*Charge Carrier Dynamics in Photovoltaic Materials*
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# Summary of PhD thesis 'Charge carrier dynamics in photovoltaic materials' by Søren Jensen

Solar energy is often mentioned as part of the solution to the worlds pressing energy problems. The sun provides ample energy for covering the earth's energy needs. Still, solar energy represents only a vanishingly small percentage of the worlds energy production. This is because of the high cost of photovoltaic (PV) energy compared to other energy sources such as coal, oil and gas.

Most PV devices employed today are based on crystalline silicon. These devices are expensive because costly cleaning procedures are necessary for producing PV grade silicon. Moreover, the energy conversion efficiency of conventional PV devices is limited to a theoretical maximum of 33.7 %, the Shockley-Queisser limit, due to energy loss mechanisms such as the absence of absorption of below bandgap photons and thermalization and recombination of carriers excited above the bandgap.

In this thesis the optical and electronic properties of potential alternative PV materials are examined using THz time domain spectroscopy. With this method, charge carriers are optically excited by an ultrashort laser pulse, and subsequently probed by a freely propagating single-cycle electromagnetic field oscillating at THz frequencies. At these frequencies the THz probe pulse is particularly sensitive to the motion of free and weakly confined charge carriers. Therefore optical pump - THz probe experiments can provide information on the efficiency of photoexcitation, and on the THz frequency dependent mobility of the photoexcited charge carriers.

We examine the efficiency of Carrier Multiplication (CM) in bulk indium nitride. Carrier multiplication is the process of generating multiple electron-hole pairs from one absorbed photon. In this way, the excess energy of high energy photons, initially exciting charge carriers high above the bandgap, can be used to excite additional carriers across the bandgap. Thus, through an increase of the photocurrent, CM can increase the energy conversion efficiency of a photovoltaic device. InN possesses a number of properties making it a promising material for achieving efficient solar energy conversion through CM. Its bandgap of roughly 0.7 eV was shown to correspond to the highest theoretical energy conversion efficiency of 44.4 %, assuming ideal CM behavior. Additionally, InN possesses a favorable phononic band structure, meaning that competing losses through phonon emission are expected to be small; and an asymmetric electronic band structure which causes the excess energy of an absorbed photon to be preferentially transferred to the electron rather than the hole, making it more likely to undergo CM. Notwithstanding these facts, we find that while the CM onset occurs at relatively low photon energies in InN (1.7±0.2 eV) - corresponding to $2.7 \pm 0.3$ times its bandgap - the excitation efficiency above the onset increases linearly with a very modest slope of only $\sim$13 %/$E_\mathrm{g}$. Based on

these numbers, the efficiency increase of an InN based photovoltaic device owing to CM is limited to maximum 1 percentage point. Similar small conversion efficiency gains due to CM are found for other semiconductor materials based on literature values. We conclude that, in the bulk semiconductors studied to date, CM will only contribute to the efficiency of a solar cell by a very small amount.

In a similar study we investigate the mechanism of energy transfer from an absorbed photon into the electronic system in monolayer graphene deposited on a supporting substrate. We find that photoexcitation of graphene samples causes a decrease in the conductivity. This can be understood by noting that supported graphene is intrinsically doped, meaning that there is an intrinsic conductivity present which can be reduced by photoexcitation. We find that as a high energy electron-hole pair is excited by an optical photon, the energy is quickly transferred to the dopant population. This process increases the mean temperature of the carriers, which in turn causes a reduction in the overall conductivity. Indeed, at high absorbed photon densities we observe a saturation of the photoconductivity consistent with a quenching in the conductivity of the dopant states. At these high photon densities the pump induced THz transmission change approaches the total THz absorption of the unexcited sample, meaning that the sample tends toward transparency to the THz probe as the conductivity of the conducting carrier population is reduced. This observation strengthens the notion that the negative photoconductivity in supported graphene does indeed arise from a temperature induced change in the conductivity of the population of intrinsic dopant carriers. We further prove this picture by controlling the dopant concentration with an electronic back-gate and monitoring the THz resolved photoconductivity change. By optically exciting the sample with various excitation densities and photon energies, we quantify the efficiency of energy transfer from an absorbed photon to the electrons via the process of 'multiple hot carrier generation'. We find that the photoinduced conductivity change per absorbed photon increases almost linearly with photon energy, indicating very efficient energy transfer from the absorbed photons to the charge carriers. Comparing the measured data to a theoretical model, the efficiency of energy transfer from an optically excited carrier into the intrinsic dopant carriers was found to be on the order of 75 %. This high energy conversion efficiency is a positive result for graphene based optoelectronic applications. However, owing to its vanishing bandgap, graphene is ill suited for a number of such applications.

A bandgap can be induced via quantum confinement by physically confining the graphene in one dimension. We conduct a comparative study of ultrafast photoconductivity in two different forms of semiconducting one-dimensional (1D) quantum-confined graphene nanostructures: flat, structurally well-defined semiconducting graphene nanoribbons (GNRs) fabricated by a 'bottom-up' chemical synthesis approach, and semiconducting carbon nanotubes (CNTs) with similar dimensions and a similar bandgap energy. We find that, while the THz photoresponse seems very different for the two systems, a single model of free carriers experiencing backscattering when moving along the long axis of the CNTs or GNRs provides a quantitative description of both sets of results. The model reveals significantly longer carrier scattering times for CNTs (ca. 150 fs) than for GNRs (ca. 30 fs) and in turn

higher carrier mobilities. This difference can be explained by differences in band structures and phonon scattering and the greater structural rigidity of CNTs as compared to GNRs, minimizing the influence of bending and/or torsional defects on the electron transport. At longer pump-probe delays (10 ps after excitation) we observe a THz frequency resolved complex conductivity in the GNRs that indicates localized charge carriers. Indeed, the response is found to be very similar to that of a molecule of similar chemical composition to that of GNRs, but much smaller in the length dimension so that charge carriers are physically confined in all dimensions. The observation of localized or 'bound' charge carriers in GNRs 10 ps after excitation indicates that the photoexcitation in these systems gives rise to the formation of excitons, which could potentially be extracted in an organic donor-acceptor heterojunction solar cell.

Finally, we study the charge transport in films consisting of sintered $TiO_2$ particles of very different sizes. $TiO_2$ nanoparticle films are widely used in photovoltaic and photocatalytic applications, and the nature of electrical conductivity in such materials is therefore of both fundamental and practical interest. The conductive properties of colloidal $TiO_2$ films depend strongly on their morphology and deviate greatly from the properties of the bulk material. Remarkably, identical photoconductivity spectra are observed for films of particles with diameters of tens of nm and hundreds of nm respectively. The independence of photoconductivity on particle size demonstrates that the terahertz photoconductive response of colloidal $TiO_2$ films is not affected by carrier backscattering at particle boundaries as has previously been concluded, but rather by depolarization fields resulting from the spatial inhomogeneities in the dielectric function inherent to these types of films. Comparing the observed spectral data to a model, we see that the observed photoconductivity spectra reflect percolated pathways in the colloidal $TiO_2$ nanoparticles films, through which charge carrier diffusion can occur over macroscopic length scales. These pathways give the material the long range conductive properties that are crucial for device applications.