Chapter 53
Phononic Engineering for Hot Carrier Solar Cells

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ABSTRACT

The concept underlying the hot carrier solar cell is to slow the rate of photo-excited carrier cooling to allow time for the carriers to be collected while they are still at elevated energies ("hot"), and thus allowing higher voltages to be achieved from the cell. Significant reduction in carrier cooling has been observed in Quantum Well (QW) nano-structures at very high illumination intensities due to a "phonon bottleneck" mechanism. With the phononic gaps in nano-structures, the optical phonon lifetime can be prolonged by blocking the main phonon decay from optical branches to acoustical branches (such as the Klemens or Ridley decay channels). Si-based hot carrier cell is a very active topic and Si-Ge nano-structures are especially interesting for the application, as their fabrication process is well developed.

In this chapter, the authors first analyse the operation of a hot carrier solar cell and lay down the general principles. They then discuss the opportunity of phonon engineering to improve the phonon bottleneck. Finally, they present how these can be modeled in nanostuctures comprising several thousand atoms, where true 3D phonon dispersion relations for Si-Ge nano-structures are obtained using first principles methods. The effects of the nano-structure size and geometry on the phonon dispersion relations are investigated. The possible phonon decay processes in the nano-structures are discussed and compared with the bulk crystal materials. The performance of calculated nano-structures on the hot carrier solar cell is evaluated with the acquired knowledge of phonon modes.

1. THE HOT CARRIER SOLAR CELL CONCEPT

1.1. Principles of the Hot Carrier Solar Cell

The concept of hot carrier solar cell was first introduced by Ross and Nozik (1982). In standard devices, the photon energy in excess of the threshold absorption energy is given to the photogenerated carrier population, and then to the lattice as heat, with only the band gap energy being converted as electrical energy. If the carrier thermalization (thermal equilibration of carriers with the lattice) is suppressed, then the conversion of the total available energy into potential energy is possible and leads to higher conversion efficiency.

The energy distribution of the photogenerated carriers is, immediately after absorption, a non-equilibrium distribution that depends on the energy distribution of the incident photons, and on the electron and hole effective masses and density of states. After absorption, the fate of the carrier distribution can be:

- **Hot Non-Equilibration:** The carriers are not even equilibrated among themselves, the carrier temperature cannot be defined.
- **Hot Equilibration:** The carriers equilibrate among themselves but not with the lattice, resulting in a hot carrier population at $T_H > T_C$, where T_C is the temperature of the lattice.
- **Full Thermalization:** The common situation where carriers are at thermal equilibrium with the environment at ambient temperature.

The comparison between the thermalization rate (due to interactions with phonons, see section 1.3), the carrier-carrier scattering rate, and the carrier extraction rate (the rate at which carriers are removed from the system through contacts or by radiative recombination) will determine which one of the above cases applies.

Typical time constants for these different mechanisms in III-V materials are given in Table 1, from Othonos (1998).

The carrier-carrier scattering time constant is usually below the picosecond, and decreases with an increasing carrier density, while the time constant for the carrier-phonon interaction is of the order of the picosecond. Considering these time constants and without carrier extraction, the dynamics of the carrier after a pulsed monochromatic excitation is described in Figure 1 from Green (2003). Immediately after absorption at t = 0, carriers are generated in a narrow energy range (2). Carrier-carrier scattering then occurs and carriers are redistributed in a hot thermal distribution (3)-(4), within a picosecond. This distribution is then cooled towards the lattice temperature because of interaction with phonons (5). Finally, carriers recombine with a sub-microsecond time constant (7).

If the excitation rate is higher than the thermalization rate, and lower than the carrier-carrier scattering rate, a steady state hot distribution can be established, and the carrier kinetic energy, which is usually lost as heat, can be used and contributes to the conversion efficiency.

Assuming such steady state hot carrier population is achieved, a specific care is required regarding carrier extraction. If the photogenerated

Table 1. Typical time constants of various carrier interaction mechanisms in semiconductors, from Othonos (1998)

Type of Interaction	Characteristic Time (s)
Carrier-Carrier scattering	$10^{-15} - 10^{-12}$
Carrier - Optical phonon interaction	$\geq 10^{-12}$
Optical phonon - Acoustic phonon interaction	$\sim 10^{-11}$
Auger recombination	$\sim 10^{-10}$
Radiative recombination	$\geq 10^{-9}$

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