Raman spectra of graphene exfoliated on insulating crystalline substrates

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Abstract. We have investigated single layer, bilayer and few-layer graphene exfoliated on SiO₂ and on single crystal surfaces of SrTiO₃, Al₂O₃ and TiO₂ using Raman spectroscopy. The typical ‘fingerprint’ 2D peak turns out to be indicative of the number of graphene layers independent of the substrate material. The morphological quality of the graphene is as good as on SiO₂ substrates for all the materials. We find evidence for substrate-induced changes due to doping. With most substrates, hole doping is observed, but with SrTiO₃ we have identified a dielectric substrate with which electron accumulation in graphene can be achieved.

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1. Introduction

The first graphene flakes to be reported were exfoliated on a 300 nm SiO$_2$/Si substrate [1]. As is now well known, this method not only yields single and bilayer graphene of very high quality, but also provides a non-conducting substrate for electrical insulation purposes as well as an extremely easy way of identifying graphene by optical inspection [2]. Therefore, exfoliation is still the method of choice for experiments investigating the transport properties of graphene. However, graphene and its electronic properties are substantially affected by the underlying substrate. For example, it has been pointed out that a bandgap opening in the case of graphene epitaxially grown on SiC might be connected with the substrate [3, 4].

The influence of the substrate has been investigated on free-standing films [5], and some groups have tried to use other materials than SiO$_2$ [6–11]. Except for the functionalized SiO$_2$ surfaces used by Wang et al, none of the insulating substrates yielded $n$-doped graphene. We recently showed that the optical contrast of graphene on crystalline insulating substrates, e.g. SrTiO$_3$, is less than that on SiO$_2$, but is still sufficient for visual inspection [12]. Therefore, these graphene flakes should also be accessible by Raman spectroscopy. In this paper, we have applied Raman spectroscopy to identify graphene on non-SiO$_2$ substrates and to study the charge carrier accumulation induced by those substrates by exploiting the following facts.

- The $D$ mode at $\approx 1350$ cm$^{-1}$ is activated by defects, and its intensity is a measure of short-range disorder [13–18].
- The Raman shift $\tilde{\nu}_G$ and line width of the $G$ peak at $\approx 1580$ cm$^{-1}$ vary with the doping level of graphene [19].
- The shape of the 2$D$ phonon mode at $\approx 2700$ cm$^{-1}$ reflects changes in the electron bands and electron–phonon interactions. The 2$D$ mode has been shown to be indicative of single and bilayer graphene, respectively [20]. Its position $\tilde{\nu}_{2D}$ can be used to distinguish between electron doping and hole doping [21], although the 2$D$ shift is not very sensitive to the doping level [22]. The intensity ratio of the 2$D$ peak and $G$ mode depends on charge carrier concentration [23] and on polarization [24].

2. Experimental

We prepared several graphene crystallites on 90 nm SiO$_2$/Si substrates (Fraunhofer Institute IMS, Duisburg), as well as on three different crystalline insulators (SrTiO$_3$(100), TiO$_2$(100), Al$_2$O$_3$(1102); Crystec, Berlin), by mechanical exfoliation with adhesive tape from high-quality natural graphite flakes (Graphenium, NGS Naturgraphit, Leinburg). The SiO$_2$/Si substrate was cleaned by sonification in isopropanol; all other substrates were polished to optical quality by the supplier and were used without further cleaning. An optical microscope was used to identify regions with graphene flakes, and atomic force microscopy (AFM Veeco DI 3100, tapping mode) and Raman spectroscopy were used for the identification of single-layer graphene (SLG) and bilayer graphene (BLG). We took care that all SLG and BLG crystallites were isolated flakes in order to minimize self-doping from thicker graphene layers [25]. The following samples were studied; the number of individual samples are given in parentheses: SLG and BLG on SiO$_2$ (23, 11), on SrTiO$_3$ (12, 4), on Al$_2$O$_3$ (5, 3) and on TiO$_2$ (5, 3).

The samples were measured with a LabRam Micro-Raman spectrometer (Jobin Yvon/Horiba) using non-polarized radiation with a wavelength of 514.5 nm ($E_L = 2.41$ eV)
from an Ar laser, a 100\times objective and a grating of 1800 grooves per mm, yielding a spectral resolution of \( \approx 5 \text{ cm}^{-1} \); the spot size was \( \approx 1 \mu\text{m}^2 \). We avoided excessive heating of the graphene by limiting the laser power to \( P_{\text{max}} = 1 \text{ mW} \). Spectra were taken from all the samples under ambient conditions. As references for background subtraction, we used substrates without graphene. For calibration purpose, a Si single crystal was used. All Raman features were fitted using either a Voigt function for SLG modes or Lorentzians profiles for BLG modes. From these fits we determined the peak width (full-width at half-maximum (FWHM)), the peak positions \( \tilde{\nu}_k \) and the peak intensities \( I \) (calculated as integrated areas), respectively. All spectra were rescaled to achieve better comparability.

3. Results and discussion

3.1. Identification of single-layer graphene and bilayer graphene and their morphology

As an example of the prepared graphene flakes, we show an image obtained by optical microscopy as well as an AFM image of SLG on an SrTiO\(_3\) surface; see figures 1(a) and (b). The overall morphology of the flake resembles that found on SiO\(_2\) substrates. A detailed analysis reveals that the average step height of SLG sheets on all the crystalline substrates investigated here is \( d_c = 3.5 \pm 1.5 \text{ Å} \) and is thus close to the nominal value of 3.35 Å. In addition, it is much smaller than the value found here for SiO\(_2\) substrates of \( d_{\text{SiO}_2} = 8 \pm 2 \text{ Å} \) and these in earlier papers [12, 26]. The reason for this difference is still unknown.

All graphene samples had sufficient optical contrast to be inspected by Raman spectroscopy. Due to the material-dependent lower contrast, the signal-to-noise ratio is not as good as that in the case of SiO\(_2\), but is for SrTiO\(_3\) in particular still sufficient to easily distinguish the signal from SLG, BLG and FLG, respectively. Graphene on either TiO\(_2\) or Al\(_2\)O\(_3\) exhibits a clearly worse optical contrast than graphene on SrTiO\(_3\), making it more difficult to find BLG and SLG flakes.

In figure 2, the Raman 2D bands of all three crystalline substrates, as well as SiO\(_2\) with exfoliated graphene, are shown and the corresponding values can be found in table 1. Figure 2 clearly reveals that the overall characteristics of the electron and phonon dispersion do not change and that Raman spectra can be used as an unambiguous method for the identification of SLG and BLG independent of the substrate.

The rather large standard deviation in table 1 is due to the significantly large variation between different flakes. In the case of preparation and measurement under ambient conditions, hole doping from adsorbed water or other species can be significant (see section 3.3). Each Raman spectrum represents only the local properties, which might vary due to inhomogeneously distributed impurities [22]. Another reason for the variation could be local strain caused by the substrate morphology [27].

To investigate if the various substrates induce any structural changes in the graphene, we recorded spectra in the region of the 2D peak at around 1350 cm\(^{-1}\). This mode is solely activated by the presence of defects. In defect-free graphene edges act as defects, yielding a 2D peak but no change in the G and 2D peaks, respectively [17, 18]. In figure 3, we show Raman spectra taken from SLG, BLG, FLG and graphite on the four substrates. As can be seen from the figure we detect no peaks in the 2D band, indicating the high structural quality of the exfoliated graphene on those substrates.
3.2. Electronic bandstructure

Both the $D$ and the $2D$ mode involve two scattering events. In the case of the $2D$ mode both processes are inelastic—two iTO phonons are required [28]. In SLG there is only one main (either double or triple resonance, respectively) process contributing to the $2D$ band. In the case of BLG the situation is more complicated. Both the electronic bands and the phonon branches split into two components. Therefore, both could be the reason for the four components contributing to the $2D$ peak (see figure 4). Ferrari et al argued that the splitting of the phonon branches is much smaller than the experimentally observed splitting of the peaks and therefore must be due to electronic effects. The two phonons in the highest optical branch are almost degenerate and they couple all electron bands among each other. The four components correspond to the four different $q$-momenta associated with the possible transitions between the split bands of the electron (and hole) dispersion curves along $\Gamma-K-M-K'-\Gamma$ [20].
Figure 2. Raman 2D peaks for SLG (black), BLG (red), FLG (blue) and graphite (green) prepared on different substrates. The curves are offset for clarity.

Table 1. Experimentally determined Raman shifts $\tilde{\nu}$ of the 2D peak in cm$^{-1}$ for SLG and BLG prepared on four different substrates. The Voigt function is used to fit the SLG peak, and the respective peak positions of the Lorentzian fits for the four components $\tilde{\nu}_k$ for the 2D peak of the BLG.

| Substrate  | $\tilde{\nu}_{2D}$ | $\tilde{\nu}_{1B}$ | $\tilde{\nu}_{1A}$ | $\tilde{\nu}_{2A}$ | $\tilde{\nu}_{2B}$ |
|------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| SiO$_2$    | 2670 ± 4            | 2649 ± 5            | 2684 ± 5            | 2703 ± 4            | 2718 ± 5            |
| Al$_2$O$_3$| 2682 ± 1            | 2651 ± 3            | 2685 ± 4            | 2703 ± 4            | 2718 ± 3            |
| SrTiO$_3$  | 2674 ± 5            | 2646 ± 1            | 2685 ± 1            | 2703 ± 2            | 2716 ± 2            |
| TiO$_2$    | 2687 ± 1            | 2656 ± 1            | 2691 ± 4            | 2708 ± 6            | 2723 ± 4            |

The single peak for SLG (solid lines in figure 4) and the four different peaks (green lines in figure 4) for BLG can be clearly seen in the Raman spectra of graphene on all four substrates studied here. In addition, we observe changes in the shift of the SLG 2D peak corresponding to the underlying substrate. This indicates a possible doping of the graphene from the substrate (see section 3.3). A detailed analysis of the BLG splitting reveals that the values of all four components for BLG on SiO$_2$ are in good agreement with previous studies [20]. The corresponding values for the other substrates show no significant deviation from the values found for SiO$_2$; see table 2. That is, for all substrates the Raman transitions are dominated by electronic effects.

3.3. Substrate doping

One of the possible effects of the substrate on graphene is the accumulation of charge carriers due to different work functions. When graphene is exfoliated on a substrate with a higher work
Figure 3. Comparison of the Raman spectra in the range encompassing the $D$ mode as well as the $G$ mode measured from SLG (black), BLG (red), FLG (blue) and graphite (green) exfoliated on four different substrates. The $D$ mode is absent in all substrates. The curves are offset for clarity.

function, electrons will be transferred to the substrate. A substrate with a lower work function will, vice versa, lead to an accumulation of electrons in the graphene. If this doping effect is induced or can even be controlled by the substrate, this will have important implications for possible applications of graphene, e.g. in electrical devices. The work function of graphene can be directly determined by Kelvin probe force microscopy [29, 30]. The charge accumulation can be monitored with Raman spectroscopy as it shifts the Fermi level away from the neutrality point. This is reflected in the $G$ peak position and its FWHM. It has been shown that the line width of the $G$ peak decreases at first and then saturates for both electron and hole accumulation, while the peak position shifts to higher wave numbers with increasing charge accumulation [19]. We therefore investigated the position and FWHM of the $G$ mode for SLG on different substrates. From figure 5 a clear trend can be observed. With respect to graphene/SiO$_2$, the FWHM decreases and the wave number increases for all other substrates. Following the line of reasoning of Wang et al [11], we used the non-adiabatic approach presented in [31, 32] to fit our data and find similar agreement as in the case of functionalized substrates. From this we conclude that the carrier concentration in graphene is affected by the substrates investigated here.

Das et al [21, 33] performed a detailed analysis of Raman spectra as a function of injected charges. They utilized the variation in gating voltage in a graphene transistor to control the carrier type as well as their density. Apart from the above-mentioned changes in the position and FWHM of the $G$ mode, it was shown that the intensity ratio $I_{2D}/I_G$ and the position of the $2D$ mode are affected by injection of charge carriers, too. Whereas the $G$ mode shifts to higher wave numbers and the intensity ratio $I_{2D}/I_G$ decreases for both electron and hole doping, the $2D$ mode reacts differently to electron (lower) or hole (higher wave number than
Figure 4. Measured (symbols) and fitted (solid lines) Raman 2D peaks for SLG (left) and BLG (right) prepared on different substrates. The green solid lines represent the four components of the fit.

Table 2. Relative splitting of the 2D components in BLG in cm\(^{-1}\) with respect to the average Raman shift of the two main components \(\tilde{\nu}_{1A}^{BLG}\) and \(\tilde{\nu}_{2A}^{BLG}\).

|          | \(q_{1B}\) | \(q_{1A}\) | \(q_{2A}\) | \(q_{2B}\) |
|----------|------------|------------|------------|------------|
| BLG/SiO\(_2\) | -44        | -10        | +10        | +25        |
| BLG/SiO\(_2\) | -(44 \(\pm\) 1) | -(9 \(\pm\) 0) | +(9 \(\pm\) 0) | +(24 \(\pm\) 0) |
| BLG/Al\(_2\)O\(_3\) | -(-43 \(\pm\) 2) | -(9 \(\pm\) 0) | +(9 \(\pm\) 0) | +(24 \(\pm\) 1) |
| BLG/SrTiO\(_3\) | -(48 \(\pm\) 3) | -(9 \(\pm\) 1) | +(9 \(\pm\) 1) | +(23 \(\pm\) 1) |
| BLG/TiO\(_2\) | -(-44 \(\pm\) 6) | -(9 \(\pm\) 1) | +(9 \(\pm\) 1) | +(24 \(\pm\) 2) |

at the neutrality point) accumulation. Currently, we have no way of gating our samples; we therefore compare our data with the results of [33, 34] to determine the carrier type and density.

From our data in figure 5, one can see that the \(G\) mode of graphene/SiO\(_2\) samples has the largest FWHM of up to \(\approx 14\) cm\(^{-1}\). This value agrees well with the reported value for undoped graphene on SiO\(_2\) [33]. We therefore used all of our graphene/SiO\(_2\) samples that exhibited an FWHM of \(\geq 13.5\) cm\(^{-1}\) and determined the average position of the 2D peak from these samples. This value of \(\tilde{\nu}_{2D} = 2672.1 \pm 2.8\) cm\(^{-1}\) is used as a reference position for an undoped graphene sheet.

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To determine the type of charge carrier, we plotted the position of the 2D peak as a function of the G peak for all samples investigated here. As one can see from figure 6, the data points from graphene/SiO$_2$, graphene/TiO$_2$ and graphene/Al$_2$O$_3$ follow an upward trend (dashed line). In the case of graphene/SrTiO$_3$ we find significantly shifted G peak positions in comparison to graphene/SiO$_2$ samples with the same 2D position. As was shown in [34], the upshift of the 2D as well as the G peak beyond 1580 cm$^{-1}$ indicates $p$-type doping, while different G peak positions are a clear sign of $n$-doping. From this we conclude that in the case of Al$_2$O$_3$ and TiO$_2$ an accumulation of holes always occurs, whereas for SrTiO$_3$ substrates the graphene sheets are doped with electrons. The shifts are, of course, limited in comparison to [34], as highly doped samples are not available without gating. Kelvin probe data from our samples reveal Fermi level shifts of $E_F = 160$ meV before outgassing ($|\text{CPD}_{\text{FLG}} - \text{CPD}_{\text{SLG}}|$), see figure 7). This corresponds to a carrier density of $n_e = \frac{1}{\pi} \left( \frac{E_F}{h v_F} \right)^2 \simeq 2 \times 10^{12}$ cm$^{-2}$ if we assume $v_F = 1 \times 10^6$ m s$^{-1}$ for the Fermi velocity. If we compare the ratio $I_{2D}/I_G$ and the FWHM of the G mode [33], we will find carrier densities of up to $n \approx 5 \times 10^{12}$ cm$^{-2}$ (see table 3) on SrTiO$_3$, substrates. However, one should keep in mind that these ratios depend not only on the substrate, but also on the exact experimental conditions. Therefore, these numbers should be treated with caution.

It is surprising at first that electron accumulation is not always observed. SrTiO$_3$ ($\Phi_{\text{SrTiO}_3} = 3.98$ eV [30]), as well as TiO$_2$ ($\Phi_{\text{TiO}_2} = 4.1$ [35]), has lower work functions than SLG, and in a very simplified picture this should lead to electron transfer into the graphene. Here, we observe only electron doping in the case of SrTiO$_3$. The reason for this might be connected with contamination present under ambient conditions. It is known that water acts as an electron acceptor and would thus lead to hole doping [36–38]. This effect might be strong enough to cancel or even over-compensate the electron doping from the substrate. In the case of SrTiO$_3$, the
**Figure 6.** The position of the 2D peak as a function of the position of the G peak for all samples. The dashed line serves as a guide to the eye. The upward trend is an indication of $p$-type doping, while the large differences in the G peak position of graphene/SrTiO$_3$ compared to that of graphene/SiO$_2$ indicate that there is electron accumulation.

**Figure 7.** Topography and Kelvin probe data from graphene/SrTiO$_3$ recorded under UHV conditions (base pressure $p \leq 3 \times 10^{-10}$ mbar). The left panel shows the data that were obtained directly after transfer into the system, while the right panel shows the data that were recorded a month later. With respect to the graphite (marked FLG), the CPD of the SLG has increased by 68 mV after outgassing.

existence of SrO terminated patches with an extremely low work function ($\Phi_{\text{SRO}} = 3.3 \text{ eV}$ [39]) might be responsible for a sufficiently strong electron doping that cannot be cancelled out by doping due to adsorbates. In TiO$_2$, such surface terminations with a lower work function do not exist.
Table 3. Experimentally determined peak positions $\tilde{\nu}_G$ and FWHM of the $G$ peak in cm$^{-1}$ and intensity ratios $I_{2D}/I_G$ (integrated area) for graphene prepared on four different substrates. $n_k$ are the charge carrier densities obtained from a comparison of the $n_k$ equivalent to the FWHM of $G$ and that equivalent to $I_{2D}/I_G$ values taken from [33].

| Substrate | $\tilde{\nu}_G^{SLG}$ (cm$^{-1}$) | FWHM$^{SLG}$ (cm$^{-1}$) | $I_{2D}/I_G$ (10$^{13}$ cm$^{-2}$) | $I_{2D}/I_G$ $n_f$ (10$^{13}$ cm$^{-2}$) |
|-----------|---------------------------------|-------------------------|----------------------------------|----------------------------------|
| SiO$_2$   | 1578 ± 2                        | 14 ± 1                  | 6.1 ± 0.2                         | 6.1 ± 0.2                        |
| Al$_2$O$_3$ | 1583 ± 0                        | 12 ± 1                  | 7.8 ± 0.4                         | 7.8 ± 0.4                        |
| SrTiO$_3$ | 1587 ± 2                        | 8 ± 1                   | 5.4 ± 0.7                         | 5.4 ± 0.7                        |
| TiO$_2$   | 1589 ± 3                        | 10 ± 2                  | 5.9 ± 0.7                         | 5.9 ± 0.7                        |

To investigate the influence of ambient conditions we have introduced one of our SrTiO$_3$ samples into an ultrahigh vacuum (UHV) system and measured the contact potential difference (CPD) via a Kelvin probe force microscope directly after the transfer and a month later. From the data (figure 7) two things can be seen. Firstly, graphene on SrTiO$_3$ is doped with electrons in agreement with our Raman data (for details see [30]). Secondly, after outgassing, the CPD value for the SLG with respect to graphite (FLG) increases by almost 70 mV. An increase in the CPD value corresponds to a lowering of the work function, i.e. an enhanced accumulation of electrons in the SLG. From these data we infer that under ambient conditions adsorbates indeed act as strong electron acceptors, which can diminish (SrTiO$_3$) or even prevent (TiO$_2$) the accumulation of electrons in graphene.

4. Conclusions

Raman spectra reflect the high morphological quality of exfoliated graphene sheets on various crystalline substrates. An unambiguous identification of SLG and BLG independent of the underlying material is possible. The substrate-induced charge carrier accumulation in SLG was investigated, and we found doping effects for graphene prepared on all substrates. In the case of SrTiO$_3$, mechanically exfoliated graphene doped with electrons could be prepared on a crystalline dielectric for the first time. Thus, the charge accumulation in graphene can be influenced by the substrate, as has been suggested e.g. by Jones et al [40], but we also found a strong influence of contamination. To really use substrates to control charge accumulation in graphene impurities must be avoided, which is not possible with the current preparation procedure. Apart from the need to establish improved preparation conditions, e.g. exfoliation under UHV conditions, for a better control of charge transfer it would be interesting to investigate whether under such conditions these substrates can also be used to initiate a band gap opening in exfoliated graphene.

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