentration of the barrier [25,29-30], so one must interpret these conclusions carefully. Nonetheless, the lifetimes for room temperature are nearly in agreement, hinting that interface recombination is present but not significant in these test structures.

### 3.2 Decoupling Interface and Bulk Recombination

The decoupling of bulk and interface recombination pathways is performed using effective lifetime measurements on samples of different GaInP thicknesses in order to exploit the thickness dependence as

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S}{d},
\]

where $\tau_{\text{eff}}$ is the effective photoluminescence lifetime of the absorbing GaInP layer, $\tau_{\text{bulk}}$ is the bulk lifetime, d is the thickness of the GaInP layer and S is the experimentally calculated effective interface recombination velocity (IRV), which is assumed equal between both front and rear interfaces of the DH, and encompasses a thermionic emission component which depends on the confinement in the DH. Note that three samples of various thicknesses were measured for the ensuing analysis. However, due to the minority carrier lifetime’s strong dependence on carrier concentration [8,31-32], in parallel with photon recycling’s important dependence on thickness [21,33-34], the thinnest (300 nm) structure is probed at a 2-4× higher carrier concentration and thus a longer effective lifetime than the other two samples, which introduces significant errors in the analysis due to the inverse nature of the lifetime. As a result, only two samples of different thicknesses (600 and 1200 nm) were probed to decouple interface from bulk effects. Uncertainties can be extracted for bulk and interface components assuming a 5% lifetime uncertainty based on the PL measurement setup, equipment and reproducibility [21], but lifetime dependence on carrier concentration is assumed to be negligible for the thicknesses of 600-1200 nm [8].

The bulk lifetimes extracted using equation (1) are illustrated in Figure 2a as a function of temperature for samples D with Al$_{0.35}$InP barriers and samples C with AlInP barriers. A reminder that for this analysis only, the set of low barrier samples (D) have a GaInP doping of 1E17 cm$^{-3}$,
whereas the higher barrier samples (C) have the nominal GaInP doping of 6E16 cm⁻³. The impact of doping should result in a longer radiative lifetime in samples C with lower GaInP doping based on \( \tau_{rad} = 1/[(1-f)B_{rad}N_d] \), where \( B_{rad} \) is the radiative recombination coefficient of GaInP (estimated to be 1.6E-10 cm³/s⁻¹) [21], \( N_d \) is the doping concentration and \( f \) is the photon recycling factor which depends on thickness and temperature [21,33-34]. The bulk lifetime shows a steady decrease from 100 ns at room temperature to 30 ns at 500 K for the low Al₀.35GaInP barrier sample (D). The high barrier sample (C) containing AlInP also shows similar trends, but a lifetime of 366 ns at room temperature and decreasing to 20 ns at 500 K. Note here that the lifetime of 366 ns appears quite long for this doping concentration of 6E16 cm⁻³, but the impact of photon recycling can result in a lifetime of up to 500 ns for GaInP thicknesses of 1 µm [21]. An increase in bulk lifetime as a function of temperature is expected since the radiative lifetime should increase as a function of temperature [19,21,28]. This confirms that nonradiative recombination and/or thermionic emission results in the decreased effective lifetime over temperature. Overall, the reported decreasing lifetimes as a function of temperature is in agreement with previous results [22], and may be due to increasing capture cross-sections as a function of temperature [36].

The extracted effective interface recombination velocities corresponding to these samples are illustrated in Figure 2b, and show a strong increase from 300 cm/s at room temperature to 4500 cm/s at 500 K for sample D with low Al-containing barriers composed of Al₀.35GaInP. This supports the hypothesis that nonradiative recombination is becoming increasingly dominant as a function of temperature. However, thermionic emission can also be expected to play an important role depending on the Al₀.35GaInP barrier heights [22]. This hypothesis is supported by an increased PL signal originating from the GaAs buffer layer below the GaInP DH for increasing temperature for both samples. This is illustrated in Figure 2c, which shows the maximum PL signal from the GaAs wavelength range divided by the maximum signal from the GaInP wavelength range as a function of temperature (both subtracted by the background detector noise). Figure 2c illustrates that an overall 30x increase in the GaAs PL over the studied temperature range for Al₀.35GaInP barriers (sample D). The same ratio of GaAs to GaInP PL is also illustrated for the sample with AlInP barriers (sample C), and demonstrates a 3x reduction in the apparent leakage out of the DH at 500 K compared to sample D with low Al-containing barriers. Although Figure 2a shows the bulk lifetime of the high barrier sample, which is not directly comparable to the low barrier sample due to their difference in doping concentration, the calculated effective interface recombination velocity should be comparable, assuming that the GaInP doping in this range does not significantly impact the IRV [37]; note that the thermionic emission out of the DH is inherent within this experimentally extracted effective IRV. It is apparent that this effective IRV is reduced by a factor of 15 at 500 K for barriers composed of AlInP (sample C) compared to barriers composed of Al₀.35GaInP (sample D). Maximizing the Al-content in Al₀.35GaInP therefore allows for an important increase in the barrier height (discussed in the next sub-section), which exponentially inhibits thermionic emission out of the DHs; this enables a more accurate extraction of minority carrier lifetime components, namely the IRV. Note that the maximum doping of the AlInP (of 1E17 cm⁻³) may limit the benefit of increased barrier height from the increased bandgap.

3.3 Influence of Barrier Heights on Carrier Dynamics

For high temperatures, the confinement of minority carriers within the DH can become insufficient depending on the potential barrier’s height [22]. For GaInP, the choice of lattice matched materials is restricted to Al₀.35GaInP. The energy band diagram of the Al₀.35GaInP/GaInP/Al₀.35GaInP DH is illustrated in Figure 3a and b for sample D with an Al₀.35GaInP barrier and sample C with an AlInP barrier.
respectively, both for 300 K and 500 K. Note the doping of the GaInP layer is decreased from 1E17 cm$^{-3}$ in sample D to 6E16 cm$^{-3}$ in sample C, which is apparent in the overall conduction band energy, and that the thickness of the barrier is increased from 30 nm in sample D to 50 nm in sample A in an effort to reduce the thermionic emission over said barrier. For room temperature, the barrier height is $\sim$280 meV, and increases to $\sim$313 meV at 500 K for sample D with Al$_{0.35}$GaInP barriers. Increasing the Al-content to AlInP first results in an indirect bandgap close to $x$=0.57 (where the X-band has the lowest energy in the conduction band) [19], and results in an increased barrier height of 432 meV at room temperature and 451 meV at 500 K, as illustrated in Figure 3b. This increase in barrier height is primarily responsible for the inhibition of thermionic emission over the barrier, which is supported by numerical simulations (discussed below). For comparison, the confinement in a GaAs/Al$_{0.3}$Ga$_{0.7}$As DH is $\sim$350 meV at room temperature for the same doping concentrations, whereas the thermal energy is 3kBT 77 meV at room temperature and 128 meV at 500 K. Furthermore, the impact of temperature increases the barriers by as much as 5%. The extraction of a constant barrier height over this temperature range is therefore reasonable within uncertainties [22].

Simulating the quasi-equilibrium state in these devices as a function of temperature yields insight into the carrier dynamics. One example is the asymmetry of the thermionic emission at both interfaces of the DH (assuming no significant Fermi-level pinning at the semiconductor/air surface). The simulated front side and back side thermionic emission losses are illustrated in Figure 3c as a function of temperature for both Al$_{0.35}$GaInP barriers (samples D) and AllnP barriers (samples C), where the loss rate ratio is defined as the ratio of carriers escaping the DH normalized to the integrated optical generation of the structure. The simulation results indicate that leakage is significant even at room temperature for the low barrier sample, amounting to $\sim$50% (sum of front and rear sides). The thermionic emission losses become significantly worse for increasing temperature, amounting to nearly 90% out of the DH at 500 K. This shows that carriers are readily escaping the potential barriers in samples A and D with Al$_{0.35}$GaInP barriers, and even sample B to a reasonable extent, whereas they are strongly reduced in sample C when AlInP is used as the barrier material. The implication is that as significant fluxes of carriers escape the confinement of the DH, recombination events will occur within the barrier material and thus impact the PL signal. Another interesting result from modeling this system is the rear-side leakage into the GaAs buffer underlying the GaInP DH is consistently larger than the front-side leakage, and is nearly 30% higher at 500 K. This asymmetry originates from the higher carrier concentration in the front barrier compared to the rear barrier due to the 18-

### 3.4 Decoupling Thermionic Emission Losses from Interface Recombination

A term representing the thermionic emission losses must be added to equation (1) to extract a more accurate interface recombination velocity and bulk recombination lifetime. Since thermionic emission losses out of the DH and interface recombination are both loss mechanisms through a 2-dimensional surface, the leakage term can be accounted for analytically as a recombination velocity (henceforth referred to as a leakage velocity), such that it serves as a correction for the calculated effective interface recombination velocity. In other words, one can re-write equation (1) as

$$\frac{1}{\tau_{PL}} = \frac{1}{\tau_{bulk}} + \frac{2}{d} (S_0 + S_L),$$

where $S_0$ is the true interface recombination velocity and $S_L$ is the leakage velocity. The leakage velocity is dependent on temperature and barrier height as well as the carrier concentrations in the DH and barrier, both of which also depend on temperature. However, a simplification can be made by assuming the excess carrier concentration is negligible in the barrier (i.e. all photons are absorbed by the absorber layer, which may not be reasonable for the front-side barrier since it absorbs 18-40% of the incident light, but it is reasonable for the rear-side barrier), as [35]

![Image](image_url)
The impact of thermionic emission at high temperature on extracting bulk minority carrier lifetimes and interface recombination velocities using double-heterostructures is critical and can lead to significant errors if it is not properly accounted for. AlGaInP/GaInP double-heterostructure samples of different thicknesses with low and high Al-containing barriers were studied using TRPL to estimate the contribution of thermionic emission to the carrier dynamics. Increasing the potential barrier from Al0.35GaInP to AlInP decreased the experimentally extracted interface recombination velocity from 4500 cm/s to <500 cm/s at 500 K due to this increased potential barrier. A correction procedure is proposed to account for the observed carrier leakage using a supplementary leakage term modeled using thermionic emission theory. This correction procedure is useful when performing TRPL experiments on samples with limited barrier choices to extract a more accurate estimate of the true bulk lifetime and interface recombination velocity.

Acknowledgements

The authors acknowledge financial contributions by the EU European Commission FP7-Energy Project ProME3ThE2US2 ‘Production Method of Electrical Energy by Enhanced Thermal Electron Emission by the Use of Superior Semiconductors’, Grant Agreement n. 308975.

References


