

## The effect of substrates on the Raman spectrum of graphene: Graphene-on-sapphire and graphene-on-glass

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(Received 19 August 2007; accepted 12 October 2007; published online 13 November 2007)

The authors investigated the influence of substrates on Raman scattering spectrum from graphene. The room-temperature Raman signatures from graphene layers on GaAs, sapphire, and glass substrates were compared with those from graphene on the standard Si/SiO<sub>2</sub> (300 nm) substrate, which served as a reference. It was found that while *G* peak of graphene on Si/SiO<sub>2</sub> and GaAs is positioned at 1580 cm<sup>-1</sup>, it is downshifted by ~5 cm<sup>-1</sup> for graphene on sapphire and, in some cases, splits into doublets for graphene on glass with the central frequency around 1580 cm<sup>-1</sup>. The obtained results are important for nanometrology of graphene and graphene-based devices. © 2007 American Institute of Physics. [DOI: 10.1063/1.2805024]

Graphene has recently attracted major attention from the physics and device research communities.<sup>1-6</sup> In addition to its unusual physical properties, it also shows promise as a material for the electronic applications. Geim and Novoselov<sup>7</sup> suggested that a band gap of  $\Delta E_G \sim 0.3$  eV can be induced in the bilayer graphene (BLG) and engineered in the single-layer graphene (SLG) by the spatial confinement or lateral superlattice-type potential. The extremely high carrier mobility of  $\sim 15\,000$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at room temperature<sup>1-3</sup> represents an advantage over Si, making graphene a candidate for applications in the circuits beyond the conventional complementary metal-oxide-semiconductor technology.

Raman spectroscopy has been successfully utilized as a convenient technique for identifying and counting graphene layers.<sup>8-13</sup> Specifically, it was shown<sup>8</sup> that the evolution of the two dimensional (2D) band Raman signatures with the addition of each extra layer of graphene can be used to accurately count the number of layers. It was also found<sup>9</sup> that the position of *G* peak upshifts linearly relative to that of graphite with increasing  $1/n$ . The overall shift, as  $n$  changes from 19 to a single layer, is  $\sim 5-6$  cm<sup>-1</sup>. We have recently reported the temperature dependence of the *G* peak and 2D band in graphene on Si/SiO<sub>2</sub> substrates.<sup>10,11</sup> The extracted values of the temperature coefficients  $\chi_G$  for the *G* peak in the spectra of SLG and BLG are  $-(1.6 \pm 0.2) \times 10^{-2}$  and  $-(1.5 \pm 0.06) \times 10^{-2}$  cm<sup>-1</sup>/K, respectively.<sup>11</sup>

Most, if not all, Raman spectroscopy studies of graphene reported to date were limited to either graphene layers on Si/SiO<sub>2</sub> substrates<sup>8-13</sup> with a very carefully selected thickness of the SiO<sub>2</sub> layer or to tiny dispersed flat carbon clusters, which were also referred to as graphene.<sup>14,15</sup> The reason for choosing a specific substrate for the mechanically exfoliated graphene is the observation that it becomes visible in an

optical microscope when placed on top of Si wafer with 300-nm-thick oxide layer.<sup>1,2</sup> Even a small deviation (by ~5%) in the oxide thickness from 300 nm can make SLG invisible. Thus, it is easier to carry out Raman spectroscopy of graphene layers on the standard Si/SiO<sub>2</sub> (300 nm) substrates because one can pinpoint the exact location of a graphene sample (which typically has the lateral dimensions of a few micrometers) and carry out an initial identification of the number of layers under the optical microscope.

Future studies of graphene's unique properties and its application as an electronic material call for graphene integration with a variety of different materials and substrates. However, presently very little is known about the visibility or property of graphene on substrates other than Si/SiO<sub>2</sub>, and there is no confirmed experimental tool for determining the number of layers in few-layer graphites on these substrates. Thus, it is important to expand Raman spectroscopy as a nanometrology tool for graphene and graphene-based devices to various substrates. Another motivation for the study of the substrate influence on graphene Raman spectrum is a fundamental question of the role played by the graphene-substrate interface. In this sense, the measurements of Raman spectra from graphene on different substrates can shed light on the strength of the graphene-substrate coupling for different phonon modes.

In this letter, we report the room-temperature spectroscopic Raman microscopy of a single-layer and a few-layer graphene (FLG) deposited on different substrates. SLG and FLG were obtained by micromechanical cleavage of bulk graphite using the process outline in Refs. 1 and 2. An identical procedure was used to place graphene layers on a reference Si/SiO<sub>2</sub> (300 nm) substrate and on a set of distinctively different substrates, which included *n*-type (100) GaAs wafer, *A*-plane (11-20) sapphire (Al<sub>2</sub>O<sub>3</sub>), and glass substrates. The number of layers was determined from the visual inspection of graphene on Si/SiO<sub>2</sub> (300 nm), atomic-force microscopy (AFM), and analysis of the 2D band features

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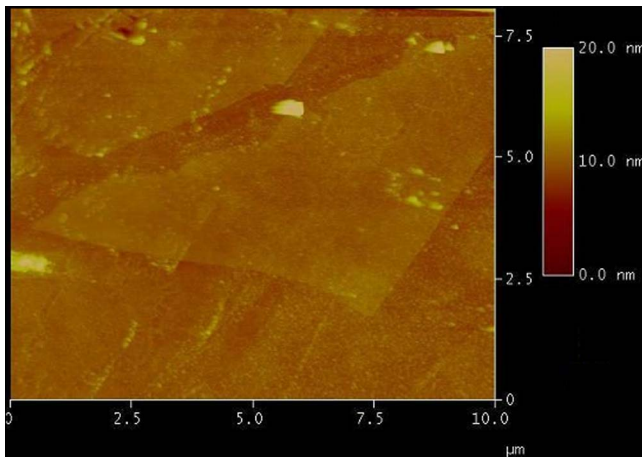


FIG. 1. (Color online) Atomic-force microscopy image of graphene layers on a glass substrate.

using the approach outlined in Ref. 8. For GaAs substrate, we only succeeded in transferring five-layer graphene as confirmed by AFM and Raman spectrum of the 2D band. The AFM inspection of graphene on sapphire and glass substrates revealed spots with thickness of  $<2$  nm, indicating the presence of less than four layers. Figure 1 shows AFM image of graphene on a glass substrate. The following Raman analysis allowed us to conclude that the transferred graphene samples on sapphire and glass are most likely SLG.

In order to provide additional verification for the number of layers and graphene quality, we carried out transport studies for some of the samples on the Si/SiO<sub>2</sub> substrate by attaching the electrodes using the standard nanofabrication techniques, which we described elsewhere.<sup>6,10</sup> The electrical measurements were performed at low temperature in a sorption pumped <sup>3</sup>He refrigerator. The extracted high values of the carrier mobility ( $\sim 8000$ – $15\,000$  cm<sup>2</sup>/V s) and the anomalous “half-integer” plateau, which is a unique signature of the band structure of graphene, attested to the high quality of our samples.

The Raman microscopy was carried out using the Renishaw instrument under 488 nm excitation at low power level to avoid the laser heating effects.<sup>16</sup> A Leica optical microscope with a 50 $\times$  objective was used to collect the backscattered light from the graphene samples. Since it was important to separate the effect of the substrate from spatial variations in the graphene properties, we took 10–20 spectra in different locations for each of the examined samples. Figure 2(a) presents a close-up of 2D bands for graphene as the number of layers increases from one to five. The observed features are consistent with the previously reported data.<sup>8,10,11</sup> After taking Raman spectra from graphene layers on the standard substrate, we investigated graphene placed on GaAs, sapphire, and glass substrates. The adherence of SLG and FLG to different substrates was similar. Since all the measurements were conducted at RT under small excitation power, the role of the coefficient of thermal expansion on the results has been eliminated. To avoid the fabrication damage and charge transfer, no contacts were fabricated on the samples subjected to detail Raman study.

Figure 2(b) shows a typical spectrum of FLG on *n*-type GaAs substrate. Two pronounced features in the spectrum are the *G* peak at 1580 cm<sup>-1</sup> and the 2D band at  $\sim 2736$  cm<sup>-1</sup>. The decomposition and analysis of the 2D band features con-

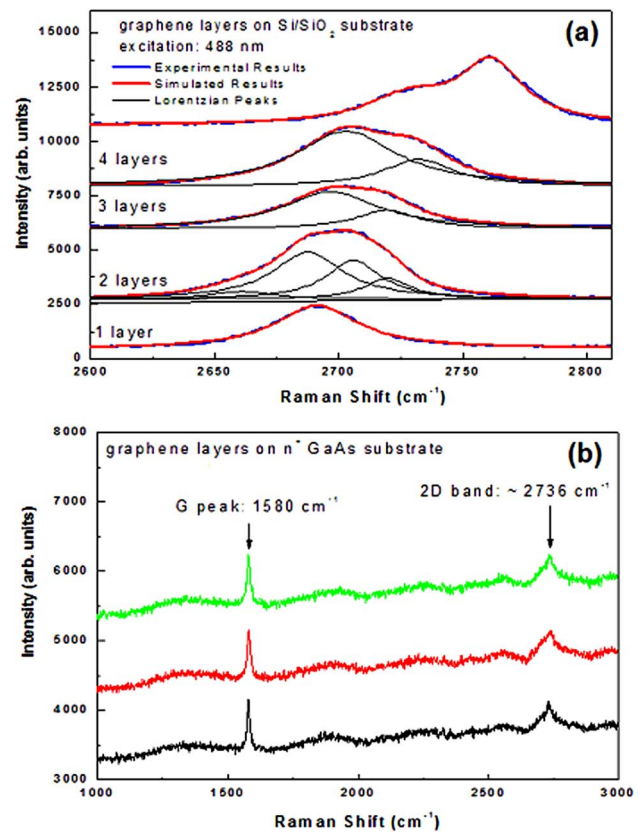


FIG. 2. (Color online) (a) Raman spectrum of 2D band of graphene on Si/SiO<sub>2</sub> substrates as a number of layers changes from one to five. The analysis of the 2D band was used to verify the number of graphene layers. (b) Raman spectrum of graphene layers on GaAs substrate showing *G* peak and 2D band. Three spectra are taken from different locations on the sample to demonstrate reproducibility and uniformity.

firm that the number of layers is five. The measured spectrum features, e.g., *G*-peak position and shape and 2D band shape, are very similar to those observed for FLG on the standard Si/SiO<sub>2</sub> (300 nm) substrate. Three curves in Fig. 2(b) correspond to the spectra taken from three different locations. Since there are virtually no variations in the spectra, one can conclude that the sample is uniform and the measured results are reproducible. *G* peak recorded for graphene on GaAs substrate is essentially in the same location and of the same shape as the one measured by us<sup>10,11</sup> and by Ferrari *et al.*<sup>8</sup> and Gupta *et al.*<sup>9</sup> for graphene layers on Si/SiO<sub>2</sub> (300 nm).

The spectra measured for graphene on the glass and sapphire substrates were much noisier than those for graphene on Si/SiO<sub>2</sub> (300 nm) or GaAs substrates. Specifically, the spectra from graphene on a glass substrate manifested a large number of peaks attributed to the amorphous nature of the substrate, which resulted in many local vibrational modes. At the same time, it was always possible to identify *G* peak and 2D band. Figures 3(a) and 3(b) present a close-up of *G* peak for a single-layer graphene on sapphire (GOS) and graphene on glass (GOG), respectively. One can see in Fig. 3(a) that *G* peak in GOS spectra is redshifted from its position in the spectra from SLG on a standard substrate by  $\sim 5$  cm<sup>-1</sup>. This shift is observed for all locations; a small spot-to-spot variation in the peak position of about  $\sim 1$  cm<sup>-1</sup> is equal to the spectral resolution of the instrument.

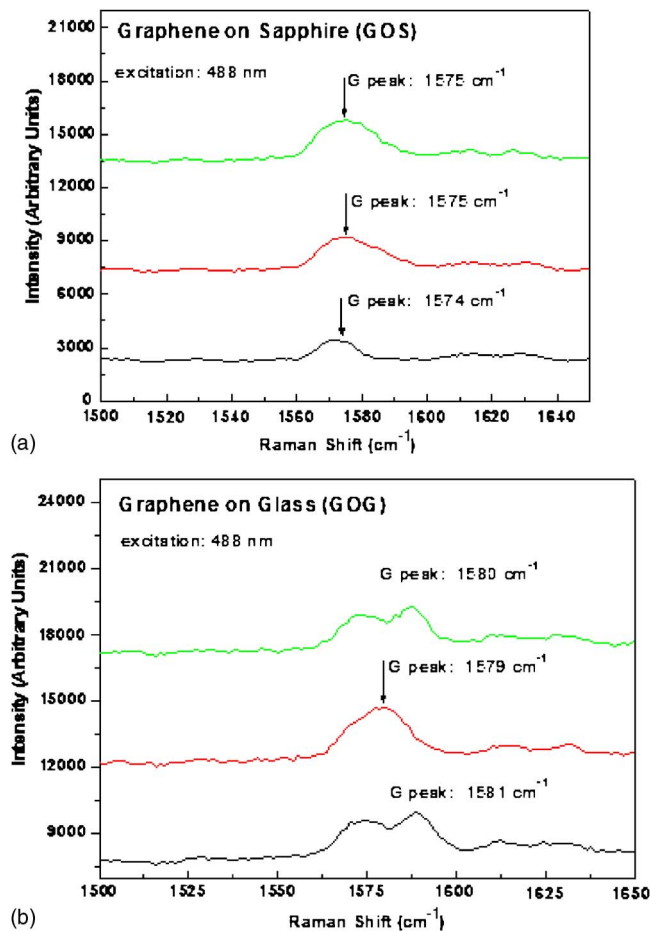


FIG. 3. (Color online) Raman spectra of graphene layers on (a) sapphire and (b) glass substrates showing  $G$ -peak region. Three spectra for each substrate are taken from different locations.

An unusual feature in the spectra from GOG in Fig. 3(b) is a splitting of  $G$  peak into an asymmetric doublet for approximately half of the examined locations. When the  $G$  peak is not split, it is located at  $1579\text{ cm}^{-1}$ , which is consistent with its position in graphene on the standard substrate. In the spectra where  $G$  peak is split, its central frequency is  $\sim 1580\text{ cm}^{-1}$ . Thus, the  $G$ -peak position in GOG spectra is close to the one in SLG spectra on the standard Si/SiO<sub>2</sub> (300 nm) substrate. The  $G$ -peak splitting in Raman spectra from some locations on GOG can be attributed to the presence of the randomly distributed impurities or surface charges. The localized vibrational modes of the impurities can interact with the extended phonon modes of graphene leading to the observed splitting. The  $G$ -peak positions and their full width at half maximum (FWHM) for different substrates are summarized in Table I. One can see that FWHM

TABLE I. Raman  $G$ -peak position for graphene on different substrates.

Substrate	$G$ -peak position (cm <sup>-1</sup> )	$G$ -peak FWHM (cm <sup>-1</sup> )
Si/SiO <sub>2</sub>	1580	15
GaAs	1580	15
Sapphire	1575	20
Glass	1580 <sup>a</sup>	35

<sup>a</sup>This value corresponds to the middle frequency if  $G$  peak is split.

for  $G$  feature from GOG is the largest. The latter is likely related to the amorphous nature of the glass substrate and inhomogeneous properties of graphene layers on a given substrate.

The relatively weak dependence of  $G$  band on the substrate can be explained by that fact that it is made up of the long-wavelength optical phonons of particular symmetry. The  $G$ -band optical phonons in graphene represent the in-plane vibrations since the  $E_{2G}$  symmetry of this band restricts the atomic motion to the plane of the carbon atoms.<sup>17</sup> According to the first-principles calculations, the out-of-plane vibrations in graphene are not coupled to the in-plane motion.<sup>18</sup> The dependence is stronger for graphene on the  $A$ -plane sapphire substrate, where we observed consistent  $\sim 5\text{ cm}^{-1}$  shift of  $G$  mode. The latter can be related to the specifics of the carbon-sapphire binding similar to the phenomenon reported in Ref. 19. Han *et al.*<sup>19</sup> observed the formation of the highly aligned single-wall carbon nanotube (CNT) arrays on  $A$ -plane and  $R$ -plane sapphire substrates with negligible miscut, i.e., without apparent involvement of the step edges. Such spontaneous self-orientation was not observed for other types of the substrates. From their AFM studies, the authors concluded that strong CNT-sapphire substrate interaction plays a major role in the CNT alignment. Similar interaction forces may lead to the  $G$ -mode position change in our GOS samples. Another possibility is a presence of the surfaces charges, which lead to the changes in the graphene lattice parameter with the corresponding peak shift.

A.A.B. acknowledges support from the Focus Center Research Program (FCRP) - Center on Functional Engineered Nano Architectonics (FENA).

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