RF Photoreflectance Characterization of Binary and Quasi-Binary Substrates and Antimonide-Based TPV Devices

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Both starting substrates and complete TPV device structures have been characterized 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. The initial exponential transient decay, indicative of bulk recombination and surface recombination mechanisms as demonstrated previously for doubly-capped sample structures, is approximately 30-40 ns for GaSb substrates, with the decay constant increasing with increasing optical excitation (similar to Shockley-Read-Hall (SRH) high injection behavior). In the InGaAsSb quasi-binary substrates two distinct decays are observed, an initial decay transient of 15-20 ns which is independent of optical intensity and a subsequent decay of 30-60 ns which decreases with increasing optical intensity. This latter dependence on optical intensity was observed with doubly-capped epitaxial layers and is indicative of radiative recombination.

Similar measurements on quaternary device structures indicate that both the pulse amplitude and initial decay are reduced significantly without a front-surface capping layer that reduces surface recombination velocity. With reduction of the front surface recombination velocity, initial decays of 20-25 ns were obtained under open-circuit conditions. These results indicate that the RF photoreflectance technique can be useful in characterizing and qualifying starting substrates and can be used to qualify epitaxial structures as well, particularly when doubly-capped standards are available for initial understanding of recombination processes in the material systems being investigated.

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) devices1,2.
A radio-frequency (RF) photoreflectance technique, similar to that reported by Yablonovitch and Gmitter and Ahrenkel, et al., is employed to measure recombination in unprocessed substrates and epitaxial layers using double heterostructure confinement or capping layers to isolate the bulk lifetime from the interface recombination. Variation of the laser pulse energy was used to differentiate between the recombination mechanisms in these capped structures, as well as in TPV device structures and substrates (binary and quasi-binary).

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 with a nominal pulse width and decay time of 13.5 ns and 5 ns, respectively.

A schematic of the RF system as shown in Figure 1 has been described elsewhere. The system is designed to detect the sample conductivity using the probe coil (inductor) to sense currents induced in the sample by the continuous-wave (CW) RF signal from the generator. When the sample is illuminated by the laser, excess carriers are generated causing an increase in conductivity. This produces 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.
THEORETICAL ANALYSIS

Analysis of the photoreflectance decay transient in thick boule samples was accomplished by solving the transient diffusion equation for a uniform distribution of bulk recombination centers with the assumption that the RF signal penetrates the entire sample and that the optical excitation is an impulse. The latter assumption is valid for times greater than the laser pulse decay time. The boundary conditions for the solution follow a Beer's law distribution with \( N_{ph} \) incident photons/cm\(^2\) for the excess carriers at \( t=0 \), a surface recombination velocity (SRV) of \( S_p \) at the front surface, and a vanishing excess carrier concentration at the back surface for a semi-infinite solid. For p-type material with bulk lifetime \( \tau_B \) and electron diffusion constant \( D_n \), the excess electron concentration obeys the relations:

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

and \( \frac{\partial n}{\partial x} \bigg|_{x=0} = S_p n, \quad n(\infty, t) = 0 \),

where \( \alpha \) is the absorption constant of the monochromatic light. The preceding equations are simplified by substituting

\[
n(x, t) = f(x, t) e^{-\frac{t}{\tau_B}}
\]

in the continuity equation, thus giving

\[
D_n \frac{\partial^2 f}{\partial x^2} = \frac{\partial f}{\partial t}
\]

Solution of this equation (subject to the boundary conditions given above) is accomplished through the Laplace transform in the time domain as follows:

\[
\mathcal{L} \left[ \frac{\partial f(x,t)}{\partial t} \right] = sF(x,s) - f(x,0+) = sF(x,s) - \alpha N_{ph} e^{-\alpha x}
\]

\[
D_n \frac{d^2 F(x,s)}{dx^2} - sF(x,s) = -\alpha N_{ph} e^{-\alpha x}
\]

\[
\Rightarrow F(x,s) = Ae^{-\lambda x} + Be^{\lambda x} + \frac{\alpha N_{ph}}{s - \alpha^2 D_n} e^{-\alpha x}, \quad \lambda = \sqrt{s \frac{s}{D_n}}
\]

The value of the constant B must be 0 for the solution to remain finite throughout the semi-infinite slab and the value of the constant A can be obtained by applying the boundary condition on the front surface, giving
\[ F(x, s) = \frac{\alpha N_{ph}}{s - \alpha^2 D_n} \left( e^{-\alpha x} \left( \frac{S_R + \alpha D_n}{S_R + \lambda D_n} e^{-\lambda x} \right) \right) . \] (5)

Integrating \( F(x, s) \) over the thickness to obtain the total free carrier concentration in the Laplace domain, i.e. \( G(s) \), yields

\[ G(s) = \int_0^\infty F(x, s) dx = \frac{N_{ph}}{s - \alpha^2 D_n} - \frac{N_{ph} \alpha (S_R + \alpha D_n)}{\sqrt{s}} \left( \frac{S_R}{\sqrt{S_R + \frac{S_R}{\sqrt{D_n}}}} \left( s - \alpha^2 D_n \right) \right) , \] (6)

which has poles at \( s = 0, s = \alpha^2 D_n, \) and \( \sqrt{s} = -S_R/\sqrt{D_n} \). This expression can be rewritten using partial fraction expansion as

\[ G(s) = \frac{A}{\sqrt{s}} + \frac{B}{\sqrt{s} + \frac{S_R}{\sqrt{D_n}}} \]

\[ A = \frac{N_{ph} (S_R + \alpha D_n)}{\alpha S_R \sqrt{D_n}} , \quad B = \frac{N_{ph} \alpha D_n^{3/2}}{S_R (S_R - \alpha D_n)} . \] (7)

Taking the inverse Laplace transform, the integrated carrier concentration is

\[ N(t) = \left[ \frac{S_R}{\alpha (S_R - \alpha D_n) \sqrt{\pi D_n t}} - \frac{\alpha D_n}{S_R - \alpha D_n} \frac{S_R^{3/2} t}{D_n} \text{erfc} \left( \frac{t}{D_n} \right) \right] N_{ph} e^{-\frac{t}{\tau_p}} . \] (8)

For low and high values of SRV, the above expression simplifies to the following

\[ N(t) = \begin{cases} 
N_{ph} e^{-\frac{t}{\tau_p}}, & S_R = 0 \\
\frac{N_{ph}}{\alpha \sqrt{\pi D_n t}} e^{-\frac{t}{\tau_p}}, & S_R \to \infty \end{cases} . \] (9)

For intermediate values of SRV, the solution can be simplified for \( t >> D_n/S_R^2 \) using the approximation

\[ \text{erfc} \ x = \frac{e^{-x^2}}{x \sqrt{\pi}} \quad \text{for} \ x >> 1 \] (10)
to give

\[ N(t) = \frac{N_{ph}(S_R + \alpha D_n)}{\alpha S_R} \cdot \frac{t}{\pi D_n t} \]  \hspace{1cm} (11)

By plotting \( \ln[\sqrt{T}N(t)] \), a linear plot is obtained with a slope of \(-1/\tau_B\) and, extrapolating back to the y-axis, a y-intercept of

\[ \ln \left( \frac{N_{ph}(S_R + \alpha D_n)}{\alpha S_R \sqrt{\pi D_n}} \right) \]

\hspace{1cm} (12)

Thus, it is possible to extract the bulk lifetime and SRV from the decay transient through this analysis.

For passivated samples (i.e. SRV < 10⁴ cm/s) the expressions in Eqs. (11) and (12) are applicable to the long decay of the transient. In this case, the analysis of the initial decay is achieved by first integrating the transient diffusion equation, Eq. (1), over the thickness of the sample to give

\[ D_n \frac{\partial n(x,t)}{\partial x} \bigg|_0^\infty - \frac{N(t)}{\tau_B} = \frac{dN(t)}{dt} \]  \hspace{1cm} (13)

Substituting the boundary conditions of Eq. (1) for the first term results in

\[ -S_R n(0,t) - \frac{N(t)}{\tau_B} = \frac{dN(t)}{dt} \]  \hspace{1cm} (14)

from which the instantaneous exponential decay time may be obtained by dividing by \( N(t) \). Evaluating the result at \( t=0 \) gives the following expression for the initial decay:

\[ \left. \left( \frac{-1}{N(t)} \frac{dN(t)}{dt} \right) \right|_{t=0} = \frac{S_R n(0,0)}{N(0)} + \frac{1}{\tau_B} \]  \hspace{1cm} (15)

From the initial condition in Eq. (1) and the fact that \( N(0) = N_{ph} \), the initial decay time can be expressed as

\[ \frac{1}{\tau_{eff}} = \alpha S_R + \frac{1}{\tau_B} \]  \hspace{1cm} (16)

Thus, for passivated samples the initial decay time will depend on the bulk lifetime, the SRV, and the absorption constant, i.e. wavelength of light, whereas the long decay time will depend on the bulk lifetime; the effect of bulk traps have not been considered here.
The bulk lifetime, \( \tau_b \), depends on SRH, radiative, and Auger recombination. Separation of the more conventional SRH recombination from radiative and Auger recombination is important to guide material research and to design optimum TPV device structures. For SRH recombination, the lifetime is given by \( \tau_b \), under low-level injection, and \( \tau_b + \tau_r \) under high-level injection levels, where \( \tau_{np} = \sigma_{np} v_{th} N_t \), \( \sigma_{np} \) is the electron (hole) capture cross-section, \( v_{th} \) is the thermal velocity, and \( N_t \) is the defect density. The full intensity of the 1.06 \( \mu \)m laser is 1 mJ, which results in 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.

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

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

where \( G_{th} \) is the thermal generation rate; \( n_0 \) and \( p_0 \) are the equilibrium electron and hole concentrations, respectively; and \( n_t \) 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 (low SRV) on a thin epitaxial layer, the resulting ordinary differential equation can be solved to give:

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

where \( n(0) \) is the initial concentration of excess carriers following the photo excitation. A similar analysis for the thick samples requires a numerical solution as the spatial dependence is significant.

Auger recombination involves three carriers and is therefore a relatively weak effect except in heavily doped semiconductors or in the case of high level injection. Under high level injection, the Auger lifetime is approximated by \( \tau_a = 2\tau_v n_t^2 n(0)^2 \) which has an inverse dependence on the excitation level squared. Assuming \( n_t = 3 \times 10^{13} \) cm\(^{-3}\) in 0.55 eV TPV devices and a conservative estimate for \( \tau_v \) of 39 ms, extremely short values for \( \tau_a \) of \( 10^{16} \) to \( 10^8 \) s are obtained for similar injection levels as for the radiative recombination analysis. Thus, the effects of Auger recombination will not impact the measured decay times with the present setup.

The bulk recombination processes may be combined into a bulk lifetime by \( \frac{1}{\tau_b} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{rad}} \). Since these components exhibit a different dependence on excitation level, varying the laser pulse energy can differentiate between SRH and radiative
recombination.

This paper reports on the experimental results with uncapped GaSb and InGaAsSb boule samples. A comparison is made with capped and uncapped organometallic vapor phase epitaxy (OMVPE) grown InGaAsSb devices for which electrical measurements have been taken.

RESULTS WITH CAPPED AND UNCAPPED QUATERNARY OMVPE DEVICE STRUCTURES

Three p/n junctions were grown on Te-doped GaSb substrates with an emitter (p-layer) thickness of 3 μm. One sample had a bare (uncapped) InGaAsSb surface, while the other two samples had a cap of either p-GaSb or p-AlGaAsSb to provide a retarding field for minority carriers at the surface. The 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 1.

A typical waveform of the photoreflectance decay transient is shown in Figure 2 along with a graphical depiction of the parameters measured. Analysis of thin active layer samples presented previously indicates that the initial decay depends only on surface and bulk recombination. As expected from the electrical data, the uncapped device had the shortest initial decay due to the high SRV at the front surface (estimated to be on the order of 10⁷ cm/s from electrical and optical 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 (\( W=3 \mu m \)) is about 1 ns. However, the data in Table 1 were measured with the device open-circuited, allowing the separated charges to build up in each layer within a few nanoseconds, creating a retarding field a short time after the optical pulse.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capping Layer</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>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-AlGaAsSb</td>
<td>88</td>
<td>22</td>
<td>83</td>
<td>13</td>
</tr>
</tbody>
</table>
The decay times measured as a function of the laser intensity using neutral density filters to reduce the optical intensity are plotted in Figure 3. 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 an inverse dependence on excitation level. This behavior was also obtained in doubly capped OMVPE InGaAsSb structures which showed a good fit to the radiative recombination model yielding radiative lifetimes on the order of 95 ns. This similarity in dependence upon optical intensity provides further evidence of radiative recombination being dominant in these materials.

**EXPERIMENTAL RESULTS: BINARY AND QUASI-BINARY SUBSTRATE MATERIALS**

The initial decay time from a commercial bulk p-GaSb (compensated) wafer from Firebird® (FB1), and Rensselaer grown bulk compensated p-GaSb (GaSb15) and uncompensated p-GaSb (GaSb17) were measured as a function of excitation level and is presented in Figure 4. The dependence on intensity is opposite to that of the OMPVE InGaAsSb material in each case; that is, the decay times increase with intensity and resembles classic SRH high level injection behavior, even though the decay times are of comparable value.

Three InGaAsSb quasi-binary samples (IGAS1, IGAS2, IGAS3) were grown by
the vertical Bridgman method from GaSb and InAs sources and polished at Rensselaer\textsuperscript{9,10} in a manner similar to that of the GaSb15 and GaSb17 samples. Comparing the transients of the quasi-binaries (Figure 6) with those of the binary samples (Figure 5) it is evident that these samples have at least two distinct decays (plotted in Figures 7a and 7b) preceding a long decay (latter presumably due to bulk traps). No trend is observed in the initial decay, whereas the second decay time decreases with increasing intensity, as did the OMVPE InGaAsSb material.
Such behavior can be characteristic of the presence of ordering and the separation of carriers at the type II heterointerfaces of the resulting domains. These effects were observed in InGaAs materials lattice matched to InP, where transmission electron diffraction images show evidence of ordering on \{111\} planes (CuPt-type ordering). However, such ordering does not appear to be present in these antimonides based upon recent X-ray diffraction images.

Three additional quasi-binary samples were prepared with differing amounts of mixing prior to crystal growth. As before, two decays were observed preceding a long exponential tail. The initial and second decay times are shown in Figure 8a and 8b. For the relatively unmixed sample, the initial decay does not show a significant dependence on laser intensity while the second decay shows a strong inverse dependence similar to the previous quasi-binary samples. As the mixing time is increased, the initial decay shows increasing dependence on intensity. One hypothesis is that well mixed samples should be homogenous and exhibit no ordering. While this data supports the assumption, further
FIGURE 8. Initial (a) and second (b) decays from quasi-binary samples with different mixing times

material characterization is required for corroboration.

CONCLUSION

An RF photoreflectance system was used as a non-contacting, non-destructive tool for the characterization of recombination processes in GaSb and InGaAsSb samples. The system was applied to both TPV device structures and starting material. The strong difference in pulse height and decay time between capped and uncapped devices demonstrates the system's ability to discriminate surface passivation. In both the InGaAsSb device structures and the InGaAsSb quasi-binary material a dependence on optical intensity was observed which is indicative of radiative recombination being dominant. In contrast, in the GaSb boule material the optical intensity exhibited SRH recombination behavior.

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