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Raman study on the interlayer interactions and the band structure of bilayer graphene synthesized by alcohol chemical vapor deposition

Makoto Okano,¹ Ryusuke Matsunaga,^{1,a)} Kazunari Matsuda,^{1,b)} Satoru Masubuchi,² Tomoki Machida,² and Yoshihiko Kanemitsu^{1,3,c)}

¹*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

²*Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan*

³*Photonics and Electronics Science and Engineering Center, Kyoto University, Kyoto 615-8510, Japan*

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We investigated the electronic band structure and interlayer interactions in graphene synthesized by alcohol-chemical vapor deposition (a-CVD) using microprobe Raman spectroscopy and tight-binding band-structure calculations. The number of graphene layers was determined from the spectrally integrated intensity ratios of the *G* phonon to 2*D* phonon peaks. We found that the value of the parameter determining interlayer interactions in a-CVD bilayer graphene was less than half that of exfoliated bilayer graphene. The weak interlayer interaction in a-CVD bilayer graphene was attributed to non-*AB* stacking order. © 2011 American Institute of Physics. [doi:10.1063/1.3651325]

Graphene has attracted interest because of its utility in fundamental physics research and potential device applications.^{1–4} The electronic band structure of single-layer graphene has a characteristic linear gapless dispersion at the K point; thus, an electron of graphene is a massless Dirac fermion. The band structure of bilayer graphene differs from that of single-layer graphene due to interactions between the layers, which depend on the stacking of graphene layer. Layer stacking of exfoliated bilayer graphene fabricated by the Scotch tape method⁵ is usually *AB* (Bernal) stacking, leading to band splitting and modification of the dispersion near the K point. This stacking behavior has been confirmed by both theoretical calculations and experimental studies including Raman spectra.^{6–8} Furthermore, an understanding of interlayer interactions in bilayer graphene is important for device applications because the anisotropic potential formation in bilayer graphene causes electric-field-induced opening of the band gap.⁹

For device applications, we need to produce large-area samples and control the shape and number of the graphene layer. Recently, fabrication of large-area graphene on transition-metal substrates was successfully demonstrated using chemical vapor deposition (CVD).^{10–14} In particular, alcohol-CVD (a-CVD) synthesis of graphene has advantages such as low cost, easy handling, and controllability of the layer number.¹⁵ However, graphene fabricated by CVD has not been studied in detail using Raman spectroscopy, although it is one of the most powerful methods for determining the number of layers and interlayer interactions in graphene. For a-CVD graphene, the band structure and interlayer interactions are not well understood.

In this study, we fabricated graphene samples consisting of a few layers by a-CVD and studied their electronic properties using microprobe Raman (micro-Raman) spectroscopy.

The number of layers was determined from the spectrally integrated intensity ratio of *G* phonon to 2*D* phonon peaks (I_G/I_{2D}) in Raman spectra and was compared with that of exfoliated graphene. From spectral shape analysis of the Raman signal and tight-binding (TB) energy-structure calculations, we evaluated the parameters determining the energy band structure of a-CVD bilayer graphene. The strength of the interlayer interactions, determined by parameters of a-CVD bilayer graphene, is less than half that of exfoliated bilayer graphene.

Graphene samples were synthesized by flash cooling a-CVD according to Ref. 15. A polycrystalline Ni substrate (20 μm thick) was inserted into a quartz tube (3 cm in diameter, 75 cm in length) at room temperature. The CVD system, including the quartz tube, was evacuated to 2 Pa, and Ar gas was introduced to the system at a flow rate of 300 sccm. The quartz tube was heated to 900 °C in a furnace, and the Ar flow was stopped. Ethanol was introduced as a carbon source at a flow rate of 1 sccm for 10–30 s. After growth was complete, the quartz tube was immediately cooled at room temperature for 30 min. Graphene grew on both sides of the Ni substrate, and the back side of the Ni substrate was polished for easy transfer from the Ni substrate onto SiO₂/Si substrates. Poly(methyl methacrylate) (PMMA) was spin coated on the front side of the Ni substrate as a protective film, and the Ni substrate was etched away using HNO₃ solution at 80 °C.¹⁰ Finally, graphene with a PMMA film was transferred to the SiO₂/Si substrate, and the PMMA was rinsed with acetone three times for 5 min.

We performed micro-Raman spectroscopy to characterize the number of layers in a-CVD graphene because our samples were spatially inhomogeneous. The samples were excited by a single-mode diode-pumped solid-state laser with a wavelength of $\lambda_{\text{exc}} = 532 \text{ nm}$. Raman spectra were measured in back-scattering geometry and detected with a cooled charge-coupled-device detector via a monochromator. From the Raman intensity map, the grain size was estimated to be $\sim 10 \mu\text{m}$, which afforded a micro-Raman spatial resolution of $\sim 1 \mu\text{m}$ and was comparable to the grain size reported previously.¹⁵

^{a)}Present address: Department of Physics, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

^{b)}Present address: Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan.

^{c)}Electronic mail: kanemitsu@scl.kyoto-u.ac.jp.

Figure 1(a) shows typical Raman spectra of a-CVD graphene and exfoliated graphene samples. In both samples, three characteristic Raman peaks were observed at ~ 1350 , 1580 , and 2700 cm^{-1} . These peaks are known as the D , G , and $2D$ phonon peaks.⁶ The low intensity ratio of D to G phonon peaks indicates that the crystal quality of a-CVD graphene is relatively high.¹⁶ In exfoliated graphene, the intensity ratio of G to $2D$ phonon peaks can be used to determine the number of graphene layers because it depends strongly on the number of layers.⁶ Therefore, we measured the Raman spectra at various positions and determined the number of layers in a-CVD samples using I_G/I_{2D} , and compared the results with that of exfoliated graphene samples. Using previous Raman data,^{6,17} we found that exfoliated single-layer and bilayer graphene exhibited $I_G/I_{2D} \sim 0.2$ and 0.45 , respectively. Next, we determined the single-layer and the bilayer graphene region of the a-CVD sample using these values.

It is well known that the spectral shape of the $2D$ peak reflects the electronic interaction between layers.⁶ If interlayer interactions between graphene layers do not exist or are very weak, it is likely that the full-width at half-maximum (FWHM) of the $2D$ peaks is independent of the layer number and that the intensity ratios are similar. Actually, bilayer graphene fabricated by the roll-to-roll method showed almost the same intensity ratio as single-layer graphene because of weak interlayer interactions due to random orientation.¹⁸ In our sample, the intensity ratios of single-layer and bilayer graphene are not the same, and the intensity ratio and spectral shape of bilayer graphene are independent of spatial position, as shown in Fig. 1(b). Therefore, we discuss the interlayer interactions of a-CVD graphene based on spectral fitting of $2D$ peaks.

The thick solid curves in Figs. 2(a) and 2(b) show the Raman spectra of $2D$ phonon peaks in exfoliated and a-CVD bilayer graphene. There is a large difference in the spectral shape between the exfoliated and a-CVD graphene. We

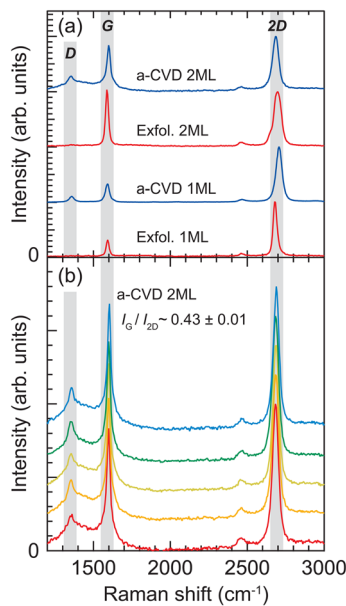


FIG. 1. (Color online) (a) Typical Raman spectra of single-layer and bilayer graphene in a-CVD and exfoliated samples. (b) Raman spectra of bilayer graphene in the a-CVD sample at various positions. Gray regions correspond to G , D , and $2D$ phonon bands.

decomposed the $2D$ peak in exfoliated bilayer graphene into four Lorentzian components (thin solid curves in Fig. 2(a)), due to band splitting induced by the interlayer interaction and four different double-resonance (DR) Raman processes.⁶ The fitted results (dotted curve) of the intensity ratio and the FWHM are consistent with previous results.⁶ For a-CVD bilayer graphene, we assumed that the $2D$ peak decomposed into four components similar to exfoliated graphene. To minimize decomposition ambiguity, we assumed that the intensity ratios of the four Lorentzian components for a-CVD graphene were the same as that of the exfoliated graphene and that the FWHMs of the four Lorentzian components have the same value ($\sim 30\text{ cm}^{-1}$). Thus, we determined each peak energy using least-squares fitting. Our fitting reproduces the experimental results well, as shown in Fig. 2(b). We evaluate interlayer interactions using the numerical analysis¹⁹ because the peak energies in Fig. 2(b) provide information on the band structure and splitting in a-CVD bilayer graphene.

We adopt the modified Slonczewski-Weiss-McClure (SWM) model to calculate the electronic band structure.¹⁹ The SWM model is based on TB theory and has been used widely for graphites.^{20–22} Malard *et al.* modified the SWM model for $2D$ phonon peak shape analysis in exfoliated bilayer graphene.¹⁹ According to their model, the energy dispersions of upper (lower) valence and conduction bands $E_{\pi_{1(2)}}$, $E_{\pi_{2(1)}^*}$ are given by

$$E_{\pi_{1,2}} = \frac{1}{2}(\pm\gamma_1 \pm v_3\sigma - \xi_{\mp}), \quad (1)$$

$$E_{\pi_{2,1}^*} = \frac{1}{2}(\pm\gamma_1 \pm v_3\sigma + \xi_{\mp}), \quad (2)$$

$$\xi_{\pm} = \sqrt{(\gamma_1 - v_3\sigma)^2 + 4(1 \pm v_4)^2\sigma^2},$$

$$\sigma = \gamma_0 \left[2\cos\left(\frac{2\pi}{3} - \frac{\sqrt{3}ka}{2}\right) + 1 \right],$$

$$v_n = \frac{\gamma_n}{\gamma_0} (n = 1, 3, 4).$$

Here, k is the wave number measured from the K point, $a = 0.142\text{ nm}$ is the in-plane nearest-neighbor carbon distance, and γ_0 , γ_1 , γ_3 , and γ_4 are overlap and transfer integrals calculated for nearest-neighbor carbon atoms (Fig. 3(a)). The excitation photon energy E_{ex} determines the momentum k_i of an excited electron

$$E_{\text{ex}} = E_{\pi_i^*}(k_i) - E_{\pi_i}(k_i). \quad (3)$$

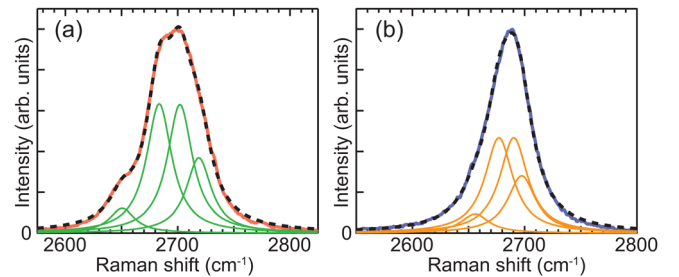


FIG. 2. (Color online) Observed Raman spectra (thick solid curves), four Lorentzian components (thin solid curves), and fitting curves (dotted curves) of the $2D$ phonon band in (a) the exfoliated and (b) the a-CVD bilayer graphene at 532-nm excitation.

The excited electron is then resonantly scattered from near the K point to near K' points by emission of an iTO phonon with energy E_p^{ij} given by

$$E_p^{ij}(k_i + k'_j) = E_{\pi_i^*}(k_i) - E_{\pi_j^*}(k'_j) (i, j = 1, 2). \quad (4)$$

Each E_p^{ij} corresponds to the energy of half a phonon obtained by spectral fitting. The iTO phonon dispersion near the K point is defined as $A + B(k_i + k'_j)$, and we assume that the values of A and B are similar to those from a previous study.¹⁹ The γ_0 value is the same as that of graphite because an in-plane interaction should be almost the same as that in graphite. From each component of the fitted 2D phonon peak, the values of γ_1 , γ_3 , and γ_4 can be determined. The γ values of a-CVD graphene are obtained by numerical analysis: $\gamma_1 = 0.15$, $\gamma_3 = 0.12$, and $\gamma_4 = 0.10$. Note that the estimated values of exfoliated bilayer graphene are identical to those reported previously: $\gamma_1 = 0.3$, $\gamma_3 = 0.1$, and $\gamma_4 = 0.12$.¹⁹

The electronic band structures of exfoliated and a-CVD bilayer graphene near the K point were calculated using the modified SWM model (Figs. 3(b) and 3(c)). It is clear that the band splitting Δ of a-CVD bilayer graphene is smaller than that of exfoliated bilayer graphene. We predict the possible stacking orders of our a-CVD graphene sample by obtaining the γ parameter difference between the a-CVD and exfoliated bilayer graphene samples. Two physically reasonable non-AB stacking orders are predicted, translated, and twisted orders (Fig. 3(d)), and they deviate from the AB stacking of exfoliated graphene. The SWM model is suitable for AB stacking; however, the band structure of twisted graphene calculated by first-principle calculations^{23–25} is in qualitative agreement with our calculated results. This suggests that our analysis is reasonable. Finally, we comment on the band-splitting Δ determined primarily by γ_1 . The magnitude of the band gap is determined by an applied electric field and the γ_1 value.⁹ The γ_1 value of a-CVD bilayer gra-

phene is half that of exfoliated bilayer graphene, suggesting that band-gap opening due to a lateral electric field can be achieved in a-CVD bilayer graphene. Thus, a-CVD bilayer graphene has potential applications in graphene-based electronic devices.

In conclusion, we studied micro-Raman spectra of graphene synthesized by a-CVD. The number of layers in a-CVD graphene was determined by the spectrally integrated intensity ratio of G to $2D$ phonon peaks, similar to that of exfoliated graphene. From the detailed analysis of the $2D$ phonon line shape, the band structure of a-CVD bilayer graphene was calculated by the modified SWM model. The strength of the interlayer interactions in a-CVD bilayer graphene was less than half that in exfoliated bilayer graphene.

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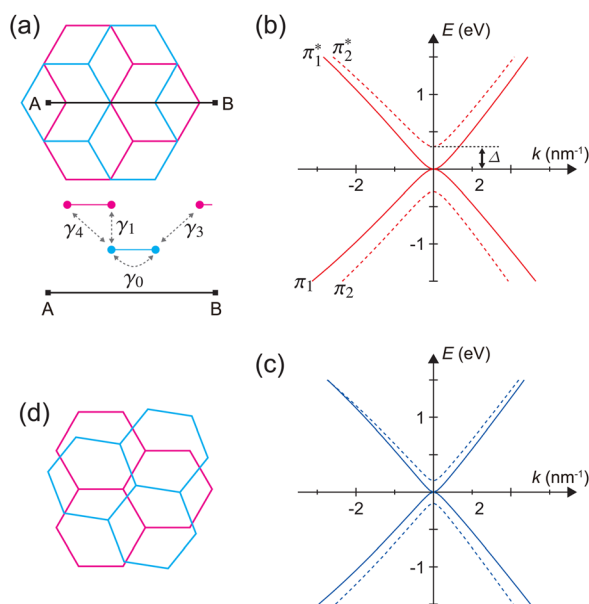


FIG. 3. (Color online) (a) Modified SWM model based on the TB theory. Calculated electronic band structures in (b) exfoliated and (c) a-CVD bilayer graphene near the K point. (d) Possible stacking order of a-CVD bilayer graphene based on the calculated band structure.

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