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Far-infrared study of substrate-effect on large scale graphene

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From far-IR Drude absorption measurement we determine carrier density (N) and carrier scattering rate (Γ) of graphene deposited on buffer-layer/SiO_2 composite substrate. Two types of buffer-layers, (1) polar dielectric oxide ZnO and $SrTiO_3$ (2) organic thin film hexamethyldisilazane and polymethyl methacrylate (PMMA) were studied. N varies widely over 0.12–11.8 ($\times 10^{12}$ cm^{-2}) range depending on the buffer-layer. In contrast Γ remains almost constant, $\sim$100 cm^{-1}, irrespective of the buffer-layers. This indicates that carrier mobility (μ) of graphene depends on substrate through N, but not by Γ as commonly believed. © *2011 American Institute of Physics*. [doi:10.1063/1.3590773]

High mobility of massless Dirac fermion plays critical role in high-speed electronic device application of graphene. In free-standing graphene electron mobility as high as $\mu = 250\,000$ $cm^2/V\,s$ is reported at room temperature.[1] However when graphene is transferred on SiO_2 substrate, μ is suppressed to 3000–15 000 $cm^2/V\,s$.[2] The μ-reduction is considered to be related with carrier scattering with surface polar phonon and charged impurity of the substrate. One approach to overcome this problem is to insert second material between the graphene and SiO_2 in hope to reduce the influence of SiO_2. Indeed quasi-free-standing behavior is restored partly in graphene/Au/Ni-substrate[3] made by Au-monolayer intercalation method, and also in graphene/HMDS/SiO_2 (Ref. 4) with organic hexamethyldisilazane (HMDS) thin layer. The designed graphene/buffer-layer/SiO_2 composite is therefore a promising structure for the μ-enhancement. However the role of the b-layer (=buffer-layer) on the graphene carrier is not well understood yet.

When graphene is transferred on substrate carrier density(N) changes due to substrate-induced charge doping. Also the scattering rate (Γ) is believed to increase through surface polar phonon and/or charged impurity scattering. N and Γ are, as we will discuss later, directly related with the carrier mobility of graphene. Therefore it is important to characterize them for various types of substrate materials. N and Γ are measured commonly by Hall effect and dc-resistivity experiment. Recently we and other groups reported[5,6] that they can be determined from far-infrared (FIR) spectroscopy of free carrier Drude response. This method allows simultaneous measurement of N and Γ without need of the electrical-lead contact to the sample.

In this letter, we performed FIR transmission measurement of large scale chemical vapor deposition (CVD)-grown graphene placed on b-layer/SiO_2 composite substrate for various b-layers in following two groups: (1) polar dielectric oxide ($SrTiO_3$ and ZnO) and (2) organic polymer film HMDS($[(CH_3)_3Si]_2NH$) and polymethyl methacrylate [PMMA; $(C_5O_2H_8)_n$]. We also measured the sample with no b-layer, graphene/SiO_2. We determine N and Γ of charge carrier monitoring how they change on different types of the b-layers. Such information enables us to understand the role of the b-layer on the carrier mobility in graphene and eventually which direction we should pursue to enhance it. To study large scale graphene (LSG) is important because they are in greater need than the microscopic exfoliated sample in high-speed circuit,[7,8] flexible display,[9] and transparent conductor[10] applications.

LSG is synthesized by CVD method as described elsewhere.[11] b-layer was deposited on SiO_2 (300 nm thick)/Si-substrate using thermal evaporation method as in Ref. 12 (for $SrTiO_3$ and ZnO) and spin-coating method (HMDS and PMMA) respectively. Thickness of the b-layer was measured using AFM and ellipsometry method. LSG was transferred onto the composite substrate b-layer/SiO_2/Si after removing Cu-foil using 0.1*M* ammonium persulphate $(NH_4)_2S_2O_8$ solution. For FIR measurement we covered half of the substrate surface with LSG leaving the other half for the transmission reference (see inset of Figs. 1 and 2). Transmission spectrum through LSG/sub ($=T_s$) was normalized by that through the bare substrate ($=T_r$) and relative transmission $T_R(\omega)=T_s/T_r$ was obtained. FTIR (Bomem DA8) and bolometric detector were used for FIR measurement.

Figure 1 shows $1-T_R(\omega)$ in the FIR region measured on LSG/SiO_2(300 nm)/Si. The curve rises at low frequency (=decrease in transmission) due to Drude absorption. The transmission of the SiO_2/Si substrate is flat with frequency (inset), a typical behavior of an insulator. We fit $T_R(\omega)$ using three-layer model with dielectric function $\epsilon(\omega)$ algorithm;[13] $[\epsilon(\omega), d]=[11.6, 0.5\ mm]$ for Si and [2.5, 300 nm] for SiO_2. d is the layer thickness. $\epsilon(\omega)$ was determined from transmission data in the inset. For LSG we use $[-(4\pi/i\omega)\sigma(\omega), 3.4\ Å]$ where $\sigma(\omega)$ is the Drude optical conductivity

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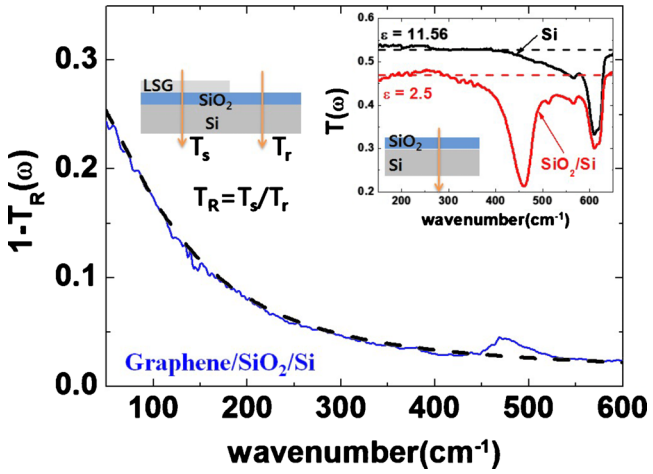

FIG. 1. (Color online) 1-$T_R(\omega)$ of graphene/SiO_2(300 nm)/Si(0.5 mm) in FIR region. $T_R(\omega)$ represents the transmission of the graphene sample relative to that of substrate. The dashed curve shows the fit result using Drude model. The dip at ω=480 cm^{-1} is an artifact due to low instrumental FIR intensity. The inset shows absolute transmission of the SiO_2(300 nm)/Si(0.5 mm) and Si (0.5mm) without graphene. We determine $\epsilon(\omega)$ of Si and SiO_2 from their transmission levels. See the dashed lines. The dip at 460 cm^{-1} (610 cm^{-1}) is due to optical phonon of SiO_2 (Si).

$$\sigma(\omega) = \frac{\omega_P^2}{4\pi} \times \frac{i}{\omega + i\Gamma}. \quad (1)$$

Here Drude strength ω_P^2 and carrier scattering rate Γ are the fitting parameters. Interference among the multiply reflected lights is accounted for coherently for LSG and SiO_2 layers. The fit agrees well with the data. The $2d$-carrier density N is related with ω_P as $\omega_P^2 \cdot d = (V_F e^2/\hbar)\sqrt{\pi N}$. Using the Fermi velocity $V_F = 1.1 \times 10^6$ m/s, we obtain $N = 4.5 \times 10^{12}$ cm^{-2} which is comparable to transport measurements.[14–16] We repeated the $T_R(\omega)$ measurement for six LSG samples and the data were reproduced with identical ω_P^2 and Γ values.

Figure 2 displays 1-$T_R(\omega)$ of LSG on ZnO and $SrTrO_3$ layers. The Drude peak for ZnO-buffer is stronger than that for the SiO_2 layer of Fig. 1, while it is similar for STO. From four-layer model fit, we obtain $N = 9.8 \times 10^{12}$ cm^{-2}

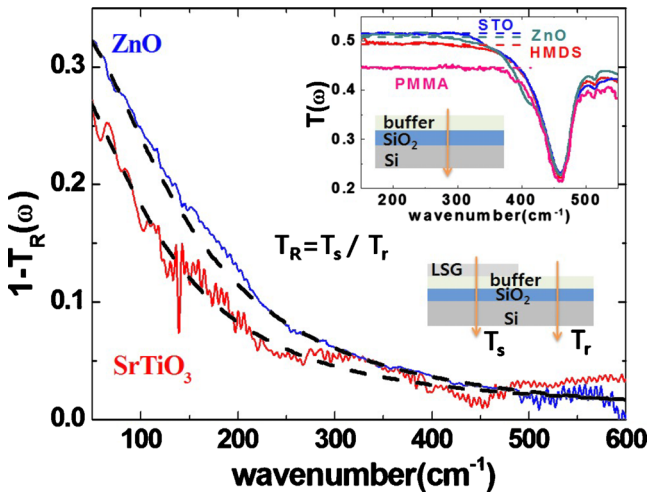

FIG. 2. (Color online) 1-$T_R(\omega)$ of graphene transferred on b-layer/SiO_2/Si with polar oxide buffer b-layer=STO and ZnO. The dashed curves show the fit from the multilayer optical transmission analysis. Inset shows the absolute transmission of the insulating composite substrates. ϵ of the buffer-layer is determined from the transmission level at low frequency region.

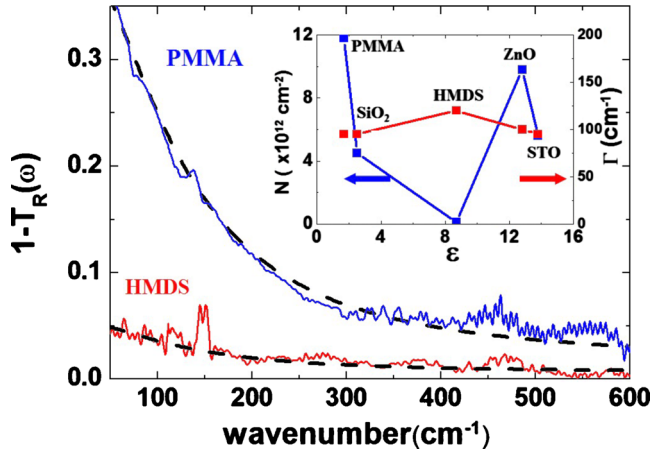

FIG. 3. (Color online) 1-$T_R(\omega)$ of graphene on b-layer/SiO_2/Si with organic polymer buffer PMMA and HMDS. Inset shows the carrier density (n) and scattering rate (Γ) as function of ϵ for the different buffer-layers.

and $N = 5.6 \times 10^{12}$ cm^{-2} for ZnO and STO respectively. $\Gamma = 95-100$ cm^{-1} is the same as that of Fig. 1. The inset shows absolute transmission of the b-layer/SiO_2/Si substrate without graphene. The transmission level at low frequency allows us to determine $\epsilon(\omega)$ of the b-layer's from the three-layer analysis (dashed lines).

Figure 3 depicts $1-T_R(\omega)$ of LSG on organic films PMMA and HMDS. In PMMA Drude strength is substantially enhanced resulting in the increase in N to 11.8 $\times 10^{12}$ cm^{-2}. For HMDS, N is suppressed largely to $N = 0.1 \times 10^{12}$ cm^{-2}, which is 1/40 of that for SiO_2. In contrast to the N-change Γ is almost the same as for the other b-layers. Again the transmission of the bare HMDS (PMMA)/SiO_2/Si, inset of Fig. 2, shows the insulating behavior of the buffer-layers. The fitting parameters for the graphene layer and for the b-layers are summarized in Table I.

Γ is in 95–120 cm^{-1} range for the 5 different substrates studied in our work. The little dependence of Γ on the b-layer is an unexpected result: In polar oxide substrate remote surface polar phonon (SPP) is considered as important scattering source for graphene at room-T.[17,18] On the other hand HMDS is a nonpolar material where SPP is absent or, if any, weak. Γ shows no difference for the two material groups. Charged impurity in the substrate is another scattering source for the carrier in graphene. In high-ϵ substrate, the Coulomb potential is screened more effectively by the dielectric polarization of the lattice. However while ϵ of the b-layer varies from 2.5 (for SiO_2) to 11 (for STO) in our measurement, Γ remains constant showing no correlation

TABLE I. Drude model fit result for different buffer-layers: plasma frequency ω_p, scattering rate Γ, carrier density N, and mobility μ. d and ϵ are the thickness and dielectric constant, respectively.

Type	d (nm)	ϵ	ω_p ($\times 10^3$ cm^{-1})	Γ (cm^{-1})	N ($\times 10^{12}$ cm^{-2})	μ ($cm^2/V\,s$)
SiO_2	300	2.5	17.4	95.0	4.5	2467
ZnO	30	12.8	21.1	100.0	9.8	1594
$SrTiO_3$	30	13.8	18.3	95.0	5.6	2216
HMDS	2	8.7	7.1	120.0	0.1	11680
PMMA	30	1.7	22.1	95.0	11.8	1527

with ϵ (Inset of Fig. 3).[19] The robustness of Γ may indicate that Γ is dominated by intrinsic scattering due to such as phonon of the graphene itself, the nanoripples, and the grain boundary.

In graphene carrier mobility μ is given as $\mu = (e/\sqrt{\pi}h)\cdot(v_F/\sqrt{N})\frac{1}{\Gamma}$ in contrast with the familiar semiclassical relation $\mu = (e/m^*)\cdot(1/\Gamma)$.[17] Using N and Γ of Table I we calculate μ for each b-layer (Table I). For LSG on SiO_2 we have $\mu \simeq 2500$ $cm^2/V\,s$ which is close to other reports.[20] Notably μ increases to 11 700 $cm^2/V\,s$ for HMDS. This effect was seen also in the transport measurement by Lafkioit *et al.*[4] The significant μ-enhancement is due to the exceptionally small N of HMDS but not by reduced scattering rate. In fact Γ of HMDS is larger than other b-layers. To find a b-layer material with small N is one guideline toward better μ. However when LSG is applied as a field effect device N can increase by the gate voltage and in such situation μ-drop cannot be avoided. Ultimately μ-increase through the reduced Γ is highly needed. Next step of our work is to find a way to improve Γ such as, for example, thermal annealing.

In conclusion we have performed FIR spectroscopy measurement to investigate the effect of buffer-layer on graphene in the LSG/buffer-layer/SiO_2(300 nm)/Si samples. The Drude response of graphene showed that (1) carrier density N changes depending on the five b-layers, polar oxide thin layer ZnO and $SrTiO_3$, organic film PMMA and HMDS, and the bare SiO_2. (2) However surprisingly the carrier scattering rate Γ has little dependence on the buffer-layers. That the carrier mobility μ varies on different substrates—including the fourfold enhancement to 11 700 $(cm^2/V\,s)$ for HMDS-layer—results through the N-change, but not from the Γ change as many people believe. Our finding indicates that in addition to the N-control further room is left open for μ-enhancement through Γ improvement.

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