Introduction and Motivation
In modern society, the demand for energy is constantly increasing. Although the reliability and cleanliness of fossil fuel based energy remains questionable, the demand will almost definitely outweigh the supply in the next few decades. The question posed is: How will we meet global energy needs in the future of increased demands, finite supplies of fossil fuels, and political issues with some of the sources of these fuels? The field of Organic Photovoltaics (OPV) is one possible answer.

Silicon based photovoltaics have existed since the middle of the 20th century. Russell Ohl patented the modern solar cell in 1946. Ten years later, Bell Laboratories learned that doped silicon was very sensitive to light. Although silicon based photovoltaics can be made very efficient (30% for a single junction device), the fabrication process is expensive. The cost of modern photovoltaics renders them unable to compete with fossil based energy sources except when these sources are unavailable (remote locations, satellites etc.)

Organic Photovoltaics can be made much cheaper than their silicon based counterparts. They can be fabricated so cheaply, that efficiencies as low as 7% may make them compatible with on the grid power sources.* Current efficiencies are near 5%, and 10% is a reasonable goal. The challenge in increasing efficiency lies in the fact that organic semiconductors considerably lower charge mobility than crystalline silicon. In short, it’s possible to create charges from sunlight, but it’s difficult to get them out of the device in a useful way. OPV faces many other challenges, such as scalability and long-term stability, but this paper will focus on efficiency, and more specifically, charge generation and conductivity.

Organic Photovoltaics: The Bulk Heterojunction Device
A bulk heterojunction is one type of photovoltaic device. The active layer is the material that creates charges from incident photons. This active layer is sandwiched between two electrodes. At least one of these electrodes must be transparent. The active layer is a 20 nanometer film, so the entire device is very thin. An incident photon can excite an electron in the active layer to form an exciton. An exciton is a bound electron-hole pair that is localized on the molecule. If this exciton can dissociate to form unbound e-h pairs, these charges are free to move about the active layer. The electrodes have different work functions, so the electrons are attracted to one side, and the holes are attracted to the other.

Polymerized Regioregular Poly (3-Hexylthiophene) (P3HT) is used in the active layer as the charge generator. Excitons on this polymer recombine very quickly, so the polymer is mixed in solution with [6,6]-Phenyl C61 butyric acid methyl ester (PCBM), a C-60 fullerene. The PCBM acts as an electron acceptor, and allows the excitons in P3HT to dissociate into unbound e-h pairs.
The film contains domains of P3HT and PCBM. Charges are free to move within these domains, but they must hop from one domain to the next in order to be able to leave the device. This can make it difficult to measure charge conductivity within the domains, because the hopping is the limiting factor. TRMC will address this issue.
The Optical Parametric Oscillator

Nonlinear Optics
The Optical Parametric Oscillator is a device that takes advantage of nonlinear optics. When we studied polarization in E&M, we made the assumption that polarization is always parallel to applied electric field, and that its magnitude increased linearly with the magnitude of the electric field. This led to the equation:

\[ \hat{P} = \chi \hat{E} \]

If we include the diagonal elements of the polarization, we introduce the possibility of an electric field in the x direction producing a polarization in the y direction, for example. The equation now becomes:

\[ P_i = \chi_{ij} E_j \]

If we now consider that both the polarization and the electric field are time and space varying functions of the frequency and wave number, the equation becomes:

\[ P_i(\omega, \vec{k}) = \chi_{ij}(\omega, \vec{k}) E_j(\omega, \vec{k}) \]

Next we will include the next (squared) term of the Taylor expansion of \( \chi \). The polarization at a frequency \( \omega \) and wavevector \( \vec{k} \) due to the presence of two external fields is given by this (very complicated) equation:

\[
P_i(\omega, \vec{k}) = \chi_{ij}^{(1)}(-\omega, -\vec{k}; \omega_1, \vec{k}_1) E_j(\omega, \vec{k}) + \chi_{ij}^{(1)}(-\omega, -\vec{k}; \omega_2, \vec{k}_2) E_j(\omega, \vec{k}) + \sum_{ij} \chi_{ijk}^{(2)}(-\omega, -\vec{k}; \omega_1, \vec{k}_1, \omega_2, \vec{k}_2) \]

\[
E_j(\omega, \vec{k}) E_k(\omega, \vec{k}) + \sum_{ijk} \chi_{ijkl}^{(2)}(-\omega, -\vec{k}; \omega_1, \vec{k}_1, \omega_2, \vec{k}_2) \]

\[
E_j(\omega, \vec{k}) E_k(\omega, \vec{k}) E_l(\omega, \vec{k}) + \sum_{ijkl} \chi_{ijkl}^{(2)}(-\omega, -\vec{k}; \omega_1, \vec{k}_1, \omega_2, \vec{k}_2, \omega_3, \vec{k}_3) \]

\[
E_j(\omega, \vec{k}) E_k(\omega, \vec{k}) E_l(\omega, \vec{k}) E_m(\omega, \vec{k}) + \sum_{ijklm} \chi_{ijklm}^{(2)}(-\omega, -\vec{k}; \omega_1, \vec{k}_1, \omega_2, \vec{k}_2, \omega_3, \vec{k}_3, \omega_4, \vec{k}_4) \]

Here, Band has changed notation. Negative \( \omega \) and \( \vec{k} \) values correspond to complex conjugated E fields, which represent the creation of photons, while positive values and non-conjugated fields represent destruction of photons. For example, the term:

\[ P_i(\omega, \vec{k}) = \ldots + \chi_{ijk}^{(2)}(-\omega, -\vec{k}; \omega_1, \vec{k}_1) E_j(\omega, \vec{k}) E_k(\omega, \vec{k}) + \ldots \]
Corresponds to the destruction of photons $\left(\omega_2, k_2\right)$ polarized in the j direction, and $\left(\omega_1, k_1\right)$ polarized in the k direction, and the creation of a photon $\left(\omega, k\right)$, polarized in the i direction. Conservation of energy implies that

$$\omega = \omega_2 + \omega_2, \; k = k_1 + k_2$$

This particular term can create a photon with a frequency that is the sum of 2 others. Others can split 1 photon into 2 with lower frequencies. It can be seen that a material with these characteristics can be very useful in the manipulation of light.

**In Practice**

Certain crystal structures can have nonzero values for some of these higher order $\chi$ terms. The specific values can depend on lattice spacing, thus the values can be temperature dependant. Since the values are directional, the orientation of the crystal can also affect the emitted light. In general, these nonlinear terms only show up for very high intensities of light.

A device called the Optical Parametric Oscillator (OPO) can take advantage of the nonlinear optical properties of crystals. The OPO has 3 distinct waves: the pump wave, the signal wave, and the idler wave (the last 2 of these are interchangeable). Generally the frequency of the pump wave is split into the other two, using the nonlinear optical properties of a crystal. The amount of the split can be fine tuned by the orientation of temperature of the crystal. This technique is useful for creating a signal with a lower frequency than the pump frequency. If a higher frequency is needed, a process called Second Harmonic Generation (SHG) can be used first, in which the pump frequency is first doubled, then split down to the desired signal frequency. The end result is that the OPO can be used as a tool to create coherent light of any specific frequency from a single-frequency laser.

**Time Resolved Microwave Conductivity:**

**An application of the OPO for the use of OPV**

Time resolved microwave conductivity (TRMC) is a process that can measure the conductivity of a thin film material without the use of electrodes.

A thin film is exposed to light from one normal direction, and microwaves (9GHz) from the other. The microwaves pass through the material, reflect off of a microwave mirror, pass through the material a second time, and are then directed through a waveguide. There is an amplifier at the end of the waveguide which measures the reflected radiation. When there are no free charges in the film, it is transparent to the microwave radiation. When light is incident on the photosensitive material, free charges are created. These charges are able to absorb the incident microwave radiation, which is dissipated as heat through the material’s resistance. The intensity of the reflected microwaves is inversely related to the density of free charges in the material.
TRMC employs the use of waveguides, which are explained in Griffiths, Intro to E&M, 9.5.

TRMC measures charge carrier density without regard to large scale mobility. This means that an accurate view of the inside of a photovoltaic device can be found, without the need of large scale charge transport. Long range transport is important, but TRMC allows charge generation to be studied separately. In addition, TRMC is time resolved. This allows recombination rates to be measured. Studying the graph of conductivity vs. time is important, because the longer that the charges exist before recombination, the more time the device has to get them out into a circuit. Since the microwaves are polarized in the waveguide, the in-plane anisotropy of aligned polymer layers can be measured.6

![Diagram](image1)

**FIG. 2.** Schematic representation of the microwave resonant cavity containing a thin-layer sample (not to scale). The sinusoidally varying dashed lines represent the standing-wave pattern of the microwave electric field.

![Graph](image2)

**FIG. 3.** The change in conductance, $\Delta G$, of a 110-nm-thick film of P3HT on a 3 ns FWHM pulsed photoexcitation at 500 nm (2.48 eV) with $I_0=4.3\times10^{15}$ photons/cm$^2$/pulse.
The optical parametric oscillator is a powerful tool for TRMC, because it allows carrier density measurements as a function of frequency for the entire optical spectrum. This helps to create detailed band-gap information for different materials.

**Results of TRMC:**
P3HT alone isn’t a good material for organic photovoltaics. Charges are generated, but recombination rates are way too fast; often too fast for TRMC to notice them. In a P3HT/PCBM blend, the fullerenes act as electron acceptors, allowing excitons to dissociate. By allowing the excitons to split into true electron-hole pairs, the PCBM allows enough time for the charges to leave the device before recombination.

At higher intensities, charge lifetimes decrease. The suggested reason for this is that since there are so many electron-hole pairs floating around; they are more likely to find each other and recombine. This puts a limit on the efficiency of a device at high intensity. Many organic semiconductors are able to create enough charges for successful OPV, but getting those charges out is another challenge.

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1. Ohl Patent
2. Band eq. 8.5 pp.456-458
3. See Table in Band, pp. 462-463
4. R-p photonics website
5. Dicker Paper
6. Dicker Paper
7. Dicker Paper
This thesis is about the mechanisms governing charge generation and transport in the organic semiconductor Poly(3-hexylthiophene) (P3HT). The intent is to use this semiconductor in the manufacture of organic photovoltaics. In the second chapter, the author presents methods of measuring charge carrier generation and lifespan in organic semiconductors. Time Resolved Microwave Conductivity (TRMC) measurements allow for the detection of charge carriers without the use of electrodes or contacts. Chapters 4, 6, and 8 present results of TRMC measurements which determine quantum yield, recombination rates, and dynamics of charge carriers in P3HT thin films.

(Paper) Electrodeless time-resolved microwave conductivity study of charge-carrier photogeneration in regioregular poly(3-hexylthiophene) thin films
http://prola.aps.org/abstract/PRB/v70/i4/e045203

The authors use TRMC to determine charge generation, charge lifetimes and quantum efficiency of P3HT thin films. Quantum efficiency is found to be 2-7% depending on the photon energy in relation to the first excitation energy of the P3HT polymer.

The mobility and relaxation kinetics of charge carriers in molecular materials studied by means of pulse-radiolysis time-resolved microwave conductivity: dialkoxy-substituted phenylene-vinylene polymers
http://iopscience.iop.org/0953-8984/14/42/308/?ejredirect=iopscience

The authors use TRMC to obtain information about the mobility and lifespan of photogenerated charge carriers in bulk organic polymers. Results tie the electronic properties of these polymers to their morphology. Mobilities and recombination rates are found to vary with different annealing times and temperatures. High temperature annealing has a substantial positive effect on both mobility and lifetime of charge carriers. This is postulated to be due to the self-assembly of structures made possible from heating.

www.rp-photonics.com/phase_matching.html
www.rp-photonics.com/parametric_amplification.html
Both articles on this website describe the physics, and some of the math behind the Optical Parametric Amplifier. The author owns a photonics consulting firm, and cites valid sources in his articles.

Ohl Patent
**Light Sensitive Electric Device**
This is the patent on the first solar cell, from 1956.

Griffiths, Prentice-Hall Inc. 1999
**Introduction to Electrodynamics, 3rd ed.**
This is an undergraduate textbook in electricity and magnetism. Chapter 9, section 5 discusses waveguides, which are useful in the TRMC discussed in this handout.

Band, John Wiley & Sons, Ltd 2006
**Light and Matter**
This graduate-level text discusses applications of optics and electromagnetism. Chapter 8 discusses nonlinear optics; the science behind the Optical Parametric Oscillator