CHARACTERIZATION OF RECOMBINATION PROCESSES IN EPITAXIAL THIN FILMS AND SUBSTRATES FOR ANTIMONIDE BASED THERMOPHOTOVOLTAIC DEVICES

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Characterization of Recombination Processes in Epitaxial Thin Films and Substrates for Antimonide-Based Thermophotovoltaic Devices

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Abstract - Recombination processes in antimonide-based materials for thermophotovoltaic (TPV) devices have been investigated using a radio-frequency (RF) photoreflectance technique, in which a Nd-YAG pulsed laser is used to excite excess carriers, and the short-pulse response and photoconductivity decay are monitored with an inductively-coupled non-contacting RF probe. Double-capped lattice-matched GaInAsSb organometallic vapor phase epitaxy (OMVPE) - grown layers on GaSb substrates have been used to evaluate bulk lifetime and surface recombination velocity with different layer thicknesses. With an active layer doping of 2x10^{17} cm^{-3}, effective bulk lifetimes of 95 ns and surface recombination velocities of 1900 cm/s have been obtained. As the laser intensity is increased the lifetime decreases, which may be indicative of radiative recombination under these high level injection conditions. Similar measurements have been taken on both commercially available GaSb boules as well as in-house grown quaternary GaInAsSb boules. A two-step decay is observed with the quaternary boules, an initial decay of nominally 15 ns which is relatively independent of laser intensity and a second decay of 30-60 ns which increases with decreasing laser intensity. This behavior may be indicative of free charge separation as a result of short-range ordering in the quaternary crystals. GaSb boules, both commercially available and those grown in-house, exhibit more classical characteristics.

INTRODUCTION

The optimization of minority carrier devices, including photovoltaic devices, depends heavily on the various recombination processes which exist to return an excited system to its equilibrium state. These processes include recombination at surfaces and interfaces, Shockley-Read-Hall (SRH) recombination, Auger recombination, and especially in III-V compounds, radiative recombination. An understanding of these processes is critical to the improvement of materials and the design of antimonide-based thermophotovoltaic (TPV) devices.

A radio-frequency (RF) photoreflectance technique, similar to that reported by Yablonovitch and Gmitter and Ahrenkiel, et al., is employed to measure these effects on unprocessed substrates and epitaxial layers using double heterostructure confinement layers to isolate the bulk lifetime from the interface recombination. In addition, variation of the laser pulse energy was used to characterize radiative recombination in these materials. These results are applied to TPV device structures and are compared to binary and quaternary substrates.
EXPERIMENTAL TECHNIQUE

Measurements of the bulk and surface lifetimes were made using a contactless inductively-coupled RF reflectance system. The system senses changes in the sample conductivity as carriers recombine following excitation by a Laser Photonics YQL-102 Q-switched Nd:YAG laser operating at 1.06 μm having a nominal pulse width and decay time of 13.5 ns and 5 ns, respectively.

A schematic of the RF system is shown in Figure 1. The constant-wave (CW) RF carrier signal, obtained from a variable frequency oscillator set at 410 MHz, is fed to a tuned inductor-capacitor circuit forming the RF probe. The capacitor is adjusted to obtain a critically coupled resonance at the operating frequency, i.e. the RF signal is reflected from the probe in the absence of a sample. When the coil (i.e., inductor) is brought in proximity to any conducting sample, a transformer is formed with the coil as the primary and the induced eddy currents as a 1-turn secondary. The sheet resistance of the sample is then transformed into an effective load resistance in the primary. When the system is in steady-state without photo excitation, a fraction of the RF signal is reflected according to $\Gamma = \frac{Z_L - Z_0}{Z_L + Z_0}$, due to the mismatch between the 50 Ω impedance of the measurement system and the effective load resistance, where $Z_L$ is the transformed sheet resistance, $Z_0$ is the impedance of the measurement system, and $\Gamma$ is the fraction of signal reflected (dependent upon the sample conductivity). The amplitude and phase of the reflected signal are detected by the balanced mixer and converted to a DC voltage which is then digitized.

When the sample is illuminated by the laser, excess carriers are generated causing an increase in conductivity. This modulates the reflected signal, which when demodulated by the mixer, gives rise to a transient signal whose height is proportional to the change in sample conductivity, assuming the change in sample resistivity is small compared to the system impedance. Plotting the transient response on a log scale allows the decay time of this signal to be readily extracted. Typically, more than one decay time is observed, the origin of which can be understood via modeling of the recombination processes.

Figure 1. RF reflectance system diagram
THEORETICAL ANALYSIS

Analysis of the photoreflectance decay transient was accomplished by solving the transient diffusion equation for a uniform distribution of bulk recombination centers assuming an impulse excitation. This assumption is valid for times greater than the laser pulse decay time. The boundary conditions for the solution are then a Beer's law distribution for the excess carriers at $t=0$, and surface recombination velocities (SRV) of $S_1$ and $S_2$ at the front and back surfaces. For p-type material, the excess electron concentration obeys the relations:

$$\frac{\partial n}{\partial t} = -\frac{n}{\tau_B} + D_n \frac{\partial^2 n}{\partial x^2}, \quad n(x,0) = \alpha N_{ph} e^{-ax}$$

and

$$D_n \frac{\partial n}{\partial x} \bigg|_{x=0} = S_1 n, \quad D_n \frac{\partial n}{\partial x} \bigg|_{x=W} = -S_2 n.$$ 

The preceding equations can be solved by separation of variables and results in the solution:

$$n(x,t) = e^{-\frac{t}{\tau_B}} \sum_i A_i e^{-k_i^2 D_i t} \left( \cos k_i x + \frac{S_1}{D_n k_i} \sin k_i x \right),$$

where

$$A_i = \frac{\int_0^W n(x,0) \left( \cos k_i x + \frac{S_1}{D_n k_i} \sin k_i x \right) dx}{\int_0^W \left( \cos k_i x + \frac{S_1}{D_n k_i} \sin k_i x \right) dx}.$$

$D_n$ is the electron diffusion constant, and $W$ is the thickness of the active area. The $k_i$'s are obtained by solving

$$\tan k_i W = \frac{k_i W \frac{S_1 + S_2}{D_n/W}}{\left(k_i W\right)^2 - \frac{S_1 S_2}{\left(D_n/W\right)^2}}.$$

The transcendental equation must be solved numerically to give the eigenvalues $k_i$. This solution represents a series of exponentials of amplitude $A_i$, with decay times given by:

$$\frac{1}{\tau_i} = \frac{1}{\tau_B} + k_i^2 D_n.$$

For very poor ($S >> D_n/W$) or very good ($S << D_n/W$) surfaces, the sum reduces to a single exponential with an effective decay time as:
Thus, for low SRV values the effective decay time depends on both the bulk lifetime and the sum of the SRV at each surface. For very high values of SRV the effective decay time depends only on the bulk lifetime. When one or both of the surfaces have a large $S$, the excess carriers recombine at the surface on the order of the time required for carriers to diffuse across $W$ if the diffusion length ($L_n = \sqrt{D_n \tau_B}$) is long. If $W >> L_n$, the carriers recombine by bulk recombination (e.g., at SRH centers) before reaching the surface. However, when both surfaces have low SRVs, as in the case of the double heterostructure confinement layers, the sum of the SRVs can be separated from the bulk lifetime using samples of different $W$. By plotting $1/\tau_{eff}$ versus $1/W$, the sum of the SRVs can be extracted from the slope and the bulk lifetime from the extrapolated y-intercept.

The bulk lifetime, $\tau_B$, depends on SRH, radiative, and Auger recombination. For SRH recombination, the lifetime is given by $\tau_n$ under low-level injection, and $\tau_n + \tau_p$ under high-level injection levels, where $\tau_{n,p} = \sigma_{n,p} v_{th} N_i$, $\sigma_{n,p}$ is the electron (hole) capture cross-section, $v_{th}$ is the thermal velocity, and $N_i$ is the defect density. Separation of the more conventional SRH recombination from radiative and Auger recombination is important in guiding material research and in designing optimum TPV device structures.

If radiative recombination is the dominant bulk recombination process, the following equation describes the distribution of excess carriers:

$$\frac{\partial n}{\partial t} = -G_{th} (n_0 + p_0 + n)n + \frac{\partial^2 n}{\partial x^2},$$

where $G_{th}$ is the thermal generation rate; $n_0$ and $p_0$ are the equilibrium electron and hole concentrations, respectively; and $n_i$ is the intrinsic carrier concentration. A closed form solution of the above partial differential equation is not possible in general; but if the carrier concentration is assumed to be uniform, as is the case when both surfaces are good, the resulting ordinary differential equation can be solved to give:

$$n(t) = \frac{(n_0 + p_0)n(0)}{(n_0 + p_0 + n(0))e^{t/\tau_{rad}} - n(0)}, \quad \tau_{rad} = \frac{n_i^2}{G_{th} (n_0 + p_0)},$$

where $n(0)$ is the initial concentration of excess carriers following the photo excitation. The solution is not purely exponential; in particular, for times shorter than $\tau_{rad}$ the following inverse time relationship can be obtained:
For longer times ($t > \tau_{rad}$), the solution becomes exponential with the behavior:

$$n(t) = \begin{cases} 
\frac{\tau_{rad}(n_0 + p_0)}{t}, & n(0) \gg n_0 + p_0 \\
\frac{n(0)}{1 + \frac{t}{\tau_{rad}}}, & n(0) << n_0 + p_0
\end{cases}$$

Under low level conditions, the amplitude of the asymptotic solution is proportional to the initial carrier concentration, and hence the optical excitation level. However, for high level injection, the asymptotic solution does not depend on the injection level in either the amplitude or the decay time. The complete solution is plotted in Figures 2 and 3 for $\tau_{rad} = 50$ ns, a background doping concentration of $2 \times 10^{17}$ cm$^{-3}$, and the initial excess carrier concentration ranging from $10^{16}$ to $10^{21}$ cm$^{-3}$.

Figure 2. Radiative recombination solution

Figure 3. Exponential decay time of radiative recombination solution

Figure 3 shows the effective decay time extracted from the slope of Figure 2. Before the solution asymptotically approaches the exponentials given above, the effective decay time shows a dependence on the excitation level. If the decay time is measured at a time 10 ns after the excitation pulse (to allow for a system response time of 5 ns) as a function of initial excess carrier concentration, the effective decay time decreases with increasing excitation level as depicted in Figure 4.

Auger recombination involves three carriers as well as a phonon, and is therefore a relatively weak effect except in heavily doped semiconductors or in the case of high level injection. The carrier
distribution obeys the relationship:

\[
\frac{\partial n}{\partial t} = -\frac{(n_0 + p_0 + n)(n_0 + \beta p_0 + (1 + \beta)n)n}{2n_i^2 \tau_i},
\]

where: \( \beta = \frac{\mu^2(1+2\mu)}{(2+\mu)} e^{-\frac{(1-\mu)E_g}{kT}} \), \( \mu = \frac{m_c}{m_v} \),

\[
\tau_i = \frac{3.8 \times 10^{-18} k^2 (1+\mu)^2(1+2\mu)e^{\frac{E_g + E_{ae}}{kT}}}{m_0 m_c |F_1| F_2 |kT|^{3/2}},
\]

\[
F_1 = \int u_c^* u_v \, dr, \quad F_2 = \int u_c^* u_c \, dr.
\]

\( m_c \) and \( m_v \) are the conduction and valence band effective masses, respectively, \( E_g \) is the semiconductor bandgap, \( E_{ae} \) is Auger electron excess energy, \( m_0 \) is the electron rest mass, and \( u_c \) and \( u_v \) are the conduction and valence band wavefunctions, respectively. Under high level injection, the Auger lifetime is given by \( \tau_A = 2\tau_i n_i^2 n(0)^2 \) which has an inverse dependence on the excitation level squared. Assuming \( n_i = 3 \times 10^{13} \text{ cm}^{-3} \) in 0.55 eV TPV devices and a conservative estimate for \( \tau_i \) of 50 ns, while using the same injection levels as for the radiative recombination analysis, one obtains extremely short values for \( \tau_A \) of \( 10^{-20} \) to \( 10^{-12} \) s. Thus, the effects of Auger recombination will not have an impact on the measured decay times with the present setup.

\[\text{Figure 4. Effective radiative recombination decay time at } t=10 \text{ ns}\]

The bulk recombination processes may be combined into a bulk lifetime by \( 1/\tau_B = 1/\tau_{GRH} + 1/\tau_{rad} \).

As described above, the components exhibit a different dependence on excitation level, which implies
that varying the laser pulse energy will lead to separation of the effects.

This paper reports on the experimental results of: (1) InGaAsSb quaternary layers with double heterostructure carrier confinement layers, (2) thick-emitter p/n OMVPE quaternary junctions with and without surface carrier confinement layers, and (3) bulk binary and quaternary substrate materials.

EXPERIMENTAL RESULTS

1. Quaternary Layers with Double Heterostructure Carrier Confinement Layers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Active Layer thickness, p-type doping density</th>
<th>Pulse Height (mV)</th>
<th>Initial Decay (ns)</th>
<th>Long Decay (ns)</th>
<th>Long Decay Amp (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>98-725</td>
<td>4 μm, 2x10^{17} cm^{-3}</td>
<td>128</td>
<td>25</td>
<td>185</td>
<td>16</td>
</tr>
<tr>
<td>98-723</td>
<td>6 μm, 2x10^{17} cm^{-3}</td>
<td>120</td>
<td>28</td>
<td>203</td>
<td>18</td>
</tr>
<tr>
<td>98-728</td>
<td>8 μm, 2x10^{17} cm^{-3}</td>
<td>136</td>
<td>33</td>
<td>189</td>
<td>21</td>
</tr>
</tbody>
</table>

The above structures were grown in a vertical organometallic vapor phase epitaxy (OMVPE) system with the thickness of the InGaAsSb active layer varied as indicated in Figure 5. This 0.55 eV layer is capped on the front and back surfaces with undoped AlGaAsSb layers having a bandgap of about 1 eV. An undoped GaSb layer is grown on the front surface to prevent oxidation of the high Al content cap. The resulting heterostructure provides retarding fields for the minority carriers (electrons) at both surfaces, thus significantly reducing the effect of interface recombination. Similar structures have been used in the AlGaAs / GaAs material system in the same capacity, with reported recombination velocities as low as 450 cm/s.

Table 1. Photoreflectance data from double heterostructure OMVPE InGaAsSb (see Fig. 6)
Table 1 shows the pulse heights and decay times measured on samples of three thicknesses for a 1 mJ optical pulse excitation; all other parameters are nominally the same. The measured quantities in the table are shown graphically for the 6 μm structure in Figure 6. The initial decay depends only on surface and bulk recombination and is seen to increase with active layer thickness. This decay time is plotted with the thickness on a 1/τ versus 1/W plot in Figure 7. Similar data taken

RF Photoreflectance from 98-723

![Graphical depiction of measured parameters](image)

**Figure 6.** Graphical depiction of measured parameters

![Extraction of SRV from bulk lifetime for different optical intensities](image)

**Figure 7.** Extraction of SRV from bulk lifetime for different optical intensities
with filters in place to reduce the pulse energy are also plotted in this figure with the relative intensities indicated.

At 1.06 μm, the full intensity excitation of 1 mJ corresponds to an initial excess carrier concentration of roughly $10^{20}$ cm$^{-3}$. This high level of injection (almost 3 orders of magnitude above the active layer doping of $2 \times 10^{17}$ cm$^{-3}$) necessitates the inclusion of high level injection effects on radiative and SRH recombination when interpreting the extrapolated value for bulk lifetime.

![Figure 8. Initial decay time dependence on optical intensity](image)

The initial decay times versus the relative intensity (on a log scale) are plotted for each sample in Figure 8. Due to the similarity of this data with the plot of the solution of the effective radiative recombination equation 10 ns following the laser pulse (Figure 4), as well as the absence of a slow initial decay followed by a faster decay which is typical of SRH high level injection, radiative recombination appears to be the dominant mode in high level injection. Fitting the plot of Figure 4 to the data above (Figure 9), with $\tau_{\text{rad}}$, the background doping $p_0$, and the excitation level $n(0)$ as parameters gives values of 73, 95, and 80 ns for the radiative lifetime of samples 98-725, 723, and 728, respectively. This variance in radiative lifetime, larger than the experimental error of the system ($\pm 3$ ns with filters), is attributed to the closeness of the fitting algorithm and/or run-to-run repeatability in the growth process (which can be manifested as variation in the bandgap). Since radiative recombination plays a greater role at high injection levels, the variance observed increases the error in the extrapolated bulk lifetime and SRV of Figure 7. This is also evident from the more linear trend at 8% and 17% relative optical intensity, as compared to the higher intensity data in the same figure. Thus, the most accurate value for the bulk lifetime of InGaAsSb layers and the SRV of the InGaAsSb/AlGaAsSb interface are obtained from the lowest intensity data (i.e., $\tau_y=95$ ns, $S_f=S_{S_y}=1900$ cm/s).
Three p/n junctions were grown on Te-doped GaSb substrates with an emitter (p layer) thickness of 3 \( \mu m \). One sample was measured with a bare (uncapped) InGaAsSb surface, while the other two samples had a cap of either p-GaSb or p-AlGaAsSb, as in the double heterostructure layers. Pieces of these samples were later subjected to metal deposition and patterning to form a TPV cell. These samples were subsequently characterized electrically using current-voltage (I-V) and quantum efficiency (QE) measurements. The photoreflectance data for these samples at full intensity is shown in Table 2.

**Table 2. p/n InGaAsSb junction photoreflectance data**

| Sample | Capping Layer | Pulse Height (mV) | Initial Decay (ns) | Long Decay (ns) | Long Decay Amp (%)
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>97-463</td>
<td>uncapped</td>
<td>54</td>
<td>9</td>
<td>179</td>
<td>7</td>
</tr>
<tr>
<td>97-570</td>
<td>p-GaSb</td>
<td>77</td>
<td>23</td>
<td>71</td>
<td>19</td>
</tr>
<tr>
<td>97-548</td>
<td>p-GaSb/p-AlGaAsSb</td>
<td>88</td>
<td>22</td>
<td>83</td>
<td>13</td>
</tr>
</tbody>
</table>

As expected, the uncapped device had the shortest initial decay due to the high SRV at the front surface (estimated to be on the order of \( 10^7 \) cm/s from electrical characterization). There is no significant difference in the initial decay times of the capped devices, but a higher pulse height was obtained with the GaSb/AlGaAsSb cap. It has been reported that in the presence of a junction, the effective lifetime reduces to the diffusion lifetime \( \tau_d = 4W^2/\pi^2D_n \), which in this case is about 1 ns. However, these measurements were taken with the device open-circuited, allowing the separated charges to build up in each layer, creating a retarding field a short time after the optical pulse.
The decay times measured as a function of the laser intensity using the same filters are plotted in Figure 10. Due to the low response, a decay time could not be extracted from sample 97-463 at the lowest intensity. Note that the decay times exhibit the same dependence on excitation level as the double heterostructure layers, which provides further evidence of radiative recombination being dominant in these materials.

![Graph of initial decay time vs. log(relative intensity)](image)

**Figure 10.** Photoreflectance from InGaAsSb junctions vs. Intensity

![Graph of photoreflectance from bulk GaSb vs. log(relative intensity)](image)

**Figure 11.** Photoreflectance from bulk GaSb vs. Relative Intensity

3. Bulk GaSb and InGaAsSb

The initial decay time from a bulk p-GaSb (compensated) commercial wafer from Firebird®
Figure 12. Photoreflectance from bulk GaSb

Figure 13. Photoreflectance from IGAS1

was measured as a function of excitation level and is presented in Figure 11. The dependence on intensity is opposite to that of the OMPVE InGaAsSb material, that is, the decay time increases with intensity and resembles classic SRH high level injection behavior.

Three polished InGaAsSb samples were grown by the vertical Bridgman method under the following conditions:

1. IGAS1: 720 °C, low In concentration, B₂O₃ encapsulant,
2. IGAS2: 950 °C, high In concentration, B₂O₃ encapsulant, and
3. IGAS3: 720 °C, high In concentration, salt encapsulant.

These samples have at least two distinct decays preceding a long decay (presumably due to bulk traps). The initial and second decays are shown in Figures 14a and 14b, respectively. No trend is observed in the initial decay, whereas the second decay time decreases with increasing intensity, as did the OMVPE InGaAsSb material. This result is in contrast to the bulk GaSb, where the initial decay is followed by a non-exponential tail.

Figure 14. Initial (a) and second (b) decays from bulk quaternary samples
Such behavior is characteristic of the presence of short range ordering and the separation of carriers at the type II heterointerfaces of the resulting domains. These effects have been observed\(^7\) in InGaAs materials lattice matched to InP, where transmission electron diffraction images show clear evidence of ordering on \{111\} planes (CuPt-type ordering).

**CONCLUSION**

An RF photoreflectance system was used as a noncontacting, non-destructive tool for the characterization of recombination processes in GaSb and InGaAsSb samples. With the use of double heterostructure carrier confinement layers, separation of bulk and surface effects yielded a 95 ns bulk lifetime in InGaAsSb and 1900 cm/s surface recombination velocity at the InGaAsSb/AlGaAsSb interface. Radiative recombination was found to be of particular importance in the InGaAsSb system, implying that photon recycling which leads to long effective diffusion lengths, must be considered in the design of antimonide-based TPV devices. Fitting of the decay time versus excitation level revealed that the radiative lifetime lies in the range of 73 to 95 ns. Radiative recombination was also dominant in InGaAsSb homojunctions as well as bulk substrate material. SRH recombination was observed to be dominant only in the bulk GaSb sample. Evidence of short-range ordering in bulk InGaAsSb was found in the multiple decay times present and the short initial decay.

**References**


