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Time-Resolved Photoluminescence and Photovoltaics

W.K. Metzger, R.K. Ahrenkiel, P. Dippo, J. Geisz, M.W. Wanlass, and S. Kurtz

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W. K. Metzger, R. K. Ahrenkiel, P. Dippo, J. Geisz, M. W. Wanlass, S. Kurtz
National Renewable Energy Laboratory (NREL)
1617 Cole Blvd, Golden, CO 80401; Wyatt_Metzger@nrel.gov

ABSTRACT

The time-resolved photoluminescence (TRPL) technique and its ability to characterize recombination in bulk photovoltaic semiconductor materials are reviewed. Results from a variety of materials and a few recent studies are summarized and compared.

1. Objectives

TRPL is a contactless method to characterize recombination and transport in photovoltaic materials. In this article we outline the theory, strengths, and weaknesses of the technique, and exemplary studies.

2. Technical Approach

TRPL is measured by exciting luminescence from a sample with a pulsed light source, and then measuring the subsequent decay in photoluminescence (PL) as a function of time. A wide variety of experimental configurations can accomplish this. Most experiments excite the sample with a pulsed laser source, and detect the PL with a photodiode, streak camera, or photomultiplier tube (PMT) set up for up-conversion or single-photon counting. The system response time, wavelength range, sensitivity, operational difficulty, and cost vary widely for each configuration.

We most often use the single-photon counting technique. In this technique, the laser pulse is split into two beams with a beam splitter. The first beam triggers a time-amplitude converter (TAC) to start ramping up a voltage. The second beam excites PL from the sample. Some of the PL is passed through a long pass filter and monochromator onto a PMT. The first emitted photon to be detected by the PMT sends a stop signal to the TAC, and the TAC voltage is read and stored by a pulse height analyzer. The experiment is repeated at the repetition rate of the laser, typically 250,000 times per second with our new laser system. The optical system is configured so that a single photon is detected on the order of once every 200 pulses. Given these statistics, after a collection time on the order of 10 minutes, a histogram with on the order of 10^6 photon counts vs. time is generated that corresponds to the PL decay of the sample. The advantages of this technique are that, with appropriate electronics, the system response time is on the order of 30 ps to 100 ps, the sensitivity is excellent, and experimental versatility and sample throughput are fairly high. With this system, we have studied the PL decay of CdTe, CIGS, GaAs, InGaAsP, GaInP, GaAsN, GaInAsN, GaNP, GaInN, amorphous Si, carbon nanotubes, III-V quantum dots, and measured lifetimes ranging from tens of picoseconds to tens of microseconds. Indirect bandgap, such as Ge and Si, do not emit enough light to be suitable for TRPL.

The PL intensity is proportional to the rate of radiative recombination. For direct bandgap recombination, the radiative recombination rate per unit volume, R_{rad}, is given by

$$R_{rad}(t) = B\left[p(\mathbf{r},t)n(\mathbf{r},t) \quad p_0(\mathbf{r})n_0(\mathbf{r})\right], \tag{1}$$

where B is the radiative recombination coefficient and p_0 and n_0 are the equilibrium hole and electron concentrations, respectively. For p-type material, $p_0 >> n_0$ and substitution of $p = p_0 + \quad p$ and $n = n_0 + \quad n$ into Eq. 1 gives

$$R_{rad}(t) = B\left[p_0(\mathbf{r}) + \quad p(\mathbf{r},t)\right] \quad n(\mathbf{r},t), \tag{2}$$

where $\quad p$ and $\quad n$ are the excess hole and electron concentrations, respectively. In low-injection conditions, $\quad p << p_o$, Eq. 2 indicates that the rate of radiative recombination is linearly proportional to the number of minority carriers. So, the PL decay tracks minority carrier recombination, even if this recombination is due primarily to nonradiative processes such as Shockley-Read-Hall (SRH) or Auger recombination. In high injection conditions, $\quad p >> p_o$ and the PL intensity is proportional to p^2. Although more complicated in form, the PL intensity still tracks the decay of excess carriers.

Minority carriers can decay via midgap states created by surface states, grain boundaries, structural defects, point defects, and impurities, or by radiative recombination, Auger recombination, and other processes. By varying sample temperature, sample dimensions, and injection levels, and conducting ancillary experiments, we can use TRPL to help determine which recombination processes are dominant. However, the technique can rarely pinpoint the source of SRH type recombination.

3. Results and Accomplishments

For III-V and III-V-N materials, lifetime studies are typically conducted on double heterostructures (DHs) that confine excess carriers to the material layer of interest, passivate the surfaces of this layer, and simplify analysis. Figure 1 indicates low-injection lifetime measurements on n- and p-type InP/$In_{0.53}Ga_{0.47}As$/InP DHs for a wide range of carrier concentrations [1,2]. The figure includes lifetime data from resonant coupled photoconductive decay and TRPL by upconversion. A combination of SRH, radiative, and Auger recombination contribute to the overall lifetime. Although each of these processes is quite complex, in ideal conditions and low injection, the measured lifetime, , can be written as

$$= (A + B_{eff}N_o + CN_0^2)^{-1}. \tag{3}$$

The three terms on the right-hand side correspond to SRH, radiative, and Auger recombination, respectively. N_o is the majority carrier concentration, A is the inverse of the SRH

lifetime, B_{eff} is the radiative recombination coefficient corrected for photon recycling, and C is the Auger

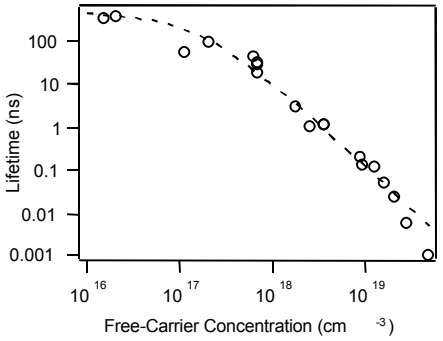

Fig. 1. Lifetime vs. Carrier Concentration for $In_{0.53}Ga_{0.47}As$.

coefficient. The fit shown in Fig. 1 gives $_{srh}$ = 500 ns, $B_{eff}=2x10^{-11}$ cm^3/s, and $C=8x10^{-29}$ cm^6/s, and shows that the Auger, radiative, and SRH recombination are dominant for high, moderate, and low carrier concentrations, respectively. This behavior is typical for low-bandgap III-V materials. By mapping out lifetime vs. carrier concentration in this form, one can understand the recombination mechanisms that limit lifetime, and determine the ideal carrier concentrations for solar cells.

The addition of nitrogen into III-V materials changes recombination characteristics appreciably. Lifetimes typically fall in the range of 100 ps to 10 ns, with the larger lifetimes limited to very dilute N concentrations. The lifetimes do not change substantially with injection, and the radiative efficiency is very poor; this is consistent with SRH type recombination. Figure 2 shows lifetime data from a study conducted on $GaN_{0.02}P_{0.98}$ epilayers grown by MOCVD [3]. It was found that certain growth conditions that favored better device performance incorporated less C and H into the $GaN_{0.02}P_{0.98}$, and less C and H was correlated with longer lifetimes. The latter was also found for GaAsN. Consequently, it appears that C and H help form a recombination center in both GaNP and GaAsN.

CdTe and CIGS cannot be incorporated into DH structures suitable for lifetime measurements. Consequently, TRPL is typically measured on either completed devices or absorber layers with a free surface.

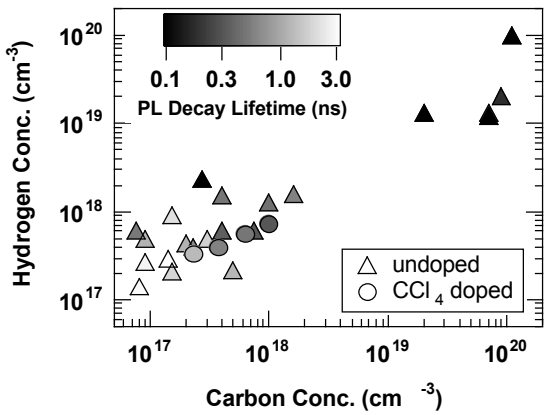

Fig. 2 Lifetime vs. C and H Concentration in $GaN_{0.02}P_{0.98}$.

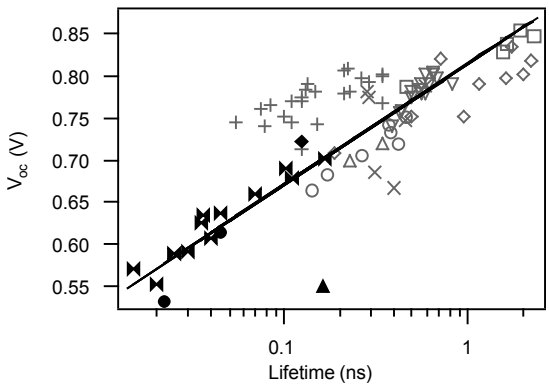

Fig. 3. Voc vs. Lifetime for CdTe Solar Cells.

The PL decay times on CIGS absorber layers are on the order of hundreds of ps, but generally improve to several nanoseconds with the addition of CdS and ZnO. CdTe thin films generally have PL decay times that range from several hundred picoseconds to 1 or 2 ns. The fast lifetimes and poor radiative efficiency are consistent with SRH type recombination; but the inability to control the structures makes it difficult to separate out grain boundary, surface, and bulk recombination. The PL decay time is often correlated with open-circuit voltage (V_{oc}), even though many other variables can contribute to V_{oc}. Figure 3 shows lifetime data for more than 80 CdTe solar cells [4].

4. Conclusions

TRPL is a contactless technique that has been used to characterize and understand recombination in numerous photovoltaic materials. III-V, III-V-N alloys, and polycrystalline films all show consistent and distinct recombination characteristics.

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