Dielectric constant of graphene-on-polarized substrate: A tight-binding model study

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Abstract. We report here a microscopic tight-binding theoretical study of the dynamic dielectric response of graphene-on-polarizable substrate with impurity. The Hamiltonian consists of first, second and third nearest-neighbour electron hopping interactions besides doping and substrate-induced effects on graphene. We have introduced electron–electron correlation effect at A and B sublattices of graphene which is considered within Hartree–Fock mean-field approximation. The electron occupancies at both sublattices are calculated and solved self-consistently and numerically for both up- and down-spin orientations. The polarization function appearing in the dielectric function is a two-particle Green's function which is calculated by using Zubarev's Green's function technique. The temperature and optical frequency-dependent dielectric function is evaluated and compared with experimental data by varying Coulomb correlation energy, substrate-induced gap and impurity concentrations.

1. Introduction

The synthesis of pristine graphene by Novoselov *et al* [1] has stimulated intense experimental and theoretical studies of graphene. The interaction between two intralayer carbon atoms in graphene is much larger and arises due to sigma bonds. The π electrons play the role of itinerant electrons. The optical spectrum studies are helpful for investigating the excitation properties of graphene [2]. This study shows that the π plasmon frequency in graphene is in the range of 7–12 eV. It is, therefore, convenient for theoretical studies of q-dependent plasmon. The optical frequency response of graphene leads to a dielectric function which incorporates all the information about the effects of impurity, defects, ad-atoms, different substrates, Coulomb correlation etc. [3]. There are a few theoretical studies on frequency and temperature-dependent dielectric function taking into account the electron dispersion throughout the Brillouin zone [4,5]. Recently, Hwang and Sarma [6] have reported a theoretical study of dielectric function and plasmon dispersion in two dimensions. We report here a tight-binding model calculation of dielectric function of graphene-on-substrate and compare the results with the experimental data.

2. Model Hamiltonian

The model Hamiltonian for monolayer graphene consisting of site energy, impurity effects and the substrate effects is given by

$$H_1 = \sum_{k,\sigma}(\epsilon_a a_{k,\sigma}^\dagger a_{k,\sigma} + \epsilon_b b_{k,\sigma}^\dagger b_{k,\sigma}), \tag{1}$$

$$H_2 = \sum_{k,\sigma} V(x_a a_{k,\sigma}^\dagger a_{k,\sigma} - x_b\, b_{k,\sigma}^\dagger b_{k,\sigma}), \tag{2}$$

$$H_3 = \sum_{k,\sigma} \Delta(a_{k,\sigma}^\dagger a_{k,\sigma} - b_{k,\sigma}^\dagger b_{k,\sigma}). \tag{3}$$

Here H_1 represents the on-site hopping of electrons with site energies ϵ_a and ϵ_b at A and B sites respectively. The Hamiltonian H_2 represents the external doping effect with doping concentrations x_a and x_b respectively at A and B sublattices with the same impurity potential V. The Hamiltonian H_3 represents the substrate effect on graphene which raises the A site energy by Δ and lowers the B site energy by $-\Delta$, thereby introducing a substrate-induced gap 2Δ. Based on our earlier publications [7,8], the tight-binding Hamiltonian consisting

of electron hoppings up to third nearest-neighbours is written as

$$
\begin{aligned}
&H_4 \\
&= -\sum_{\beta=1,3}\sum_{k,\sigma} t_\beta(\gamma_\beta(k)\, a_{k,\sigma}^\dagger\, b_{k,\sigma} - \gamma_\beta^*(k)\, b_{k,\sigma}^\dagger a_{k,\sigma}).
\end{aligned}
\tag{4}
$$

The Hamiltonian H_4 represents the electron hopping between the nearest-neighbours, second nearest-neighbours and the third nearest-neighbours represented by $\beta = 1, 2, 3$. The corresponding electron dispersions are: $\epsilon_1(k) = -t_1\gamma_1(k)$, $\epsilon_2(k) = -t_2\gamma_2(k)$ and $\epsilon_3(k) = -t_3\gamma_3(k)$ respectively. Here t_β and $\gamma_\beta(k)$ represent the hopping integrals and band dispersions. The electron–electron correlation effect is described by Hubbard model [9] at A and B sites of the carbon atoms, i.e.

$$
H_U = U\sum_i n_{i,\uparrow}^a\, n_{i,\downarrow}^a + U\sum_j n_{j,\uparrow}^b\, n_{j,\downarrow}^b,
\tag{5}
$$

where $n_{i,\sigma}^a = a_{i,\sigma}^\dagger a_{i,\sigma}$ and $n_{j,\sigma}^b = b_{j,\sigma}^\dagger b_{j,\sigma}$ are the electron occupation numbers at A and B sublattices respectively. In the present work, we have considered electron hoppings up to third nearest-neighbours in honeycomb lattice of graphene. The computational work is carried out for electron momentum throughout the Brillouin zone. To make the calculation simpler, we have considered here the above Coulomb correlation effect within Hartree–Fock mean-field approximation.

3. Calculation of dynamic dielectric function

The Fourier transferred dynamic dielectric function for wave vector q and frequency ω for graphene is written as

$$
\epsilon(q,\omega) = 1 + \Pi(q,\omega),
\tag{6}
$$

where the frequency and wave vector-dependent polarization function is defined as

$$
\Pi(q,\omega) = \langle\langle \rho(q,t); \rho(-q,t)\rangle\rangle_\omega,
\tag{7}
$$

where charge function due to A and B site electrons is given by

$$
\rho(q,t) = \sum_{k,\sigma}(a_{k+q,\sigma}^\dagger a_{k,\sigma} + b_{k+q,\sigma}^\dagger b_{k,\sigma}).
\tag{8}
$$

The polarization function $\Pi(q,\omega)$ describes the charge–charge correlation which is a two-particle Green's

function. $\Pi(q,\omega)$ defined in eq. (7) is rewritten as

$$
\Pi(q,\omega) = \sum_{k,\sigma}\sum_{k',q',\sigma'}[\Pi_1 + \Pi_2 + \Pi_3 + \Pi_4].
\tag{9}
$$

The two-particle Green's functions are defined as $\Pi_1 = \langle\langle \alpha_1; \beta_1\rangle\rangle_\omega$, $\Pi_2 = \langle\langle \alpha_2; \beta_1\rangle\rangle_\omega$, $\Pi_3 = \langle\langle \alpha_1; \beta_2\rangle\rangle_\omega$ and $\Pi_4 = \langle\langle \alpha_2; \beta_2\rangle\rangle_\omega$, where $\alpha_1 = a_{k+q,\sigma}^\dagger a_{k,\sigma}$, $\alpha_2 = b_{k+q,\sigma}^\dagger b_{k,\sigma}$, $\beta_1 = a_{k'-q',\sigma'}^\dagger a_{k',\sigma'}$ and $\beta_2 = b_{k'-q',\sigma'}^\dagger b_{k',\sigma'}$. The above two-particle Green's functions Π_i ($i = 1$–4) are calculated by using Zubarev's technique [10]. Finally, the frequency-dependent polarization function is calculated in terms of the Fermi–Dirac distribution functions.

4. Results and discussions

The frequency-dependent dynamic polarization function given in eq. (9) is computed numerically by taking 100×100 grid points for the electron momentum. In order to investigate the effect of Coulomb interaction in $\Pi(q,\omega)$, we evaluate numerically and self-consistently the electron occupancies at A and B sublattices. Finally, dynamic dielectric function given in eq. (6) is computed taking different physical parameters of the systems, as shown in figures 1–6. The physical parameters involved in the calculation are made dimensionless with respect to nearest-neighbour hopping integral (t_1). The parameters are $\tilde{t}_1 = -1$, $\tilde{t}_2 = t_2/t_1$, $\tilde{t}_3 = t_3/t_1$, impurity potential $v = V/t_1$, Coulomb potential $u = U/t_1$, temperature $t = k_B T/t_1$, applied external frequency $c_1 = \omega/t_1$ and substrate-induced gap $d_1 = \Delta/t_1$, plasmon momentum transfer energy $qx = v_F q/t_1$, where v_F and q are respectively the velocity of electrons at Fermi level and plasmon wave vector.

In the present work, the real part of the dielectric constant of graphene associated with the absorption of optical wave is investigated at lower energies. The frequency-dependent real part of the dielectric constant is shown in figure 1. For different values of plasmon momentum transfer energy ($qx = qy = v_F q/t_1 = 0.01$ to 0.04), the dielectric constant exhibits a sharp peak p_1 at energy qx and another high-energy step function p_2 at substrate-induced gap (d_1). The low-energy peak p_1 is a plasmon resonance peak associated with plasmon momentum transfer energy. This peak p_1 shifts to higher energies with increase of qx accompanied by the enhancement of resonance peak height. On the other hand, the step function at p_2 remains unaltered with the increase of qx. However, the dielectric constant is suppressed with the increase of qx at higher energies.
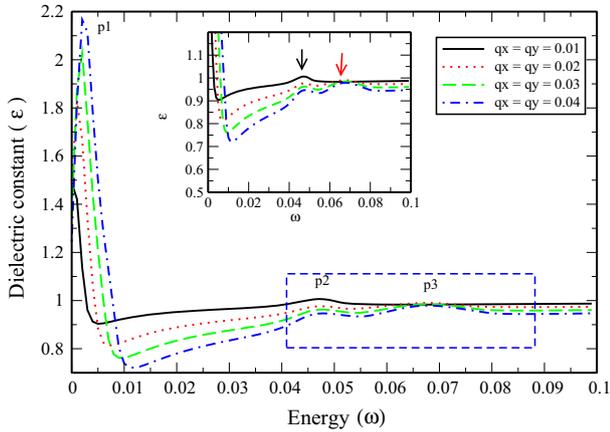
Figure 1. The plot of the real part of dielectric constant (ϵ) vs. energy (c_1) for different values of plasmon wave vector qx on substrate-induced gap $d_1 = 0.04$ for Coulomb potential $u = 2.2$ and damping factor $e_1 = 0.001$ at temperature $t = 0.025$.
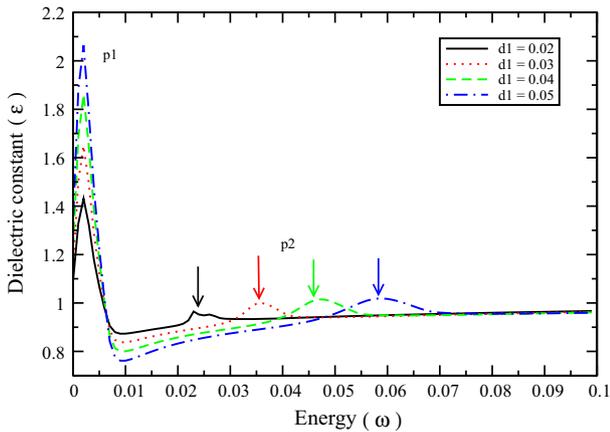

Figure 3. The plot of the real part of dielectric constant (ϵ) vs. energy (c_1) for different Coulomb potentials $u = 1.7, 2.0, 2.2, 2.5$ and fixed substrate-induced gap $d_1 = 0.04$ at temperature $t = 0.025$ for plasmon wave vector $qx = 0.03$.

Figure 2. The plot of the real part of dielectric constant (ϵ) vs. energy (c_1) for different substrate-induced gap $d_1 = 0.02, 0.03, 0.04, 0.05$, fixed Coulomb potential $u = 2.2$, damping factor $e_1 = 0.001$ and temperature $t = 0.025$ for plasmon wave vector $qx = 0.03$.

Figure 4. The plot of the real part of dielectric constant (ϵ) vs. energy (c_1) for different electron hopping $t_1 = -1, t_1 = 1, t_2 = 0.043$ and $t_1 = 1, t_2 = 0.043, t_3 = 0.024$, Coulomb potential $u = 2.2$, fixed temperature $t = 0.025$ and substrate-induced gap $d_1 = 0.04$ for plasmon wave vector $qx = 0.03$.

When graphene is placed on polarized substrates like SiC [11], gold-on-ruthenium [12] etc., the gapless semiconducting graphene system develops substrate-induced gap (d_1). Figure 2 shows the plot of frequency-dependent dielectric constant for different values of substrate-induced gap $d_1 = 0.02, 0.03, 0.04, 0.05$. It is observed that the substrate-induced gap does not alter the position of the resonance peak p_1, but enhances the peak height considerably indicating that the dielectric constant is enhanced substantially at energy qx. With increase in substrate-induced gap, the step function at p_2 shifts to higher energies. This indicates that the enhancement of substrate-induced gap can be detected experimentally from the frequency-dependent dielectric constant.
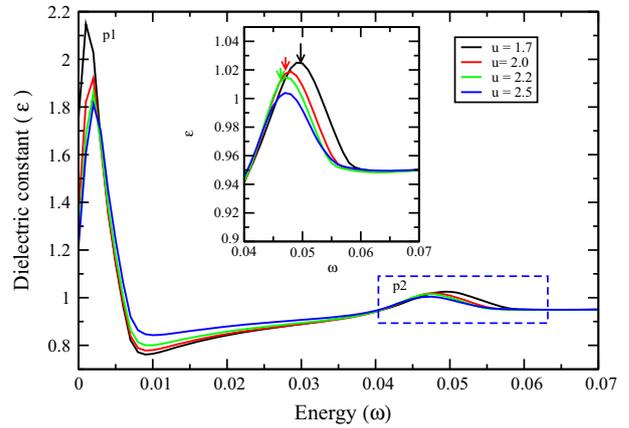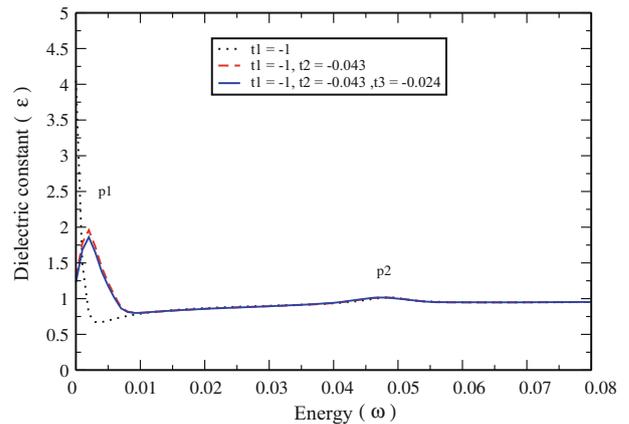
The Coulomb correlation of electrons is found to be absent in pristine graphene. However, Coulomb correlation plays an important role in doped graphene-on-polarized substrate. Therefore, we present here the tight-binding model calculation taking electron–electron interaction into account. Figure 3 shows the effect of Coulomb energy $u = 1.7, 2.0, 2.2, 2.5$ on frequency-dependent dielectric constant. With increase of Coulomb energy, the peak p_1 shifts to higher energy with its peak height suppressed. On the other hand, the step function at p_2 shifts to lower energies with decrease of peak height (see inset of figure 3). This indicates that Coulomb interaction suppresses the charge-polarization
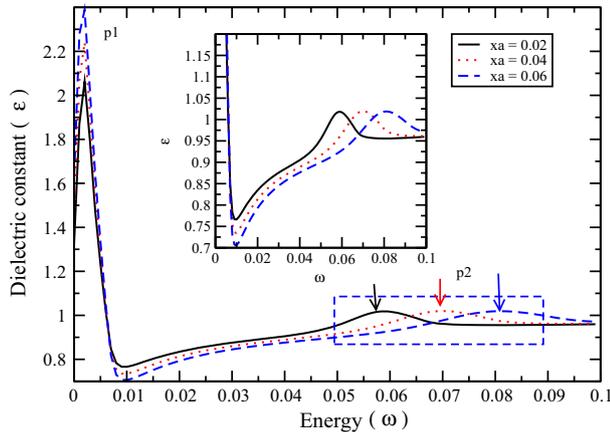
Figure 5. The plot of the real part of dielectric constant (ϵ) vs. energy (c_1) for different doping concentrations at A site $x_a = 0.02, 0.04, 0.06$ for impurity potential $v = 1$, Coulomb potential $u = 2.2$, damping factor $e_1 = 0.001$ and substrate-induced gap $d_1 = 0.04$ for plasmon wave vector $qx = 0.03$.
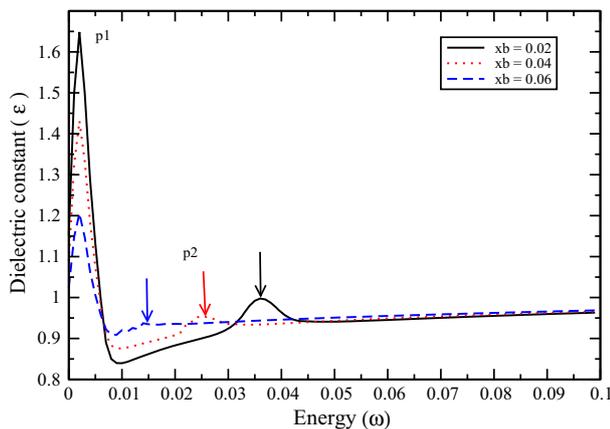

Figure 6. The plot of the real part of dielectric constant (ϵ) vs. energy (c_1) for different doping concentrations at B site $x_b = 0.02, 0.04, 0.06, 0.08$ for impurity potential $v = 1$, Coulomb potential $u = 2.2$, temperature $t = 0.025$, damping factor $e_1 = 0.001$ and substrate-induced gap $d_1 = 0.04$ for plasmon wave vector $qx = 0.03$.

effect in graphene and this results in the reduction of substrate-induced gap.

Figure 4 shows the effects of nearest-neighbour hopping integral (t_1), second nearest-neighbour hopping integral (t_2) and third nearest-neighbour hopping integral (t_3) on frequency-dependent dielectric constant ϵ. For only t_1 the dielectric constant is very large at energy ($c_1 = \omega/t_1 = 0$). The dielectric constant (ϵ) rapidly decreases with increase of frequency (c_1) and remains nearly constant. When t_1 and t_2 are considered for calculation, the dielectric constant exhibits a peak of finite height at low energy corresponding to the

plasmon momentum transfer energy qx. However, the third nearest-neighbour contribution to ϵ is negligible. It is observed that the different hopping integrals have very little effect on the step function at p_2.

The pristine graphene can be modulated by introducing electron or hole doping in it. The doping effect on the real part of dielectric constant of graphene is studied as shown in figure 5. With increase of A site doping, peak p_1 in the dielectric constant does not change its position. However, the step function at p_2 shifts to higher energy with increase of A site electron doping from $x_a = 0.02$ to 0.06. This indicates that the A site doping can enhance the substrate-induced gap from $c_1 = 0.05$ to 0.08, when doping changes from $x_a = 0.02$ to 0.06.

Figure 6 shows the effect of B site electron doping on dielectric constant. With increase of B-site doping, the height of resonance peak p_1 in ϵ is suppressed considerably and finally vanishes for higher doping concentrations. Further, the step function in ϵ shifts to lower energies with increase of B-site doping and its peak is suppressed considerably. Hence, we conclude that the B-site doping destroys the gap in graphene arising due to substrate. In other words, the B-site doping suppresses the charge polarization in graphene developed due to substrate effects.

5. Conclusions

We present here a tight-binding model calculation in the presence of electron doping and substrate-induced gap and calculate the frequency-dependent real part of the dielectric constant. We observe a plasmon resonance peak at plasmon momentum transfer energy and a step function at higher energies arising due to substrate-induced gap in graphene. This step function in dielectric constant shifts to higher energy with increase of substrate-induced gap as observed experimentally. The Coulomb correlation energy suppresses the substrate-induced gap. The first and second nearest-neighbour hoppings are sufficient for tight-binding model calculation of dielectric constant of graphene. The A-site electron doping enhances the substrate-induced gap, whereas the B-site electron doping suppresses substrate-induced gap. This indicates that electron doping introduces charge asymmetry at two sublattices.

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