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Relaxation of femtosecond photoexcited electrons in a polar indirect band-gap semiconductor nanoparticle

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Abstract. A model calculation is given for the energy relaxation of a non-equilibrium distribution of hot electrons (holes) prepared in the conduction (valence) band of a polar indirect band-gap semiconductor, which has been subjected to homogeneous photoexcitation by a femtosecond laser pulse. The model assumes that the pulsed photoexcitation creates two distinct but spatially interpenetrating electron and hole non-equilibrium subsystems that initially relax non-radiatively through the electron (hole)–phonon processes towards the conduction (valence) band minimum (maximum), and finally radiatively through the phonon-assisted electron–hole recombination across the band-gap, which is a relatively slow process. This leads to an accumulation of electrons (holes) at the conduction (valence) band minimum (maximum). The resulting peaking of the carrier density and the entire evolution of the hot electron (hole) distribution has been calculated. The latter may be time resolved by a pump-probe study. The model is particularly applicable to a divided (nanometric) polar indirect band-gap semiconductor with a low carrier concentration and strong electron–phonon coupling, where the usual two-temperature model [1–4] may not be appropriate.

Keywords. Electron gas; Fermi gas; semiconductor compounds.

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1. Introduction

Consider the kinetic evolution of a photoexcited non-equilibrium system of electrons (holes) in the conduction (valence) band of a polar, indirect band-gap semiconductor with a low carrier density and strong electron–phonon coupling with high anharmonicity, such that, $\tau_{e-e} \gg \tau_{e-p} \gg \tau_{p-p}$. Here, τ_{e-e}, τ_{e-p}, and τ_{p-p} are, respectively, the electron–electron, electron–phonon and the phonon–phonon relaxation time-scales. This is the regime, in which the usual two-temperature model is not applicable [1–4]. The photoexcited non-degenerate hot electron (hole) distribution then evolves predominately through the non-radiative electron (hole)–phonon

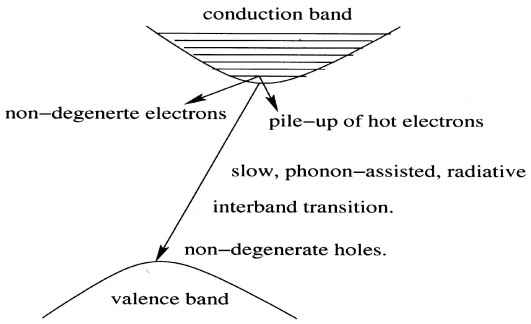

Figure 1. A polar, indirect band-gap semiconductor.

processes. Due to this quasi-continuous phononic energy loss mechanism, the photoexcited electrons (holes) tend to accumulate at the conduction (valence) band minimum (maximum). The final relaxation step (i.e., electron–hole recombination) involves a relatively slow phonon-assisted radiative interband transition across the indirect gap as shown in figure 1. There is thus a pile up of the hot electrons (holes) at the bottom (top) of the conduction (valence) band. Thus, the entire relaxation process proceeds on two time-scales, namely, the initial, fast time-scale involving the quasi-continuous intraband electron–phonon interaction, and the final slow time-scale involving the phonon-assisted radiative interband transition across the indirect gap. We have derived an analytical expression for the entire time evolution of the non-equilibrium hot-electron distribution, following the initial preparation by the femtosecond laser pulse. The fast and the slow relaxation processes, can, in principle be time resolved using the pump-probe experimental technique. Our calculations clearly capture the peaking of the electron number as the latter accumulate at the conduction band minimum. (The calculation for the holes is, of course, identical.)

2. Theory

Consider the sample as homogeneously photoexcited (i.e., no spatial diffusion) by an fs-laser pulse. Let this generate a gas of hot electrons with a non-equilibrium distribution function $f_{\rm e}(\epsilon, t)$. In this work we will consider two models of electron–phonon interaction (friction) for the relaxation of $f_{\rm e}(\epsilon, t)$, a linear model in which the phonon friction is taken to be linear in the velocity of the hot electrons, and the other in which the phonon friction is non-linear in the electron velocity. For these, we derive analytical expressions for the time-dependent non-equilibrium hot-electron distribution.

A. *Linear model*

Here the phononic friction is proportional to the electron velocity v. The kinetic equation for $f_{\rm e}(\epsilon, t)$ is

$$\frac{\partial f_{\rm e}(\epsilon,t)}{\partial t}+\dot{\epsilon}\frac{\partial f_{\rm e}(\epsilon,t)}{\partial \epsilon}=-\frac{\partial f_{\rm e}(\epsilon,t)}{\tau_r}. \tag{1}$$

Here, $\dot{\epsilon}\equiv\frac{\rm d}{{\rm d}t}(mv^2/2)=-\gamma_p v^2=-\epsilon/\tau_p$, where τ_r and τ_p are, respectively, the radiative and the non-radiative relaxation times, and $\alpha=t/\tau_p$, $\alpha_r=\tau_r/\tau_p$ are dimensionless variable parameters. With these, eq. (1) reduces to

$$\frac{\partial f_{\rm e}(\epsilon,\alpha)}{\partial\alpha}-\frac{\partial f_{\rm e}(\epsilon,\alpha)}{\partial\,\ln\,\epsilon}=-\frac{\partial f_{\rm e}(\epsilon,\alpha)}{\alpha_r}, \tag{2}$$

that can be solved analytically to give

$$f_{\rm e}(\epsilon,\alpha)={\rm e}^{-\alpha/\alpha_r}\Theta(-\alpha-\ln[\epsilon/(\epsilon_{\rm c}+\epsilon_{\rm L})]),\quad \text{for}\quad t>0 \tag{3}$$

with the initial condition imposed at $t=0$. Here, Θ is the Heavyside step function. We have assumed here an initial delta-function laser pulse of photon energy $\epsilon_{\rm L}$ that excites electrons uniformly in the energy interval $\epsilon_{\rm c}\le\epsilon\le\epsilon_{\rm c}+\epsilon_{\rm L}$ in the conduction band, with $\epsilon_{\rm c}$ the conduction band minimum and $\epsilon_{\rm L}>\epsilon_{\rm g}$ (the band-gap energy). In as much as physically eq. (2) has only the forward propagating solution in the energy space, we can readily incorporate the boundary condition corresponding to this slow recombination relaxation process effectively at the bottom of the conduction band simply by introducing a longer relaxation time, $\tau_{pc}>\tau_p$, there. This gives rise the peaking effect referred to above. Thus, eq. (3) is our basic result. In terms of it, we can calculate the total number $N_{\rm c}(\alpha)$ of the hot electrons piled up in the bottom of conduction band, as also the total number $N_{\rm hot}(\alpha)$ of hot electrons above $\epsilon_{\rm c}$. The number of hot electrons with energy $\epsilon>\epsilon_{\rm c}$ is $N_{>}(\epsilon)=N_{\rm hot}(\epsilon)-N_{\rm c}(\epsilon)$.

The time evolution of the hot electrons in the pile up is given by

$$\dot{N}_{{\rm c}(t)}+\dot{N}_{>(t)}=-N_{\rm c}(t)/t_{pc}.$$

Defining $\eta=\tau_p/\tau_{pc}$, the solution may be written as

$$N_{\rm c}(\alpha)=\frac{f_0(\epsilon_{\rm c}+\epsilon_{\rm L}){\rm e}^{-\eta\alpha}}{1-\eta}[1-{\rm e}^{-(1-\eta)\alpha}], \tag{4}$$

$$N_{\rm hot}(\alpha)\equiv N_{\rm c}(\alpha)+N_{>}(\alpha)=f_0(\epsilon_{\rm c}+\epsilon_{\rm L}){\rm e}^{-\alpha}\times\left[1+\frac{{\rm e}^{(1-\eta)\alpha}}{1-\eta}(1-{\rm e}^{-(1-\eta)\alpha})\right]. \tag{5}$$

Time evolution of these two populations are plotted in figures 2 and 3. Here f_0 is the initial number density of photoexcited electrons per unit energy interval for $\epsilon_{\rm c}<\epsilon<\epsilon_{\rm c}+\epsilon_{\rm L}$.

B *Non-linear model*

Here the phonon friction is non-linear in the electron velocity. The kinetic equation is

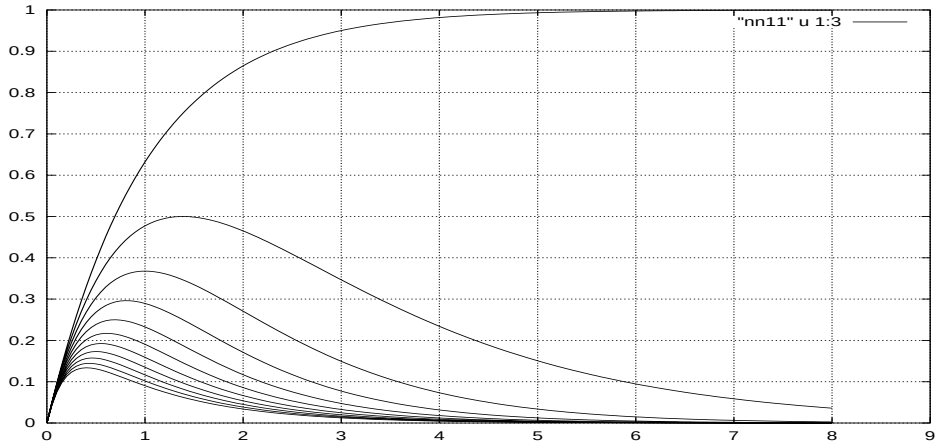

Figure 2. Decay of hot electrons $N_{\rm c}(\alpha)$ in the pile up as a function of α (α is along the horizontal axis in all the figures). Top most curve is for $\eta = 0$, lowest for $\eta = 0.9$ with a step of 0.1.

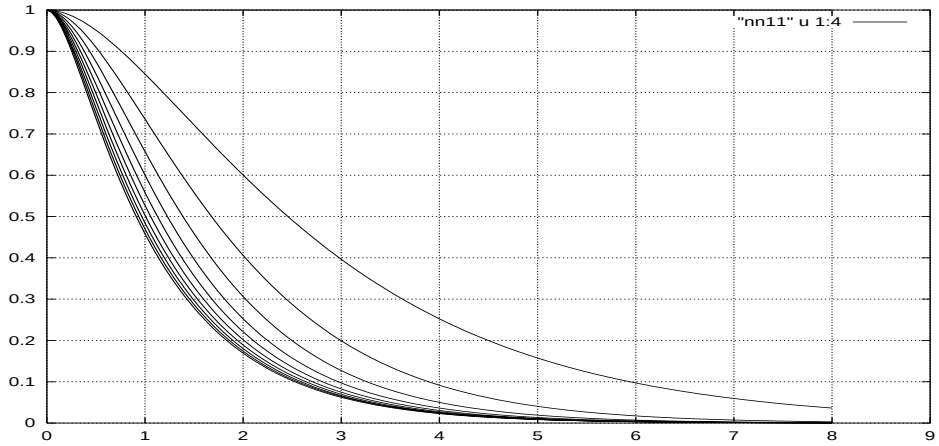

Figure 3. Decay of hot electrons $N_{\rm hot}(\alpha)$. Top most curve is for $\eta = 0$, lowest for $\eta = 0.9$ with a step of 0.1.

$$\frac{\partial f_{\rm e}(\epsilon,t;n)}{\partial t} + \dot{\epsilon}\frac{\partial f_{\rm e}(\epsilon,t;n)}{\partial \epsilon} = -\frac{\partial f_{\rm e}(\epsilon,t;n)}{\tau_r} \tag{6}$$

with $\dot{\epsilon} = -\frac{\epsilon}{\tau_p}[\frac{\epsilon}{\epsilon_0}]^n$ and ϵ_0 is an associated energy scale. In line with the linear model, this kinetic equation has the solution

$$f_{\rm e}(\epsilon,\alpha;n) = {\rm e}^{-\alpha/\alpha_r}\Theta\left(-\alpha - \frac{1}{n}\left(\frac{\epsilon_0}{\epsilon_{\rm L}+\epsilon_{\rm c}}\right)\left[1-\left(\frac{\epsilon_{\rm L}+\epsilon_{\rm c}}{\epsilon}\right)^n\right]\right). \tag{7}$$

The number $N_{>;n}(\alpha)$, of hot electrons with energy greater than $\epsilon_{\rm c}$ is

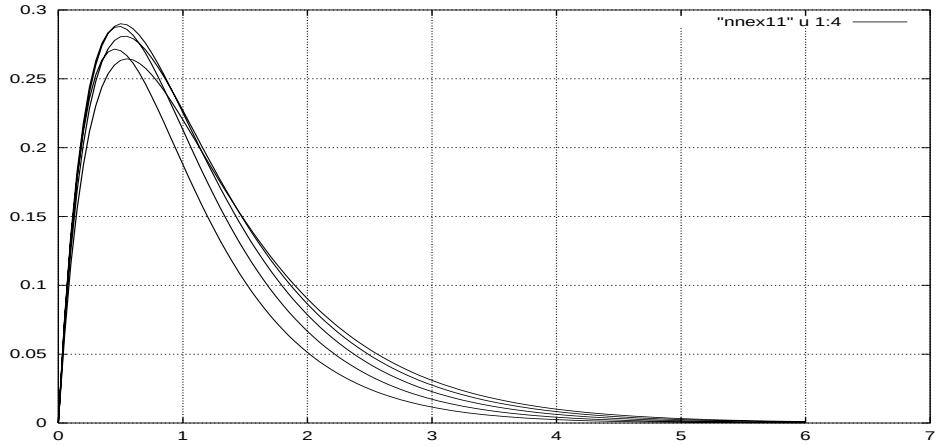

Figure 4. Decay of hot electrons $N_{\mathrm{c};n}(\alpha)$ in the pile up as a function of α, for $\eta = 0.5, \chi = 0.5$, and $0.8 < n < 1.2$, peaking effect is clear around, $\alpha = 0.5$.

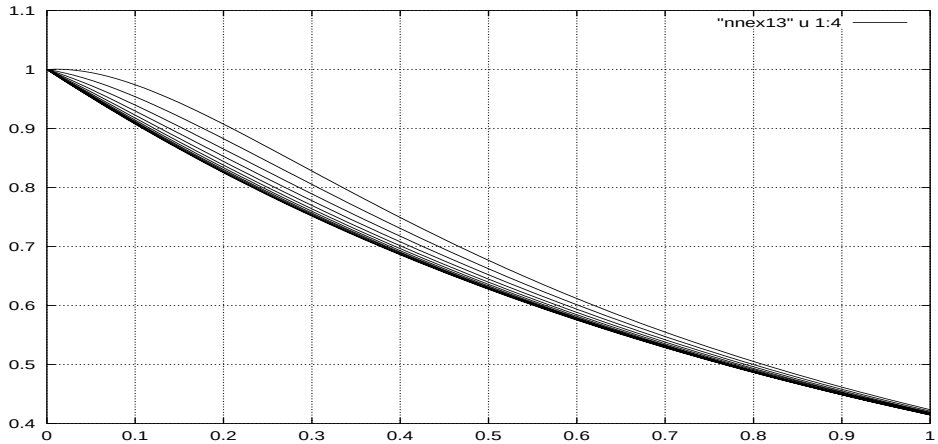

Figure 5. Decay of hot electrons $N_{\mathrm{hot};n}(\alpha)$ as a function of α. Here $n = 0.28, \chi = 1$, and $0 < \eta < 1.2$.

$$N_{>;n}(\alpha) = \int_{\epsilon_{\mathrm{c}}}^{\epsilon_{\mathrm{c}}+\epsilon_{\mathrm{L}}} f_{\mathrm{e}}(\epsilon, \alpha; n)\mathrm{d}\epsilon = f_{0;n}(\epsilon_{\mathrm{c}} + \epsilon_{\mathrm{L}}) \left[1 + \frac{\alpha}{\beta}\right]^{-1/n}, \tag{8}$$

where $\beta = \frac{1}{n}(\chi)^n, \chi = \frac{\epsilon_0}{\epsilon_{\mathrm{c}}+\epsilon_{\mathrm{L}}}$. As in the linear model, the number of hot electrons in the pile up near the bottom of the conduction band comes out to be

$$N_{\mathrm{c};n}(\alpha) = f_0(\epsilon_{\mathrm{c}} + \epsilon_{\mathrm{L}}) \left[\frac{1}{n}\right]^{n+1} \eta^{1/n} \mathrm{e}^{-\alpha(\eta+\chi^n/n)} \times \left[\int_{\eta\beta}^{\eta(\alpha+\beta)} y^{-(n+1)/n} \mathrm{e}^{y} \mathrm{d}y\right]. \tag{9}$$

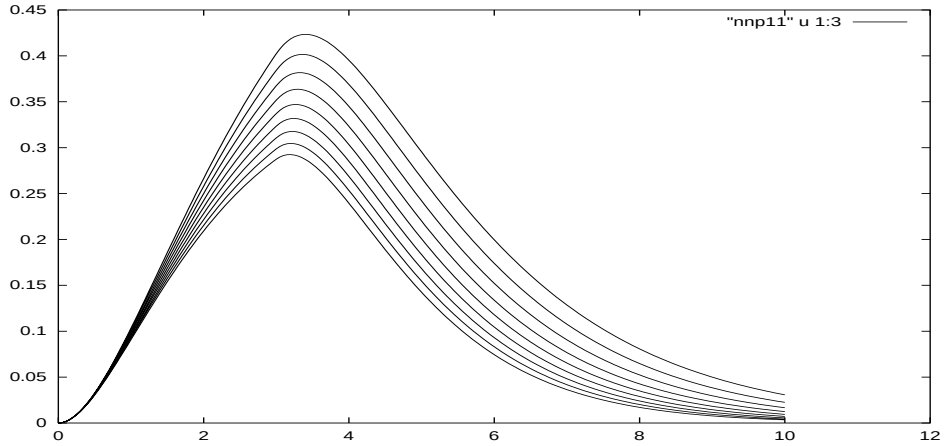

Figure 6. Decay of hot electrons $N_{\mathrm{c};p}(\alpha)$ in the pile up as a function of α in the presence of a rectangular laser pulse with width $\alpha_p = 3$. Top most curve is for $\eta = 0$, lowest for $\eta = 0.9$ with a step of 0.1.

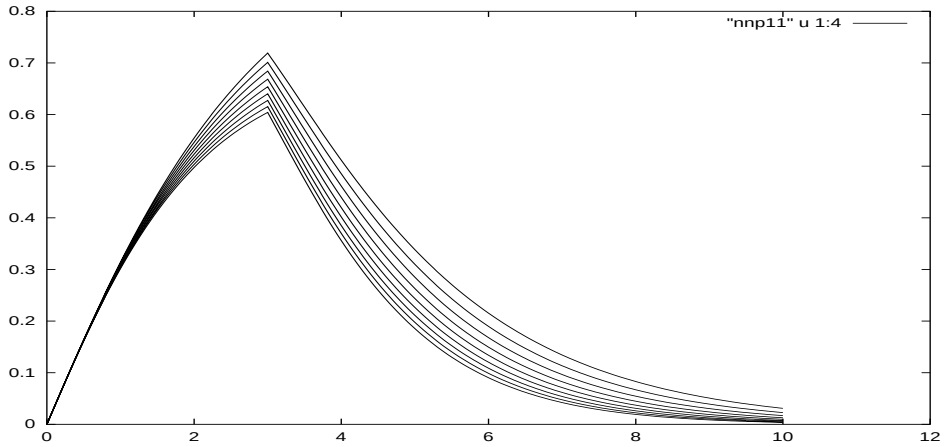

Figure 7. Decay of hot electrons $N_{\mathrm{hot};p}(\alpha)$ as a function of α, with same set of parameters as in figure 5.

The total number of hot electrons, $N_{\mathrm{hot};n}(\alpha)$, is then $N_{\mathrm{hot};n}(\alpha) = N_{>;n}(\alpha) + N_{\mathrm{c};n}(\alpha)$. These populations are plotted in figures 3 and 4.

In the limit $\alpha \ll \beta$, or $t \ll \frac{\tau_p}{n}\left(\frac{\epsilon_0}{\epsilon_\mathrm{c}+\epsilon_\mathrm{L}}\right)^n$, these expressions for the hot electrons in the pile up, and the total number of hot electrons reduce to

$$N_{\mathrm{c};n}(\alpha) = \frac{f_{0;n}(\epsilon_\mathrm{c}+\epsilon_\mathrm{L})\chi^{-n}\mathrm{e}^{-\eta\alpha}}{\chi^{-n}-\eta}[1-\mathrm{e}^{-(\chi^{-n}-\eta)\alpha}], \tag{10}$$

$$N_{\mathrm{hot};n}(\alpha) = \frac{f_{0;n}(\epsilon_{\mathrm{c}} + \epsilon_{\mathrm{L}})\chi^{-n}\mathrm{e}^{-\eta\alpha}}{\chi^{-n} - \eta}[1 - \mathrm{e}^{-(\chi^{-n}-\eta)\alpha}] + (1 + \alpha/\beta)^{-1/n}. \tag{11}$$

In the limit $n \to 0$, we recover the results of the linear model, as indeed we must.

3. Incorporating pump pulse duration

So far we have taken the pump laser pulse to be a delta-function in time. We now consider the system as being pumped by a rectangular femtosecond pulse of duration t_p. The effect of the pulse width can be taken into account as the convolution integral of the respective hot-electron time-evolution with the rectangular pulse. Thus, for the case $n = 0$ we obtain

$$N_f^p(\alpha) = \frac{1}{\alpha_p}\int_0^{\min(\alpha_p,\alpha)} N_{\mathrm{c}}(\alpha - x)\mathrm{d}x, \tag{12}$$

$$N_f^p(\alpha) = \frac{1}{\alpha_p}\int_0^{\min(\alpha_p,\alpha)} N_{\mathrm{hot}}(\alpha - x)\mathrm{d}x. \tag{13}$$

4. Discussion

One of the distinctive features of our calculated time evolution of the photoexcited electron distribution in the conduction band is the peaking effect which is clearly seen in figures 2–7. It reflects the effect of the slow radiative relaxation across the indirect band gap. This can be probed in a pump-probe experiment. This calculation refers to a situation $\tau_{\mathrm{e-p}} \ll \tau_{\mathrm{e-e}}$, not describable by the usual two-temperature model $\tau_{\mathrm{e-e}} \ll \tau_{\mathrm{e-p}}$ [1]. In our case, the non-degenerate system of electrons relaxes towards the bottom of the conduction band predominantly by a quasi-continuous energy loss to the phonons (intraband relaxation). The model is applicable under the condition $\delta \sim k_{\mathrm{B}}T_{\mathrm{D}}$ ($\sim mev$) $\ll \epsilon_{\mathrm{g}}$ ($\sim ev$), where δ is the intraband energy-level spacing in the nanometric sample. Here T_{D} is the Debye temperature of the material. Accordingly, the lower limit to the size of a nanoparticle for the application of this model is given as ($\hbar/\sqrt{2mk_{\mathrm{B}}T_{\mathrm{D}}} \sim 2$ nm) for $T_{\mathrm{D}} \sim 200$ K. Such a situation is expected in a polar, indirect band-gap semiconductor with a low electron concentration and strong electron–phonon coupling.

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