Infrared study of Large scale h-BN film and Graphene/h-BN heterostructure

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We synthesize a series of CVD h-BN films and perform critical infrared spectroscopic characterization. For high-temperature (HT, Temp = 1400 °C) grown h-BN thin film only E1u-mode infrared phonon is activated demonstrating highly aligned 2D h-BN planes over large area, whereas low-temperature (LT, Temp = 1000 °C) grown film shows two phonon peaks, E1u, and A2u, due to stacking of h-BN plane at tilted angle. For CVD graphene transferred on HT h-BN/SiO2/Si substrate, interband transition spectrum σ2 shifts strongly to lower energy compared with that on LT h-BN/SiO2/Si and on bare SiO2/Si substrate, revealing that residual carrier density n in graphene is suppressed by use of HT h-BN layer. Also the interband transition width of σ1 defined by effective temperature is reduced from 400 K for G/SiO2/Si to 300 K for HT h-BN/SiO2/Si. The behaviors of n and effective temperature show that HT h-BN film can decouple CVD graphene from the impurity and defect of SiO2 leading to large scale free-standing like graphene.

I. INTRODUCTION

Hexagonal boron nitride (h-BN) is a graphite-like layered material characterized by wide band gap ~ 6 eV.[1] The B and N atoms bond covalently to constitute BN honeycomb planes, whereas adjacent BN planes are weakly coupled by van der Waals interaction.[2] h-BN shows a range of attractive properties such as high-temperature stability, high mechanical strength, and large thermal conductivity useful for application.[3–6] In particular when used as substrate for graphene h-BN greatly enhances carrier mobility at room- and low-temperature compared with conventional SiO2/Si substrate.[7–9] The superior performance as substrate is directly associated with the ultraflat, chemically inert surface and also the high purity, defect-free bulk nature of h-BN.[10, 11] However, the exfoliated h-BN flake is limited in size by small lateral length, only ~ 10μm x 10μm, which seriously hinders its use in application. For practical industrial application large scale h-BN is strongly needed.

Recently large area h-BN thin films are synthesized by CVD technique.[12–16] Here chemical precursors containing B and N are thermally evaporated and deposited on metallic platforms (Cu, Pt, Fe)[12, 13] or α-Al2O3 crystal.[14] Hexagonal phase BN film is formed for certain ranges of vapor pressure and growth temperature. The h-BN film is isolated from its template and transferred onto desired substrate such as SiO2/Si. Further transfer of a pregrown CVD graphene sheet on h-BN/substrate completes the large scale fabrication of graphene supported by h-BN buffer layer.[17] A systematic spectroscopic study and critical comparison with the exfoliated samples, currently lacking, can lead to deeper understanding of the large area samples.

In this work we perform infrared transmission measurement on the CVD h-BN and graphene/h-BN films. For the h-BN film infrared-active phonon peaks are probed. A correlation of the phonon profile with the growth condition is found, providing a knowledge about the lattice structure of the films. For graphene/h-BN interband transition of Dirac carrier in graphene is measured using the infrared spectroscopy. From the electronic transition we are able to determine Fermi energy, carrier density, and defect-related interband transition width of graphene.

II. EXPERIMENT

We grew multilayer h-BN thin films using CVD method on Al2O3 substrate at two different temperatures (Temp) 1000 °C and 1400 °C. The details of the film synthesis were reported elsewhere.[18] The h-BN films were isolated from the Al2O3 and transferred on IR-transparent SiO2/p-Si substrate, 1 cm x 1 cm in size, by using electrochemical bubbling-based method.[14, 18] We also prepared single crystal multilayer h-BN flakes by exfoliation. Large scale monolayer graphene was grown on Cu-foil (Alfa Aesar, 99.999%) using CVD method.[19, 20] The CVD graphene was then transferred on the CVD h-BN/SiO2/p-Si following the PMMA transfer method.[17] Infrared transmission was measured using a microscope FTIR spectrometer (Bruker Vertex 70V). Optical dielectric functions were calculated by fitting transmission and reflection data using RefFit analysis program.[21]
parenthesis show the thicknesses of the h-BN films.

Figure 2(b) shows 1

\[ \frac{I_{1u}}{I_{2u}} \]

peak is activated. The 1

\( A_{2u} \) phonon in-

\[ \theta \]

is normalized by that of \( E_{1u} \) peak. For each spectrum the intensity of \( h\text{-BN/substrate} \) and bare substrate respectively. For LT h-BN, \( A_{2u} \) phonon is observed at \( \omega = 800 \text{ cm}^{-1} \) which is absent for the HT h-BN film. For each spectrum the intensity ratio \( I_{1u}/I_{2u} \) for a single crystal h-BN flake. As the tilting angle \( \theta \) increases, the \( A_{2u} \) phonon intensity increases (see the inset) and \( I(E_{1u}) \) phonon intensity decreases respectively. (b) Ratio of peak heights \( I(A_{2u}) \) and \( I(E_{1u}) \) as function of \( \theta \). The dashed curve, \( 0.24 \tan \theta \), connects the single crystal data points. Based on this curve we infer the tilting angle of LT h-BN films \( \theta = 20^{\circ} \sim 40^{\circ} \) from their phonon intensity ratio \( 0.1 < I(A_{2u})/I(E_{1u}) < 0.15 \). For HT h-BN films we have \( I(A_{2u})/I(E_{1u}) < 0.01 \) and \( \theta < 3^{\circ} \).

III. RESULT

A. h-BN thin film

Figure 1(b) shows \( 1 - T/T_0 \) of the h-BN films grown at low-temperature (LT, Temp = 1000 °C) and high-temperature (HT, Temp = 1400 °C). For LT h-BN two IR-active phonon peaks are observed at \( \omega = 800 \text{ cm}^{-1} \) and \( \omega = 1375 \text{ cm}^{-1} \). On the other hand, for HT h-BN, the low-frequency peak is absent and only the high-frequency \( E_{1u} \) peak is activated. The \( E_{1u} \) phonon represents in-plane oscillation of B and N atoms within the BN plane. The \( \omega = 800 \text{ cm}^{-1} \) phonon is considered to be a c-axis mode associated with vibration normal to the BN plane.\[22\] For our near-normal incident experiment, infrared light should couple only with the in-plane \( E_{1u} \) phonon mode if the BN-plane of the thin film were perfectly aligned with the substrate-plane. The phonon profiles of LT h-BN and HT h-BN suggest that the two kinds of films differ in their lattice alignments.

To better understand the phonon behavior we performed angle-tilted IR transmission measurement using single crystal h-BN. Here 100 nm-thick h-BN crystal is tilted from \( \theta = 0 \) to 30° with respect to the incident IR as sketched in Figure 2(a). As \( \theta \) increases \( E_{1u} \) peak intensity decrease and that of \( A_{2u} \) peak increases. The peak intensity \( I(A_{2u}) \) and \( I(E_{1u}) \) change with \( \theta \) as \( I(A_{2u}) \sim \sin \theta \) and \( I(E_{1u}) \sim \cos \theta \) (data not shown). The \( \theta \)-dependent behaviors of the IR phonons confirm that they are in-plane and out-of-plane vibration modes respectively. In Figure 2(b) we plot the intensity ratio \( I(A_{2u})/I(E_{1u}) \) as function of \( \theta \). The ratio increases in proportion to \( \tan \theta \),
the ultrathin, few-layer thickness region. To investigate how the $E_{1u}$ phonon change with thickness, we measured IR transmission for a series of HT h-BN samples with controlled thickness. Figure 3(a) shows $1 - T/T_0$ of HT h-BN from $d = 24$ layers to $d = 1$ layer. We used the relation 0.33 nm = 1 layer to convert the unit of thickness from nm to the number of layers. The characteristic phonon spectrum, prominent $E_{1u}$ peak and absence of $A_{2u}$ peak, persists for all samples, indicating the aligned growth of h-BN layer at few layer and monolayer film. Interestingly the $E_{1u}$ peak shifts to higher energy as the film becomes thinner. In Figure 3(b) we plot the phonon frequency ($\omega_0$) of h-BN film as function of h-BN thickness. $\omega_0$ measured for several exfoliated h-BN crystal flakes are shown together. For thick h-BN flakes ($d > 40$ layers) $\omega_0$ is independent with $d$ and it agrees with the frequency of bulk h-BN crystal. For HT h-BN films $\omega_0$ increases rapidly as $d$ decreases at $d < 24$ layers. The steep increase of phonon frequency in the few-layer thickness is observed in other layered compounds such as topological insulator (Bi$_2$Se$_3$) and transition metal dichalcogenide (MoS$_2$, MoTe$_2$) suggesting that it is possibly an universal behavior of layered 2D materials. The strong shift of phonon frequency shows that one can use $\omega_0$ to identify thickness of h-BN film as an alternative to AFM or TEM.

We discuss briefly about the phonon frequency of our samples. For HT h-BN film the phonon frequency agrees with that of the single crystal for both $A_{2u}$ peak and $E_{1u}$ peak. However, for LT h-BN film, the $A_{2u}$ ($E_{1u}$) phonon frequency is notable lower (higher) than HT h-BN. When the substrate temperature is lower than the optimal temperature during the growth (HT = 1400 °C for our case) the B and N atoms cannot crystallize into fully relaxed, equilibrium lattice due to insufficient migration energy, causing some strain or tension in the film. We propose that the lattice strain may be one possible reason for the phonon frequency shifts. Also LT h-BN film may contain atomic vacancy and defects, which may also cause the phonon shifts.

B. Graphene on h-BN

To study the role of h-BN thin film as substrate for large scale graphene we transfer monolayer CVD graphene sheet on three different substrates, HT h-BN(2.5 nm thick)/SiO$_2$/Si, LT h-BN(40 nm thick)/SiO$_2$/Si, and bare SiO$_2$/Si. Figure 4(a) shows the infrared transmission $T/T_0$ and reflection $R/R_0$ measured for the graphene(G)/substrate, where again the spectra $T$ and $R$ are normalized by the substrate $T_0$ and $R_0$. We extracted optical conductivity of graphene alone by applying the Kramers-Kronig constrained variational analysis to $T/T_0$ and $R/R_0$.

Figure 4(b) shows optical conductivity $\sigma_1$ of graphene. $\sigma_1$ represents interband transition $\sigma_1 = \sigma_0 (= \pi e^2/2h)$ of the Dirac carrier. At low $\omega$, $\sigma_1$ is suppressed because the transition becomes Pauli-forbidden. The $\sigma_1$ curve shifts to lower energy as substrate is changed in the order SiO$_2$ → LT h-BN → HT h-BN. Theoretically the interband optical transition is expressed as

$$\sigma_1 = \frac{\sigma_0}{2} \left[ \tanh \left( \frac{\hbar \omega + 2E_F}{4k_B T} \right) + \tanh \left( \frac{\hbar \omega - 2E_F}{4k_B T} \right) \right]$$

where $E_F$ and $T(=\text{Temp})$ stand for the Fermi energy and sample temperature respectively. We fit $\sigma_1$ using Eq.(1). The fitting parameters are summarized in Table I. For graphene on SiO$_2$, we have $E_F = 214$ meV from the fit which, from the relation $E_F = \hbar v_F \sqrt{\pi n}$ and $v_F = 1.1 \times 10^6$ cm/s, shows that Dirac band is doped by carrier, known to be hole, with density $n = 2.9 \times 10^{12}$ cm$^{-2}$.

| Substrate | $E_F$ (meV) | $n$ ($10^{12}$ cm$^{-2}$) | $\text{Temp}^*$ (K) |
|-----------|-------------|--------------------------|------------------|
| HT h-BN (2.5 nm) | 93 | 0.5 | 300 |
| LT h-BN (40 nm) | 155 | 1.5 | 370 |
| SiO$_2$ | 214 | 2.9 | 400 |

TABLE I. Dirac carrier parameters measured from the interband transition conductivity $\sigma_1$ of graphene on different substrates. $E_F$ = Fermi energy, $n$ = carrier density, and $\text{Temp}^*$ = effective temperature.
The hole-doping of graphene is caused by various defect of SiO$_2$ such as oxygen vacancy, surface dangle bonds, and others. For HT h-BN, we have significantly less values $E_F = 93$ meV and $n = 5 \times 10^{11}$ cm$^{-2}$. The latter is only 17% of that for G/SiO$_2$, showing that residual carrier has strongly decreased. It is interesting to compare the large scale CVD G/h-BN with single crystal G/h-BN. For exfoliated graphene on exfoliated h-BN, transport measurements showed $n$ is as small as $1.5 \times 10^{11}$ cm$^{-2}$ at $T$ which is 10% of $n$ for single crystal G/SiO$_2$ and 5% of $n$ for CVD G/SiO$_2$. To gain better idea on the n’s, we convert $n$ to the familiar transport $I$-$V$ curve of graphene. In the $I$-$V$ curve charge neutral voltage $V_{CNP}$ is determined by $n$ as $n = (\epsilon_r \epsilon_0 / ed) V_{CNP}$ where $\epsilon_r = 3.9$ and $d = 300$ nm are dielectric constant and thickness of SiO$_2$, respectively. For G/SiO$_2$ sample we have $V_{CNP} = 40$ V. It is reduced to $V_{CNP} = 7$ V for G/HT h-BN and $V_{CNP} = 2$ V for the single crystal G/h-BN. This result shows that large scale graphene was brought closer to the graphene on single crystal h-BN by use of the CVD h-BN, and in fact is not far from $V_{CNP} = 0$ V, the ideal free standing state. For the G/LT h-BN, we have $E_F = 155$ meV and $n = 1.5 \times 10^{12}$ cm$^{-2}$. Those values lie between SiO$_2$ and HT h-BN showing that LT h-BN is not as efficient as HT h-BN although it does reduce the residual carrier to some extent. High quality h-BN with well aligned BN planes is essential to achieve residual carrier-free graphene.

For $T = 0$, Eq.(1) predicts that $\sigma_1$ changes suddenly from $\sigma_1 = 0$ to $\sigma_1 = \sigma_0$ at $h \omega = 2E_F$. At elevated temperature ($T > 0$), the carrier is thermally populated in the Dirac band and the sharp transition of $\sigma_1$ becomes broadened. For G/HT h-BN, $\sigma_1$ data agrees well with Eq.(1) calculated with the measurement temperature $T = 300$ K. However for G/LT h-BN and G/SiO$_2$ the $\sigma_1$ transition is broader than the theory curve. Here $\sigma_1$ can be fit only using higher $T$, $T = 370$ K for LT h-BN and $T = 400$ K for SiO$_2$ as shown by black dashed curve. We define for convenience those $T$ as effective temperature $T^*$. $T^* > 300$ K implies that there are extra source other than temperature that broadens the curve. Possibly the carrier is populated or redistributed in the Dirac band due to the defect-driven perturbation from the substrate, LT h-BN and SiO$_2$. This postulation is supported by that $T^{*}$ is correlated with $E_F$, i.e. $T^*$ decreases along with the residual carrier reduction as the substrate quality is increased as SiO$_2$ → LT h-BN → HT h-BN.

**IV. CONCLUSION**

In conclusion we performed infrared measurement on large scale CVD h-BN thin film and CVD graphene/h-BN heterostructure. For CVD h-BN sample, HT ($T = 1400$ °C) grown thin film shows only $E_{1u}$ optical phonon like single crystal h-BN flake, demonstrating that 2D h-BN planes are highly aligned over the entire area of the film. On the other hand, LT ($1000$ °C) grown film shows two phonon peaks, $E_{1u}$ and $A_{2u}$, due to tilting of the h-BN plane by $\theta = 20 \sim 40^\circ$. For G/HT h-BN samples, interband transition spectrum $\sigma_1$ shows that residual carrier density of graphene is strongly suppressed to $n = 5 \times 10^{11}$ cm$^{-2}$, from $n = 2.9 \times 10^{12}$ cm$^{-2}$ of G/SiO$_2$ and becomes comparable to $n$ of single crystal graphene on single crystal h-BN. Also the interband transition width of $\sigma_1$ is reduced from $T^{*} = 400$ K for G/SiO$_2$ to the theoretical value $T^* = 300$ K by using the HT h-BN film as substrate. The behaviors of $n$ and $T^{*}$ show that HT h-BN can decouple large scale graphene from SiO$_2$ leading it closer to ideal, undoped Dirac semi-metallic state.

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[1] K. Watanabe, T. Taniguchi, and H. Kanda, Nat. Mater. 3, 404 (2004).
[2] A. K. Geim and I. V. Grigorieva, Nature 499, 419 (2013).
[3] E. Sichel, R. Miller, M. Abrahams, and C. Buioioci, Phys. Rev. B 13, 4607 (1976).
[4] K. Watanabe, T. Taniguchi, T. Niiyama, K. Miya, and M. Taniguchi, Nat. Photonics 3, 591 (2009).
[5] T. Sugino and T. Tü, Jpn. J. Appl. Phys., Part 2 39, L1101 (2000).
[6] I. Jo, M. T. Pettes, J. Kim, K. Watanabe, T. Taniguchi, Z. Yao, and L. Shi, Nano Lett. 13, 550 (2013).
[7] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. Shepard, et al., Nat. Nanotechnol. 5, 722 (2010).
[8] W. Gannett, W. Regan, K. Watanabe, T. Taniguchi, M. Crommie, and A. Zettl, Appl. Phys. Lett. 98, 242105 (2011).
[9] E. Kim, T. Yu, E. S. Song, and B. Yu, Appl. Phys. Lett. 98, 262103 (2011).
[10] G.-H. Lee, Y.-J. Yu, C. Lee, C. Dean, K. L. Shepard, P. Kim, and J. Hone, Appl. Phys. Lett. 99, 243114 (2011).
[11] J. Xue, J. Sanchez-Yamagishi, D. Bulmash, P. Jacqoud, A. Deshpande, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, and B. J. LeRoy, Nat. Mater. 10, 282 (2011).
[12] K. K. Kim, A. Hsu, X. Jia, S. M. Kim, Y. Shi, M. Hofmann, D. Nezich, J. F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, et al., Nano Lett. 12, 161 (2011).
[13] Y. Gao, W. Ren, T. Ma, Z. Liu, Y. Zhang, W.-B. Liu, L.-P. Ma, X. Ma, and H.-M. Cheng, ACS nano 7, 5199 (2013).
[14] G. Kim, A.-R. Jang, H. Y. Jeong, Z. Lee, D. J. Kang, and H. S. Shin, Nano Lett. 13, 1834 (2013).
[15] J.-H. Park, J. C. Park, S. J. Yun, H. Kim, D. H. Luong, S. M. Kim, S. H. Choi, W. Yang, J. Kong, K. K. Kim, et al., ACS nano 8, 8520 (2014).
[16] A. Ismach, H. Chou, D. A. Ferrer, Y. Wu, S. McDonnell, H. C. Floresca, A. Covacevich, C. Pope, R. Piner, M. J. Kim, et al., ACS nano 6, 6378 (2012).
[17] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg, and R. S. Ruoff, ACS Nano 5, 6916 (2011).
[18] A.-R. Jang, S. Hong, C. Hyun, S. I. Yoon, G. Kim, H. Y. Jeong, T. J. Shin, S. O. Park, K. Wong, S. K. Kwak, N. Park, K. Yu, E. Choi, A. Mishchenko, F. Withers, K. S. Novoselov, H. Lim, and H. S. Shin, Nano Lett. (2016).
[19] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, F. Tutuc, et al., Science 324, 1312 (2009).
[20] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, et al., Nat. Nanotechnol. 5, 574 (2010).
[21] A. Kuzmenko, Rev. Sci. Instrum. 76, 083108 (2005).
[22] R. Geick, C. Perry, and G. Rupprecht, Phys. Rev. 146, 543 (1966).
[23] D. Hoffman, G. Doll, and P. Eklund, Phys. Rev. B 30, 6051 (1984).
[24] R. V. Aguilar, A. Stier, W. Liu, L. Bilbro, D. George, N. Bansal, L. Wu, J. Cerne, A. Markelz, S. Oh, et al., Phys. Rev. Lett. 108, 087403 (2012).
[25] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, and S. Ryu, ACS Nano 4, 2695 (2010).
[26] M. Yamamoto, S. T. Wang, M. Ni, Y.-F. Lin, S.-L. Li, S. Aikawa, W.-B. Jian, K. Ueno, K. Wakabayashi, and K. Tsukagoshi, ACS Nano 8, 3895 (2014).
[27] V. Kravets, A. Grigorenko, R. Nair, P. Blake, S. Anisimova, K. Novoselov, and A. Geim, Phys. Rev. B 81, 155413 (2010).
[28] D.-H. Chae, T. Utikal, S. Weisenburger, H. Giessen, K. v. Klitzing, M. Lippitz, and J. Smet, Nano Lett. 11, 1379 (2011).
[29] Z. Li, E. A. Henriksen, Z. Jiang, Z. Hao, M. C. Martin, P. Kim, H. Stormer, and D. N. Basov, Nat. Phys. 4, 532 (2008).
[30] K. F. Mak, M. Y. Sfeir, Y. Wu, C. H. Lui, J. A. Misewich, and T. F. Heinz, Phys. Rev. Lett. 101, 196405 (2008).