Hot carrier solar cells: the device that did not exist (but should)

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Abstract– **Hot carriers are an unusual type of solar cell, very efficient in principle but where electronic, optical and thermal effects are inextricably mixed. Modeling was used first to understand the device operation. Then more detailed simulations were made on phononic properties of the nanostructures absorbing material using DFT-based molecular dynamics and electron-electron and electron-phonon interactions using a Monte Carlo approach.**

I. INTRODUCTION

There is no question about the merit of having high efficiency photovoltaic device. Most efficient solar cells are presently based on multijunction stacks. Yet, from present day 40% conversion efficiencies to the thermodynamic limit (~87%), there is still a lot of room for improvement. Moreover, it is desirable that the design of the solar cell be kept as simple as possible and its workings be robust to changes in operation conditions, which are weak points of the multijunction approach, in spite of its practical current achievements. Hot carrier solar cells (HCSC) provide an attractive solution to approach limiting energy conversion efficiencies, with simplicity of design, by converting with improved efficiency the high energy range of the solar spectrum, normally mainly lost to heat, into electric power [1].

To circumvent heat dissipation through absorption of high excess energy (w.r.t. band gap) photons, photogenerated electrons and holes have to be collected through specially designed contacts that are energy selective (i.e. they let through carriers only within a narrow energy range), as in this way one minimizes heat production of high kinetic energy carriers *in the contacts,* before they have lost most of their energy. In this case, efficiencies as high as 86% could in principle be achieved [1], quite close to the thermodynamic limit. Yet, high kinetic energy electron and hole carriers ("hot carriers") normally thermalize with the lattice in sub ps times, but can in some conditions (high injection) reach a regime where interaction with the lattice becomes inefficient ("hot phonon bottleneck") [2].

As efficient and attractive in principle as this device may be, it has never been made and measured. This is because its operation is quite counter-intuitive, and in an unusual regime where thermal, optical and electronic effects are involved together. Clearly, this device is a good case for simulation.

II. NANOSTRUCTURED ABSORBERS

The concept of hot carrier solar cells is based on the use of the careers excess energy induced by above bandgap photons absorption, and the collection of carriers before they thermalize. Previous experiments showed that hot-carrier thermalization rates can be reduced under strong excitation in nanostructures to the point that conversion efficiencies over 50% under concentration are possible. The thermalization rate is tightly related to the phonon-carrier interaction and ultimately is limited by LO phonon anharmonic decay [2,6]. Monte Carlo simulations have been carried out to study the detailed energy transfers by electron-electron and electron-phonon interactions.

We have explored the possibility to slow the career cooling through phonon engineering. In this work, we performed molecular dynamics based ab-initio calculations in order to investigate the phonon lifetimes in bulk materials and nanostructures. We obtained phonon lifetime modulation in Si and Ge based quantum dots, as phonon decay mechanisms in these nanostructures is altered.

First, the vibration modes of Si and Ge based superlattices and nanostructures have been accurately calculated using ab-initio force constant techniques where forces between atoms are computed at the quantum mechanical level using DFT (Density Functional Theory) formalism. These vibration modes are then a good starting point to obtain the phonon lifetimes by using molecular dynamics: because lattice vibrations consist of periodic motion of atoms, a

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Fourier transform of their motion will give the modes vibrational frequencies and their decay in time (the Fourier transform is actually carried out on the velocity autocorrelation function). Simulations were carried out on an IBM Blue Gene supercalculator, with 40000 CPUs.

The method was tested successfully on silicon lattice as shown in the previous report. Not only the fundamental frequency of the zone centre LO mode could be reproduced accurately, but its lifetime was found to fit existing data. The method was then tested on various nanostructures to check for lifetime improvements.

In figure 1, we show the velocity autocorrelation function (VAF) obtained in the case of a Si dot in a Ge matrix (left). The Fourier transform of this VAF function yields the main vibration modes in the whole structure (right).

We studied the evolution of these modes during time. Further mathematical treatments have been performed in order to obtain the phonon decay in the nanostructures. In silicon lattice, we obtained a Si LO phonon lifetime of 5 ps at zero temperature and 1.5 ps at 300 K. We obtained an increase of the silicon LO phonon lifetime in the nanostructure with a Si dot in Ge matrix (10 ps at 0 K), compared to that obtained in pure silicon lattice. Conversely, for a Ge dot in Si matrix the same phonon has a lifetime of 2.5 ps.

Finally, this demonstrates that nanostructuration can strongly modulate the phonon lifetimes. These results are in agreement with our expectations, with the target to increase phonon lifetimes, so that the carriers thermalization could be slowed.

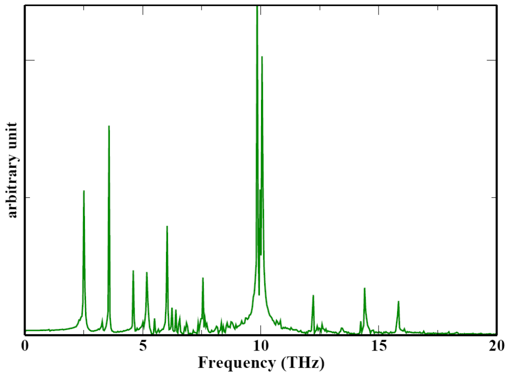

Figure 1: The main vibration modes and their decay are extracted by a Fourier transform from the velocity autocorrelation function (VAF) of the atoms in the lattice with a Si dot in Ge matrix

III. CARRIER COLLECTION

There are two main issues with such devices, one is slowing down the loss, usually very fast, of the excess kinetic energy of the photogenerated carriers and the other is collecting the photogenerated carriers with their excess energy. In both cases, key to the success, is the possibility to absorb sun's incoming photons in a small volume so that they can be collected before thermalisation. For that, absorber thicknesses have to be 100 nm or below. Therefore, current progress in nanophotonics is central to the possibility of making such devices. These can be made either from dielectric structures [3] or with plasmonic resonators as simulations have shown, both of them providing impressive enhancement of thin films absorptivity.

As a first step, detailed models have been developed, addressing the above issues. For instance, in the case of thermalization pathways, these are twofold. Excited carriers can loose energy (cool down) by interacting with the phonons in the absorber, but also in the contacts if these are not carefully designed. Theoretically [5], the best configuration is that of energy selective contacts [1,2], but real contacts cannot be perfectly selective. Investigating the influence of contact selectivity, it has been shown that semi-selective contacts (i.e. energy barriers) would do almost as well in practical cases [5] . This fact is instrumental in bringing hot carriers solar cells closer to realization. Available experimental data on carrier cooling and hot phonon bottleneck effects [2] combined with a device model including realistic carrier extraction and carrier thermalization furthermore confirm that solar conversion efficiencies above 50% are within the possibility of technologically available materials [6].

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