Real time relaxation dynamics of macroscopically photo-excited electrons toward the Fermi degeneracy formation in the conduction band of semiconductors

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Concerning with the recent experiment of time-resolved two-photon photo-emission spectral measurements on semiconductors (GaAs, InP), we theoretically study real time relaxation dynamics of macroscopically photo-excited electrons, toward the Fermi degeneracy formation in an originally vacant conduction band of these semiconductors. Very soon after the photo-excitation, the whole electrons are shown to exhibit a quite rapid relaxation, like an avalanching phenomenon, mainly due to successive multi-(optical and acoustic) phonon emission from them. Repeating this multi-phonon process, the whole energy distribution of the electrons is shown to become a multi-peaked structure largely elongated over the lower part of the wide conduction band. However, after around 1 ps from the excitation, this relaxation critically slows down, since the emission of a long-wave acoustic phonon from electrons around the Fermi level becomes prohibitively difficult. By using the electron temperature approximation, we show that this slow relaxation is inversely proportional to time. Thus, the formation of the complete Fermi degeneracy takes an infinite time. These theoretical results are quite consistent to the aforementioned recent experiment.

Presence of the Fermi surface or Fermi degeneracy is one of the most fundamental concepts in the solid state physics. In fact, one can easily see back the standard textbook, that the most of many body theories for solids, say the BCS, the Kondo and the CDW theories, all start after the Fermi surface has been already well established.¹) In the present paper, however,
let us return to a more original viewpoint, and ask how this Fermi degeneracy itself can be generated from the very beginning, or from the true electron vacuum, to which macroscopic number of electrons are photo-injected.

Generally speaking, when a macroscopically condensed system is shone by photons, electrons in this system will usually be excited, and after a while, the system will relax down to the original ground state. Nowadays, we can observe this transient relaxation process of electrons in detail as a function of real time, through the time-resolved photo-electron emission spectra.

In metallic, or highly conductive systems, rapid relaxation dynamics of optically excited electrons has already been well-known and widely investigated. In most cases, however, only a minor part of the whole electrons is excited, while the main part of electrons is still in the original ground (Fermi degenerate) state and works as an infinite heat reservoir, resulting in a quite rapid relaxation or dissipation of newly given energy and momentum. In typical cases, only a few femtoseconds (fs) after the photo-excitation, are enough to return as far as to the vicinity of the Fermi degeneracy.

Now, we may have a quite naive but interesting question. What happens if a small but macroscopic number of electrons are excited at once into a truly vacant conduction band without electronic heat reservoir at low (absolute zero) temperature? Even in this case with no electronic heat reservoir, the excited electrons will relax down toward the Fermi degeneracy at around the bottom of the conduction band.

This ideal situation is known to be experimentally realized and can be investigated as a practical phenomenon by using the direct gap semiconductors such as GaAs and InP so far, but the relaxation mechanism of photo-excited carriers is still under considerable debates.

Very recently, however, a time-resolved two-photon photo-emission spectroscopy measurement in GaAs and InP has been performed, in which we can directly access to a transient time evolution of carrier (electron) distributions in the conduction band. The essential results of this experiment are as follows: (1) The electrons are excited, by an intense visible laser pulse, to the states around 0.3 eV higher from the conduction band minimum (CBM). (2) The Fermi energy is located around 0.1 eV above this CBM, implying the carrier number is about 0.003 electrons per unit cell. (3) In the initial 1 picosecond (ps) from the photo-excitation, a rapid shift of the whole electron distribution like an avalanche is observed. In this process, a multi-peaked structure of electron distribution is observed. It is elongated over the lower part of the wide conduction band. The important point in this early stage is that such an electron distribution is far from the Fermi-Dirac one, and we cannot define the
(4) After 1 ps from the photo-excitation, the change of the electron distribution becomes very small and the relaxation keeps slowing down. This slow relaxation, in the long time limit, is inversely proportional to time. Thus, the situation is quite different from the aforementioned metallic or highly conductive cases.

In this letter, we theoretically study how a macroscopic number of photo-excited electrons will relax toward the Fermi degeneracy formation in the originally vacant conduction band of the semiconductor.

At first, we should note about usual decay channels of photo-excited carriers in the conduction band. The radiative recombination of an electron-hole pair occurs within $10^{-9}$ second. The Auger recombination of an electron-hole pair with no energy dissipation may also occur within $10^{-12}$ second or so. On the other hand, various quantum fluctuations of the electron momentum, charge and spin give no energy dissipation. Thus, the relaxation phenomenon, we have to describe here, is the intraband one which occurs in an initial few ps.

Based on above, our scenario is as follows: The intra-band coulombic scattering among electrons, being completely elastic, can give no net energy relaxation. Moreover, the number of excited carriers is still low ($\sim 0.003$ per unit cell), implying the electron-electron scattering is rather a rare event. The electron-hole pair attractive interaction does not cause any serious effects on the net energy relaxation in the energy region where we are concerning with. This is because the distribution of the electrons and holes are spatially uniform all through the energy relaxation, implying the electron-hole pair attractive interaction is almost within the mean field type. Thus, the energy relaxation will be dominated by the electron-phonon scattering. At the very beginning, the relaxation would be quite rapid, since the one-body states of electron below the Franck-Condon one are all completely vacant. As the Fermi degeneracy is approached, however, it slows down infinitely, since only low energy phonons are available. To examine this scenario, we consider a system, in which many electrons are coupled with acoustic (ac) and optical (op) phonons. Our Hamiltonian ($H$) is given as follows:

$$H \equiv H_0 + H_1,$$

$$H_0 = \sum_{k,\sigma} \varepsilon_k a_{k,\sigma}^\dagger a_{k,\sigma} + \sum_q \omega_q b_{q}^\dagger b_{q} + \omega_{op} \sum_q f_{q}^\dagger f_{q},$$

$$H_1 = \frac{S}{\sqrt{2N}} \sum_{q,k,\sigma} \left( b_q^\dagger + b_{-q} \right) a^\dagger_{k-q,\sigma} a_{k,\sigma} + \frac{1}{\sqrt{N}} \sum_{q,k,\sigma} \frac{iV}{q} \left( f_q^\dagger a_{k-q,\sigma}^\dagger a_{k,\sigma} - f_q a_{k,\sigma}^\dagger a_{k-q,\sigma} \right).$$

Here, $a^\dagger_{k,\sigma}$($a_{k,\sigma}$) is creation (annihilation) operator of an electron with wavevector $k$ and spin $\sigma$. The conduction band energy is assumed to be isotropic and parabolic: $\varepsilon_k = B \cdot (k \cdot k / \pi^2)$ with
Fig. 1. (Color online) Time evolution of DOS is shown. CFDS means completely fermi degenerated state. Thick and thin lines are plotted at every 500 and 100 fs, respectively, from $t = 0$ fs to 4000 fs.

a band width $B$, $b^\dagger_q(b_q)$ and $f^\dagger_q(f_q)$ are creation (annihilation) operators of ac and op phonons, respectively, with a wavevector $q$. The acoustic phonon energy is linearly $q$-dependent : $\omega_q = \omega_M \cdot (q/\pi)$, while the op one is $q$-independent. $S$ and $V$ are electron-ac and -op phonon coupling constants, respectively. The second term of $H_I$ describes the electron-op phonon interaction introduced in Ref.\(^{14}\). $N$ is the total number of lattice site.

The density matrix ($\equiv \rho(t)$) at a time $t$ is written as a direct product of the electron density matrix ($\equiv \rho_e(t)$) and the phonon one $\rho_p \equiv \exp (-H_p/k_B T_p)$ with a phonon temperature $T_p$. The phonon system always behaves as a heat reservoir in the present scenario, and thus $T_p = 0$ K. An expectation value of electron population at a site $l$ is given as $\langle n_{l,\sigma}(t) \rangle \equiv \text{Tr}[n_{l,\sigma}\rho(t)/\text{Tr}(\rho(t))]$, where $n_{l,\sigma} \equiv a^\dagger_{l,\sigma} a_{l,\sigma}$, and $a_{l,\sigma} \equiv N^{-1/2} \sum_k e^{ikl} a_{k,\sigma}$. It is easily shown that $\langle n_{l,\sigma}(t) \rangle$ is independent of $l$ and $t$, and we put $n_M \equiv \langle n_{l,\sigma}(t) \rangle$.

Our electronic system is in a non-equilibrium state starting from the photo-excitation. Time evolution of the density matrix is obtained by

$$\tilde{\rho}(t + \Delta t) = \exp_+ \left\{ i \int_0^{\Delta t} d\tau \tilde{H}_I(\tau) \right\} \rho_e(t) \rho_p \exp_- \left\{ -i \int_0^{\Delta t} d\tau' \tilde{H}_0(\tau') \right\},$$

where subscript $\pm$ in exponent means chronological order and $\tilde{O}(\tau) \equiv e^{i\tau H_0} O e^{-i\tau H_0}$. By expanding the exponential terms in Eq. (4) up to the second order of $H_I$, we can evaluate a time evolution of $\langle n_{k,\sigma}(t) \rangle$. After a tractable calculation with a use of the Fermi’s golden rule, we
get the rate equation for the electron population as

$$\frac{\partial n_{k,\sigma}}{\partial t} = \left(1 - \langle n_{k,\sigma}(t)\rangle\right)\left(\Gamma_{ep,k}^{(+)}(t) + \Gamma_{ep,k}^{(op)}(t)\right) - \left(\Gamma_{ep,k}^{(-)}(t)\right)\left(\Gamma_{ep,k}^{(ac)}(t) + \Gamma_{ep,k}^{(-)}(op)\right),$$

(5)

where

$$\Gamma_{ep,k}^{(i)} = C_i \sum q \langle n_{k+q,\sigma}\rangle \delta(\varepsilon_k + \omega_q - \varepsilon_{k+q}),$$

(6)

$$\Gamma_{ep,k}^{(-i)} = C_i \sum q \left(1 - \langle n_{k+q,\sigma}\rangle\right) \delta(\varepsilon_{k+q} + \omega_q - \varepsilon_k),$$

(7)

with $C_i = \pi S^2 N^{-1}$ or $2\pi V^2 N^{-1}$ for $i=ac$ or $op$, respectively. Actual numerical calculations are performed by replacing the discretized $q$ to continuous one, as $N^{-1} \sum_q \rightarrow \left(4\pi^4/3\right)^{-1} \int dq$. It should be noted that, in our model, the electronic system is relaxed all through the process by an "infinite repetition" of a phonon emission within the second order perturbation. Then, all the higher order processes, which can be reduced to this infinite repetition of this second order process, are taken into account.

We use the following parameters, which are appropriate for GaAs and InP: $B = 5$ eV, $\omega_M = 24$ meV, $\omega_{op} = 38$ meV, $S = 0.5$ eV, and $V = 0.13$ eV. In our model, there is no anisotropy in $k$-space. Then, under the polar coordinate, we use equi-spaced $10^4 k$-mesh in $[0 : \pi]$ for the radial component, and the angle dependent part is convoluted. Thus, the total number of states is given as $2N = 2 \cdot \sum k 4\pi k^2$, and the total electron number is $n_{tot} = n_M N$. Time step $\Delta t$ is set to 0.01 fs.

The time evolution of DOS from 0 fs to 4000 fs with $n_M = 0.003$ electrons per site is given in Fig. 1. We assume that the photo-excited electrons are strongly concentrated around a certain energy, and the electron population at $t = 0$ fs has a rectangular shape. We have checked even if a gaussian-shaped distribution is adopted for the initial one, the basic aspect is not altered so much. When the system is relaxed only by the electron-ac phonon scattering (Fig. 1a), the energy relaxation proceeds very slowly, and its tail can only slightly reach the CBM. Even after 4000 fs from the photo-excitation, the state has still not reached around the Fermi degeneracy, as shown in Fig. 2a. In Fig. 2a, the mean energy is defined as $\langle E \rangle \equiv E_{tot}/n_{tot}$, where $E_{tot} = \int E n(E) dE$, which are referenced from the CBM.

When we also take into account the electron-op phonon scattering, the situation changes drastically (Fig. 1b). Even in the early stage, a substantial part of electrons relaxes below the Fermi energy very rapidly, and the broadening of the electron distribution occurs. This occupation of states below the Fermi energy is attained by the energy relaxation from higher energy states. As a result, we can find a multi-peaked distribution, around 1000 fs. Thus, in
this stage, the system shows a quite rapid relaxation (avalanching) as shown in Fig. 2a.

After this avalanching phenomenon, the energy relaxation shows a critical slowing down at around $t = 1200$ fs. This is because the relaxation occurs only around the Fermi energy, in which electron scatterings with only low energy phonons are possible. More precisely, the energy of the op phonon is too large for electrons just above the Fermi energy to relax down to the unoccupied states just below the Fermi energy. Thus, the main relaxation process changes from the electron-op phonon scattering to the electron-ac phonon one. In Fig. 2a, the shift of the mean energy after the 2000 fs is almost invisible, but a quite slow relaxation still continues as seen in Fig. 2b, in which the total energy is referenced from that in the completely Fermi degenerated state (CFDS). In Fig. 3, the time evolution of the electron distribution is given. In the later time, the electron distribution approximately follows the Fermi-Dirac distribution, implying the electron temperature is well-defined, while, one can see, it can never be defined in the avalanching process.

The results in Figs. 2 and 3 lead a conclusion that it takes an infinite time to reach the complete Fermi degeneracy since the energy relaxation continues to slow down. These results have no serious carrier number dependence, provided that $n_{\text{M}} \sim 0.003$.

The long time limit, or the final stage of the energy relaxation can also be investigated
by using the electron temperature approximation (ETA). In the final stage, as mentioned before, the energy relaxation by the electron-ac phonon scattering becomes dominant. Then, we neglect the electron-op phonon interaction in this stage. At each time $t$, an electron temperature ($\equiv T_e$) will be always well established in the electronic system, prescribed by $H_e = \sum_{k,\sigma} \varepsilon_k n_{k,\sigma}$, due to intra-system multiple scattering by the elastic electron-electron interaction, though we have not written it explicitly in Eq. (1). It is weak but becomes effective in the long time limit. Then, the electron density matrix is given as $\rho_e(t) \equiv \exp \left(-\frac{H_e}{k_B T_e(t)}\right)$. $T_e(t)$ gradually decreases, as releasing its energy to the phonon system through the electron-phonon interaction. Thus, we can forget about the electron-electron interaction, except $T_e(t)$.

The electronic heat capacity is defined as

$$C(T_e(t)) \equiv \frac{\partial \langle H_e \rangle}{\partial T_e},$$

where $\langle H_e \rangle = \sum_{k,\sigma} (\varepsilon_k - \mu) \langle n_{k,\sigma} \rangle$ with chemical potential $\mu$. On the other hand, the time evolution of the phonon energy, $H_p = \sum_q \omega_q b_q^\dagger b_q$, through the electron-phonon scattering is calculated by using the aforementioned density matrix. Along the same manner with the deviation of the rate equation, we obtain

$$\langle H_p(t + \Delta t) \rangle = \Delta t \Gamma(T_e),$$

where

$$\Gamma(T_e) = \frac{\pi S^2}{N} \sum_{q_{k,\sigma}, q_{-k,\sigma}} \omega_q (1 - \langle n_{k-q,\sigma} \rangle \langle n_{k,\sigma} \rangle) \delta(\omega_q + \varepsilon_{k-q} - \varepsilon_k).$$

Then, by considering the energy conservation:

$$\Delta \langle H_e(T_e) \rangle = C(T_e) \Delta T_e = \Gamma(T_e) \Delta t = \Delta \langle H_p(T_e) \rangle,$$
we get the equation for the electronic system cooling as

\[
\frac{\partial T_e}{\partial t} = - \frac{\Gamma(T_e)}{C(T_e)}.
\] (12)

At low temperature, the electronic heat capacity is well-known to be linearly proportional to temperature.\(^1^5\) Electron-hole pair numbers around the Fermi energy and ac phonon energy are also proportional to \(T_e\), while the phonon mode density is proportional to \(T_e^2\). Then, \(\Gamma(T_e) \propto T_e^4\). From these order estimations with Eq. (12), we can finally obtain \(T_e \propto t^{-1/2}\), and thus \(\Delta \langle H_e(T_e) \rangle \propto t^{-1}\). Although our theory for the electron-ac phonon interaction in Eq.(3) is rather phenomenological, being a little different from the standard deformation potential one,\(^1^6,1^7\) this result agrees well with the experiment,\(^1^2,1^3\) and gives much slower relaxation than the aforementioned results of the real time dynamics, as shown in Fig. 2b.

In summary, the energy relaxation dynamics of the macroscopically photo-excited carriers in the conduction band is theoretically studied, by considering the phonon system as a heat reservoir. The avalanching process soon after the photo-excitation is found, and it is mainly caused by the electron-op phonon scattering. In this process, we found the appearance of an elongated multi-peaked distribution in the DOS. The slow dynamics is seen in the later time, in which only the low energy phonon is available, and thus the electron-ac phonon scattering works as a main reservoir. At around 1200 fs, main relaxation process is changed from electron-op phonon scattering to electron-ac phonon one. At that time, the relaxation shows a critical slowing down. With a use of the ETA for the electronic system cooling, we showed that the relaxation in the long time limit is proportional to \(t^{-1}\). The present results well agree with the basic aspects of the recent time-resolved two-photon photoemission.\(^1^2,1^3\) This conclusion has a close connection with the Luttinger theorem,\(^1^8\) and the theory for the life time of the quasi-particle in the Fermi liquid.\(^1^9\)

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