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A Comparison of Plasmon-induced and Photoexcited Hot Carriers in Metallic Nanostructures

by

Hangqi Zhao

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APPROVED, THESIS COMMITTEE

Naomi Halas, Chair
Stanley C. Moore Professor of Electrical and Computer Engineering, Professor of Biomedical Engineering, Chemistry, Physics & Astronomy, Director of LANP

Peter Nordlander
Wiess Chair and Professor of Physics & Astronomy, Professor of Electrical and Computer Engineering, Materials Science and NanoEngineering

Stephan Link
Associate Professor of Chemistry and of Electrical and Computer Engineering

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ABSTRACT

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The incompressible oscillations of electrons in metallic nanostructures, known as surface plasmons, have provided a promising route to increasing light-matter coupling and boosting the efficiency of solar energy conversion in photovoltaic devices. When plasmons decay, energetic electron-hole pairs are created through a non-radiative channel. These hot electrons have found applications in photodetection and photocatalysis but remain poorly understood in terms of mechanisms. In this work, we made a comprehensive comparison between plasmon-induced hot carrier generation and direct excitations of hot carriers by photon absorption. Using a gold nanowire based hot carrier device, which either forms a Schottky barrier or an Ohmic barrier between nanostructures and a wide-bandgap semiconductor substrate, we are able to distinguish between these two mechanisms of hot carrier generation. We show that plasmon-induced hot electrons have higher energies than directly excited carriers, and can be characterized by the integration of electrical field enhancement within the nanostructures, while photoexcited carriers are correlated with material absorption. Our work paves the way for increasing the energy conversion efficiency by decreasing the Schottky
barrier and collecting both the plasmonic and interband photocurrent, which may find wide applications in future photovoltaic devices.
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Chapter 1

Introduction

The capabilities of metallic nanostructures for enhancing solar energy conversion through the generation of energetic electrons, known as hot electrons, have been demonstrated and found broad applications in photodetection and photocatalytic devices in the past few decades\textsuperscript{2–5}. However, a full understanding of hot carrier generation is still missing in terms of mechanism, despite some previous experimental work\textsuperscript{6–19} and theoretical studies\textsuperscript{20–23}. These hot electrons could either be generated by direct photoexcitation or plasmon decay. Limited by the small electron-photon cross-section, hot electron generation by direct photon absorption is very inefficient. Plasmonic nanostructures, however, could exhibit significantly larger absorption cross sections than their physical cross sections, thanks to the excitation of plasmons. Thus, plasmon-induced hot carrier generation could be a much more efficient process and a promising route for photon conversion. For a long time, plasmonic hot carrier generation has been correlated with the optical
absorption of the metallic nanostructure\textsuperscript{2,3}, due to the important role of photon absorption in this process. However, this kind of analysis could not differentiate hot carriers generated by plasmon decay and by direct photoexcitation, which is an important distinction in many applications. In this work, we study these two types of hot carrier generation process by designing a metallic nanowire based hot electron device, which either forms a Schottky barrier or an Ohmic barrier. We successfully distinguish these two mechanisms and a comprehensive theoretical model is generated to explain the mechanisms behind these two processes.

In Chapter 2, a brief review of localized surface plasmons and hot electron generation is introduced. Two difference mechanisms of carrier generation, namely, plasmon-induced and direct photoexcited process, are described. The basic method for hot electron collection by forming a Schottky barrier with a semiconductor is also introduced.

In Chapter 3, a comprehensive study on the comparison of these two mechanisms is presented. The geometries of Schottky and Ohmic devices are described in Section 3.1, and their photocurrent maps are discussed in Section 3.2. Detailed numerical calculation methods are introduced in Section 3.3, including a review of FDTD method, the basic model setup and the theoretical modeling of hot carrier generation by both mechanisms. The experimentally and theoretically calculated device photocurrent responsivities and a thorough discussion on the results are given in Section 3.4.
Chapter 4 summarizes the major conclusions in this work as well as the significance in future photodetection and photovoltaic devices.
Chapter 2

Hot electron generation

2.1. Localized surface plasmons

Plasmons are incompressible oscillations of conduction electron liquids in metals, as shown in Fig. 2.1. Plasmons can be excited at plane interfaces of metal/dielectrics, known as surface plasmon polaritons (SPP), or localized at the surface of nanoparticles (LSP). Plasmons have drawn rapidly growing interests in recent years due to its capabilities to confine light in the nanoscale, which made many novel nanophotonic devices and applications possible.
Plasmons can enable strong couplings between light and matters, and can result in extraordinary strong local electromagnetic field near nanoparticles, known as plasmonic hot spots. Moreover, plasmon resonance can be highly tunable by the geometries, materials and environments of nanoparticles. Because of these properties, plasmons have found broad applications from plasmon enhanced spectroscopy\textsuperscript{24}, biomedicine\textsuperscript{25}, photocatalysis\textsuperscript{26} to light harvesting\textsuperscript{27} and photodetection\textsuperscript{11}.

2.2. Hot electron generation: two mechanisms

There is a growing interest over the past few decades in the capability of plasmonic nanoparticles to directly convert solar energy into electricity by generating hot carriers\textsuperscript{2,6,16,19,28–31}, which opens new avenues in novel photovoltaic and photocatalytic devices and applications. “Hot carriers” are referred to those carriers that are not in thermal equilibrium, whose energies are larger than those of thermal excitations at ambient temperatures\textsuperscript{4}.

These electrons can be generated in the process of plasmon decay. Plasmon decay happens in femtoseconds and through two channels: either radiatively by emitting photons, or non-radiatively by creating electron-hole pairs via Landau damping\textsuperscript{32}, in which case the plasmon energy is transferred to the conduction electrons. The ratio of these two channels depends on the radiance of the plasmon
mode, namely, super-radiance mode prefers radiative channel while subradiance mode favors non-radiative channel.

Conceptually, the non-radiative decay can take place either through transition within the conduction band of metals, or through interband transition between different bands (for example, from d band to s band in gold). However, in noble metals such as gold and silver, the d band is 2.4eV\textsuperscript{33} and 4eV below the Fermi level, respectively, making the plasmon-induced interband transition rather impossible, or unlikely for optical excitations\textsuperscript{34,23}. On the other hand, in plasmon-induced process, the perturbing potential driving the electron transition is the near field induced by the plasmon, which is localized on the surface of nanoparticles, hence the plasmon induced process favors exciting electrons from near the Fermi level\textsuperscript{20}. Thus, for plasmon-induced hot electron generation, electrons are mostly excited from below but near the Fermi energy to an energy level higher than it by the plasmon, as shown in Fig 2.2.
Figure 2.2 – Two mechanisms of hot electron generation in gold. (1) Hot electron generation by plasmon decay. Electrons from near the Fermi energy are excited to a much higher energy, corresponding to an intraband transition. (2) Hot electron generation by direct photoexcitation. Electrons from the d band of gold are excited above the Fermi energy, corresponding to an interband transition.

Another mechanism of hot carrier generation is directly photoexcitation. In this case, the electrons absorb photons directly and experience an interband transition, contrary to the intraband transition in plasmon-induced hot electron generation, from d band to s band in gold. The resulting hot electrons are above Fermi energy, but are generally lower than the plasmon-induced process, as is shown in Figure 2.2.

2.3. Hot electron collection

Hot electron generation has found applications in photocatalysis, photovoltaic and photodetection. One of the issues in these applications is an efficient collection of hot electrons. An efficient way is to form a Schottky barrier using a semiconductor contacted with the metallic nanostructures. Figure 2.3 shows the energy diagram of the interface between a plasmonic nanostructure and an n-type semiconductor, which clearly shows a Schottky barrier. Electrons from various energy levels of the metal are excited either by plasmon or photon absorption upon Fermi level, while only those electrons with higher energies than Fermi energy can be injected into the semiconductor substrate. TiO2 is a good candidate for the semiconductor due to its wide bandgap (~3eV), which enables
efficient separation of electrons and holes, as well as its high density of state in conduction band, which could lead to fast and efficient injection of hot electrons from the metal to substrate. This metal-semiconductor scheme has been used in most of current hot electron based photovoltaic and photodetection devices\textsuperscript{36,37}.

**Figure 2.3** – Hot electron collection by a Schottky barrier\textsuperscript{5}. Only electrons with energy higher than the barrier $\varphi_{SB}$ could be injected into semiconductor.
3.1. Device description

We designed two kinds of devices: a Schottky device and an Ohmic device. For Schottky device, a gold nanowire array is on top of a wide bandgap, n-doped semiconductor (TiO₂), connected with a square gold pad, as shown in Figure 3.1.

![Figure 3.1](image)

*Figure 3.1 – Scheme of (a) Schottky and (b) Ohmic device.*
All nanowires are 50nm thick and the pitch distance between nanowires is 500nm. For Ohmic device, a thin Titanium layer (2nm) is formed between gold nanowire and TiO2 substrate, so a Au-TiO2 junction is formed for Schottky contacts and an Au/Ti/TiO2 junction forms Ohmic contacts.

Figure 3.2 shows the band diagram of these two devices. In Schottky device, a Schottky barrier of ~1eV is formed between Au and TiO2. This value is in consistent with previous measurements. Schottky diodes are majority-carrier type of devices, thus the current flow is conducted by either electrons or holes. As a result, it prevents these two types of carrier from recombining and thus minimizes the current loss.

![Band diagram of Schottky and Ohmic device](image)

**Figure 3.2 – Band diagram of (left) Schottky and (right) Ohmic device. The barrier of ~eV in Schottky device was decreased to zero by the thin Ti layer in Ohmic device.**

In Schottky device, only those high energy hot electrons induced by the plasmon decay could have enough kinetic energy to overcome the Schottky barrier, while the directly photoexcited hot electrons, which are at from least 2.4eV below
the Fermi energy to at most 0.6eV above the Fermi energy by optical excitations between 1~3eV, are blocked by the Schottky barrier. Thus, in Schottky device only the hot electrons from plasmon decay are collected, and the interband electrons are filtered.

In Ohmic device, the effective barrier between Au and TiO2 is essentially decreased to zero due to the material properties of Ti. As a result, those low energy hot electrons from direct photoexcitation can also be injected, and the photocurrent is from both the contribution of plasmonic hot carriers and interband carriers. This fundamental difference between Schottky and Ohmic device provides a way to distinguishing between plasmon-induced and photoexcited hot carriers.

Figure 3.3 shows the current-voltage (I-V) curve of these two devices. The red line is the averaged signal and all devices I-V curves are the grey regions, which clearly shows the behavior of a Schottky and Ohmic barrier. The Schottky barrier height is extracted from the I-V curve by fitting with the diode equation39, and a value of 1.07eV is obtained.
3.2. Photocurrent mapping

To determine the origination of photocurrent in various regions of devices, the spatial distribution of photocurrent, namely, the photocurrent map, is experimentally measured as Figure 3.4 shows. A diffraction-limited laser spot is scanned over the whole device and the photocurrent at different positions are recorded. The laser wavelength is tuned to plasmon resonance (~675nm).
Figure 3.4 – Photocurrent mapping. (a) Schematic of TE excitation. Photocurrent maps of (b) a Schottky device and (c) an Ohmic device with TE polarization. The laser wavelength is ~675nm and nanowire width is 273nm. (d) Schematic of TM excitation. Photocurrent maps of (e) a Schottky device and (f) an Ohmic device with TM polarization.

In TE case, where the polarization of incident field is perpendicular to the orientation of nanowires, a plasmon can be excited. We observed the photocurrent generation in the nanowires, which is corresponding to the plasmon-induced hot electrons. In the gold pad, where no plasmon mode exists, nearly no photocurrent is generated, since the interband electrons are filtered by the Schottky barrier. In Ohmic device, photocurrent is produced in the nanowire region due to plasmon decay as we expected. However, a large proportion of photocurrent is also observed in the pad region, where no plasmon mode exists. The photocurrent is generated
homogeneously in the whole pad area, indicating that this is from direct absorption. Thus, in Ohmic device, both the plasmon-induced and photoexcited hot carriers contribute to the photocurrent.

In TM case, where the polarization is parallel to the orientation of nanowires, no plasmon is excited due to the ~20um length of the nanowires. As we expected, no photocurrent is generated except some junctions in the Schottky device, since the interband electrons are filtered by the Schottky barrier. However, in the Ohmic device, photocurrent is produced in the nanowires as well as the pad region. This photocurrent arises regardless of polarization and geometry, indicating that it is from direct photoexcitation instead of plasmon decay, which is strongly dependent on the geometry and polarization of incident light. All these observations confirm that in the Ohmic device, electrons from both of the two mechanisms are responsible for the photocurrent.

3.3. Numerical calculation

In this chapter, the numerical calculation methods based on Finite Difference Time Domain (FDTD) for modeling the responsivity of both devices are introduced.

3.3.1. FDTD method

FDTD is a numerical technique used for electromagnetic computations. Differential form of Maxwell's equations is taken in the time domain, and the resulting equations in a simple 1D case as shown in Equation 3.1.
Equation 3.1 – Differential form of 1D Maxwell’s equations in time domain.

\[
\frac{\partial \vec{E}}{\partial t} = -\frac{1}{\varepsilon_0} \nabla \times \vec{H} \Rightarrow \frac{\partial E_x}{\partial t} = -\frac{1}{\varepsilon_0} \frac{\partial H_y}{\partial t} \quad \frac{\partial \vec{H}}{\partial t} = -\frac{1}{\mu_0} \nabla \times \vec{E} \Rightarrow \frac{\partial H_y}{\partial t} = -\frac{1}{\mu_0} \frac{\partial E_x}{\partial t}
\]

They are further discretized using central-difference approximations to the space and time partial derivatives, resulting in Equation 3.2.

Equation 3.2 – Discretization of Maxwell’s equations using central difference approximation.

Electric and magnetic field are then calculated in a staggered way in time and space domain, as shown in Equation 3.3. This process is repeated iteratively until a steady state electromagnetic field is obtained.

\[
\begin{align*}
E_{x}^{n+\frac{1}{2}}(k) &= E_{x}^{n-\frac{1}{2}}(k) - \frac{\Delta t}{\varepsilon_0 \Delta x}\left[ H_{y}^{n}(k + \frac{1}{2}) - H_{y}^{n}(k - \frac{1}{2}) \right] \\
H_{y}^{n+1}(k + \frac{1}{2}) &= H_{y}^{n}(k + \frac{1}{2}) - \frac{\Delta t}{\mu_0 \Delta x}\left[ E_{x}^{n+\frac{1}{2}}(k + 1) - E_{x}^{n-\frac{1}{2}}(k) \right]
\end{align*}
\]
Equation 3.3 – Staggered calculation of electric and magnetic field.

FDTD method can be formulated to run on distributed memory parallel computers, and since it’s a time domain technique, it enables multiple frequency simulations in one run. It could also deal with nonlinear and inhomogeneous problems, as well as complicated systems with no symmetry.

3.3.2. Model description

A commercial software based on FDTD method (Lumerical Solutions) is used to model the device responsivity.

Simulation is performed in 2D case, since the length of nanowires (20um) can be assumed to be infinite. For simplicity, we studied the response of a single nanowire of infinite length. This approximation is justified by the fact that we find no significant differences in the calculated spectra when simulating a single nanowire or an array of nanowires. In all calculations, the sizes of the nanowires were chosen to be identical to the fabricated structures. Furthermore, the corners of the nanowires were slightly rounded to avoid numerical instabilities and match the experimental conditions more precisely. The Aluminum devices were simulated with a 3 nm oxide layer, as is used in previous studies\textsuperscript{41}. The dielectric functions of the different materials were taken from tabulated data: Au from ref.23\textsuperscript{42}, Al and Al2O3 from ref.24\textsuperscript{43} and TiO2 from ref. 25\textsuperscript{44}. The incident light was modeled as a plane wave with the polarization transverse (TE) or parallel (TM) to the orientation
of the nanowires and propagation normal to the substrate. Perfect-matched layers were used as boundary conditions to simulate the infinite substrate and absorb scattered light. All calculations have been converged to ensure the reliability and accuracy of the simulation results.

### 3.3.3. Device responsivity calculation

To calculate the device photocurrent responsivity, an assumption was made that only hot electrons produced within the mean free path from the interface of the metal and substrate were considered “effective”, namely, could be injected and contribute into the photocurrent.

For Schottky device, or plasmon induced process, the responsivity should be determined directly by the local field induced by the plasmon\textsuperscript{20}. Thus, we integrate the field intensity enhancement over the volume of one mean free path (25nm for gold\textsuperscript{45}, and 18nm for aluminum), given by Eq. 3.4. This result can also be rigorously derived by quantum mechanical calculations\textsuperscript{20}.

\[
E_{\text{MFP}}^2 = \frac{1}{V_{\text{MFP}}} \int |E(r)|^2 \, dr
\]

\textbf{Equation 3.4 – Calculation of photocurrent responsivity for Schottky device by field intensity integration.}

For Ohmic device, a common routine, namely, the optical absorption is used for describing the electron transfer, since fundamentally the hot electron generation
depends on photon absorption. Optical absorption is calculated by integrating the product of frequency $\omega$, local electric field intensity $|E|^2$, and the imaginary part of material permittivity, which determines the heating loss, as Eq. 3.5 shows.

$$P_{MFP} = \frac{1}{2} \int_{V_{MFP}} dV |E(r)|^2 \text{Im}(\epsilon)$$

**Equation 3.5 – Calculation of photocurrent responsivity for Ohmic device by optical absorption.**

Basically, the electric field intensity term describes the plasmon-induced local field, while the imaginary part of permittivity has taken the interband transition into account. Hence, the optical absorption has included the contribution from both mechanisms.

**3.4. Device responsivity**

Wavelength-dependent photocurrent responsivity for both Schottky and Ohmic devices were measured and compared with theoretical calculations, as shown in Fig 3.6. A very good match between the experiments and theory was found, which verifies the calculation methods. The width of nanowires ranges from 82nm to 273nm and the geometries are not optimized for maximum responsivity.
Figure 3.5 – Experimentally measured device photocurrent responsivities for (b) Schottky device and (c) Ohmic device, and corresponding theoretical calculation results (d)(e), with different nanowire widths shown in (a).

For TE polarization case, where a plasmon could be excited, the photocurrent responsivity for Schottky device shows a clear plasmon lineshape, which corresponds to the plasmon mode of Au nanowires. This indicates the exclusive contribution of plasmon-induced hot carrier generation. The narrower nanowires have a broader plasmon resonance, corresponding to dipolar plasmon modes, while
the nanowires with widths larger than 155nm result in quadrupolar modes, as shown in Fig. 3.7. In TM case, where no plasmon is excited, nearly no photocurrent is generated for the whole wavelength range since the interband hot electrons are filtered by the Schottky barrier. This strong polarization dependent photocurrent responsivity clearly indicates a plasmon-induced process instead of direct optical absorption. We also note from Fig. 3.7 that for both cases, the maximal electric field is at the metal-semiconductor interface, which is beneficial for the injection of hot electrons from the metal to the substrate.

In Ohmic device, low-energy electrons excited by direct photon absorption, or interband transition, are also collected, resulting in a rise in the photocurrent for energies of incident light above 2.3eV. In this regime, interband transition of gold begins to occur. This behavior is observed in the TE case, where apart from the plasmon-induced photocurrent at gold plasmons around ~600nm to ~650nm, an almost constant photocurrent generation at around ~400nm to ~500nm is also found in the spectrum, corresponding to the interband transition. This is further confirmed by the TM case, where no plasmon happens but the contribution of interband transition is still predominant. We also note that due to the damping of the thin Ti layer, the Ohmic devices overall shows a damped photocurrent response compared to the Schottky devices.
Figure 3.6 – Electric field and charge distribution for (a) nanowires with 83nm width and (b) 273nm width in Schottky device at plasmon resonance. The electric field is mostly localized at the interface, and the plasmon mode transfers from a dipole with smaller width to a quadupole with larger width.

It is of great importance to point out that in the Ohmic device, the photocurrent responsivity in TE case at plasmon resonance is strongly enhanced compared to TM polarization. Moreover, it reaches a comparable magnitude as the photocurrent in the interband transition regime, which is corresponding to the direct excited hot electron generation. This indicates that plasmon-induced hot electron generation is indeed an efficient process. Despite the fact that in Ohmic devices the thin Ti layer between the nanostructure and substrate prevents a more direct comparison of photocurrent responsivity in these two devices, we found that for both devices the responsivity at plasmon resonance are of similar magnitude, indicating that most of the hot electrons in the plasmon-induced process could have sufficient kinetic energy to overcome the Schottky barrier and be injected into the substrate.
It is interesting to compare the photocurrent responsivity of Schottky device calculated by electric field integration with optical absorption, as Figure 3.7 shows. While the plasmon-induced hot electron generation (around ~600nm to ~700nm) is shown in both cases, we note that by calculating the optical absorption, the interband transition in Schottky device is also included in the spectrum around ~400nm to ~500nm. This is experimentally (Fig. 3.6 b) not true since this part of low-energy electrons are filtered by the Schottky barrier. We thus conclude that for Schottky device and plasmon-induced hot electron generation, the photocurrent is characterized by the electric field intensity integration instead of optical absorption, which is used in most of previous studies. Previous studies have also shown that increasing the electric field is crucial for increasing the photon-conversion efficiency of hot electrons. Based on these results, we further conclude that plasmonic hot carrier generation occurs independently of optical absorption.
Figure 3.7 – Calculated responsivity of Schottky device by (left) field integration, (right) material absorption, with TE (solid) and TM (dashed) excitations.

To further explore the Ohmic device, an aluminum based device was fabricated and investigated. Aluminum for plasmonics has been investigated in the past a few years\textsuperscript{41,46–49}. Aluminum plasmon typically has higher energy than gold plasmon and could reach the UV region. The interband transition in Al, which is
from s band to d band instead, occurs around 800nm. Hence, we expect a rise of responsivity at 800nm for both TE and TM cases, which is shown in the experimentally measured responsivity for Al Ohmic devices in Fig. 3.9.

Figure 3.8 – Photocurrent responsivity for aluminium Ohmic device. (a) Experimentally measured responsivity with TE (solid) and TM (dashed) excitations. The peak at ~800nm in both cases corresponds to aluminum
interband transition. (b) Theoretically calculated absorption within one mean free path (18nm) of the interface.

The theoretical calculations capture most of the features in experiments. The rise of photocurrent at around 400nm to 500nm is the hot electron generation induced by Al plasmon, while the interband electrons are shown in the ~850nm peak. We note this slight deviation of ~50nm compared to experiment, and this is due to the over-estimation of the electric field intensity in the absorption spectrum.
Chapter 4

Summary

In summary, we compared the photocurrent generation in metal-semiconductor based Schottky and Ohmic devices and distinguished between plasmon-induced and direct excited hot electron generations. We show that in Schottky device, the photocurrent is only from the contribution of plasmon-induced process, which could be calculated by the electric field intensity integration over the volume of one electric mean free path from the interface. In Ohmic device, both the plasmon-induced and photoexcited hot carriers can be injected, and the photocurrent responsivity could be modeled by the optical absorption within the same volume. We have demonstrated that plasmon-induced hot carriers have higher energy than the directly photoexcited electrons, and a plasmon is required to overcome the Schottky barrier. We have also shown that plasmon-induced hot electron generation is indeed an efficient process. Our work points to a clear route
to increasing the solar energy conversion efficiency by enhancing the internal field, and through the collection of both plasmonic and interband photocurrent, as we have shown in the Ohmic devices. This work helps understand the fundamental mechanisms of hot carrier generation and could find broad applications in novel photovoltaic and photodetection devices.
References


