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Subgap optical conductivity in semihydrogenated graphene

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We report that for graphene with a finite band gap (such as semihydrogenated graphene or graphene with spin-orbit coupling), there exists a strong nonlinear optical response for energies lower than the band gap where the linear response is forbidden. At low temperatures, the nonlinear current in graphene with a gap is much stronger than that in gapless graphene. Our result suggests that semihydrogenated graphene can have a unique potential as a two-color nonlinear material in the terahertz frequency region. The relative intensity of the two colors can be tuned with the electric field. © *2011 American Institute of Physics*. [doi:10.1063/1.3549201]

In graphene, the conduction and valence bands touch each other at six equivalent points, the K and K' points in the Brillouin zone. This gapless band structure leads to some unique optical properties,[1–7] the chief among them is the universal conductance, $\sigma_0=\pi e^2/4h$. This was calculated theoretically long before graphene's fabrication in 2003 (Ref. 8) and has been measured experimentally and the universal conductance has been confirmed.[9–11] The optical conductivity of graphene outside the low energy Dirac regime has been calculated theoretically.[12,13]

It has been shown that the nonlinear optical response of intrinsic graphene is particularly strong.[14,15] This strong nonlinear effect is not induced by any disorder scattering, but is a direct consequence of the nonparabolic band structure. More specifically, the massless Dirac Fermi energy dispersion gives rise to a strong nonlinear effect. The potential application of the nonlinear properties of graphene is abundant in optics and photonics. For example, frequency upconversion for radiation sources in the terahertz to far-infrared regime. The conversion coefficient is shown to be much stronger in graphene as compared to traditional semiconductors.[16]

It has been hypothesized that a semihydrogenated version of graphene could be created via the blocking of a substrate, or the application of an external electric field, removing the hydrogen atoms from one side.[17] In this form, both ferromagnetic order[18] and a band gap opening[17] have been predicted due to the breaking of symmetry between hydrogen-bonded and nonbonded carbon atoms.

The purpose of this paper is to demonstrate a strong nonlinear optical response in semihydrogenated graphene (SHG) in the frequency regime well below the band gap Δ, where the linear response is strictly forbidden. In general, for systems with a finite gap, the linear response, or one photon process for frequency below Δ, is forbidden. However, multiphoton processes can still occur for frequencies below the gap. The strength of such nonlinear response is usually very weak. Here we show that the opening of a band gap at the Dirac point leads to a very strong nonlinear response below the gap. In fact the low frequency nonlinear conductance can be as strong as the universal conductance in intrinsic graphene under a rather moderate electric field of the order of 10^3 V/cm. This result is particularly useful for developing applications in nonlinear optics and nonlinear photonics since the linear process is fully suppressed in this frequency regime.

In the tight-binding approximation, the Hamiltonian for semihydrogenated graphene under a time-dependent electric field along the x-axis ($Ee^{-i\omega t}$) can be written as

$$H=\begin{bmatrix} -\Delta/2 & v_0(p_- + eA) \\ v_0(p_+ + eA) & \Delta/2 \end{bmatrix}, \tag{1}$$

where $p_\pm = p_x \pm ip_y$, $v_F=\sqrt{3}ta/2\hbar$ is the Fermi velocity which is about 10^6 m/s, $t\approx 3$ eV is the nearest neighbor hopping bandwidth, a is the lattice constant, and $A=Ee^{i\omega t}/i\omega$ is the vector potential. In the Hamiltonian, the on-site energies of the A-sublattice and B-sublattice are $-\Delta/2$ and $\Delta/2$, respectively. In the absence of the applied field, the eigenvalues are

$$\varepsilon_{\mathbf{p},s}=s\tfrac{1}{2}\sqrt{\Delta^2+4v_F^2p^2}, \tag{2}$$

with $s=\pm 1$. Correspondingly, the eigenstates can be written in the form of

$$\psi_0(\mathbf{p},s)=\sqrt{\frac{\varepsilon_+^2}{v_F^2p^2+\varepsilon_+^2}}\begin{pmatrix} \dfrac{v_Fp_-}{\varepsilon_+} \\ 1 \end{pmatrix}, \tag{3}$$

where $\varepsilon_+\equiv\varepsilon_{\mathbf{p},s}+\Delta/2$. The presence of $\Delta/2$ results in a band gap of Δ between valence and conduction bands. The velocity operator can be obtained by $\hat{\mathbf{v}}=\partial H/\partial\mathbf{p}$ and Δ is independent of $\mathbf{p}$,

$$v_x=v_F\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{4}$$

We write the two-component spinor wave function with $s=+1$ in the following form:

$$\psi(\mathbf{p})=\sum_{n=0}^{\infty}\begin{bmatrix} a_n(\mathbf{p}) \\ b_n(\mathbf{p}) \end{bmatrix}e^{i(n\omega-\varepsilon/\hbar)t}, \tag{5}$$

where we have used $\varepsilon\equiv\varepsilon_{\mathbf{p},s}$ for simplicity.

In the above equation, each term represents a specific multiphoton process. The spinor components a_n and b_n can be obtained by solving the time-dependent Schrödinger equation $i\hbar\partial\psi/\partial t=H\psi$. The time-derivative of $\psi(\mathbf{p})$ is given by

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$$\frac{\partial \psi}{\partial t}(\mathbf{p}) = \sum_{n=0}^{\infty} i(n\omega - \varepsilon/\hbar) \begin{bmatrix} a_n(\mathbf{p}) \\ b_n(\mathbf{p}) \end{bmatrix} e^{i(n\omega - \varepsilon/\hbar)t}. \quad (6)$$

Equation (6) is now inserted in the Schrödinger equation. Due to the orthogonality of $e^{in\omega t}$, we obtain the following recursion relation in the momentum representation for the spinor components:

$$(\varepsilon - n\omega\hbar)a_n = -(\Delta/2)a_n + v_0 p_- b_n + \frac{eE}{i\omega} b_{n-1},$$

$$(\varepsilon - n\omega\hbar)b_n = (\Delta/2)b_n + v_0 p_+ a_n + \frac{eE}{i\omega} a_{n-1}. \quad (7)$$

In the absence of the electric field, only $n=0$ terms are nonzero and the eigenvalue and the eigenvector are given by Eqs. (2) and (4). Equation (5) does not include negative n terms because the electrical field used here contains only $\exp(i\omega t)$ term.

Equation (8) contains information of all multiple photon process in semihydrogenated graphene. The recursion relation couples the n photon processes to the $n-1$ photon processes. From the solutions to Eq. (5) we can calculate the nth order total current which is given by

$$\mathbf{J}_\mathbf{n}^\nu = \frac{1}{4\pi^2} \int \mathrm{d}\mathbf{p} \mathbf{j}_\mathbf{n}^\nu N(\epsilon). \quad (8)$$

Here $N(\epsilon)=n_F(-\epsilon)-n_F(\epsilon)=\tanh(\epsilon/2k_BT)$, and $\widehat{v_\nu}$ is given by Eq. (2). $\mathbf{j}^\nu=\psi^\dagger \widehat{v_\nu}\psi$ and $\mathbf{j}_\mathbf{n}^\nu$ is the part of $\mathbf{j}^\nu$ that is proportional to the nth power of the electric field.

By using Eqs. (7) and (8), we obtain the third order nonlinear optical conductivity given as

$$\sigma_3(\omega) = \sigma_0 \frac{e^2E^2v_0^2}{\hbar\omega^3\left(\hbar\omega + \frac{\Delta}{2}\right)} X_0 \tanh\left(\frac{\hbar\omega}{2k_BT}\right)\Theta(\hbar\omega - \Delta) \quad (9)$$

and

$$\sigma_3(3\omega) = \sigma_0 \frac{e^2E^2v_0^2}{\hbar^2\omega^4} Y\Theta(3\hbar\omega - \Delta), \quad (10)$$

where $\sigma_0=e^2/4\hbar$, $X_0=2+\tilde{\Delta}+\tilde{\Delta}^2+\tilde{\Delta}^3/2-3\tilde{\Delta}^4/8-3\tilde{\Delta}^5/16$, $Y=X_1\tanh(\hbar\omega/4k_BT)+X_2\tanh(\hbar\omega/2k_BT)+X_3\tanh(3\hbar\omega/4k_BT)$, $X_1=(1/48)[13+2\tilde{\Delta}^2+\tilde{\Delta}^4]$, $X_2=-(1/3)[2-\tilde{\Delta}^2+\tilde{\Delta}^4/8]$, $X_3=(1/48)[45-14\tilde{\Delta}^2+\tilde{\Delta}^4]$, and $\tilde{\Delta}=\Delta/\hbar\omega$.

In Fig. 1, we plot the optical conductance versus frequency for a typical value of $\Delta=0.03$ eV. The on-site energy due to semihydrogenation removes the universal conductance. For $\hbar\omega<\Delta$, the linear conductance is zero for any temperature by the virtue of energy conservation. The third order current at single frequency, $\sigma_3(\omega)$, is also zero for $\hbar\omega<\Delta$. The frequency tripled third order term $\sigma_3(3\omega)$ persists to a low frequency of $\omega=\Delta/3$. The nonlinear effect in SHG is unique in that the response peak of the linear term and frequency tripled term is well separated $\delta\omega=2\Delta/3$. This provides a useful mechanism for two-color excitation and detection, one color is associated with the linear response and the other is associated with the nonlinear response. The relative intensities of the two colors can be tuned with the electric field. At a rather moderate electric field of 3600 V/cm, the magnitude of two peaks is roughly the same at

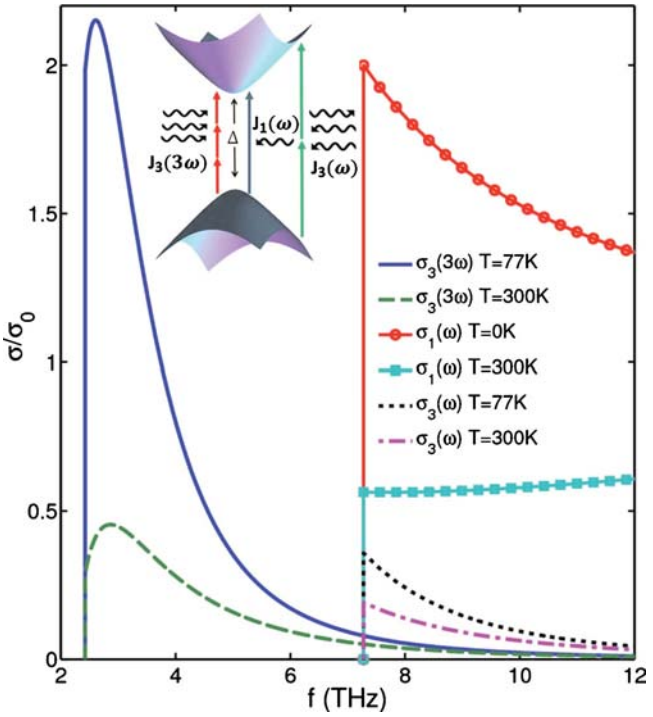

FIG. 1. (Color online) The frequency dependent optical conductance in the low frequency regime for two temperatures. The electric field is 3600 V/cm. The absorption edge for the frequency tripled response is shifted to $\Delta/3$. The inset is a schematic show of different optical processes.

77 K. At room temperature, the peak in linear conductance disappears while the nonlinear conductance still exhibits a resonance.

At the frequencies close to the energy gap, the onset linear conductance is twice the universal conductance[19] $\sigma_{1c}=2\sigma_0$. The onset nonlinear conductance $\sigma_3(3\omega)=\sigma_{1c}$ at $\omega=\Delta/3$ requires an applied field of $E=3600$ V/cm. This is a rather weak field for typical experimental conditions. On the other hand, the onset nonlinear conductance $\sigma_3(\omega)=\sigma_{1c}$ at $\omega=\Delta$ requires an electric field of around three times greater. Therefore, the potential of using the frequency tripled nonlinear effect in the frequency below the gap is very significant. The electric field required for $\sigma_3(3\omega)=\sigma_0$ at the vertical absorption edge can be determined,

$$E_c(\omega=\Delta/3) = \frac{\Delta^2}{9ev_0\hbar}\left[\frac{24}{56\tanh\left(\frac{\Delta}{12k_BT}\right) - 25\tanh\left(\frac{\Delta}{6k_BT}\right)}\right]^{1/2}. \quad (11)$$

In Fig. 2, we show the frequency dependence of the critical field at which $\sigma_3(3\omega)/\sigma_0=1$. This field measures the nonlinearity of the system at a given frequency. In the entire low frequency regime, $\Delta/3<\hbar\omega<\Delta$, we found that the critical field for SHG is smaller than that in pure graphene by around 10%–40%. This indicates that SHG is a strong nonlinear system at low frequencies and low temperatures. The reason for this is that the density of states near the band edge has a von Hove like singularity, $D(\varepsilon)\sim\varepsilon^{-1/2}$. This is qualitatively different from the case of normal two-dimensional semiconductors. In normal semiconductors, the energy dispersion near the band edge is parabolic and the density of

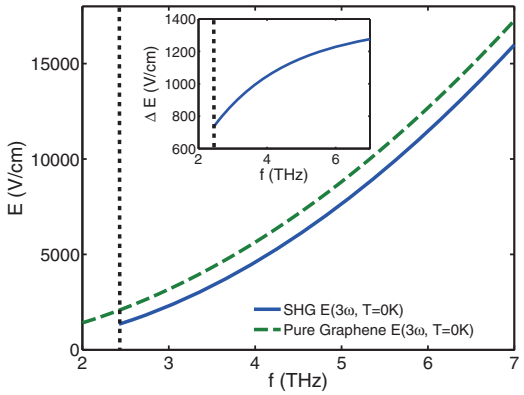

FIG. 2. (Color online) The frequency dependence of the critical field $E(3\omega)$ for SHG and pure graphene. The inset shows the reduction of the critical field in SHG. Note that there exists a cut-off frequency $f_c=\Delta/3h \approx 2.4$ THz since $\sigma_3(3\omega)=0$ at frequency smaller than f_c.

states is constant. Here in SHG the large density of state near the band edge leads to a strong nonlinear effect.

In Fig. 3 we show the temperature dependence of the critical field $E_c(3\omega)$ at two different frequencies. At low temperature $E_c(3\omega)$ is nearly constant and is smaller than that required in pure graphene. At high temperature, $E_c(3\omega)$ in SHG is larger than that required in pure graphene. As temperature increases, the Van Hove singularity becomes weaker and the critical field increases. At high temperature, $E_c(3\omega)$ increases with temperature as $E_c(3\omega) \sim T^{1/2}$. It should be pointed out that a high critical field in SHG at room temperature will not remove the key property of two-color optical response in SHG. In pure graphene, the response maximum of the linear term and frequency tripled term is not resolved.

The nonlinear effect reported is more general than that in SHG. Many effects can lead to a finite gap in the Dirac point

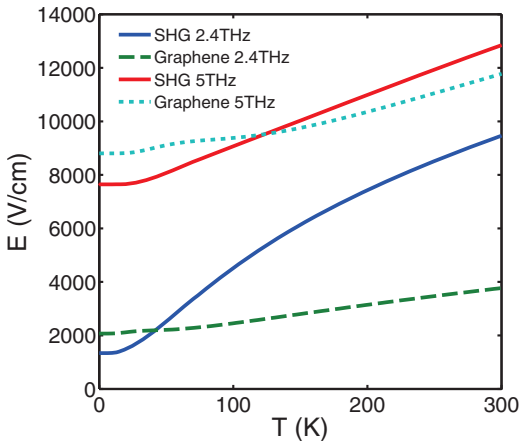

FIG. 3. (Color online) The temperature dependence of the critical field at two different frequencies of 2.4 and 5 THz.

in graphene. For example, the spin-orbit coupling can result in a gap of the size of 0.2 meV. This is a very small gap but will produce qualitatively the same nonlinear effect as in SHG. Impurity scattering included gap which is also in the form of Eq. (2). The critical field mentioned earlier for $\sigma_3(3\omega)$ is proportional to Δ^2. Therefore, in general, the smaller the gap, the weaker the critical field. If the gap can be controlled by external means, then the distance between the two peaks also becomes tunable. However, smaller gaps will result in a smaller distance between the peaks of linear response and frequency tripled response.

In conclusion, we have shown that SHG exhibits a strong frequency tripled optical response for frequencies below the band gap where the linear response is forbidden. Furthermore, it is found that in the low frequency regime, the frequency tripled response is stronger in SHG than that of pure graphene.

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