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Hot Carrier Generation in Metallic Nanostructures: Mechanisms and Novel Devices

by

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ABSTRACT

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Hot carrier generation in metallic nanostructures offers a potential route to circumventing thermodynamic efficiencies of traditional light-harvesting devices and structures. However, previous experimental realizations of hot electron devices have shown low photo-conversion efficiencies. Several theoretical works have sought to understand the fundamental processes behind hot carrier generation and explore routes toward increasing the carrier generation efficiency. In this thesis, we discriminate between hot carrier generation from interband transitions and surface plasmons by comparing photocurrent generation in Schottky and ohmic devices. By comparing the functional form of the two types of photocurrent generation, we show that hot carrier generation in metallic nanostructures obeys the field intensity inside the metallic nanostructure, paving the way towards more efficient plasmon-induced hot carrier devices. Next, I focus on plasmonic photodetectors for the mid-IR spectral region, a technologically and scientifically important spectral region where molecular vibrational resonances exist. Despite the significance of the mid-IR, the low energy of mid-IR photons poses significant challenges for efficient photodetection and light emission. We circumvent the limitations of traditional mid-IR photodetectors by exploiting hot carrier generation in metals and demonstrate a novel uncooled CMOS-compatible photodetector for the middle wave infrared (mid-IR) spectral region.
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Chapter 1

Introduction

Surface plasmons are the coherent, collective oscillations of conduction band electrons, which allows for the conversion of free-space photons into deep sub-wavelength electron oscillations. This ability to convert energy from free space photons into nanoscale volumes has attracted an immense amount of scientific interest for many applications, such as on-chip optical components, solar energy conversion, and even biomedicine. This thesis will focus on how surface plasmons directly transfer energy from the collective oscillations into its constituent electrons, called hot electron decay, and the novel optoelectronic devices that arise from this energy transfer.

First, this thesis provides an overview of the theoretical basis for hot electron decay in metallic nanostructures. Hot electrons arise from the transfer of energy from a photon into electrons. When an electron absorbs photon energy, the electron becomes excited and temporarily leaves behind a vacancy, also known as a hole. Electron-hole pairs has been observed in many, many types of materials, especially semiconductors,
and much of the mathematical machinery for understanding electron-hole pair production in metals stems from observations and theories developed for semiconductors. This thesis will provide some background into the different approaches that several groups have pursued in developing a theory of electrons and holes in metals and note some of the challenges in developing a theory for electron-hole pair production in metals.

Next, this thesis will provide some experimental results of hole electron production in metal-semiconductor solid state devices. In this section, I outline a device platform for investigating hot electron production in metal nanowires and show that the production of hot electrons in plasmonic nanostructures can be unambiguously distinguished from heating and optical impedance matching. This device platform shows that hot carrier production in metal nanostructures follows the field intensity inside the metal and not the absorption. These results have fundamental implications in how to maximize hot carrier production in metal nanostructures.

The next section focuses on a novel hot-electron based photosensor for the mid-infrared. The mid-infrared spectral region is a technologically and scientifically important spectral region, especially for telecommunications and optical spectroscopy. However, detectors for this spectral region are notoriously expensive and impractical, often requiring cryogenic cooling and exotic binary or tertiary semiconductor compounds. In this novel hot-electron based photodetector, mid-infrared light is converted into electron pairs using a plasmonic grating structure and directly injected into a semiconductor. This allows for the detection of mid-infrared light without the need for cryogenic cooling or exotic materials.
Theoretical Underpinnings of Hot Carrier Decay

Surface plasmons can lose energy through 2 decay channels: nonradiative decay and radiative decay. Radiative decay is the release of plasmon energy via a photon, also called scattering. Nonradiative decay encompasses all decay channels that do not involve the emission of a photon: heat, excitons, etc. Previously, it was believed that nonradiative plasmon decay only resulted in nanoparticle or nanostructure heating and there exists a large body of literature that clearly demonstrates that plasmonic nanoparticles undergo heating upon illumination\textsuperscript{1–9}.

However, some groups also reported light-dependent catalytic activity\textsuperscript{10–13}. These early groups showed that gold nanoparticles on certain substrates could enhance the rate of oxidation of citrate\textsuperscript{10,14,15} or could enhance the rate of hydrogen and oxygen production in a water splitting reaction\textsuperscript{16–18}. The catalytic reactions differ strongly from nanoparticle heating in that the creation of byproducts from chemical reactions cannot be energetically
explained through thermal effects alone\textsuperscript{19,20}. These pioneering experiments implicated an electron injection process and interest developed in how this phenomenon occurred and if the hot electron generation could find use in other catalytic systems or electrical devices. These experiments were further supported through experimental demonstrations using solid-state devices\textsuperscript{21–25}.

To understand the current theories about hot carrier generation in metals, it is important to visit the fundamentals of optical absorption that leads to electron-hole pair excitation. Before this thesis outlines the mathematical framework for understanding optical absorption in materials, it is important to first make a note about the nomenclature adopted by the plasmonics community.

“Hot” electrons in plasmonic nanoparticles and nanostructures refer to the effective electron temperature during optical excitation. In the absence of an incident light field, the electrons in a material follow a Fermi-Dirac distribution and the Fermi function that fits the electron occupation defines its temperature. In plasmonics, the term “hot” electron or “hot” hole describes a non-equilibrium distribution of electrons or holes, driven by an optical field that does not follow a Fermi distribution. As the excited electrons and hole lose energy through various scattering processes, their energy distribution thermalizes into a Fermi distribution called a ‘hot’ Fermi distribution and also called “hot” carriers and continue to be called hot carriers until the nanoparticle or nanostructure reaches thermal equilibrium with its surrounding.
2.1. Free Electron-Hole Pair Absorption

This particular section focuses on providing a broad overview of optical absorption in semiconductors and outlining some of the mathematical formulas and notations used to derive and analyze certain optical properties of semiconductors. This section does not strive to be exhaustive nor definitive but rather, to provide the reader a familiarity with the math and to give an intuitive explanation of why one might expect a certain functional form for plasmon-induced hot carrier generation.

Classically, the optical properties of free electrons and lattice vibrations are treated using the classical equations of motion:\(^26\)

\[
\frac{m_0 d^2 x}{dt^2} + \frac{m_0 \gamma dx}{dt} + m_0 \omega_0^2 x = -qE
\]

where \(m_0\) is the free electron mass, \(\gamma\) is a damping term, and the incident field \(E\) is described by a plane wave.

However, electron-hole pair absorption is a quantum mechanical phenomenon so the treatment of electron-hole pair absorption due to a light field must be modified. The modified approach uses quantum mechanics to treat different absorption mechanisms in the medium but retains the classical equations for the description of light. This should be noted that this semiclassical approach works well for calculating the absorption and emission properties of a material but generally fails for problems where the light field is also quantum mechanical, like in the case of stimulated emission.

In an electromagnetic field, an electron feels a force:
\[ F = -qE - \frac{q}{c} v \times B \]

So the corresponding Hamiltonian is given by:

\[ H = \frac{1}{2m_0} \left( p - \frac{q}{c} A \right)^2 + W + q\phi \]

where \( p \) is the electron momentum, \( q \) is the electron charge, \( c \) is the speed of light, \( A \) is the vector potential of the light field, \( W \) is the periodic potential of the lattice and \( \phi \) is a scalar potential. So after expanding the above Hamiltonian:

\[ H = \frac{p^2}{2m_0} + \frac{q^2}{2mc^2} A^2 - \frac{q}{2m_0c} (p \cdot A + A \cdot p) + W + q\phi \]

By using the quantum mechanical momentum operator, \( p = \frac{\hbar}{i} \nabla \), the expanded Hamiltonian becomes:

\[ H = \frac{p^2}{2m_0} - \frac{q}{m_0c} A \cdot p + \frac{iq\hbar}{2m_0c} \nabla \cdot A + \frac{q^2}{2m_0c^2} A^2 + W + q\phi \]

In general, for a given electric field, \( E \), and a given magnetic field, \( B \), the corresponding vector potential, \( A \) and the scalar potential, \( \phi \), are not uniquely defined unless constrained otherwise. So we make use of the Coulomb gauge (\( \nabla \cdot A = 0 \)) and assume that there are no free external charges or currents (at least not at optical frequencies).

This has the benefit of simplifying the Hamiltonian to something more manageable:

\[ H = \frac{p^2}{2m_0} - \frac{q}{m_0c} A \cdot p + \frac{q^2}{2m_0c^2} A^2 + W \]
This equation is simplified even further if we ignore the $A^2$ term because in general, for weak light intensities, this term is much weaker than the linear term $A$ and because it does not involve the momentum operator, does not change the momentum of electrons in the system and therefore does not alter the state of the electron.

We finally arrive at the Hamiltonian:

$$H = \frac{p^2}{2m_0} - \frac{q}{m_0c} A \cdot p + W$$

I will first note that this Hamiltonian composes of two terms which do not relate to the incident field (non-interacting terms) and one term that does (interaction term). We can think of this Hamiltonian as composed of two parts, one with the light field present ($A \cdot p$) and one without ($p^2 & W$).

Now, to calculate the probability of a field induced transition between energy eigenstates of the system, we use the Schrödinger equation for the wave function:

$$i\hbar \frac{\partial \psi'}{\partial t} = H\psi'$$

For the non-interacting terms, the solution is straightforward and has the solution:

$$H\psi_n = E_n\psi_n = -\hbar \omega_n \phi_n(r)e^{-i\omega_n t}$$

To calculate the transition probability, we relate the final excited states in the presence of a perturbing light field to these initial states in the absence of the light field.

Specifically, if $\psi'_n$ is the full wave $n$th eigenfunction, then
\[ \psi_n'(r, t) = \sum_n a_n(t) \psi_n(r, t) = \sum_n a_n(t) \phi_n(r) e^{-i\omega_n t} \]

where the spatial and time-dependent components have been made explicit and separable. Here, each \( a_n \) is the transition probability to go from any eigenstate of the unperturbed field to the \( n \)th eigenstate of the perturbed eigenfunction. The importance of this relation is to account for absorption by energy bands, which differs from transitions between two discrete levels. It should be noted that the sum of all of the coefficients, \( a_n \), equals 1 and that the \( \phi_n \) eigenfunctions are orthonormal.

Now, to find the transition rate to state \( m \) per unit time, we can plug the wavefunction into the Schrödinger equation to get:

\[
\frac{i\hbar da_m(t)}{dt} e^{-i\omega_m t} = \sum_n a_n(t) e^{-i\omega_n t} \langle q_m | H_{int} | q_n \rangle
\]

and solve for \( a_m(t) \). The solution for this equation can be found in most solid state physics textbooks so this thesis will present the final result:

\[
\Gamma_{ml} = |a_m|^2 = \left| \frac{1}{i\hbar} \int_0^t dt' \langle \phi_m | H_{int} | \phi_l \rangle e^{i\omega_{ml} t'} \right|^2
\]

In general, the interaction Hamiltonian depends on the type of incident wave and will change the evaluation of this expression. For the simple case of a plane wave, the wave is described by the plane wave equation and the interaction is described by the induced dipole moment inside the material: \( q \cdot d \), where \( d \) is the displacement vector.
I will note that in most cases for light in visible region, the dipole approximation is taken. The dipole approximation comes from the plane wave equation, which is composed of a time-varying term and a spatial term:

$$-\frac{E_0}{2} (e^{i(k\cdot r - \omega t)} + e^{-i(k\cdot r - \omega t)})$$

In general, the wavelength of visible light greatly exceeds the lattice constant so for variations of the electromagnetic wave on the atomic scale, $k \cdot r \ll 1$. A Taylor expansion of the plane wave then gives:

$$e^{ik\cdot r} = 1 + ik \cdot r + \ldots$$

The result is that all terms after the 1 become vanishingly small. The higher order terms for the plane waves would only be relevant for higher order transitions, i.e. quadrupolar transitions, octopolar transitions, etc where the wavelength of the incident light is on the order of the lattice constant or shorter. This makes intuitive sense that at visible wavelengths, the probability of exciting the quadrupolar or octopole transition of a single atom is extremely small and therefore dominated by the first term, which corresponds to a dipolar transition and hence called the dipole approximation.

The key takeaway from these derivations is that the transition probability for any type of absorption or emission should take the form:

$$I_{ml} = \left|\frac{d_{ml}E_0}{2\hbar} \right|^2 \left| \int_0^t dt' (e^{-i\omega t'} + e^{i\omega t'}) e^{i\omega_{ml}t'} \right|^2$$

which has a dependence on the electric field inside the material, $E_0$. 
2.2. Modification of Electron-Hole Pair Absorption Calculations for Metal Nanostructures

The bulk of the theoretical hot-carrier studies in plasmonics depend on this general machinery as a starting point. Still, there exist many differentiating factors for plasmonics so the above approach must be heavily modified. When one extends the theoretical framework to metal nanostructures, one must take into account the differences come from the intense field enhancement of metal nanostructures, the density of states in the metal, the collective electron oscillation as a quantum state, carrier scattering, interfacial properties, and several other factors.

In the above derivation, the field is generally assumed to be at most $E_0$ which implies zero field enhancement. For bulk dielectrics, this is generally true because there are no mechanisms for field confinement. For metallic nanostructures, the strong field confinement results in intense field enhancements, easily exceeding 1000 times the incident field. Whether or not this strong field enhancement results in a breakdown of the semiclassical approach remains difficult to probe, but it is probably sufficient to replace the $E_0$ term above with just $E$ and treat the field enhancement as a simple scalar multiple.

Next, to accommodate the density of states in metal, there are several approaches. One approach is simply to approximate the band structure as a parabola because the electron density is so high\textsuperscript{27,28} and another approach uses the realistic, experimentally derived band structure\textsuperscript{29,30} as a starting point. While the latter approach will almost certainly provide more accurate results, it remains to be seen if the extra computation really increases the accuracy by a significant amount. This is especially relevant because
some experimental studies\textsuperscript{12} indicate that electron excitation in metals may occur more preferentially near the Fermi level.

To address the collective nature of the plasmon, there has generally been one approach, simply to replace the electron wavefunctions $\phi$ with plasmon wavefunctions. It might seem odd that a theory of absorption and emission derived for a single photon and a single electron can suddenly account for oscillations of billions or trillions of electrons by a simple substitution but that is the current state of research into this topic. This approach is not unprecedented and has been approached previously under the framework of many-body perturbation theory\textsuperscript{30}.

While there exists ample literature of photoemission studies of various materials, the bulk of those studies rely on bulk metals or relatively large films. To answer many of the above questions, some experimental work has turned to photoemission experiments to directly probe electron dynamics in nanostructured metals\textsuperscript{31–36}. This thesis takes a different approach, instead by making use of solid-state devices to probe hot carrier photophysics in metallic nanostructures.
Mechanism of Hot Electron Decay in Plasmonic Nanostructures

The use of metal nanoparticles and nanostructures for enhanced solar energy conversion has shown to be a promising route towards direct light-to-fuel synthesis, or more efficient photovoltaic devices\textsuperscript{12,19,37}. Still, a full understanding of the mechanisms of plasmonic carrier generation remains elusive and many groups have sought to understand the vast body of experimental work\textsuperscript{38–42,24,25,43,10,44,18,45,11,16,46} by calculating hot carrier efficiencies through \textit{ab initio} calculations\textsuperscript{27–29,47}. Two possible hot carrier generation mechanisms in metals are direct photoexcitation and plasmon decay. Hot carrier generation by direct photon absorption is possible in metallic structures, but the small electron-photon cross-section makes this process fundamentally very inefficient. The efficiency can be somewhat compensated for in a metal with a larger density of electronic states, as in the case of the d-band electrons in Au, but it is ultimately limited by the inherent optical absorption in the metal. On the other hand, plasmonic
nanostructures exhibit extremely large absorption cross-sections, which can be significantly larger than the physical cross section of the nanostructure. Furthermore, plasmonic absorbers can obtain near perfect absorption\textsuperscript{48}, indicating that plasmon-induced hot carrier generation could be extremely efficient.

Since plasmonic hot carrier generation depends fundamentally on photon absorption, previous work has focused on correlating the experimentally measured photocatalytic activity spectrum or photocurrent responsivity with the calculated absorption spectrum.\textsuperscript{12,19} Optical absorption is a local quantity that can be calculated by integrating the product of frequency $\omega$, local electric field strength $|E|^2$, and the imaginary part of the dielectric permittivity over the full volume of the nanostructure. However, hot carriers generated far from the nanoparticle surface can undergo scattering, recombination, or lose energy in other ways and ultimately prevent its use in chemical reactions or injection over an energy barrier. Only carriers generated closer to the interface than the mean-free path, $l_{\text{MFP}}$, can participate in interfacial electron transfer\textsuperscript{43}. Thus, the relevant quantity for electron transfer is:

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

where $V_{\text{MFP}}$ is the volume within a distance of $l_{\text{MFP}}$ from the interface. However, this type of analysis cannot distinguish between directly photoexcited carrier generation and high energy carriers generated from plasmon decay, an important distinction in many applications. In photocatalysis, where chemical transformation is induced by the injection of hot carriers over an energy barrier into an unoccupied molecular orbital of an
adsorbate molecule, it is of vital importance to understand which carrier generation process can ultimately lead to useful, high energy hot carriers.

For photocurrent generation, hot carrier extraction generally involves injecting hot carriers over a Schottky barrier\textsuperscript{23,49}. A Schottky barrier is formed at a metal-semiconductor junction and only allows significant current flow in one direction. Furthermore, Schottky diodes are majority-carrier devices where the current flow is conducted by either electrons or holes, but not both. This allows a Schottky diode to exclusively collect either hot electrons or hot holes, and prevents recombination, minimizing current loss. In this work, we exploit the material properties of reduced TiO\textsubscript{2}, which preferentially transports electrons\textsuperscript{50}, to compare the properties of electrons collected across Ohmic junctions, where the effective barrier height is essentially zero, to those collected across a Schottky barrier.

### 3.1. Schottky vs. Ohmic Interfaces

The different properties of Schottky and Ohmic contacts allow us to selectively probe the two different carrier generation mechanisms in metals (Figure 1a and b). With a Schottky contact, we expect to collect only hot carriers generated from plasmon decay. This is because directly photoexcited carriers in Au are generated primarily from interband transitions and excited from the d-band with its upper edge ~2.3 eV below the Fermi level.\textsuperscript{51} For optical excitations from 1 to 3 eV, electrons are excited from the d-band to a maximum of ~0.5 eV above the Fermi energy (Fig. 1c and d). The same type of electronic excitations can occur in plasmon decay\textsuperscript{29}. However, the physical mechanism underlying electron hole pair generation in plasmon decay is different than in direct
excitation from incident plane waves. In plasmon-induced carrier generation, the perturbing potential driving the transitions is the plasmon-induced near field, which is localized to the surfaces of nanostructures. Plasmon induced carrier generation thus favors excitation of electrons from near the Fermi energy, resulting in substantially higher energy electrons. For a Schottky barrier height of 1 eV, only the high energy electrons will have sufficient kinetic energy to overcome the barrier. Therefore, the net photocurrent is exclusively from plasmon decay (Figure 1b). For an Ohmic contact, where no barrier is present, low energy electrons can also be collected, so the net photocurrent should have both plasmonic and interband contributions (Figure 1d). While it is typically assumed that carrier separation in plasmonic hot electron devices requires an electric field, the band alignment of the Ohmic device presents electrons and holes with two very different barrier heights. For electrons, the Ti barrier layer forces the Fermi level of gold to align with the conduction band of TiO₂. However, this band alignment results in a very large barrier height for holes and allows the TiO₂ to efficiently and preferentially collect photogenerated electrons.
Figure 1 Device Overview and Band Diagrams. Schematic of hot carrier generation and collection over a Schottky (a) or Ohmic barrier (b). Plasmonic hot carrier generation from surface plasmons is localized to areas of large field enhancements, while hot carriers generated from interband absorption can occur throughout the bulk material, limited instead by absorption depth. Band diagram schematics of (c) a Au-TiO$_2$ Schottky device and (d) a Au-Ti-TiO$_2$ Ohmic device. Carrier generation by direct photoexcitation results from the excitation of d-band electrons, 2.3 eV below the Fermi level, into the conduction
band. Their low energy prevents them from crossing the Schottky barrier (≈ 1 eV).

Ohmic devices have no effective barrier and allows for collection of carriers created by this process. The wide band-gap of the semiconductor allows preferential collection of electrons. (e) Representative scanning electron microscope (SEM) image of a fabricated nanostructure comprised of a contact pad and a nanowire array. Current-voltage (I-V) curves of Schottky (f) and ohmic devices (g). Red curves are the averages and all measured I-V curves fall within the gray bounded regions.

This study helps resolve a fundamental question in surface plasmon photophysics by demonstrating the large energy difference between hot carriers produced by surface plasmons and interband transitions. This large energy difference allows for a theoretical framework that largely ignores the band structure of the metal and focuses instead on field intensity enhancement. Our study further demonstrates that it is possible to collect both plasmonic and interband photocurrents without a rectifying barrier and shows a surprising deviation from the commonly observed Fowler response in silicon-based devices.

3.2. Device Geometry

We designed a simple device geometry consisting of a square metal pad and a metal nanowire array fabricated onto a TiO₂ substrate (Fig. 1e). All nanostructures were 50 nm thick and adjacent nanowires were spaced 500 nm apart for all devices. Arrays of devices of varying nanowire widths were fabricated on single-crystal rutile
<100> TiO\textsubscript{2} substrates using standard cleanroom and electron beam lithography techniques. The substrates initially exhibited extremely high resistance (>100 GΩ). Heating the substrates in vacuum introduced oxygen vacancies, n-doping the crystal substrate\textsuperscript{53}. The resistance across the crystal decreased to ~10 kΩ after heat treatment and the crystal color changed from slight yellow to blue. This color change is due to free carrier absorption from shallow mid-band trap states\textsuperscript{53}, which does not increase the number of free carriers under illumination and therefore, does not contribute to photocurrent. These trap states do not alter the bandgap of TiO\textsubscript{2} and serve as the main mechanism for conducting electrons across the substrate.

Ohmic and Schottky devices were patterned and fabricated on the same TiO\textsubscript{2} substrate using electron-beam lithography and shadow masking. Au-TiO\textsubscript{2} junctions form Schottky contacts while Au/Ti/TiO\textsubscript{2} junctions form Ohmic contacts. The Ti barrier layer is 2 nm and kept thin to minimize plasmon damping. The methods section cover the fabrication process in more detail.

### 3.3. Electrical Characterization

The current-voltage (I-V) characteristics for the two devices are shown in Figure 1f and 1g. The red line is the average device current-voltage (I-V) curve and all device I-V curves are bounded by the gray regions. The Schottky devices exhibit current rectification while Ohmic devices show linear I-V characteristics. We extracted Schottky barrier heights by fitting the I-V curves with the diode equation\textsuperscript{54} and obtained barrier heights between 1.02 eV and 1.13 eV, with an average of 1.07 eV. These measurements agree well with previous reports of Au-TiO\textsubscript{2} Schottky barrier heights (~1 eV).\textsuperscript{55} A lock-in
amplifier was used for photocurrent measurements; all devices were measured without an
applied bias voltage. We verified that the measured photocurrent in the Ohmic devices is
consistent with electron injection, and not explained by changes in device conductance or
junction resistances. In addition, we verified that photocurrent losses due to charge
recombination in the substrate were minimal.
3.4. Photocurrent Mapping

Figure 2 Photocurrent Mapping. Schematic of transverse electric (TE) (a) excitations used to generate photocurrent maps. The laser wavelength is tuned to the resonance of the plasmonic nanowires (~675 nm, wire width 273 nm). Photocurrent maps of a (b) Schottky and (c) Ohmic device using TE polarized light. (d) Schematic of transverse magnetic (TM) polarized light excitation. Photocurrent maps of a (e) Schottky and (f) Ohmic device. In the Schottky device, photocurrent production is drastically reduced while in the Ohmic device, photocurrent is observed throughout the metal nanostructure and in the nanowires.
Mapping the photocurrent as a function of polarization of the incident light in the various regions of each device allows us to determine the specific regions of the structure where the photocurrent originates, which allows us to discriminate between the plasmon-induced and directly photoexcited current contributions. We produce photocurrent maps by raster scanning a diffraction-limited laser spot (~3 µm spot size) over a device and using a lock-in amplifier to record the photocurrent signal. The substrate produces no photocurrent since the wavelength of the incident light, 675 nm, which corresponds to the plasmon excitation energy of 1.84 eV, cannot be directly absorbed by rutile TiO₂ (bandgap ~3.03 eV). For light polarized transverse to the plasmonic nanowires (TE polarization), shown schematically in Figure 2a, we observe photocurrent generation in the Schottky device (Figure 2b) when scanning over the plasmonic nanowires and at points of broken symmetry along the edges of the metal pad. In the Ohmic device (Figure 2c), photocurrent is produced when scanning over the nanowires as expected, but photocurrent is also produced throughout the entire pad region, where no plasmon mode exists. The spatial distribution of this photocurrent generation suggests that it arises from bulk absorption, since the photocurrent is generated homogeneously throughout the pad area. We also generated photocurrent maps using transverse-magnetic (TM) polarized light (Figure 2d). For the Schottky device (Figure 2e), no photocurrent is generated in the substrate and little photocurrent is produced by the metal nanostructure except at point defects and edges. In stark contrast, a significant amount of photocurrent is observed throughout the Ohmic device (Figure 2f) in the pad region as well as in the nanowires, for which no plasmon mode is excited. This photocurrent, which arises regardless of polarization and geometry, shows that the photocurrent in the Ohmic devices results from
direct excitation and not plasmon decay, where the photocurrent would exhibit a strong dependence on the geometry of the metal nanostructure as well as the polarization of incident light.

### 3.5. Device Responsivity

We provide further evidence that the nonresonant photocurrent is from interband transitions by comparing the wavelength-dependent photocurrent responsivity of plasmonic nanowires with either a Schottky or Ohmic interface. SEM images of the different wire widths are shown in Figure 3a. No attempt was made to optimize the nanowires for maximum responsivity. The increase in photocurrent for wavelengths shorter than 410 nm is due to direct absorption in TiO$_2$, corresponding to a bandgap of 3.03 eV.$^{53}$ For Schottky devices, the responsivity shows strong polarization dependence (Figure 3b). For TE polarization, the photocurrent response shows unambiguous resonances corresponding to plasmonic modes of the nanowires. The broad resonances for the small nanowire widths correspond to dipolar plasmon modes while the sharp resonances for nanowire widths of 155 nm and larger are quadrupolar plasmon modes (Supplementary Fig. 5). TM polarized excitations produced little to no photocurrent, because the excitation is detuned from any plasmon mode.

Since the Ohmic devices can collect low energy electrons excited via interband transitions, we expect a rise in the photocurrent for photon energies of the incident light above 2.3 eV, where the interband transitions in gold begin to occur. We verify using photocurrent maps that the photocurrent at shorter wavelengths is localized to the metal nanostructure and does not correspond to absorption in the TiO$_2$. Ohmic devices (Figure
3c) show the predicted increase and also show that the responsivity matches very well with the absorption spectrum (Figure 3e) calculated using Eq. 1, which includes interband transitions. In particular, the response at shorter wavelengths closely follows the onset of interband transitions as manifest in the imaginary component of the gold dielectric permittivity. Overall, the Ohmic devices show a damped photocurrent response when illuminated on resonance, which results from damping by the Ti barrier layer. We note that the photocurrent for plasmon excitation (TE) in the Ohmic devices is also strongly enhanced compared to the TM excitation and reaches a similar magnitude as for direct excitation at the interband threshold at much higher energy. This shows that plasmon-induced carrier generation indeed is an efficient process. Although the Ohmic devices have a thin Ti layer between the antenna and the substrate, preventing a direct comparison of the photocurrent responsivity of the two types of devices, the responsivity of Ohmic and Schottky devices at the plasmon resonances are similar in magnitude, suggesting that most of the plasmon-induced hot electrons have sufficient energy to traverse the Schottky barrier.
3.6. Discussion

Figure 3 Device Responsivities. (a) SEM images of the different nanowire widths used for responsivity measurements. Scale bar is 500 nm for all images. (b) Experimentally measured responsivities for Schottky devices when excited with TE (solid) and TM
(dashed) polarizations. (c) Experimentally measured responsivities of Ohmic devices. (d) Numerically calculated photocurrent response (Eq. 2) for the Schottky devices. (e) Numerically calculated absorbed power (Eq. 1) for the Ohmic devices using an lMFP = 25 nm.

Through theoretical modeling, we show that hot carrier generation is independent of interband carrier generation. Since the inherent material absorption is described by the imaginary part of the dielectric, the calculated absorbed power Eq. (1) will include interband transitions. In contrast, hot carrier formation from plasmon decay is predicted to be determined directly by the plasmon induced local electric field $|E(r)|^2$. To model the contribution to the photocurrent of carriers from plasmon decay, we thus integrate the field intensity enhancement over the volume $V_{MFP}$:

$$E^2_{MFP} = \frac{1}{V_{MFP}} \int |E(r)|^2 \, dr$$

(2)

Using this method, we obtain excellent agreement between the calculated (Figure 3d) and measured (Figure 3c) photocurrent responsivity for the Schottky devices. We note that the enhancement for our devices is strongest at the metal-semiconductor interface and that all integrations for these devices were performed within one mean free path of the interface (25 nm). Previous work has shown that increasing the field enhancement near the interface is important for increasing the efficiency of hot electron devices. Since the photocurrent response matches with the field intensity enhancement rather than with the material-dependent absorption, we have shown that plasmonic hot carrier generation occurs independently of material absorption.
It is important to note that we do not observe a Fowler-type response for the Schottky devices. In general, Fowler theory is used to explain a quadratic increase in the photocurrent responsivity for higher photon energies\textsuperscript{27} and derived using a quadratic density of states, equal probability of excitation for all states, and an isotropic momentum distribution for excited carriers. Our result indicates that one or more of these assumptions is not likely to be applicable to plasmonic carrier generation. It is unclear why this work and other experiments with rutile TiO\textsubscript{2}\textsuperscript{18,11} do not observe a Fowler-type response but we speculate that it could be related to the behavior of indirect semiconductors like Si, or anatase TiO\textsubscript{2}\textsuperscript{58}, for which absorption also increases quadratically near the band edge\textsuperscript{59}. On the contrary, rutile TiO\textsubscript{2} has a direct bandgap, which results in an absorption coefficient that increases sharply at the band edge. Therefore, all measured photocurrent is directly attributed to surface plasmons and independent of any absorption in the semiconductor substrate.
Figure 4: Hot Carriers in Aluminum Nanowires. (a) Photocurrent responsivities of ohmic aluminum structures. The peak at ~800 nm in both TE and TM polarizations corresponds to aluminum interband transitions. (b) Numerically calculated absorbed power within one mean-free path of the interface (18 nm) for a single nanowire.
By comparing gold Ohmic devices with equivalently fabricated aluminum Ohmic devices, we establish that the Ohmic devices collect hot carriers generated from interband transitions. One major difference between gold and aluminum is that aluminum interband transitions occur at a much longer wavelength, near \( \sim 800 \) nm (\( \sim 1.5 \) eV).\(^6\) Therefore, we predict that Ohmic aluminum devices will exhibit a peak at 800 nm for both TE and TM polarizations. Our measured responsivities, shown in Figure 4 Hot Carriers in Aluminum Nanowires, confirm this prediction. Theoretical modelling reproduces most features of the experimental results (Figure 4 Hot Carriers in Aluminum Nanowires\(^b\)). We note that the theoretical calculations likely overestimate the intensity inside the nanostructure, which leads to a peak at \( \sim 850 \) nm, as opposed to the interband peak at 800 nm. We did not measure significant photocurrent generation in aluminum Schottky devices. We speculate that the relatively thick Au barrier layer (6 nm) which was required to form a continuous film significantly damps the optical response.

In summary, by comparing the photocurrent generation through plasmon excitation and from direct excitation in simple Schottky and Ohmic devices, we have demonstrated that plasmonic hot carrier generation results in higher energy electrons than direct excitation. We have shown that for the Schottky device, the photocurrent responsivity can be calculated by integrating the electric field enhancements over a volume within the electronic mean free path of the surface of the plasmonic nanoparticle. For the Ohmic device, the responsivity can be calculated by integrating the imaginary part of the metallic permittivity over the same volume and is dominated by interband transitions. Our results open up new avenues for increasing photo-conversion efficiency
through the collection of both plasmonic and interband photocurrent and could find broad applicability in novel optoelectronic devices.
Chapter 4

Hot-Electron Devices in the Mid-Infrared

The middle wave infrared (mid-IR) spectral region is a technologically and scientifically important spectral region but poses significant challenges for light emission and detection. In this region (2-10 µm), a large number of molecular vibrations exhibit resonances and therefore many materials can be uniquely identified according to its mid-IR absorption spectrum. This spectral region is also used for thermal imaging, which has a number of important industrial and scientific applications, from gas-leak detection to night vision to energy auditing.

4.1. Challenges of Mid-IR sensing

Despite the technological and scientific importance of the midIR, photodetection in the mid-IR poses significant challenges. These challenges arise from the low energy of mid-IR photons (0.1 eV to 0.5 eV). In order to absorb low energy photons and convert it
into an electrical signal, mid-IR photodetectors exotic materials with small bandgaps (e.g. HgCdTe, InSb, etc.)\textsuperscript{61}, gapless materials (e.g. graphene)\textsuperscript{41,62–64}, inter-subband transitions\textsuperscript{65}, quantum dots\textsuperscript{66}, or quantum wells\textsuperscript{67}. These types of detectors almost always require cryogenic cooling as thermionic noise at room temperatures becomes a dominant noise source. Other approaches to mid-IR light sensing have focused on converting the mid-IR photon into heat, and then measuring the corresponding output voltage or current. Such devices include MEMS-based microbolometers, vanadium dioxide bolometers, and other pyroelectric sensors\textsuperscript{68}. However, these types of detectors are generally not suitable for high-speed applications and less sensitive than cooled detectors. An ultra-fast room temperature mid-IR photodetector made from earth-abundant materials significantly advances mid-IR photodetection.

Here we show an ultrafast photodetector where the active optical element comprises of a metallic nanostructure that generates photocurrent from hot-carriers. Metallic nanostructures support surface plasmons, or coherent oscillations of conduction band electrons and can efficiently couple with free-space light into resonant electronic oscillations without the use of dipolar single electron transitions. These oscillations occur at room temperature and can be deterministically controlled through proper geometric and material selection. As plasmons oscillations decay, they can give some of their energy into excited electron-hole pairs, or “hot” carriers, which results in a measurable electrical signal. While surface plasmon-based optical sensors for the mid-IR have been demonstrated\textsuperscript{69–71}, plasmon-derived photodetectors remain unrealized.

The difficulty in using surface plasmons for mid-IR photodetectors arises from injection of a generated hot carrier over non-zero barrier height. Typically, hot carrier
injection from the metal nanostructure into an adjacent semiconductor occurs over a Schottky barrier, which exceeds 0.4 eV for most combinations of metals and semiconductors. Therefore, surface plasmon-derived photodetectors have only been demonstrated in the near-infrared\textsuperscript{24,25,46,23}.

### 4.2. Mid-IR sensing with ohmic devices

While it was previously assumed that hot carrier injection required a rectifying barrier\textsuperscript{12}, recent experiments\textsuperscript{72,73} have shown that hot carrier extraction over a zero-energy ohmic barrier is possible with proper band alignment between materials.

Figure 5 Schematic of a plasmon-based photodetector for the mid-infrared. The device is composed of an aluminum metallic nanoantenna with a resonance tuned for the midinfrared. The excitation of a surface plasmon in the metallic nanostructure results in
the creation of electron hole pairs. Due to the band alignment of aluminum and silicon (inset), there exists different barriers for electrons and holes. Excited electrons are effectively blocked from collection whereas excited holes see an ohmic barrier. The difference in the barrier heights for electrons and holes results in a net current flow.

A schematic of the device in Figure 5 demonstrates the working principle of this type of device. The metal nanostructure acts as the active optical element and its surface plasmon resonance allows for the strong coupling of mid-IR light into surface plasmons, which create energetic electron-hole pairs. An ohmic barrier collects excited holes and the band alignment of Al and p-type Si establishes an electron-blocking barrier, which results in net current flow that produces a measurable signal. It is important to note that the Al-Si ohmic interface only presents holes with a zero-energy barrier. For electrons, the effective barrier height is the full bandgap of silicon, effectively blocking all electrons from collection in the semiconductor. Since the Al-Si interface only allows one type of carrier to pass through, this photodetector can generate photocurrent under mid-IR illumination at room temperature.
4.3. Device Electrical Characterization

Figure 6 Device Characterization. Scanning electron microscope (SEM) image of a representative device with grating pitch 1 μm. b) Current-voltage curve of the device presented in a), as well as the difference between the dark current and the current under illumination for small biases (inset). The inset shows a open-circuit potential and a short
circuit current. c) power dependence of the device, showing linear behavior under laser illumination. The laser wavelength is 4 µm.

First, we electrically characterize this type of detector. A scanning electron microscope image, shown in Figure 6a, shows a representative photodetector, consisting of an aluminum plasmonic grating on a p-type silicon wafer. The current-voltage (IV) curve for the representative device is shown in Figure 6b. For small biases near zero voltage, the change in the IV curve (inset) shows an open-circuit potential and a short-circuit current, which indicates a charge injection or generation mechanism as opposed to purely bolometric. While the absorptivity in moderately and heavily-doped silicon increases in the mid-IR spectral region, the increased absorption results from free carrier absorption, which cannot produce an open-circuit potential since the number of free carriers does not change. We also show that the photocurrent response of an unbiased detector remains linear over 2 decades of illumination power (Figure 6c), which eliminates any multiple-photon absorption processes as possible sources for the photocurrent. For larger biases, the photocurrent response increases to 2.36 mA, or a responsivity of 2.04 A/W, which corresponds to a calculated noise-equivalent power of 27.9 pW/√Hz.
Figure 7 Photocurrent mapping. a) Bright-field microscope image of a fabricated device with a measurement probe tip. b) Photocurrent map of the same area obtained by raster scanning a laser spot over the sample (4 µm wavelength, ~10 µm spot size, polarized transverse to the grating).

We show that the photocurrent signal does not originate from the silicon substrate through photocurrent mapping. By raster-scanning a laser spot (4 µm laser wavelength, ~10 µm spot size) over the sample and recording the photocurrent at each position, we build up a spatial map of where the photocurrent is produced. From the photocurrent map, we clearly see the most photocurrent produced when the laser spot illuminates the device grating and decreases as the laser spot moves away from the device.
4.4. Device Optical and Optoelectronic Characterization

Figure 8 Device optoelectronic response. Fourier transform Infrared (FTIR) spectra a) of several devices with grating pitch ranging from 750 nm to 2000 nm. b-g) Photocurrent responsivity curves for the devices in a). The illumination was polarized transverse to the long axis of the grating.
We show that the photodetector can be tuned for specific wavelength bands by examining the wavelength-dependent response of the photodetector. In Figure 8 Device optoelectronic response. Fourier transform Infrared (FTIR) spectra a) of several devices with grating pitch ranging from 750 nm to 2000 nm. b-g) Photocurrent responsivity curves for the devices in a). The illumination was polarized transverse to the long axis of the gratinga, we show Fourier Transform IR (FTIR) spectra of several grating structures. The spectra have broad dipolar resonances in the 3-10 μm range and for shorter wavelengths near the NIR spectral region, the structures exhibit narrower resonances, corresponding to higher-order grating modes. The absorption resonances of the structures increase with grating pitch and strongly polarization-dependent throughout the mid-IR “fingerprint” region. The device photocurrent responsivities shows excellent agreement with the FTIR spectra.

4.5. Discussion

We have demonstrated an uncooled photodetector for the mid-IR spectral region using earth-abundant materials that eliminates the need for exotic materials and cryogenic cooling of typical mid-IR sensors. The high responsivity of the demonstrated devices compare comparably to commercially available devices which could lead to a dramatic reduction in the cost of mid-IR sensor technologies. Since each sensor can tune to maximize or minimize sensitivity for specific spectral regions of the mid-IR, this type of photodetector could lead to novel hyperspectral spectroscopic techniques with broad applications in infrared spectroscopy.
Chapter 5

Summary

This work has investigated the fundamentals of hot carrier photophysics in metallic nanostructures and developed a novel sensor based on these results. In order to design and develop better devices based on hot carrier generation, many factors must be considered and optimized. First, the plasmonic nanostructure must maximize the field intensity inside the metal, which requires extremely strong field oscillations. From the intuitive physics derived from simple harmonic motion, this necessarily implies a minimally-damped oscillator, and therefore, in the oscillator model of the plasmon, it is of vital importance to decrease losses in the plasmonic material, even if the overall absorption must be high. Second, the band alignment of the metal to a nearby material must also be considered. This alignment between the two materials sets limits on the carrier energy, and therefore, limits the usefulness of carriers produced by certain absorptive process, either through plasmon decay or direct transitions.
This work has also demonstrated that a novel method of detecting middle wave infrared light can be achieved using the combination of a nanostructured element and a charge-selective transport material. This approach allows for the strong coupling of infrared light into a compact volume at room temperatures and splits the roles of light absorption and carrier transport. In previous infrared sensors, the focus has been on the development or synthesis of single, bulk material sensors which inherently ties the issues of electron transport with a material’s ability to absorb IR light. Through the development of a nanostructure-based IR sensor, light absorption can be treated as a separate problem and tackled independently of the charge transport problem, easing some constraints in the design and construction of a mid-IR sensing pixel.
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