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Three-wave collinear difference-frequency mixing and terahertz coherent emission from gapped graphene

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ABSTRACT

The second-order nonlinear optical susceptibility $\chi^{(2)}(-\omega_3;\omega_1,\omega_2)$ corresponding to three-wave mixing of coherent radiation of the form $\omega_3=\omega_1-\omega_2$ is calculated for epitaxial graphene on a SiC substrate inducing the sublattice (inversion) asymmetry of the graphene and opening up a gap of about 0.26 eV in its π-electron-energy spectrum. The analytical treatment of the $\chi^{(2)}$ is based on the tight-binding approximation for π electrons and the original Genkin–Mednis nonlinear-conductivity-theory formalism including mixed intra- and interband terms. It is found that throughout the transparency region of the graphene, the absolute magnitude of the $\chi^{(2)}$ may be as large as 10^{-5} esu, which opens up new opportunities to generate terahertz (THz) coherent output from the graphene excited by two collinear mid-infrared ω_1 and ω_2 laser beams normally incident on its surface. The output power density produced at the difference frequency $\omega_1-\omega_2$ of 10 THz is estimated to be 0.1 μW/cm^2 for 10 MW/cm^2 pump peak intensities, and conditions are discussed under which a few orders of magnitude enhancement of the output power could be achieved in future experiments.

1. Introduction

Among many interesting properties of graphene (a single atomic layer of graphite), the unusually large nonlinear optical (NLO) response has received much attention recently, and several excellent reviews of the state-of-the-art of this subject are available in the literature at present [1–3]. However, aside from a theoretical study of the NLO excitation of surface plasmons of definite wave vector in electron-doped graphene [4], no one seems to have explored the feasibility of a new way to examine the subject. We have in mind difference-frequency generation (DFG), a second-order (three-wave mixing) coherent process which takes place when a material without a center of inversion is subjected to two optical pump fields of frequencies ω_1 and ω_2, combined to produce a third field of frequency $\omega_3=\omega_1-\omega_2$ [5,6]. Such a process is described in terms of a third-rank NLO susceptibility tensor $\chi^{(2)}_{\alpha\beta\gamma}(-\omega_3;\omega_1,\omega_2)$, where Greek subscripts refer to the Cartesian space directions x, y, and z. Due to centrosymmetric honeycomb lattice structure of pristine graphene, which is composed of two equivalent interpenetrating triangular sublattices, all the tensor elements $\chi^{(2)}_{\alpha\beta\gamma}$ for this monolayer should vanish in the electric-dipole (local) limit. Therefore, the nonvanishing electric-dipole-induced DFG from graphene can be acquired only through breaking its (the graphene) sublattice (inversion) symmetry in some or other way. In particular, such a symmetry breaking occurs in graphene grown by C-face epitaxy on SiC [7]. The underlying lattice of SiC, more precisely, a buffer layer between graphene and the SiC substrate, induces the electrostatic potential asymmetry of the two above-mentioned sublattices of graphene, generating a gap of about 0.26 eV at the Dirac points (two inequivalent corners K and K') of the Brillouin zone of the two-dimensional (2D) hexagonal lattice structure. This gives rise to a finite second-order optical nonlinearity of the overlying graphene, which has been studied in our previous work [8,9] focused on second-harmonic generation (SHG) and optical rectification.

In this paper, we further develop the above concept by showing how the strong second-order optical nonlinearity of graphene on SiC, which we will refer to as "gapped graphene" hereafter, manifests itself in the rise of a difference-frequency output in the presence of two normally incident pump laser beams at frequencies ω_1 and ω_2. We also discuss the possibility to generate coherent THz radiation in such a way, which, if realized, may become a new, very interesting application of graphene.

The rest of the paper is organized as follows. In Section 2, we describe the band structure model used in our study. In Section 3, an analytical expression for the DFG susceptibility of gapped graphene is obtained. This is followed by some numerical calculation and a discussion of the results (Section 4). Finally, a conclusion is

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drawn in Section 5.

2. Model

To describe the electronic structure of graphene in our study, we employ the tight-binding model, which has become the explanatory point of reference in almost all discussions of graphene, both experimental and theoretical (for reviews, see, e.g., [10–12]). Within the framework of the model, the perturbation caused by the graphene–substrate interaction breaking the sublattice (inversion) symmetry of pristine graphene can be expressed in terms of a "staggered" electrostatic potential Δ that has the opposite sign on the two sublattices [13]. This leads to the following two-band solution for the π-electron energies $E_{s\mathbf{k}}$ in a basis of Bloch orbitals $\Psi_{s\mathbf{k}}(\mathbf{r}) = U_{s\mathbf{k}}(\mathbf{r})\exp(i\mathbf{kr})$ near the K point:

$$E_{s\mathbf{k}} = \pm\sqrt{\Delta^2 + |h_{\mathbf{k}}|^2}, \tag{1}$$

where the plus and minus signs refer to the conduction (c) and valence (v) bands, respectively, $s(=\mathrm{c}, \mathrm{v})$ is the band index, $\mathbf{k}$ is the 2D electron wave vector measured relative to the K point [the endpoint of the vector $\mathbf{K} = (2\pi/3a)(1/\sqrt{3}, 1)$], and

$$h_{\mathbf{k}} = -(\hbar v_0/a)\left[k_+ a + (k_- a/2)^2\right]\exp(i2\pi/3) \tag{2}$$

with $k_\pm = k_x \pm ik_y$. Here, the x-axis is taken along the zigzag direction on the graphene plane (xy plane), and v_0 is the model parameter linked to the transfer integral t_0 between π orbitals of two nearest-neighboring atoms on the plane by the following relation: $\hbar v_0 = 3t_0 a/2$, where a is the distance between those atoms.

Eq. (1) explicitly takes into account the trigonal warping of the π-electron-energy bands in graphene, originating from the second term in the square brackets on the right-hand side of Eq. (2). As shown in [8,9], actually, it is the trigonal warping of the energy bands involved which gives rise to a finite second-order optical nonlinearity of gapped graphene at the normal incidence of radiation on its surface. In contrast, a few other mechanisms of the $\chi^{(2)}$ nonlinearity in gapless graphene, discussed in the literature previously [4,14–20], may cause this effect either at the oblique incidence of radiation [4,14,15] or in the presence of a direct electric current flowing in the graphene plane [16–20].

On a low-energy scale, the modulation amplitude $U_{s\mathbf{k}}(\mathbf{r})$ of the Bloch eigenfunction $\Psi_{s\mathbf{k}}(\mathbf{r})$ corresponding to $E_{s\mathbf{k}}$ of Eq. (1) is expressed in terms of atomic $2p_z$ orbitals $\varphi(\mathbf{r}-\mathbf{R}_n)$ as follows:

$$U_{s\mathbf{k}}(\mathbf{r}) = \sum_l C_{s\mathbf{k}}^{(l)} \sum_{n=1}^{N} \varphi(\mathbf{r}-\mathbf{R}_n-\boldsymbol{\tau}_l)\exp\left[-i\mathbf{K}(\mathbf{r}-\mathbf{R}_n-\boldsymbol{\tau}_l)\right]/\sqrt{N}, \tag{3}$$

where $l=1, 2$ is the sublattice index, $\mathbf{R}_n$ stands for the positions vector of the nth primitive two-atomic unit cell of the 2D lattice structure under consideration, N is the total number of the lattice sites occupied by carbon atoms, $\boldsymbol{\tau}_l$ denotes the position vector of the lth site, measured relative to the endpoint of the $\mathbf{R}_n$, and the coefficients $C_{s\mathbf{k}}^{(l)}$ are given by

$$C_{s\mathbf{k}}^{(1)} = \frac{1}{\sqrt{2}}\frac{h_{\mathbf{k}}}{\sqrt{(E_{c\mathbf{k}} \mp \Delta)E_{c\mathbf{k}}}}, \tag{4}$$

$$C_{s\mathbf{k}}^{(2)} = \pm\frac{1}{\sqrt{2}}\sqrt{1 \mp \frac{\Delta}{E_{c\mathbf{k}}}}, \tag{5}$$

The upper (lower) sign on the right-hand side of these equations refers to the conduction (valence) band.

In the following, we will ascribe an effective thickness d to monolayer graphene, which allows the second-order NLO properties of this material to be described in terms of the effective volume NLO susceptibility tensor $\chi^{(2)}_{\alpha\beta\gamma}$. This is especially convenient for assessing optical nonlinearities of mono- or few-layer structures as compared to those of truly three-dimensional (bulk) materials [14,21–23]. A value of d ($\simeq$0.34 nm), normally used for this purpose in the case of graphene, is equal to the extension of the π orbitals out of the graphene plane or, what is almost the same, to the layer separation in graphite.

The SiC-substrate-induced breaking of the inversion symmetry of graphene reduces its symmetry class to D_{3h}. With this symmetry, the second-order NLO susceptibility tensor $\chi^{(2)}_{\alpha\beta\gamma}$ has four nonvanishing surface elements with indices yyy, yxx, xyx, and xxy, among which only one is independent [5,24,25]:

$$\chi^{(2)}_{yyy} = -\chi^{(2)}_{yxx} = -\chi^{(2)}_{xyx} = -\chi^{(2)}_{xxy}. \tag{6}$$

If both the normally incident ω_1 and ω_2 pump beams are linearly polarized along the y-axis (i.e., in parallel to the armchair direction on the graphene plane), then it is enough to consider only the element $\chi^{(2)}_{yyy}$, which we will denote simply $\chi^{(2)}$ in what follows.

3. Difference-frequency generation susceptibility

To derive a formula for the DFG susceptibility $\chi^{(2)}(-\omega_3; \omega_1, \omega_2)$, we adapt the microscopic approach developed by Genkin and Mednis [26] in their nonlinear conductivity theory of bulk semiconductors. We refer the readers, who are unfamiliar with this approach, to our previous papers [27,28] where a detailed account of the theory has been given. It is worth stressing that our nowadays understanding of the NLO response of semiconductors on the whole is also based on the fundamental results obtained by Sipe et al. [29–31], whose methodology is close, in spirit, to that of the Genkin–Mednis theory.

For the two-band model described above, the relevant general expression for the $\chi^{(2)}$ can be partitioned as follows:

$$\chi^{(2)}(-\omega_3; \omega_1, \omega_2) = \chi_A^{(2)}(-\omega_3; \omega_1, \omega_2) + \chi_B^{(2)}(-\omega_3; \omega_1, \omega_2), \tag{7}$$

where

$$\chi_A^{(2)}(-\omega_3; \omega_1, \omega_2) = \frac{ie^3}{2V\hbar^2}\sum_{\mathbf{k}}\sum_P [\Omega_{\mathrm{vv}}(\mathbf{k}) - \Omega_{\mathrm{cc}}(\mathbf{k})] \times \Phi_{\mathrm{vc1}}(\mathbf{k})\Phi_{\mathrm{cv2}}(\mathbf{k}), \tag{8}$$

$$\chi_B^{(2)}(-\omega_3; \omega_1, \omega_2) = \frac{ie^3}{4V\hbar^2}\sum_{\mathbf{k}}\sum_P \left[\Phi_{\mathrm{cv1}}(\mathbf{k})\frac{\partial}{\partial k_y}\Phi_{\mathrm{vc2}}(\mathbf{k}) - \Phi_{\mathrm{vc1}}(\mathbf{k})\frac{\partial}{\partial k_y}\Phi_{\mathrm{cv2}}(\mathbf{k})\right] \tag{9}$$

with $\Omega_{ss'}(\mathbf{k})$ and $\Phi_{ss'j}(\mathbf{k})$ defined by

$$\Omega_{ss'}(\mathbf{k}) = \int U^*_{s\mathbf{k}}(\mathbf{r})\frac{\partial}{\partial k_y}U_{s'\mathbf{k}}(\mathbf{r})\,\mathrm{d}^3r \tag{10}$$

and

$$\Phi_{ss'j}(\mathbf{k}) = \frac{\Omega_{ss'}(\mathbf{k})}{\omega_{ss'}(\mathbf{k}) - \omega_j} \quad (j = 1, 2), \tag{11}$$

respectively. In the above equations, e is the magnitude of the electron charge, V is a normalization volume of the system, $\sum_P$ stands for the summation over the different permutations of the frequencies ω_1, ω_2, and $-\omega_3$, resulting in six terms, and, finally, $\hbar\omega_{ss'} = E_{s\mathbf{k}} - E_{s'\mathbf{k}}$ is the energy distance between the two bands involved at fixed value of $\mathbf{k}$. The damping of the excited electronic states due to relaxation effects neglected in Eqs. (8) and (9) can be taken into account by changing the frequency from $\omega_{ss'}(\mathbf{k})$ to