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Temperature-dependent far-infrared response of epitaxial multilayer graphene

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The optical response of pristine and FeCl₃-intercalated epitaxial graphene has been studied over the temperature range from 11 K to 296 K. The far-infrared (FIR) Drude conductivity of pristine graphene rises with increasing temperature, opposite to the behavior of intercalated graphene. This is a result of intercalation-induced *p*-type doping compensating the intrinsic *n*-doping in epitaxial graphene. Temperature-dependent Drude parameters are obtained by fitting the FIR response. This study demonstrates the influence of temperature variation on the optical properties of graphene, which should be a vital factor to be considered for graphene-based device applications.

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Graphene has many fascinating features such as high mobility massless Dirac fermions, 97% optical transparency, and low electron-phonon coupling. Considering that it typically consists of a single layer or few layers of carbon atoms, the interaction of graphene with light is strong over a wide range of the electromagnetic spectrum, compared with conventional semiconductors. This offers promising applications in optoelectronic devices, for example, photodetectors with varied spectral response from visible to far infrared (FIR).¹ In addition to studies in the visible and mid-infrared (MIR) ranges, where inter-band optical transitions dominate, intra-band transition based FIR optical response has attracted attention recently.^{2–5} The FIR study can determine charge dynamics by fitting spectra using the Drude model, including the sheet carrier density, carrier scattering rate, and mobility. The Drude response is essentially a result of the free-carrier effect. Intrinsic charges (electrons) typically exist in epitaxial graphene due to charge transfer from the substrate and influence the band gap and electronic density-of-states.⁶ Previous studies^{2–4} have focused on the room-temperature FIR properties.

Chemical intercalation is a mean to modify graphene's electronic properties, for example, changing the carrier concentration, and electronic structure by altering the interlayer coupling.⁷ In this letter, we study temperature-dependent FIR optical response of two graphene samples: pristine and FeCl₃-intercalated graphene. The FeCl₃ intercalants inserted between the layers of graphene act as electron-acceptors, resulting in *p*-type doping (holes). This allows a platform to understand the influence of intercalation-induced hole doping and substrate-to-graphene electron transfer on the FIR optical properties over a temperature range between 11 K and 296 K. We show that the pristine and FeCl₃-intercalated graphene have opposite temperature dependences of the charge density, resulting from the compensation of holes induced by FeCl₃ intercalants. Owing to reduced charge

density at higher temperatures, the intercalated sample shows a slight increase in the mobility at higher temperatures.

Graphene samples were grown on the C-face of semi-insulating 4H SiC (000 $\bar{1}$) wafers by thermal decomposition.^{8,9} The intercalated graphene under study has one FeCl₃-intercalant layer every one layer of graphene (i.e., stage 1). The transmission spectra were measured by mounting samples in a cryostat and acquired by using a Fourier transform infrared (FTIR) spectrometer (Bruker Vertex 70), schematically shown in the inset of Fig. 1. The pristine graphene (51.1-Å thick) is used to extract the temperature behavior of intrinsic charges (electrons), to compare with that of the charge density in the FeCl₃-intercalated sample (21.8-Å thick before intercalation). The total sheet charge density was extracted by fitting the FIR conductivity spectra. The determined temperature dependency does not rely on the thickness of graphene.

Room-temperature absorption spectra of two graphene samples denoted by $[1 - T/T_S]$ are shown in Fig. 1, where T and T_S are the transmission of the sample and bare SiC substrate, respectively. The spectral range between 600 and 1900 cm⁻¹ is not shown and corresponds to the Reststrahlen region of SiC. The optical conductivity $[\sigma(\omega)]$ of graphene relates to normalized transmission T/T_S through the following expression:² $T/T_S = |1 + Z_0\sigma(\omega)/(n_S + 1)|^{-2}$, where Z_0 is the vacuum impedance ($\sqrt{\mu_0/\epsilon_0}$) and n_S is the refractive index of SiC. Therefore, the real part of optical conductivity $[\sigma_1(\omega)]$ can be extracted from transmission data.³ The obtained $\sigma_1(\omega)$ normalized by the universal conductivity, $\sigma_0 = (\pi/2) e^2/h$, is shown in the inset of Fig. 1. In the MIR region, dominant inter-band transitions result in a near wavelength-independent conductivity with the value of $N_L\sigma_0$. This estimates the number of graphene layers to be $N_L = \sim 15$ and 4 for the pristine and intercalated graphene, in near agreement with their respective thicknesses.

In addition to this MIR feature, there exists a Drude response in the FIR range in both of graphene samples, i.e., optical conductivity increasing with decreasing frequency, as shown in the inset of Fig. 1. This typically results from the

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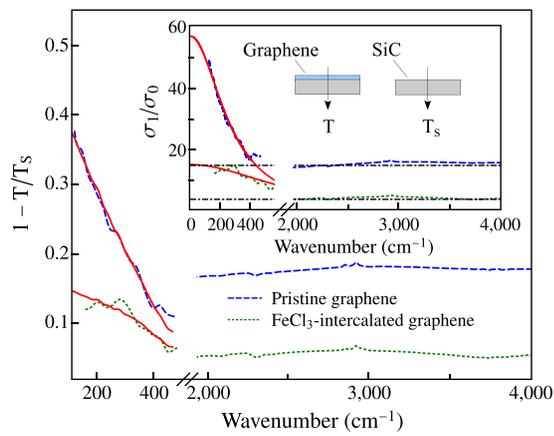


FIG. 1. Room-temperature absorption spectra of two epitaxial graphene samples, denoted by the normalized transmission $[1 - T/T_S]$ (dashed lines). Solid lines are fittings to the FIR range based on the Drude model. Measurements of T and T_S are schematically shown in the inset. The inset also shows the extracted real part (dashed line) of the optical conductivity. The dashed-dotted horizontal lines indicate the near wavelength-independent conductivities ($N_L\sigma_0$) due to inter-band transitions.

presence of intrinsic and intercalation induced charges in graphene. The Fermi level should lie at the Dirac point; however, it is shifted by electron transfer from SiC substrate for the epitaxial graphene,⁹ leading to n -type doped graphene.¹⁰ The free-carrier properties can be understood in terms of the Drude conductivity model, expressed as⁴

$$\sigma_1^{\text{FIR}}(\omega) = \frac{iD}{\pi(\omega + i\Gamma)}, \quad (1)$$

where D is the Drude weight proportional to the integrated intra-band absorption, and Γ is the scattering rate. D is related to the sheet charge density N_{2d} via $D = 2\pi V_F \sqrt{\pi N_{2d}} \cdot e^2/h$, where V_F is the Fermi velocity. D and Γ can be determined by fitting the experimental FIR conductivity using Eq. (1). Figure 1 shows the room-temperature fitting.

Temperature-dependent transmission spectra are plotted in Fig. 2(a) for SiC, the pristine, and FeCl₃-intercalated graphene samples, respectively. Following a similar procedure in determining the room-temperature Drude parameters, i.e., extracting the FIR conductivity and performing Drude model fittings, as shown in Figs. 2(b) and 2(c), various temperature-dependent parameters regarding the charge dynamics can be obtained, as illustrated in Figs. 3(b)–3(d). It can be seen that

the Drude peak increases with increasing temperature for the pristine graphene sample [Fig. 2(b)], whereas it slightly decreases at higher temperatures for the intercalated sample [Fig. 2(c)]. This opposite temperature variation can also be seen in the comparison of fitted Drude weights and sheet charge densities between these two samples, as shown in Figs. 3(a) and 3(b), respectively. For the pristine graphene, free carriers are only the electrons induced by the electric dipole field at the graphene-SiC interface which applies an electrostatic asymmetry on the graphene. Since the electron density is reduced in pristine graphene, such a dipole effect is mitigated at lower temperatures but cannot be fully eliminated. The electron density reaches a minimum of $\sim 1.8 \times 10^{12} \text{ cm}^{-2}$ by extrapolating to 0 K (or $\sim 1.2 \times 10^{11} \text{ cm}^{-2}$ per layer if equally distributed carriers in each layer of graphene are assumed⁴). In contrast, the intercalated sample has shown a decrease in the charge density with increasing temperatures. This indicates a different carrier type in this sample compared to the pristine graphene, agreeing with the fact of p -type doping introduced by FeCl₃ intercalants. The presence of holes means a full compensation of the intrinsic n -type doping. In principle, more free holes will be activated at higher temperatures. However, electron transfer from the SiC substrate also increases with increasing temperature. The combined results thus contribute to a reduction in the total charge density for the intercalated sample as shown in Fig. 3(b). By comparing the charge density at different temperatures [Fig. 3(b)], its variation from 11 K to 290 K in the intercalated sample is less than that in the pristine sample. In addition to carrier compensation, intercalation partially decoupling the graphene layers from the substrate¹¹ may also reduce the substrate-to-graphene electron transfer. The temperature behavior of the charge density in the intercalated sample also implies that the variation of p -doping provided by FeCl₃ intercalants as temperature varies is not that large to dominate over that of n -doping due to electron transfer. The p -doping density as high as more than 10^{13} cm^{-2} can be possibly achieved by intercalation. In such a case, p -doping will be one order of magnitude greater than the intrinsic n -doping, which could result in the increase of charge density with increasing temperature. On the contrary, the advantage of using slightly p -doping could be to achieve high room-temperature mobility.

Previous studies of exfoliated graphene on SiO₂ (Ref. 12) has concluded that the temperature dependence

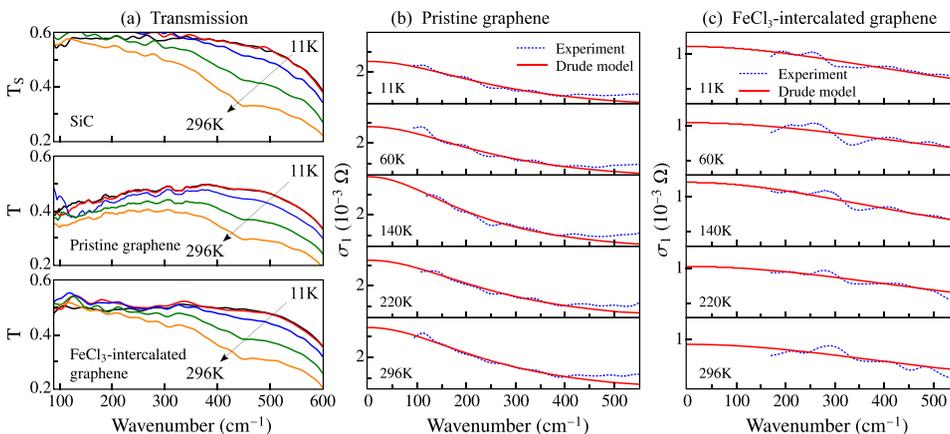


FIG. 2. (a) FIR transmission spectra of SiC, pristine, and FeCl₃-intercalated graphene. Shown temperatures are 11 K, 60 K, 140 K, 220 K, and 296 K. (b) and (c) The Drude-model fittings (solid lines) to the optical conductivities (dashed lines) for pristine and intercalated graphene samples, respectively.

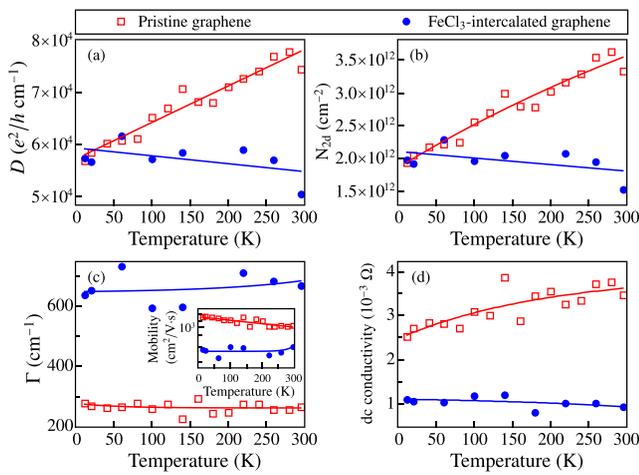


FIG. 3. Fitted parameters of (a) Drude weight (D), (b) sheet carrier density (N_{2d}), (c) carrier scattering rate (Γ) (mobility shown in the inset), and (d) dc conductivity. The pristine and FeCl₃-intercalated graphene samples have the opposite temperature variations in D and N_{2d} . This is due to the hole compensating effect owing to FeCl₃ intercalants in the intercalated sample, whereas only intrinsic electrons are present in pristine graphene.

correlates with carrier scattering by acoustic phonons in graphene and scattering by surface phonons of the substrate. The former is independent of the carrier density, while the latter is carrier-density dependent but mainly has the strong effect for $T > 200$ K. In the present case, the carrier scattering rate in the intercalated graphene is much greater than that of the pristine sample. An additional scattering source could be the scattering with intercalants. Owing to the composite effects from temperature-dependent scattering rate and charge density, the mobility of intercalated graphene slightly increases with temperature, as shown in the inset of Fig. 3(c), where mobility is calculated using $\mu = (e/\sqrt{\pi h}) \cdot (V_F/\sqrt{N_{2d}})/\Gamma$.⁵ For the same reason, the dc conductivity ($\sigma_{dc} = D/\pi\Gamma$) exhibits different temperature behaviors between pristine and intercalated graphene as shown in Fig. 2(d). In addition to phonon scattering and possible carrier scattering with intercalants, another important cause of low mobility in the epitaxial graphene is the covalent bonding at the SiC-graphene interface.¹¹ Intercalation toward the formation of quasi-free standing graphene layers¹¹ can improve the mobility. While such a result is not observed in the present study, it has been observed that the p -doping compensating the intrinsic n -doping leads to higher mobility at high temperature than that at low temperature. It may be anticipated that intercalated graphene exhibiting a slight p -type doping (thus lower density of intercalant than the present case) shows significantly high value of room-temperature mobility. This will be useful for the graphene-based device

applications. With respect to the temperature-dependent charge dynamics, temperature-induced effects should play an important role in determining the optical as well as transport properties of epitaxial graphene.

To conclude, we have studied the temperature-dependent Drude conductivity of epitaxial graphene in the FIR range. The sheet charge density of the intercalated graphene decreases with increasing temperature, whereas it increases by nearly two fold for the pristine graphene for temperature varied from 11 K to 296 K. A slight increase of carrier mobility with temperature in the intercalated sample is observed, opposite to its variation in the pristine sample. This results from p -type doping induced by FeCl₃ intercalants which compensates the intrinsic n -doping originating from substrate-to-graphene electron transfer. Since the electronic structure of graphene is sensitive to the charge distribution, temperature variation is expected to have the effects on its electronic and optical properties.

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