Terahertz plasmonic properties of highly oriented pyrolytic graphite

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We demonstrate that highly oriented pyrolytic graphite is a potentially useful material for plasmonic applications in the terahertz (THz) spectral range. Using THz time-domain spectroscopy, we studied the transmission properties of a ~7.5 µm thick graphite film made via mechanical exfoliation and found that the complex dielectric constant follows the Drude model with a plasma frequency \( \nu_p \sim 34 \text{THz} \). To assess the graphite plasmonic properties, we fabricated a subwavelength periodic aperture array in the graphite film and in a free-standing stainless steel film. Despite the low conductivity of graphite compared to conventional metals, the resonant transmission properties are similar. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4803548]

The many different allotropes of carbon are fascinating in that they can possess remarkably different transport and optical properties. Among the various allotropes, graphene has elicited the most interest in recent years. Single layer graphene exhibits a constant 2.3% absorption at normal incidence, and its infrared absorption can be tuned by electrically tuning the Fermi level.¹⁻³ While a number of interesting device implementations have been demonstrated recently using graphene,³⁻⁷ the high transmissivity of graphene limits its utility in THz plasmonics applications.

Multilayer graphene, in the form of graphite, is perhaps the most common allotrope of carbon and is readily available in thick film form. In fact, the optical properties of graphite have been well studied across the entire electromagnetic spectrum.⁸⁻¹² However reflection measurements are usually required because of the highly absorbing nature of graphite, which arises from its unique electronic properties, where the intraband and interband optical transitions within the π electron band extend up to 7 eV.⁸ In these measurements, since only the reflected optical power is readily measured, Kramers-Kronig (K-K) relations are necessary to compute the complex dielectric constant \( \varepsilon(\omega) \). Given the limitations in spectral measurements, the use of such a transformation often yields data that have limited accuracy. Despite the strong interest in the optical properties of graphite over the years, optical studies using transmission spectroscopy through thin graphite films, which yields a more accurate \( \varepsilon(\omega) \), have not been demonstrated.

Within the field of plasmonics, the phenomenon of enhanced optical transmission (EOT) through perforated metal films with periodic subwavelength hole arrays (HAs) [or plasmonic lattices] has also been extensively studied over the last two decades.¹³⁻¹⁵ The EOT spectrum consists of a number of relatively sharp resonances and correlated anti-resonance features, which are closely related with the reciprocal vectors in the HA structure factor.¹⁵ The EOT resonances are more pronounced for good conductors such as silver and gold at visible frequencies. However at THz frequencies, even relatively poor metals such as stainless steel¹⁵ and lead¹⁶ have very high THz conductivities and therefore support surface plasmon polariton (SPP) excitations, a precursor for obtaining EOT through the perforated film. In fact, a broad range of exotic metals that include heavily doped conducting polymers¹⁷ and one dimensional multi-walled carbon nanotube sheets¹⁸ have been found to support relatively low loss SPP propagation and thus may be useful for THz optoelectronics technology in the near future.

In this work we characterize the THz optical spectra of a thin highly oriented pyrolytic graphite (HOPG) film using THz time-domain spectroscopy (THz-TDS). Using incident radiation that is polarized perpendicular to the c axis of the graphite film, we obtained the complex \( \varepsilon(\omega) \) spectrum of the material without the need for K-K approximations. This is possible because the THz electric field is measured in this type of spectroscopy that yields both the transmission amplitude and phase spectra. The graphite plasma frequency, \( \nu_p \sim 34 \text{THz} \), is obtained by simultaneously fitting the real \( \varepsilon'(\omega) \) and imaginary \( \varepsilon''(\omega) \) part of the dielectric constant \( \varepsilon(\omega) \) \( (=\varepsilon'(\omega) + i\varepsilon''(\omega)) \) using the Drude model approximation, in agreement with the theoretical value. We also studied THz EOT through perforated graphite films with periodic subwavelength HAs and show that graphite supports SPP excitations. The “effective” dielectric constant \( \varepsilon^*(\omega) \) of the obtained plasmonic lattice is investigated in comparison with \( \varepsilon^*(\omega) \) of a corresponding stainless steel plasmonic lattice. From this comparison we conclude that despite the fact that graphite exhibits a lower conductivity compared to that of conventional metals such as stainless steel, the transmission properties of their plasmonic lattice structures are in fact similar in nature.

The HOPG graphite with dimension of 10 mm × 10 mm × 1 mm was purchased from SPI Supplies. It is a relatively new form of high purity graphite that consists of a lamellar structure of stacked graphene planes, which yields the relatively easy “exfoliation properties” of the material. The
reported intra-plane electrical resistivity is \( \rho = 4 \times 10^{-3} \Omega \text{cm} \), whereas the inter-plane \( \rho = 0.2 \Omega \text{cm} \); four orders of magnitude difference in \( \rho \) shows the known marked anisotropic physical properties of the graphite. Graphite has a relatively low carrier density of \( \sim 10^{19} \text{cm}^{-3} \) at room temperature because of its semimetal characteristics.\(^{19}\) In order to obtain a thin graphite film, we used the well-developed scotch tape technique with a smooth surface; this method formed films of \( \sim 7-10 \mu \text{m} \) thick and \( 1 \times 1 \text{cm}^2 \) area. The film roughness was measured by a profilometer to be of the order of few tens of nanometers. For the graphite HA fabrication, we used an excimer laser to mill holes in the graphite sheets. We fabricated a 12 \times 12 square HA structure that consisted of 0.3 mm diameter circular holes having lattice constant (or nearest neighbor hole distance) \( a = 0.7 \text{mm} \).

We used a THz-TDS setup for measuring the optical transmission spectra \( t(\omega) \) of the unperforated and perforated graphite films. Photoconductive devices were utilized for both emission and coherent detection of the THz field (see the detail in Ref. \( 15 \)). The detected transient photocurrent \( \text{PC}(\tau) \) was recorded as a function of the pump/probe translation stage path that determined the time delay, \( \tau \), between the “pump” beam that hits the emitter and the “probe” beam that arrives at the detector. \( \text{PC}(\tau) \) was subsequently Fourier transformed and normalized to a reference transmission, yielding both the electric field transmission amplitude and phase \( t(\omega) \) in the spectral range of \( \sim 0.1 \text{THz}–0.5 \text{THz} \) for the plasmonic lattice measurements and \( 0.4 \text{THz}–1.8 \text{THz} \) for the unperforated films. These different spectral ranges were obtained using different THz systems, which were required because of the significantly different transmission properties of the two types of structures. The resulting Fourier transformed data was described by the relation

\[
\begin{align*}
    t(\omega) &= |t(\omega)| \exp[i \varphi(\omega)] = \frac{E_{\text{transmitted}}(\omega)}{E_{\text{incident}}(\omega)}. \\
\end{align*}
\]

In this expression, \( E_{\text{incident}} \) and \( E_{\text{transmitted}} \) are the incident and transmitted THz fields, respectively, and the respective \(|t(\omega)|\) and \(\varphi(\omega)\) are the amplitude and phase of the transmission. From \( t(\omega) \) both real and imaginary components of the refractive index \( n(\omega) \) can be directly obtained without the need for K-K approximations, where somewhat arbitrary assumptions about asymptotic behavior are typically made.

We first present the obtained transmission spectra of a \( \sim 7.5 \mu \text{m} \) thick HOPG film, where the THz beam polarization is perpendicular to the graphite c axis. The Fourier transform of the transmission in the time domain (not shown here) yields the transmission amplitude and phase spectra shown in Fig. 1(a). Since the graphite film is quite thick, a small transmission of less than \( \sim 0.4% \) was obtained in the THz range. Based on the fact that a single layer graphene sheet exhibits a constant transmission of \( \sim 98\% \),\(^{1,2}\) we estimate that our HOPG film consists of about a thousand graphene layers, in fair agreement with the estimated film thickness. From the obtained transmission amplitude and phase spectra, we could readily calculate the complex index of refraction \( n(\omega) \) spectrum \( n(\omega) + i \kappa(\omega) \), as shown in Fig. 1(b). Both \( n \) and \( \kappa \) increase at low frequencies, in agreement with previous measurements of the graphite refractive index obtained using reflectivity measurements.\(^{12}\) The absorption coefficient spectrum is given by the relation \( \alpha(\nu) = 2\pi \nu \kappa(\nu)/c \), where the electric field decay is given by \( \exp[-\alpha(\nu)d] \), \( \nu \) is the THz frequency, and \( c \) is the speed of light in vacuum. Based on the data in Fig. 1(b), \( \alpha(\nu) \) increases at low photon energy, which is also in agreement with previous studies.\(^{12}\)

Next we calculated both \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \) spectra from \( n(\omega) \) and \( \kappa(\omega) \) spectra, as shown in Fig. 2. In order for a
medium to support SPP excitations, it is necessary that \(\epsilon'(\omega) = -\frac{\omega^2}{\omega^2 - \epsilon'\omega + \epsilon''\omega} \) be negative. Based on the spectrum in Fig. 2, \(\epsilon''(\omega)\) is indeed negative over the entire THz spectral range studied here, demonstrating that SPPs may be supported in our HOPG film. To obtain the plasma frequency of the HOPG film, we simultaneously fit \(\epsilon'(\omega)\) and \(\epsilon''(\omega)\) spectra using the Drude model for the conductivity of carriers subjected to the momentum relaxation rate \(\gamma\)

\[
\epsilon(i) = \epsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right),
\]

where \(\omega = 2\pi\nu\), \(\epsilon_{\infty} = \epsilon'\) at high frequency, and \(\omega_p\) is the plasma frequency of the material. Fig. 2 shows the best fit of \(\alpha(\omega)\) using the Drude model (Eq. (2)), where the fitting parameters are provided in the figure. The best-fit plasma frequency is \(\omega_p = 213.6\) rad/ps (corresponding to \(\nu_p = 34\) THz or \(136\) meV), which is more than a factor of 40 smaller than the plasma frequency of typical metals such as Al and Ag. The reason for the small \(\omega_p\) is that graphite has a significantly smaller carrier density \(N \sim 10^{10}/\text{cm}^2\) due to its semimetal characteristics. Our fitted plasma frequency is in good agreement with some values reported in the literature.\(^{19,21}\)

We note that in spite of the complicated graphite band structure at the Fermi energy, the obtained \(\omega_p\) is consistent with the simple plasma frequency formula, namely \(\omega_p = (4\pi Ne^2/\text{m}^*\nu_p)^{1/2}\), taking into account the graphite DC dielectric constant \(\epsilon\) and an effective electron mass \(\text{m}^* \sim 0.1 m_e\).

It is interesting to study SPP propagation in graphite, where the conductivity anisotropy is large. A simple way to study this is via the EOT spectrum on a perforated graphite sheet since SPP propagation is needed for the transmission. Fig. 3(a) shows the THz transmission spectrum through a graphite plasmonic lattice having hole diameter \(D = 0.3\) mm and lattice constant \(a = 0.7\) mm. The occurrence of EOT resonances confirms that graphite indeed supports SPPs due to its “metallic properties.” For comparison, we fabricated an identical plasmonic lattice on a stainless steel foil and studied its THz transmission (Fig. 3(a)). Comparing the EOT spectra of the two plasmonic lattices, Fig. 3(a) clearly shows that the low energy anti-resonance feature occurs exactly at the same frequency \(\nu_r \sim 0.43\) THz. This is the expected frequency for the (1,0) plasmonic lattice mode that corresponds to the plasmonic lattice constant \(a = 0.7\) mm, with \(\nu_r = c/\lambda\). However, as clearly seen in Fig. 3(a) the graphite (1,0) resonance is weaker and broader than that in the stainless steel and, in addition, is red-shifted compared to the stainless steel resonance. These differences in the resonant mode are probably due to different strengths of the SPP loss in the two materials,\(^{17}\) which determines the resonance shape. The higher loss in the graphite film may be due to its poorer metallic properties and small intra-plane conductivity that results in larger skin depth.

In order to more quantitatively compare the EOT spectra of the two fabricated plasmonic lattices, we studied the effective complex dielectric constant \(\epsilon^*(\omega)\) of the graphite and stainless steel HA structures. Figures 3(b) and 3(c) show the real and imaginary components of \(\epsilon^*(\omega)\) in graphite and stainless steel HAs calculated from the amplitude and phase of their respective EOT spectra, obtained the same way as for the unperforated graphite film discussed above. It is clear that \(\epsilon^*(\omega)\) spectra are similar in the two plasmonic lattices even though the optical properties of graphite and stainless steel are very different from each other. Using a theoretical approach that is slightly modified from that described by Agrawal et al., we modeled \(\epsilon^*(\omega)\) spectra of the two plasmonic lattices using the following formulae:\(^{20}\)

\[
\epsilon(i) = \epsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right),
\]

\[
\epsilon(i) = \epsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right),
\]

\[
\epsilon(i) = \epsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right),
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\[
\epsilon(i) = \epsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right),
\]
The plasma frequency $\omega_p$ of graphite is $7.5 \text{ THz}$, this value is consistent with the low carrier density of graphite at room temperature. Although graphite exhibits a lower conductivity than other conventional metals such as stainless steel, the resonant transmission properties are similar in nature. This demonstrates that a broad range of similar materials may be useful for THz plasmonic applications.

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