<table>
<thead>
<tr>
<th>Title</th>
<th>Raman study on the interlayer interactions and the band structure of bilayer graphene synthesized by alcohol chemical vapor deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Okano, Makoto; Matsunaga, Ryusuke; Matsuda, Kazunari; Masubuchi, Satoru; Machida, Tomoki; Kanemitsu, Yoshihiko</td>
</tr>
<tr>
<td>Citation</td>
<td>Applied Physics Letters (2011), 99(15)</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2011-10-13</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/159451">http://hdl.handle.net/2433/159451</a></td>
</tr>
<tr>
<td>Right</td>
<td>© 2011 American Institute of Physics</td>
</tr>
<tr>
<td>Type</td>
<td>Journal Article</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
<tr>
<td>Source</td>
<td>Kyoto University</td>
</tr>
</tbody>
</table>
Raman study on the interlayer interactions and the band structure of bilayer graphene synthesized by alcohol chemical vapor deposition

Makoto Okano, Ryusuke Matsunaga, Kazunari Matsuda, Satoru Masubuchi, Tomoki Machida et al.

Citation: Appl. Phys. Lett. 99, 151916 (2011); doi: 10.1063/1.3651325

View online: http://dx.doi.org/10.1063/1.3651325

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v99/i15

Published by the American Institute of Physics.

Related Articles

A Raman spectroscopic investigation of graphite oxide derived graphene
AIP Advances 2, 032183 (2012)

Micro-Raman spectroscopy of graphene grown on stepped 4H-SiC (0001) surface

Infrared absorbance of silicene and germanene

Direct observation of inner and outer G' band double-resonance Raman scattering in free standing graphene

High photocurrent from planar strips of vertical and horizontal aligned multi wall carbon nanotubes

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: http://apl.aip.org/authors
Raman study on the interlayer interactions and the band structure of bilayer graphene synthesized by alcohol chemical vapor deposition

Makoto Okano,1 Ryusuke Matsunaga1,a) Kazunari Matsuda,1,b) Satoru Masubuchi,2
Tomoki Machida,2 and Yoshihiko Kanemitsu1,3,c)
1Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
2Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan
3Photonics and Electronics Science and Engineering Center, Kyoto University, Kyoto 615-8510, Japan

(Received 8 July 2011; accepted 23 September 2011; published online 13 October 2011)

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 2D 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 2D 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 scm. 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 scm 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 washed away using HNO3 solution at 80°C. 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 λ_exc = 532 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 ~10 μm, which afforded a micro-Raman spatial resolution of ~1 μm 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.
Present address: Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan.
b)Electronic mail: kanemitsu@scl.kyoto-u.ac.jp.

© 2011 American Institute of Physics
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 week, 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 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 FWHMs 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 (~30 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 analysis\(^19\) 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 \(E_{\pi(c)}\), \(E_{\pi(c)}^{\pm}\) are given by

\[
E_{\pi(c)} = \frac{1}{2}(\pm \gamma_1 \pm v_3 \sigma - \xi_\pm),
\]

\[
E_{\pi(c)}^{\pm} = \frac{1}{2}(\pm \gamma_1 \pm v_3 \sigma + \xi_\pm),
\]

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

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

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

Here, \(k\) is the wave number measured from the K point, \(a = 0.142\) nm is the in-plane nearest-neighbor carbon distance, and \(\gamma_0, \gamma_1, \gamma_3, \gamma_4\) are overlap and transfer integrals calculated for nearest-neighbor carbon atoms (Fig. 3(a)). The excitation photon energy \(E_{\text{ex}}\) determines the momentum \(k_e\) of an excited electron

\[
E_{\text{ex}} = E_{\pi(c)}^\pm(k_e) - E_{\pi(c)}(k_i).
\]
The excited electron is then resonantly scattered from near the K point to near K’ points by emission of an iTO phonon with energy $E_p^c$ given by

$$E_p^c(k_i + k_f) = E_{\pi^c}(k_i) - E_{\pi^c}(k_f)(i, j = 1, 2). \quad (4)$$

Each $E_p^c$ corresponds to the energy of half a phonon obtained by spectral fitting. The iTO phonon dispersion near the K point is defined as $A + B(k_i + k_f)$, and we assume that the values of A and B are similar to those from a previous study.$^{19}$ The $\gamma_0$ 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 $\gamma_1$, $\gamma_3$, and $\gamma_4$ can be determined.

The magnitudes of the band gap is determined by an applied electric field and the $\pi^c$ parameter difference between the a-CVD and exfoliated bilayer graphene. 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.

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.

Part of the study at Kyoto University was supported by the MEXT Project of Integrated Research on Chemical Synthesis and The Sumitomo Electric Industries Group CSR Foundation.