SCANNING PHOTOCURRENT MICROSCOPY IN SEMICONDUCTOR NANOSTRUCTURES

RION GRAHAM and DONG YU*
Physics Department, University of California, Davis, CA 95616, USA
*yu@physics.ucdavis.edu

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Scanning photocurrent microscopy (SPCM) is a powerful experimental tool used to investigate spatially resolved optoelectronic properties of semiconductors and their nanostructures. Raster-scanned laser excitation generates a position-dependent photocurrent map from which carrier diffusion length, electric field distribution, doping concentration and more can be explored. In this review, we will briefly discuss the history of the technique, the theory behind locally injected carrier transport in semiconductors, the SPCM experimental setup, and recent applications of SPCM in semiconductor nanostructures. Particularly, we have shown that the minority carrier diffusion length can also be obtained by SPCM in two-dimensional semiconductors and that the local excitation can result in an internal electric field because of the difference in electron and hole mobilities.

Keywords: Scanning photocurrent microscopy; nanostructures; charge transport; charge recombination; photocurrent.

1. Overview

Scanning photocurrent microscopy (SPCM) is a powerful experimental technique that provides a wealth of information on semiconductors, including internal electric field, charge transport, and recombination dynamics. Generally, this technique can be considered as one member of the scanning probe microscopy (SPM) family. Unlike other SPM techniques such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), electrostatic force microscopy (EFM) and scanning gate microscopy (SGM), SPCM exploits a focused light beam instead of a probe tip as a local excitation source. The focused beam locally excites a semiconductor into non-equilibrium, from which point the injected electrons and holes go through a relaxation process which includes thermal relaxation, recombination, diffusion, and drift in the semiconductor. If these injected charge carriers can reach the nearby electrodes before they recombine, a photocurrent is measured. This technique yields a spatial mapping of photocurrent as a function of excitation location and provides...
rich information that can be used to explore optoelectronic properties of semiconductors.

In the last decade, this technique has been actively used in analyzing semiconductor nanostructures. In particular, it has been used to characterize semiconductor nanowires (NWs),\textsuperscript{1–4} carbon nanotubes,\textsuperscript{5–7} graphene,\textsuperscript{8–11} and colloidal semiconductor quantum dots (QDs).\textsuperscript{12} Furthermore, the technique has provided a range of quantitative information, including minority carrier diffusion length, internal electric field distribution, doping concentration profiles, and photothermal properties in semiconductor nanostructures. Though the experimental SPCM investigation of semiconductor nanostructures has been abundant, a review paper has not yet been published on this topic. In addition, the analysis of SPCM data is often not trivial as the observed photocurrent can originate via several different mechanisms. This brief review will focus on the principles of SPCM analysis and recent applications of this technique on semiconductor nanostructures. We will first review briefly the historical development of SPCM in Sec. 2, then discuss the basic theory governing transport and recombination of local excitation in Sec. 3. We will subsequently present the configuration of the SPCM experimental setup in Sec. 4 and examine recent experiments using SPCM to analyze semiconductor nanostructures in Sec. 5. Finally, we will provide a conclusion and an outlook.

\section{Brief History}

The concept of scanned excitation on a semiconductor for quantitative determination of material properties is hardly new. In 1949, Haynes and Shockley published results\textsuperscript{13} of an experiment in which a probe is scanned over the surface of $n$-type germanium, recording current as a function of time for several locations. From these data, they were able to deduce the carrier mobility and an estimate of the hole lifetime. The wealth of information produced from this relatively simple experimental setup was sufficient to generate interest and served as a conceptual predecessor to scanning measurements that followed.

Just five years later, in 1954, Van Roosebroeck published a paper\textsuperscript{14} on the determination of lifetimes and surface recombination velocities for various excitation sources into a $p$–$n$ junction. Both theoretical and experimental considerations were made for each calculation, providing researchers with a means of deducing relevant parameters from experimental data. Despite the significance of this publication, it was not explicitly designed for scanning experiments. However, in 1983, Marek published a paper entitled “Light-beam-induced current characterization of grain boundaries”,\textsuperscript{15} that presented a quantitative theory for the evaluation of photocurrent profiles at grain boundaries. Comparison is made between the derived theory and experiment, with consideration given to material absorption cross section, wavelength, and laser spot size, showing excellent agreement, giving experimentalists a means of analyzing such data in a quantitative and universal way. This paper
signifies the relative popularity of such measurements at the time and demonstrates that the scanning technique had become well established by this point.

Having matured as a viable method of measuring both fundamental material properties, as well as device structure characteristics, such scanning measurements have become a common tool in the semiconductor industry. Also known as optical beam-induced current (OBIC), everything from poly-crystalline silicon grain densities to defective junctions in integrated circuits are measured.\textsuperscript{16}

3. Theory on the Charge Transport and Recombination Under Local Excitation

Essential to the understanding of data generated by the SPCM technique is a model of the generation, subsequent motion, and collection of locally injected free carriers in the structure being studied. The necessary equations are well established for bulk semiconductor materials and serve as the basis for analysis in SPCM experiments. The goal of the following is to derive the photocurrent decay length one measures with SPCM in terms of fundamental semiconductor parameters; specifically, the minority carrier mobility and lifetime. We will first present a simple model that only considers the minority carrier diffusion in both one — (Sec. 3.1) and two-dimensional (Sec. 3.2) materials and then justify this simple model in practical devices (Sec. 3.3). Finally, we look beyond the simple model to consider more complicated cases (Sec. 3.4).

One begins with the charge continuity equation, written as

\[ \frac{1}{e} \frac{\partial \rho}{\partial t} = G - R - \frac{1}{e} \vec{\nabla} \cdot \vec{J}, \]

where \( \rho \) is the charge density, \( G \) is the carrier generation rate, \( R \) is the carrier recombination rate, \( e \) is the positive fundamental electronic charge, and \( \vec{J} \) is the current density. In order to solve this equation analytically, certain simplifying assumptions must be made. The first assumption we will make is that there is only one carrier type. For the sake of clarity, we have chosen to label them as holes. This assumption seems to deviate from the real case, as one always injects the same amount of electrons and holes. However, as we will justify in Sec. 3.3, in many cases, the photocurrent is dominated by one type of carrier (minority carrier). Second, we will assume that there is no electric field within the semiconductor outside of the region of excitation, which will be taken as a delta function.

For minority carriers (holes), the recombination term can be expressed as

\[ R = -\frac{\Delta p}{\tau_h}, \]

where \( \tau_h \) is the hole recombination lifetime, \( \Delta p = p - p_{\text{dark}} \) represents the excited hole density, \( p \) is the total hole density, and \( p_{\text{dark}} \) is the hole density in the dark. Outside the injection area, this leads to a continuity equation of the form

\[ \frac{\partial p}{\partial t} = -\frac{\Delta p}{\tau_h} - \frac{1}{e} \vec{\nabla} \cdot \vec{J}_h, \]
where $J_h$ is the hole current density. In general, the hole current density is comprised of both a drift component and a diffusion component,

$$J_h = pe \mu_h \vec{E} - eD_h \nabla p,$$

(4)

where $\mu_h$ is the hole mobility, $\vec{E}$ is the electric field, and $D_h$ is the hole diffusion coefficient. The diffusion coefficient is related to the mobility given by the Einstein relation as

$$D_h = \frac{k_B T}{e \mu_h},$$

(5)

where $k_B$ is the Boltzmann constant, and $T$ is temperature. It should be noted that an additional thermoelectric term, $\sigma S \nabla T$, where $\sigma$ is the electrical conductivity and $S$ is the Seebeck coefficient, could be included in Eq. (4). However, in many semiconductor materials, the drift and diffusion current is dominating and this thermoelectric term is negligible, as has been numerically verified.\textsuperscript{17}

### 3.1. One-dimensional system

The majority of recent SPCM experiments have been performed on semiconductor NWs; hence, we will first consider a solution in one-dimension (1D). This is justified by the fact that carrier diffusion lengths are generally much larger than the NW diameter. Plugging Eq. (4) into Eq. (3) results in a current continuity equation of the form

$$\frac{\partial p}{\partial t} = -\frac{\Delta p}{\tau_h} - p \mu_h \frac{\partial E}{\partial x} - E \mu_h \frac{\partial p}{\partial x} + D_h \frac{\partial^2 p}{\partial x^2},$$

(6)

where $E$ is the internal electric field along the $x$-axis (the NW axis). We have assumed the electric field is zero, hence the equation becomes

$$\frac{\partial p}{\partial t} = -\frac{\Delta p}{\tau_h} + D_h \frac{\partial^2 \Delta p}{\partial x^2}. $$

(7)

Here, we have changed $p$ to $\Delta p$ in the last term because $p_{\text{dark}}$ is spatially uniform. In the steady state, $\frac{\partial p}{\partial t} = 0$, which results in an equation of the form

$$D_h \frac{\partial^2 \Delta p}{\partial x^2} - \frac{\Delta p}{\tau_h} = 0.$$

(8)

Assuming an infinite material, with the excitation point at $x = 0$, the appropriate solution in the range of $x > 0$ is

$$\Delta p = \Delta p_0 e^{\frac{-x}{L_h}},$$

(9)

where $\Delta p_0$ is the excited hole density at $x = 0$, and $L_h$ is the hole diffusion length, where

$$L_h^2 = D_h \tau_h.$$

(10)
Fig. 1. Schematic of a 2D material studied by SPCM. The material extends in the x–y plane, with carriers being injected at the origin. Excited carriers then diffuse to the contact at \( x = L \), contributing to the measured photocurrent.

Thus, we have seen that the excited carrier density decays exponentially from the injection point with a characteristic decay length that equals to the minority carrier (hole) diffusion length in 1D semiconductor NWs. Furthermore, because the only contribution to current is charge diffusion, the current density is proportional to the gradient of excited carriers, leading to a collected current of the form

\[
J_h = -eD_h \frac{\partial \Delta p}{\partial x} \propto e^{-\frac{x}{L_h}}.
\]

It must be noted that the barrier formed between the collecting electrode and the material in study can influence the shape of the collected current as a function of excitation position. A Schottky junction between the NW and the contact will result in a photocurrent decay in the form of Eq. (11). More details will be discussed in Sec. 3.3.

3.2. Two-dimensional system

Recently, SPCM has been employed to study drift and diffusion related properties of 2D materials, such as graphene and quantum dot thin films.\(^{18}\) Using the assumptions given above for the 1D case, the appropriate continuity equation becomes

\[
-D_h \frac{\partial^2 \Delta p(x,y)}{\partial x^2} - D_h \frac{\partial^2 \Delta p(x,y)}{\partial y^2} = G(x,y) - \frac{\Delta p(x,y)}{\tau_h},
\]

where \( G(x,y) \) is the generation term. In most experiments, the excitation source is point-like and can be represented as \( G(x,y) = G_0 \delta(x) \delta(y) \), where \( G_0 \) is a constant proportional to the intensity of the excitation source. Solving for the steady state charge distribution as a function of position results in

\[
\Delta p(x,y) = \frac{1}{2\pi} K_0 \left( \frac{r}{L_h} \right),
\]
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Fig. 2. Plots of calculated photocurrent as a function of distance between the excitation and the collecting electrode ($L$). The photocurrent is normalized to 1 at $L = 0$. When fitted with an exponential curve in (a), the measured decay length is equal to that imposed in the calculation. The unit of $D_h \tau_h$ is $\mu m^2$. (b) Semi-log plot of the same data to demonstrate the exponential nature of the photocurrent decay.

where, $L_h = \sqrt{D_h \tau_h}$, $r = \sqrt{x^2 + y^2}$, and $K_0$ is the modified Bessel function of the second kind. Unlike in the 1D case, it is not immediately clear that this charge distribution will result in an exponential photocurrent decay. Assuming an infinitely wide charge collecting contact $L$ away from the injection point (Fig. 1), we can calculate the current by integrating over the entire contact, $I = -eD_h \int_{-\infty}^{\infty} \partial \Delta p(x,y) / \partial x |_{x=L} dy$.

Both the linear and semi-log plots of the numerically calculated current as a function of $L$ are shown in Fig. 2 for different $L_h$ values. The plots clearly show that the photocurrent decays exponentially over the distance from the collection electrode and furthermore that the decay length remains as $L_h = \sqrt{D_h \tau_h}$, just as in the 1D case. Thus, we have shown that SPCM can be used to extract the minority carrier diffusion length in a 2D semiconductor if the width of the contact is much longer than the diffusion length.

3.3. Extension of the simple model to two carrier types

To derive the analytical form of the photocurrent decay length above, we have assumed only a single carrier type and the absence of an electrical field in the material being studied. In reality, there are two carrier types, majority and minority, which are generated and conduct in semiconductors studied by SPCM. We will consider an $n$-type semiconductor with electrons as majority carriers. Continuing in 1D for convenience, we will demonstrate the validity of Eq. (11) in the presence of majority carriers below.

When considering both carrier types, the total current is the sum of four components in general: electron diffusion, electron drift, hole diffusion, and hole drift. In the low-injection regime, where the density of injected carriers is much less than
the majority (electron) carrier density ($\Delta p \ll n$), the minority (hole) drift current is much smaller than the other three components and can be ignored. Furthermore, though both the diffusion and drift components of the electron current are large, they cancel each other if at least one contact is Schottky-type, as supported by the simulation results.\textsuperscript{16} Therefore, the total current is dominated by the minority (hole) diffusion current, which justifies the models used in Secs. 3.1 and 3.2.

If an electric field is applied, the hole drift current can be comparable to the hole diffusion current or even dominating. We can estimate a threshold electric field by comparing the drift and diffusion components. The hole drift component of the photocurrent is equal to

$$e\Delta p \mu_h E,$$

and the magnitude of the diffusion current is

$$eD_h \left| \frac{\partial \Delta p}{\partial x} \right| \approx eD_h \frac{\Delta p}{L_h},$$

where we have assumed that the current is dominated by diffusion in the last step.

Therefore, we can define a critical electric field by comparing Eqs. (14) and (15),

$$E_c = \frac{k_B T}{e L_h},$$

below which the minority carrier conduction will be diffusion dominated and the previous derivation of decay length is valid. Above $E_c$, the drift component has to be considered. The result is that external electric field can extend the photocurrent decay length as shown experimentally.\textsuperscript{19}

In summary, we have shown that even when considering the presence of majority carriers, the photocurrent will decay with a minority carrier diffusion length ($L_h$) when the internal electric field is less than the critical field, $E_c$. We want to emphasize that this is only true when the electrode collecting the photocurrent forms a Schottky barrier with the semiconductor being studied. The Schottky contact ensures that the drift and diffusion components of the majority current balance each other. In other words, the electric field established at such a contact acts to filter majority carriers, thereby giving a photocurrent dominated by the minority carriers.

Even though the photocurrent is dominated by the minority diffusion current, the majority carriers do have effects on the electric field distribution in the semiconductors. If the mobilities are different for the two types of carriers, the injected electrons and holes will diffuse/drift at different speeds and the charge neutrality will be broken locally, resulting in an internal electric field. Such a perturbation is usually negligible in the low-injection regime, but it can become significant in the high-injection regime.

We will now give an example of how an internal electric field is created by mobility-mismatch. We will follow partially the derivation given by Smith.\textsuperscript{20} As the current is dominated by minority (hole) diffusion, we have the hole current at
position \( x \):

\[
J_h = J_{h0} e^{-x/L_h},
\]  

(17)

where \( J_{h0} \) is the hole current at the injection position, \( x = 0 \).

The steady state requires that the total current \( J = J_h + J_e \) is a constant everywhere. We introduce a quantity \( \theta \), the injection ratio, defined by

\[
J_{h0} = \theta J,
\]  

(18)

so that

\[
J_e = J - J_h = J(1 - \theta e^{-x/L_h}).
\]  

(19)

The electron current is also equal to the addition of the drift and diffusion components,

\[
J_e = e n \mu_e E + e D_e \frac{\partial \Delta n}{\partial x}.
\]  

(20)

The first term on the right-hand side can be written as \( \sigma E \), since \( n \gg p \). In the second term, we replace \( \Delta n \) by \( \Delta p \), since electrons and holes are balanced everywhere in the first order approximation. Also, we can define the ratio \( D_e/D_h = b \), such that the electron diffusion current is also given by \(-b J_h\). The total electron current is then

\[
J_e = \sigma E - b J_{h0} e^{-x/L_h}.
\]  

(21)

Compare Eqs. (19) and (21) and we have

\[
J = \sigma E - (b - 1) \theta J e^{-x/L_h},
\]  

(22)

and

\[
E = E_\infty [1 + (b - 1) \theta e^{-x/L_h}],
\]  

(23)

where \( E_\infty = J/\sigma \) is the value of the electric field at points far away from injection. As clearly seen in Eq. (23), an extra electric field term is created by the mobility ratio \( b \). If electrons and holes have the same mobility and \( b = 1 \), the electric field remains unchanged after carrier injection.

### 3.4. Beyond the simple model

The analytical models detailed above describe the transport of excited carriers with sufficient accuracy to be useful in a wide array of SPCM experiments. However, they fail to account for many details that may be important in some situations. For example, under high-level injection, when the injected minority carrier density is equal to or greater than the equilibrium majority carrier density, an electric field will be developed due to different rates of diffusion between carriers, as indicated in Eq. (23), which will in turn alter the carrier decay profile. The resulting photocurrent profiles are difficult to calculate analytically and are generally best determined through simulation.
The nature of the metal-semiconductor contacts also plays a major role in the measured photocurrent profile. Fu et al.\textsuperscript{17} have simulated the photocurrent generated in a 1D semiconductor NW when the two contacting electrodes are both Ohmic, Ohmic and Schottky, and both Schottky, respectively. The results show that when the separation between the electrodes is much greater than the minority carrier diffusion length, an Ohmic–Schottky configuration is ideal as it results in a single photocurrent spot with a decay length equal to the minority carrier diffusion length. As the separation between electrodes approaches the minority carrier diffusion length, the measured photocurrent decay no longer accurately represents the minority carrier diffusion length. In the devices with two Ohmic contacts, mobility mismatch results in internal electric field and drift currents are significant comparable to diffusion currents even in the absence of the source-drain bias.

4. Experimental Setup of SPCM

SPCM is composed of four components: an excitation source, focusing optics, a position controller, and an electrical measurement unit. A typical SPCM setup is based upon a confocal microscope, as shown in Fig. 3. Light is generated by a continuous wave (CW) laser, passed through a spatial filter, then a variable neutral-density (ND) filter, and then an electronically controlled $X-Y$ scan mirror. The light then passes through a beam expander and into a microscope with a high numerical aperture objective lens, where it is focused into a diffraction-limited spot onto a sample below. The photocurrent generated in the sample is measured by a preamplifier. This setup provides sufficient flexibility for modification, allowing for

![Fig. 3. Schematic diagram of the SPCM setup.](image-url)
a range of experiments to be performed. An alternative setup is to fix the laser position and scan the sample with a piezo-stage, as in AFM.

The purpose of the spatial filter composed of a pinhole and two lenses is to physically “condition” the laser signal, that is, to filter out higher-order spatial modes, providing a Gaussian laser profile to pass through the subsequent optics. This spatial filter is important as it improves the spatial resolution of SPCM. The ND filter allows one to control the intensity of the laser on the sample in study. In order to reduce the electrical noise of the photocurrent signal, the setup often includes an optical chopper, which modulates the light source. The resulting AC photocurrent signal will then be detected with a lock-in amplifier locked at the frequency output from the optical chopper. A photodetector is included to measure the light reflected by the sample as a function of laser position. This provides a reflection image of the sample which can be matched to the photocurrent map, so that the physical position of the photocurrent spot can be determined. Another essential component is the beam expander, which increases the diameter of the laser beam. The beam should be expanded to a diameter commensurate with the objective lens opening in order to produce a diffraction-limited beam size on the sample, which in turn maximizes the spatial resolution. For the reflecting mirror into the objective lens, one may choose a dichroic mirror that reflects light of wavelengths similar to the laser light, but passes light of different frequencies. This would be useful when performing photoluminescence measurements, with the light passing through the dichroic mirror being collected by the appropriate spectroscopic equipment.

The system described above may be considered typical, but it is by no means the only configuration in use. As SPCM has matured, the range of experimental schema used has increased greatly to include a variety of excitation sources, optics, geometries, etc. To overcome the resolution limitations imposed by objective lenses, several groups have instead used near-field scanning optical microscopes (NSOM). Such microscopes feed laser light through an ultrathin optical fiber near the surface of the sample. This allows for measurement of very short decay lengths and expands the range of materials that can be studied by SPCM. An *ACS Nano* perspective entitled “High-Resolution Photocurrent Mapping of Carbon Nanostructures” reviews several recent publications which rely on SNOM-type techniques.

Another variation of the typical system described above is electron beam induced current (EBIC). Rather than using an optical excitation source, one uses an electron beam, often from a scanning electron microscope (SEM). As with NSOM, EBIC usually has a better spatial resolution than SPCM based on optical microscopes, with the dominating factor on resolution being the interaction volume, which ranges from sub-100 nm to microns. Limitations of EBIC include the necessary high-vacuum environment and a potential of electrical charging as a function of sample conductivity.

Another experimental scheme, recently described by Jagadish et al. is called two-photon optical beam induced current (TOBIC), and it is capable of recording
5. Applications of SPCM in Investigating the Optoelectronics of Nanostructures

A key factor in the widespread study of nanostructures via SPCM is the broad array of information that can be gathered through such experiments. Data generated by SPCM include spatially resolved photocurrent profiles that can be used to indicate the photo-sensitive regions, defects and/or heterogeneity in samples, the direction of the photocurrent, which can be used to indicate the local electric field direction and the local band bending at the homo- or hetero-junctions in semiconductor devices, and the magnitude of the photocurrent, which can be analyzed to estimate the charge separation efficiencies in photovoltaic devices or internal gain in photodetection devices. SPCM images as a function of source-drain voltage, gate voltage, and excitation wavelengths and intensity can provide detailed information on local band bending, charge transport, and recombination mechanisms. Combined with other experimental techniques, e.g., Kelvin probe microscopy (KPM), SPCM can also be used to understand the doping profiles in nanostructures. In this brief review, we will focus on SPCM analysis of (1) carrier diffusion length, (2) internal electric field, (3) doping distribution, and (4) thermoelectric effects. It is important to note that these topics are by no means a full coverage of all possible usages. Given that SPCM has been applied to the investigation of nanostructures for only a few years, we expect that many innovative ways of using this powerful technique will continue to be invented.

5.1. Extracting carrier diffusion length

By far the most common use of SPCM is the measurement of minority carrier diffusion lengths. The minority carrier diffusion length is one of the key physical parameters in semiconductors, particularly important to solar energy applications. A typical solar cell is composed of an n-type and p-type region for efficient charge separation, with the total semiconductor layer thick enough to allow for sufficient absorption of impinging sunlight. Minority carriers have to diffuse over this long distance before recombination occurs in order to have a high power conversion efficiency. Defect-induced mid-gap states can substantially increase the recombination rate. Thus, semiconductors have to be purified to remove these defects and this purification process often requires high temperature, thereby increasing the cost of photovoltaic devices. The geometry of NWs helps to alleviate this problem by providing a sufficiently long path for light absorption along the length of the wires, and a short, radial diffusion path for photogenerated carriers. Thus, the minority carrier diffusion length is only required to be large compared with the diameter of the NWs in NW solar cells. On the other hand, because of an enhanced surface
to volume ratio, surface states can significantly increase the recombination rate and lower the minority carrier diffusion length. The enormous surface-to-volume ratio of the nanostructures is crucial to their novel applications, but creates new challenges as well. One needs experimentally determine the key parameters in the nanostructures such as minority carrier diffusion length in order to optimize their device performance.

SPCM provides a unique method for extracting the minority carrier diffusion length in NWs. As shown in Eq. (10), the diffusion length can be determined by the minority carrier lifetime and mobility. Without using SPCM, one must perform Hall-bar measurements to determine the Hall mobility of carriers and ultra-fast spectroscopic measurements to determine the carrier recombination lifetime and then calculate the carrier diffusion length. The preparation of a Hall bar may be very difficult or impossible with nanostructured samples, while ultra-fast spectroscopic techniques may produce several characteristic lifetimes which are difficult to interpret without complete models of recombination dynamics. Furthermore, such spectroscopic data are generally extracted from ensemble measurements, producing values averaged over sensitive parameters such as NW diameter and surface state density. On the other hand, SPCM provides a direct measure of the minority carrier diffusion length of single NWs as a function of gate and source-drain bias.

Recently, there have been several reports on using SPCM to characterize the minority carrier diffusion length. Planar devices incorporating individual NWs are required for such investigation and can be achieved by either photo- or electron beam lithography. In addition, as mentioned earlier, at least one Schottky contact is necessary in order to correctly obtain the minority carrier diffusion lengths. Schottky contacts can be achieved by using a low work function metal\textsuperscript{27} or by controlled damage of one contact through electric shock to create an energy barrier.\textsuperscript{4} The minority carrier diffusion lengths that have been measured have a wide range, from tens of nanometers up to 10 μm.

The highest value achieved so far is the electron diffusion length of 10 μm in 1 μm-diameter Si NWs grown by the vapor-liquid-solid (VLS) method using Cu as catalysts, reported by Atwater \textit{et al.}\textsuperscript{29} By removing the native oxide coating from the NW with hydrofluoric acid, followed by sputtering of Al (with 1% Si), one electrode formed an Ohmic contact, while direct sputtering of Al on the native oxide formed a Schottky barrier for the other electrode. Interestingly, they found that the decay length changes from <0.7 μm to 10.5 μm if the NW is exposed to low-intensity, broad-area illumination. They attribute this great increase to an injection of electrons into the oxide layer surrounding the NW, which is known to have a high density of fixed positive charge.\textsuperscript{29,30} The Lauhon group reported hole diffusion lengths from 25 to 80 nm for Si NWs 30 to 100 nm in diameter,\textsuperscript{31} respectively. This strong diameter dependence suggests that surface recombination is likely the dominating factor determining the charge dynamics in these low-dimensional semiconductors.
The surface recombination rate seems to sensitively depend on the preparation of the samples. Htoon et al.\textsuperscript{32} measured the minority decay lengths on either side of an axial $p$–$n$ junction in a VLS grown Si NW, demonstrating an electron (hole) recombination length of 1.0 $\mu$m (0.66 $\mu$m), which are an order of magnitude larger than previously reported values for Si NWs of the same diameter. If the surface of the NWs is not well passivated, dangling bonds at the surface can scatter charge carriers and create surface traps which substantially increase the charge recombination rates.\textsuperscript{31} The effective charge recombination rate in NWs, $1/\tau_{NW}$, depends on the surface recombination velocity $S$ and the radius of the NW, $R$, following $1/\tau_{NW} = 1/\tau_{\text{bulk}} + 2S/R$ and $S = v_{th} \sigma n_{\text{trap}}$, where $v_{th}$ is the carrier thermal velocity, $\sigma$ is the carrier capture cross sections by traps, and $n_{\text{trap}}$ is the trap density. $S$ in Si NWs, as reported by different groups, varies by more than four orders of magnitude, from 20 cm/s (Ref. 33) to $3 \times 10^5$ cm/s.\textsuperscript{31} This demonstrates the sensitive dependence of $S$ on NW growth and surface passivation methods. In addition to Si NWs, the minority carrier diffusion length in both $n$- and $p$-type GaAs NWs have been measured by EBIC to be about 100 nm, one order of magnitude lower than the bulk values. The diameter dependence indicates $S \sim 3 \times 10^5$ cm/s.\textsuperscript{34} Soudi et al. reported a minority carrier diffusion length up to 250 nm in ZnO NWs.\textsuperscript{35}

Chemical treatment can permanently passivate a surface by reducing the number of dangling bonds. This is especially true for colloidally grown NWs and QDs, for which a post-growth ligand replacement step has become standard practice, largely to improve passivation. Graham and Yu's\textsuperscript{36} demonstration has an increase in minority carrier diffusion length from 2.5 $\mu$m to 4.5 $\mu$m in colloidal PbSe NWs with $\sim$10 nm diameter after surface passivation with ammonium thiocyanate. Surface passivation decreases the density of surface states, which in turn increases the carrier lifetime, leading to a longer diffusion length. This effect is supported by a factor of 10 increase in the mobility of those devices that are treated with ammonium thiocyanate over those that are not.

The recombination rate also sensitively depends on the carrier concentration. A recent paper by Yang et al.\textsuperscript{37} details the measured minority carrier diffusion lengths as a function of applied gate voltage in single VLS grown PbS NW field effect transistors (FETs). Rather than having to grow a large variety of wires whose equilibrium charge carrier density varies incrementally, while trying to maintain all other variables, the applied gate voltage acts to change the carrier concentration, and with it, the band-to-band recombination rate, which leads to a change in minority carrier diffusion length. This study not only demonstrates a gate-dependent diffusion length in a NW, but also provides a method of tailoring carrier concentration for a desired diffusion length.

The distance that minority carriers can travel before recombination also depends on the source-drain voltage. As shown in Sec. 3.3, when the external electric field is above the critical field $E_c = k_B T/eL_D$, where $L_D$ is the minority diffusion length, the photocurrent decay length is dominated by carrier drift and is proportional to the external electric field.\textsuperscript{13}
to electric field \((L_E = \mu T E)\). This has been demonstrated experimentally in PbS NWs.\(^{19}\)

Finally, we will briefly discuss some interesting SPCM results in NW devices with Ohmic contacts. The Lauhon group has investigated with SPCM single nearly intrinsic CdS NW devices with Ohmic contacts.\(^{2}\) No photocurrent spots are observed adjacent to the Ohmic contacts as expected. Instead, the maximum photocurrent spots appear a distance away from the contacts. The peak position is determined by matching the electron and hole currents, i.e. when \(L_e/x = L_h/(D - x)\), where \(x\) is the distance between injection point and the electron collecting contact and \(D\) is the separation between contacts. It is also found that the external longitudinal electric field can shift the photocurrent peak position, as the field changes the ratio between \(L_h\) and \(L_e\). Recently, Yang \textit{et al.} have demonstrated a similar photocurrent profiles in nearly intrinsic PbS NW devices with Ohmic contacts.\(^{37}\)

Instead of using longitudinal electric field, they find that the transverse field can also shift the photocurrent peak position as both \(L_e\) and \(L_h\) depend on the gate modulated carrier concentration.

### 5.2. Probing internal electric field

In the presence of an electric field, photogenerated electrons and holes are separated. Thus, spatially resolved photocurrent can be used to map local electric field distributions. There are many sources for such an electric field, including semiconductor homo- or hetero-junctions in axially or radially modulated NWs or NW cross-bars,\(^{38}\) Schottky contacts, local charge accumulation, defects, and externally applied electric field by source-drain voltage or gate voltage. Analysis of the electric-field driven photocurrent provides a wealth of information, e.g. the location of the photocurrent spots indicates where bending of the conduction and valence bands occurs due to Fermi level equilibration, the sign of the photocurrent gives the direction of the electric field, and the magnitude of the photocurrent is proportional to the field strength, etc.

In 2004, one of the first SPCM studies of carbon nanotubes demonstrated the presence of an electric field at the contacts.\(^{39}\) Ahn \textit{et al.} have studied the local band bending profile due to Schottky contacts in Si NW FETs and have also demonstrated that both the polarity and magnitude of the photocurrent vary with gate voltage.\(^{40}\) Ahn \textit{et al.} have also imaged \(p-n\) junctions in carbon nanotube FETs, where the \(p-n\) junction is achieved by application of a gate voltage or by partially suspending nanotubes.\(^{7}\) Avouris \textit{et al.} have also imaged the Schottky barriers of carbon nanotubes and concluded that the space charge region can grow to many microns when the device is depleted.\(^{41}\) Lauhon \textit{et al.} also showed the contact band bending in CdS NW photodetectors.\(^{42}\) Removing the contact band bending by using \(Ar^+\) plasma to selectively bombard the electrode contact region leads to Ohmic contacts and the elimination of a contact photocurrent.\(^{2}\)
Ohmic and Schottky contacts formed between colloidal QD thin films and metal electrodes have also been imaged by SPCM. Bawendi et al.\textsuperscript{12} varied the contact type made to colloidal PbS QD thin films. They conclude that Au results in an Ohmic contact to QDs, while Ti produces a Schottky contact. The SPCM results also suggest a depletion width of up to $1.8 \, \mu\text{m}$, significantly longer than in vertical devices. The difference has been attributed to the lateral device configuration and/or surface state charges on the SiO$_2$ interface. Alternatively, the long photocurrent decay length may be caused by diffusion, as recently indicated by Otto et al.\textsuperscript{18} supported by a gate-dependent long minority carrier lifetime due to charge trapping.

Miller et al.\textsuperscript{43} studied the junction between metal and insulator domains in VO$_2$ nanobeams using SPCM. Photocurrent spots were observed at the domain boundaries, indicating the presence of a local electric field and band bending. The barrier height estimated from the photocurrent magnitude can shed light on the nature of the metal-insulator transition itself. On the other hand, a recent report by Cobden suggests that the photocurrent at the junction is caused by a thermoelectric effect instead of a Schottky field.\textsuperscript{44} Further investigation is required to clarify the mechanisms.

5.3. Analysis of doping distribution

Contact barriers, metal and insulator domains, and $p$–$n$ junctions all create relatively abrupt changes in charge carrier density, at least on the scale of the spatial resolution achievable with SPCM techniques. Gradual changes in doping concentration will also lead to band-bending, and will therefore generate photocurrent. Lauhon et al.\textsuperscript{45} used SPCM to calculate the doping gradient profile in $n$-type Si NWs grown by the VLS method. By assuming a drift-dominated photocurrent, using Ohm’s Law, a position dependent charge concentration can be estimated from axial cross sections of the SPCM image. With this method at hand, one can test various growth conditions, such as He versus H carrier gas in a VLS growth,\textsuperscript{46} or post-growth treatments, such as annealing. Non-uniform radial doping, including surface doping, will lead to radial electric field components that cannot be measured by this technique. However, surface etching can be used to reveal the radial doping gradient.\textsuperscript{1} In addition to SPCM, KPM, which measures changes in local electric potential at the surface, and Auger electron spectroscopy (AES), which identifies the chemical and compositional characteristics of a material, can be used as complementary techniques to analyze doping profiles.\textsuperscript{46–49}

5.4. Thermoelectrically driven current

Most semiconductors have a sufficiently low Seebeck coefficient that when connected to metal electrodes, which act as heat sinks, the thermal gradient generated by laser heating produces negligible photocurrents.\textsuperscript{17} However, there are some cases when the diffusion and drift components of photocurrent are negligible, and the thermoelectric term, mentioned in Sec. 3, dominates.\textsuperscript{50} McEuen et al.\textsuperscript{10} used
SPCM to study the photocurrent generation mechanism at the interface of a single and double graphene layer. By comparing the polarity of the photocurrent spots to the gate-tuned position of the Fermi level, they showed the Seebeck coefficient correlates to the photocurrent. Low-temperature measurements allowed them to estimate the thermal conductivity temperature dependence as $T^{1.5}$, below $\sim$100 K, which agrees with theoretical predictions. Park et al.\textsuperscript{9} generated a thermoelectric photocurrent in single layer graphene (SLG) by using a 410 nm laser as the excitation source, which is strongly absorbed by the gold electrodes making contact to the SLG, thereby creating a sufficiently large temperature gradient to produce a photocurrent. By varying the applied gate voltage, they used the polarity of the thermoelectric photocurrent to determine the majority carrier. Buscema et al.\textsuperscript{50} performed SPCM on single layer MoS$_2$ with Ohmic contacts, demonstrating a thermoelectrically driven photocurrent and a measured Seebeck coefficient that varied with applied gate voltage from $4 \times 10^2$ to $1 \times 10^5$ $\mu$V/K.

6. Conclusion

To conclude, we have introduced SPCM as a powerful experimental method capable of measuring a wide array of optoelectronic parameters and investigating interfacial properties, charge transport, and recombination in semiconductor nanostructures. We have used a simple model considering only the minority carrier diffusion to show that the photocurrent decay length is equal to the square root of the product of minority carrier diffusion coefficient and lifetime in both 1D and 2D cases. We then showed that this simple model is relevant to real devices with at least one Schottky contact. We briefly discussed the experimental setup and finally, reviewed the recent applications of SPCM to studying NWs, carbon nanotubes, graphene, and QD thin films.

We have seen in the above discussion that the photocurrent can be driven by electric field, carrier concentration gradient, and temperature gradient. In addition, there are two types of carriers and a local charge imbalance may lead to an internal electric field, resulting in complications in the analysis of SPCM data. Careful modeling and simulation are often required to better interpret experimental results. Other complementary experimental techniques such as KPM can be used to further confirm the origin of the photocurrent and extend the capability of SPCM.

As the range of nanotechnology applications increases, so too will the need for complete understanding of fundamental and operational characteristics of the materials in use. Developments such as NSOM, EBIC, and TOBIC have already produced interesting results and are likely to continue to expand the realm of what SPCM can do. Spatially resolved photovoltage, photoluminescence, and electroluminescence\textsuperscript{51} can also be obtained in addition to photocurrent, giving rich information on the optoelectronic nature of nanostructures. The combination of ultrafast spectroscopy with high spatial resolution has also emerged\textsuperscript{52} and may lead to exciting discoveries.
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References