Ultrafast carrier recombination and generation rates for plasmon emission and absorption in graphene

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Electron-hole generation and recombination rates for plasmon emission and absorption in graphene are presented. The recombination times of carriers due to plasmon emission are found to be in the tens of femtoseconds to hundreds of picoseconds range. The recombination times depend sensitively on the carrier energy, carrier density, temperature, and plasmon dispersion. Carriers near the Dirac point are found to have much longer lifetimes compared to carriers at higher energies. Plasmons in a graphene layer on a polar substrate hybridize with the surface optical phonons and this hybridization modifies the plasmon dispersion. We also present generation and recombination rates of carriers due to plasmon emission and absorption in graphene layers on polar substrates.

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I. INTRODUCTION

The high carrier mobility and the large optical absorption in graphene have opened up unique opportunities for this material in electronics and optoelectronics. The performance of graphene in many of these applications depends on the electron-hole generation and recombination rates in graphene. It is therefore important to understand the mechanisms that are responsible for electron-hole generation and recombination in graphene and the associated time scales. Previously, carrier generation and recombination rates in graphene due to Auger scattering and impact ionization and due to optical phonon emission and absorption have been reported. The strong interaction between electrons/holes and plasmons in graphene has been used to explain observed features in the angle-resolved photoemission (ARPES) data. In this paper, we present electron-hole generation and recombination rates due to plasmon emission and absorption. Our results show that the recombination times of carriers due to plasmon emission are in the range of tens of femtoseconds to hundreds of picoseconds and depend sensitively on the carrier energy, carrier density, temperature, and plasmon dispersion. The available phase space for plasmon emission is restricted because of energy and momentum conservation requirements and also because of Pauli’s exclusion principle, and carriers near the Dirac point have much longer lifetimes compared to carriers at higher energies. Plasmons in a graphene layer on a polar substrate hybridize with the surface optical phonons, and this hybridization modifies the plasmon dispersion. We also present generation and recombination rates of carriers due to plasmon emission and absorption in graphene layers on polar substrates.

II. THEORETICAL MODEL FOR SUSPENDED GRAPHENE

We first consider a graphene sheet in the plane $z = 0$ sandwiched by media with free-space permittivity [Fig. 1(a)], as in the case of suspended graphene. The electron energy dispersion is given by $E_s(\mathbf{k}) = \hbar v_F k$, where $s$ equals $+1$ and $-1$ for conduction and valence bands, respectively. The dispersion for plasmons is given by $\epsilon(q, \omega) = 0$, where

$$\epsilon(q, \omega) = 1 - \frac{q^2}{2\epsilon_0 q} \Pi(q, \omega).$$

The electron-hole propagator $\Pi(q, \omega)$ is given by

$$\Pi(q, \omega) = 4 \sum_{s,s'} \int \frac{d^2\mathbf{k}}{(2\pi)^2} \left| \langle \psi^s_{k+q}(\mathbf{r}) | e^{i\mathbf{q} \cdot \mathbf{r}} | \psi^{s'}_{k}(\mathbf{r}) \rangle \right|^2$$

$$\times \frac{f_s(k) - f_s(\tilde{k} + q)}{\hbar \omega + E_s(\mathbf{k}) - E_s(\mathbf{\tilde{k}} + q) + i\eta},$$

where $\eta$ is the imaginary part of the dielectric function. The matrix element between the Bloch functions in the above expression is

$$\left| \langle \psi^s_{k+q}(\mathbf{r}) | e^{i\mathbf{q} \cdot \mathbf{r}} | \psi^{s'}_{k}(\mathbf{r}) \rangle \right|^2 = \frac{1}{2} \left[ 1 + s s' \frac{k + q + \cos(\theta)}{|k + q|} \right].$$

Here, $\theta$ is the angle between $\mathbf{k}$ and $\mathbf{q}$. To calculate the recombination and generation rates, we consider a plasmon wave with the electric field given by

$$\mathbf{E}(\mathbf{r}, z, t) = \frac{1}{2} (\mathbf{q} \pm i\tilde{z}) E_0 e^{i\mathbf{q} \cdot \mathbf{r}} e^{i\tilde{z} \cdot \mathbf{r} - i\omega t} + c.c.$$}

The transition rate for an electron in the conduction band to go into the valence band via stimulated emission of a plasmon of wave vector $\mathbf{q}$ is given by Fermi’s Golden Rule,

$$\Gamma = \frac{1}{\hbar} \int d\mathbf{k} \left| \langle \psi^-_{\mathbf{k}-\mathbf{q}}(\mathbf{r}) | e^{-i\mathbf{q} \cdot \mathbf{r}} | \psi^+_\mathbf{k}(\mathbf{r}) \rangle \right|^2 \frac{2|E_0|^2}{4q^2} [1 - f_-(\mathbf{k} - \mathbf{q}) - f_+(\mathbf{k} + \mathbf{q}) - f_-(\mathbf{k} + \mathbf{q}) - f_+(\mathbf{k} - \mathbf{q})].$$

The energy density $W$ of the plasmon wave has contributions from both the field and the kinetic energy of the carriers. Assuming no plasmon dissipation, the total energy density can be found from the complex electromagnetic energy theorem:

$$W = W_F + W_{KE}$$

$$= \frac{\epsilon_0}{2q} |E_0|^2 - \frac{1}{4} |E_0|^2 \text{Im} \left\{ \frac{\partial \sigma(q, \omega)}{\partial \omega} \right\} \bigg|_{q(\omega)}.$$
Since the conductivity $\sigma(q, \omega)$ is related to the dielectric constant $\epsilon(q, \omega)$ as
\[
\epsilon(q, \omega) = 1 + i \frac{q \sigma(q, \omega)}{2 \epsilon_0 \omega},
\]
the expression for the energy density $W$ becomes
\[
W = \frac{\epsilon_0}{2q} |E_0|^2 \text{Re} \left\{ \omega \frac{\partial \epsilon(q, \omega)}{\partial \omega} \right\} \omega(q). \tag{7}
\]

$W$ must also equal $n(\tilde{q}) \hbar \omega_{\text{o}}(q)/A$, where $n(\tilde{q})$ is the number of plasmons in mode $\tilde{q}$ and $A$ is the area of the crystal. Therefore, using (5) and (8), the lifetime of an electron in the conduction band due to both stimulated and spontaneous emission into all plasmon modes becomes
\[
\frac{1}{\tau_k} = \frac{2 \pi}{\hbar} \int \frac{d^2 \tilde{q}}{(2\pi)^2} \left\{ n(\tilde{q}) + 1 \right\} |1 - f_-(\tilde{k} - \tilde{q})| \times \frac{e^2}{2 \epsilon_0 \omega q} \left[ 1 - \frac{k - q \cos(\theta)}{|\tilde{k} - \tilde{q}|} \right] \times \hbar \delta(E_+(\tilde{k}) - E_-(\tilde{k} - \tilde{q}) - \hbar \omega_{\text{o}}(q)) \text{Re} \left\{ \frac{\partial \epsilon(q, \omega)}{\partial \omega} \right\} \omega(q). \tag{9}
\]

The recombination and generation rates, $R$ and $G$ (units: number/cm²-s), due to plasmon emission and absorption can be written as
\[
R = 8\pi \int \frac{d^2 \tilde{k}}{(2\pi)^2} \int \frac{d^2 \tilde{q}}{(2\pi)^2} |n(\tilde{q}) + 1| f_+(\tilde{k}) |1 - f_-(\tilde{k} - \tilde{q})| \frac{e^2}{2 \epsilon_0 \omega q} \left[ 1 - \frac{k - q \cos(\theta)}{|\tilde{k} - \tilde{q}|} \right] \times \delta(E_+(\tilde{k}) - E_-(\tilde{k} - \tilde{q}) - \hbar \omega_{\text{o}}(q)) \text{Re} \left\{ \frac{\partial \epsilon(q, \omega)}{\partial \omega} \right\} \omega(q), \tag{10}
\]
and
\[
G = 8\pi \int \frac{d^2 \tilde{k}}{(2\pi)^2} \int \frac{d^2 \tilde{q}}{(2\pi)^2} n(\tilde{q}) |1 - f_+(\tilde{k})| f_-(\tilde{k} - \tilde{q}) \frac{e^2}{2 \epsilon_0 \omega q} \left[ 1 - \frac{k - q \cos(\theta)}{|\tilde{k} - \tilde{q}|} \right] \times \delta(E_+(\tilde{k}) - E_-(\tilde{k} - \tilde{q}) - \hbar \omega_{\text{o}}(q)) \text{Re} \left\{ \frac{\partial \epsilon(q, \omega)}{\partial \omega} \right\} \omega(q) \times \frac{\delta(E_+(\tilde{k}) - E_-(\tilde{k} - \tilde{q}) - \hbar \omega_{\text{o}}(q))}{\text{Re} \left\{ \frac{\partial \epsilon(q, \omega)}{\partial \omega} \right\} \omega(q)}. \tag{11}
\]

In thermal equilibrium, the plasmon number $n(\tilde{q})$ equals the Bose factor $[\exp(\hbar \omega_{\text{o}}(q)/kT) - 1]^{-1}$. Similar results can be obtained starting from the self-energy of an electron in the conduction band. Assuming thermal equilibrium, and using the imaginary-time Green’s function approach, the relevant contribution to the conduction band electron self-energy can be written as
\[
\sum(\tilde{k}, i \omega_m) = -\int \frac{d^2 \tilde{q}}{(2\pi)^2} \frac{1}{2} \left[ 1 - \frac{k - q \cos(\theta)}{|\tilde{k} - \tilde{q}|} \right] \times \frac{1}{\beta \hbar} \sum_m \frac{e^2}{2 \epsilon_0 \omega_{\text{o}}} \frac{\epsilon_{q,i\nu_m}}{\epsilon_{q,i\nu_m}} G(\tilde{k} - \tilde{q}, i \omega_m - i \nu_m), \tag{12}
\]
where $G(\tilde{k} - \tilde{q}, i \omega_m - i \nu_m)$ is the valence-band Green’s function. The summation over the Matsubara frequencies can be performed by first isolating the pole coming from the zero of $\epsilon(q, i \nu_m)$ in the denominator at the plasmon frequency. Finally, if one excludes from (12) contributions coming from plasmon absorption processes and then calculates the lifetime of the conduction electron using the expression
\[
\frac{1}{\tau_k} = -\frac{2 \hbar}{\beta} \text{Im} \left\{ \sum(\tilde{k}, E_+(\tilde{k}) - E_f)/\hbar + i \eta \right\}, \tag{13}
\]
then the result obtained is identical to the one given in (9). It should be mentioned here that focusing on the collective excitation pole coming from the zero of $\epsilon(q, i \nu_m)$ allows one to calculate the interband scattering rate due to electron-plasmon interaction. Contributions from other processes, such as Auger scattering and impact ionization, are therefore excluded. From the results obtained above it follows that the electron-plasmon interaction in graphene can be approximately described by the following Hamiltonian in the second quantized form,
\[
\hat{H}_{\text{el-pl}} = \sum_{s,s',\sigma,\tilde{k},\tilde{q}} M_{s,s',\tilde{k},\tilde{q}} (\hat{b}_{\tilde{k}} + \hat{b}_{\tilde{k}}^\dagger) \hat{e}_{s',\sigma,\tilde{k},\tilde{q}}^\dagger \hat{e}_{s,\sigma,\tilde{k}}, \tag{14}
\]
where $\hat{b}_{\tilde{k}}$ and $\hat{e}_{s,\sigma,\tilde{k}}$ are the plasmon and the electron destruction operators, respectively, $\sigma$ stands for different spins and valleys, and the coupling constant $M_{s,s',\tilde{k},\tilde{q}}$ is given by
\[
|M_{s,s',\tilde{k},\tilde{q}}|^2 = \frac{\epsilon_0}{2 \epsilon_0 q A} \text{Re} \left\{ \frac{\partial \epsilon(q, \omega)}{\partial \omega} \right\} \omega(q). \tag{15}
\]
Here, $\theta$ is the angle between $\tilde{k}$ and $\tilde{q}$ and $A$ is the area of the graphene crystal.

### A. Results and discussion

The plasmon dispersion is first found numerically using the expression for $\Pi(q, \omega)$ in (2). The recombination and
generation rates and lifetimes are then calculated using (9), (10), and (11). The dominant contribution to the propagator in (2) comes from the intraband part. The interband part modifies the plasmon dispersion slightly and also imparts an imaginary part to the plasmon frequency. If the interband contribution is ignored, the error in the calculated plasmon frequency has been found to be generally small (less than 10%) for small plasmon wave vectors. This small error comes with the enormous simplicity of having to find zeros of $\epsilon(q, \omega)$ on only the real frequency axis, and therefore this approach has been adopted in numerical simulations. The results we present are also not self-consistent in the sense that the quasiparticle density of states has been assumed to be that of the noninteracting electron system. It is known that Re$\{\epsilon(q, \omega)\}$ in (9) becomes large when $\omega(q)$ approaches $q v$, which happens for very large wave vectors and this also reduces the probability of emission of large-wave-vector plasmons. Figure 3 shows that the electron spontaneous emission lifetimes can range from values as small as 10 fs to hundreds of picoseconds. Figure 5 shows the average minority carrier (electron) recombination time $\tau_R$ plotted as a function of the minority carrier density for different temperatures in p-doped graphene ($p = 10^{12}$ cm$^{-2}$). As expected from the results in Fig. 3, the average recombination time decreases with increases in the temperature because the minority carrier distribution spreads to higher energies.

In many optical studies and in graphene-based optoelectronic devices, photoexcitation followed by rapid
thermalization results in an equal number of thermally distributed electrons and holes in an otherwise near-intrinsic graphene layer [Fig. 1(d)]. It is therefore important to understand the recombination and generation times in such situations. Figure 6 shows the recombination times \( \tau_R \) (solid curves) and the generation times \( \tau_G \) (dashed curves) plotted as a function of the electron and hole density (assumed to be equal) for different temperatures. The number of plasmons \( n(q) \) in different modes is assumed to be given by the Bose factor. This assumption may not be valid in a nonequilibrium situation immediately following photoexcitation. Figure 7 shows the recombination times \( \tau_R \) (solid curves) and the generation times \( \tau_G \) (dashed curves) plotted as a function of the temperature for different electron and hole densities. Figures 6 and 7 show that the recombination times can be much smaller than a picosecond for carrier densities higher than \( 10^{11} \) cm\(^{-2} \) at all temperatures. Figures 6 and 7 show that the generation times can also be very short, and this implies that carrier generation cannot be ignored in experiments where a hot carrier distribution is created via photoexcitation in ultrafast optical studies.\(^{25-32} \)

III. THEORETICAL MODEL FOR GRAPHENE ON POLAR SUBSTRATES

The results presented above suggest that it might be possible to alter the plasmon-assisted recombination and generation rates in graphene by altering the dielectric environment, thereby modifying the strength of the Coulomb interaction.\(^{21} \)

Specifically, a substrate with a large dielectric constant could potentially reduce the recombination and generation rates. However, polar materials with large dielectric constants have surface optical phonon modes that couple strongly with the graphene plasmons.\(^{23} \)

To study this further, we consider a graphene sheet at a distance \( d \) away from a polar substrate [Fig. 1(b)]. The dielectric constant of the substrate is assumed to be given by the expression

\[
\epsilon_{\text{sub}}(\omega) = \epsilon_{\text{sub}}(\infty) \left( \frac{\omega^2 - \omega_{\text{LO}}^2}{\omega^2 - \omega_{\text{TO}}^2} \right). \tag{17}
\]

Here, \( \epsilon_{\text{sub}}(0)/\epsilon_{\text{sub}}(\infty) = \omega_{\text{LO}}^2/\omega_{\text{TO}}^2 \). The surface optical phonon frequency \( \omega_{\text{SO}} \) is obtained by setting \( \epsilon_{\text{sub}}(\omega) \) equal to \(-1\) and equals

\[
\omega_{\text{SO}} = \omega_{\text{TO}} \sqrt{\frac{\epsilon_{\text{sub}}(0) + 1}{\epsilon_{\text{sub}}(\infty) + 1}}. \tag{18}
\]

The dielectric constant \( \epsilon(q,\omega) \) of the graphene sheet can be found by placing a test charge in the sheet and finding the resulting potential. The result is

\[
\epsilon(q,\omega) = \frac{1}{2} + \frac{1}{2} \left[ \frac{\epsilon_{\text{sub}}(\omega) + 1}{\epsilon_{\text{sub}}(\omega) + 1} e^{2qd} + \frac{\epsilon_{\text{sub}}(\omega) - 1}{\epsilon_{\text{sub}}(\omega) - 1} e^{2qd} - \epsilon_{\text{sub}}(\omega) - 1 \right] - \frac{\epsilon^2}{2\epsilon_{\text{eff}}} \Pi(q,\omega). \tag{19}
\]

The dispersion of the coupled plasmon-phonon longitudinal mode can be found as before by setting \( \epsilon(q,\omega) \) equal to
Now one finds two longitudinal collective modes. In the $q \rightarrow 0$ limit, the lower frequency mode is plasmon-like, with $\omega(q) \rightarrow 0$ as $q \rightarrow 0$, and the higher frequency mode is phonon-like, with $\omega(q) \rightarrow \omega_{\text{SO}}$ as $q \rightarrow 0$. For large wave vectors, the lower frequency mode becomes plasmon-like, with $\omega(q) \rightarrow qv$ as $q \rightarrow \infty$. As an example, we consider the technologically relevant case of a graphene layer on a silicon carbide (SiC) substrate. The values of different parameters are as follows: $d = 5 \text{ Å}$, $\bar{h}\omega_{\text{LO}} = 120 \text{ meV}$, $\bar{h}\omega_{\text{TO}} = 98 \text{ meV}$, and $\epsilon_{\infty} = 6.5$. These give $\bar{h}\omega_{\text{SO}} \approx 117 \text{ meV}$. Figure 8 shows the dispersions of the coupled plasmon-phonon modes for a p-doped graphene sheet on a SiC substrate for different hole densities. Comparing Figs. 2 and 8, it can be seen that plasmon-phonon coupling significantly modifies the dispersion, and this has recently been verified experimentally. The recombination and generation rates can be obtained using the same expressions as those given in (9), (10), and (11), with the exception that contributions from both branches of the dispersion must be included. Therefore, the surface optical phonons of the polar substrate provide an additional channel for carrier recombination and generation. It should be mentioned here that large-wave-vector surface optical phonon modes can also cause intervalley recombination and generation processes. However, the square of the coupling matrix element between the surface optical phonons and the carriers is proportional to $\frac{e^2}{\sqrt{2\epsilon_0 q^2 \bar{h}\omega_{\text{SO}}}} \left( \frac{1}{\epsilon_{\text{sub}}(\infty) + 1} - \frac{1}{\epsilon_{\text{sub}}(0) + 1} \right)$ and becomes small for the large wave vectors needed for the intervalley transitions in graphene. Therefore, intervalley processes are ignored here.

A. Results and discussion

Figure 9 shows the calculated lifetime of an electron in the conduction band due to spontaneous emission as a function of the electron energy for different hole densities and temperatures in p-doped graphene on a SiC substrate.
function of the electron energy for different hole densities and temperatures for a p-doped graphene sheet on a SiC substrate. Figure 9 displays the same general trends as does Fig. 3 in the case of a suspended graphene sheet. However, lifetimes are shorter for the low-energy electrons in the case of graphene on SiC. For electrons with energies near the Dirac point, the electron energy, while lifetimes due to the upper frequency branch are becoming shorter. As in the suspended graphene case, the spontaneous emission lifetimes can range from tens of femtoseconds to hundreds of picoseconds. Figure 10 shows the recombination time \( \tau_R \) (dashed curves) plotted as a function of the electron and hole density (assumed to be equal) for different temperatures in a p-doped graphene (\( p = 10^{12} \text{ cm}^{-2} \)) on a SiC substrate. Compared to the suspended graphene case (Fig. 5), the recombination times for graphene on SiC are shorter for low minority carrier densities. Next, we consider the case where the electron and hole densities are the same (as is the situation in photoexcitation experiments). Figure 11 shows the recombination times \( \tau_R \) (solid curves) and the generation times \( \tau_G \) (dashed curves) plotted as a function of the electron and hole density (assumed to be equal) for different temperatures for a graphene sheet on a SiC substrate. The recombination and generation times in graphene on SiC are generally of the same order as in the case of suspended graphene discussed earlier. The role of the higher dielectric constant of the SiC substrate in reducing plasmon-assisted recombination and generation rates, compared to those of suspended graphene, is compensated by the presence of surface optical phonons, which not only modify the plasmon dispersion but also provide an additional channel for recombination and generation.

**IV. CONCLUSION**

In this paper we have presented electron-hole recombination and generation times due to spontaneous and stimulated emission and absorption of plasmons in graphene. Our results indicate that plasmon-assisted recombination times in graphene can vary over a wide range of values, ranging from tens of femtoseconds to hundreds of picoseconds. In many proposed and demonstrated optoelectronic devices, the plasmon-assisted recombination and generation rates could be fast enough to significantly impact device performance.

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