Optimising graphene visibility in van der Waals heterostructures

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Abstract
Graphene constitutes one of the key elements in many functional van der Waals heterostructures. However, it has negligible optical visibility due to its monolayer nature. Here we study the visibility of graphene in various van der Waals heterostructures and include the effects of the source spectrum, oblique incidence and the spectral sensitivity of the detector to obtain a realistic model. A visibility experiment is performed at different wavelengths, resulting in a very good agreement with our calculations. This allows us to reliably predict the conditions for better visibility of graphene in van der Waals heterostructures. The framework and the codes provided in this work can be extended to study the visibility of any 2D material within an arbitrary van der Waals heterostructure.

Keywords: visibility, graphene, van der Waal heterostructures

(Some figures may appear in colour only in the online journal)

Introduction

The family of van der Waals materials has now expanded beyond graphene and offers a wide range of material functionalities, such as semiconductors [1, 2], insulators [3–5], superconductors [6, 7] and ferromagnets [8, 9]. In addition, van der Waals heterostructures are fabricated by stacking individual 2D materials to obtain compound materials with novel functionalities [10–12]. However, graphene is often difficult to locate through an optical microscope during or after the heterostructure assembly due to its near-optical transparency. While the visibility of graphene on SiO2/Si substrate has been studied before [13–19], its visibility in various configurations of van der Waals heterostructures has not yet been explored. In this paper, we develop a stepwise, robust formalism to study the visibility of graphene in various heterostructures and include practical considerations such as the details of the source spectrum, oblique incidence which is necessary at high magnifications [15, 18–23], and the spectral sensitivity of the detector. We perform the visibility calculations for graphene–boron nitride (BN), graphene–BN-MoS2, graphene–MoS2–BN and graphene–MoS2 heterostructures on SiO2 substrate and suggest conditions for better visibility. In order to corroborate our theoretical calculations, we experimentally determine the
optical visibility of a graphene-BN-MoS₂ and graphene-MoS₂ heterostructures at different wavelengths. Our methods, codes and table of information can be employed to study the visibility of most 2D van der Waals materials in an arbitrary heterostructure configuration.

**Methods**

For the theoretical calculations, a thin film interference model was assumed where the reflection coefficients were calculated using Snell’s equations. Reflection coefficients \( r_{i,i+1} \) and \( r_{i,p} \) (for \( s \) and \( p \) polarisations, respectively) for the interface between \( i \)-th and \( i+1 \)-th layer (see figure 1(b)) can be written as \([24, 25]\):

\[
\begin{align*}
    r_{i,s} &= \frac{\tilde{n}_i \cos(\theta_i) - \tilde{n}_{i+1} \cos(\theta_{i+1})}{\tilde{n}_i \cos(\theta_i) + \tilde{n}_{i+1} \cos(\theta_{i+1})}, \\
    r_{i,p} &= \frac{\tilde{n}_{i+1} \cos(\theta_i) - \tilde{n}_i \cos(\theta_{i+1})}{\tilde{n}_{i+1} \cos(\theta_i) + \tilde{n}_i \cos(\theta_{i+1})},
\end{align*}
\]

(1)

(2)

where \( \tilde{n}_i \) and \( \tilde{n}_{i+1} \) are the in-plane and out-of-plane polarisation refractive indices, respectively.

After calculating \( r_i \) (for \( s \)- and \( p \)-polarisations), the reflectivity can be obtained from the \( N \)-layer reflection formula, \( R_N \) which is obtained recursively as follows \([26, 27]\):

\[
R_N = R_N e^{i\delta_N} = \frac{r_0 + \bar{R}_{N-1} e^{-i\delta_N}}{1 + r_0 \bar{R}_{N-1} e^{-i\delta_N}},
\]

(3)

where \( \delta_N \) is the total phase acquired after transmission through \( N \) layers, \( r_0 \) is the reflection coefficient of the topmost interface (see figure 1(b)) and is given by \( (1) \) or \( (2) \) depending on the polarisation of incident light, and \( \bar{R}_{N-1} \) is the reflection from \( N-1 \) layers which is computed by applying \( (4) \) to the substrate and using \( r_1 \) and \( \phi_1 \) instead of \( r_0 \) and \( \phi_0 \). This method is repeated for subsequent layers till we reach \( \bar{R}_0 = r_N \) which is the reflection from the interface between the \( N \)-th layer and semi-infinite medium of silicon. The reflected intensity from the entire stack is given by \( I = |\bar{R}_N|^2 \).

Accounting for oblique incidence is especially important when viewing the samples at large magnifications (especially \( 100\times \)) because of the high numerical aperture \((\alpha_{\text{NA}})\) of the objective. To take this into account, we assume that the incident beam has a Gaussian profile \([21]\) and integrate the reflected intensity for both polarisations over angles from 0 to \( \theta_M = a \sin(\alpha_{\text{NA}}) \):

\[
I(\lambda) = \int_0^{\theta_M} I(\theta, \lambda) e^{-\rho^2/2} \sin \theta \, d\theta,
\]

(4)

where \( \rho = \tan \theta \) and \( \tan \theta_M = \tan \theta_{\text{NA}} \) (see figure 1(b)).

In the visibility calculation, the normalisation constants for the Gaussian distribution cancel out eventually. As the incident beam is unpolarised, the reflected intensity is the
average of the reflected intensities due to s and p polarisations.

The visibility (also known as Michelson’s contrast) [28, 29] is defined as:

$$\text{Visibility(in %)} = 100 \times \frac{I_s - I_g}{I_s + I_g}$$  \hspace{1cm} (6)

$I_s$ corresponds to the reflection from the substrate and $I_g$ refers to the reflection from the entire heterostructure. Positive or negative value of visibility corresponds to graphene appearing darker or lighter than the substrate, respectively.

Often the spectrum of the source and the spectral sensitivity of the detector must also be included to obtain a more accurate value of the visibility. For a typical RGB digital camera, if the red, green and blue channel spectral sensitivities are $\omega_d(\lambda)$, $\omega_g(\lambda)$ and $\omega_b(\lambda)$ and the spectrum of the source is $S(\lambda)$, then the reflected intensities picked up by the red, green and blue channels are [20, 30]:

$$I_j = \int_0^{\infty} I(\lambda) \omega_j(\lambda) S(\lambda) \, d\lambda,$$  \hspace{1cm} (7)

where $j = R, G, B$.

By substituting these intensities in the visibility formula (6), one can calculate the visibility for each colour channel. One should also include the spectral dependence of lenses, mirrors, etc for more sensitive applications.

The dependence of graphene’s visibility on wavelength for different angles of incidence is shown in figures 1(c) and (d) for graphene-$\text{SiO}_2$ and graphene-$\text{BN-SiO}_2$ heterostructures, respectively. Although there is a shift in the peak position for both heterostructures, the relative shifts in the height of the peaks are different for both heterostructure configurations. Specifically, comparing between incidence at $60^\circ$ and normal incidence, there is a greater difference in the height of the peaks for graphene-$\text{BN-SiO}_2$ than for graphene-$\text{SiO}_2$. This explains why accounting for oblique incidence is important for complicated heterostructure configurations. The codes employed in this work have been made available on GitHub.

The heterostructures presented in this work were prepared by mechanically exfoliating the individual flakes of graphene, BN and MoS$_2$ on separate SiO$_2$ substrates followed by micro-mechanical transfer technique using a polydimethylsiloxane (PDMS) stamp spin-coated with a transparent sacrificial polymer layer [31–33]. Similarly prepared graphene-based heterostructures have been previously shown to exhibit relatively high mobilities when encapsulated by BN [33, 34] and have also found widespread functionality as ultra-sensitive photodetectors due to their efficient interlayer charge transfer [32, 35].

We have analysed and performed visibility calculations for three heterostructure configurations: graphene-$\text{BN-SiO}_2$ and graphene-$\text{MoS}_2-\text{SiO}_2$, and graphene-$\text{BN-MoS}_2-\text{SiO}_2$. The images were taken using an Olympus UC30 camera mounted on an Olympus BX51 microscope through a 100× objective. The heterostructures were illuminated using standard light emitting diodes (LEDs) of different wavelengths at a constant power of 2 mW and the exposure time (1–2 s) was set so as not to saturate any of the channels but also yield sufficient signal-to-noise ratio. The images were split into three RGB channels and were analysed using ImageJ software. The relative intensities of these channels depend on the particular LED being used. The channel with the maximum signal-to-noise ratio for each LED was used in the calculations. To minimise errors due to uneven illumination, $I_g$ was recorded at a point on the substrate close to the point on graphene where $I_s$ was recorded and then visibility was calculated using (6). This was done multiple times over the whole sample for the same LED and the average visibility is plotted. The spectrum of the LEDs and the spectral sensitivity of the camera (see supplementary information figure S1 available online at stacks.iop.org/NANO/30/395704/mmedia) were incorporated in the calculations using (7). The experiment was performed using standard LEDs rather than the microscope’s incandescent light source since it provides a better control over the choice and range of the source wavelength and also avoids complications that arise from digital image processing of a white-light image (such as white-balance), unique to each camera and its imaging software. The thickness of BN used in the stack was determined to be 11 nm using atomic force microscopy and Raman spectroscopy was used to verify that MoS$_2$ and graphene were monolayers. We used a standard SiO$_2$-$\text{Si}$ substrate with an SiO$_2$ thickness of 285 nm. We have used both the in-plane and out-of-plane refractive indices of graphene [36] and MoS$_2$ [37] and the refractive indices of BN [38] and SiO$_2$ [39] (both of which have zero extinction coefficients) as well as that of Si [40].

**Results and discussion**

Figures 2(a) and (c) show the experimental results along with the theoretical calculations for two-layer graphene-BN and graphene-MoS$_2$ heterostructures with SiO$_2$ as substrate. The respective thicknesses were fixed at the experimentally determined values. To the right of figures 2(a) and (c) are the microscope images of the respective heterostructures illuminated with LEDs of different wavelengths. Although we have performed the visibility experiment using seven LEDs with wavelengths spread over the visible regime, we have shown only selected images in those colour channels with maximum signal-to-noise ratio. $\alpha_{NA}$ obtained from the best fit of the visibilities was $\sim$0.88 which is very close to the value of 0.9 provided by Olympus. We can see very close agreement between theory and experiment, which suggests that our model for computing visibilities is sufficiently accurate. Minor deviations of the experimental values from the theoretical values may be due to the incident beam not being strictly Gaussian in nature. In figures 2(b) and (d), we have presented the results of our visibility calculations for the graphene-BN and graphene-MoS$_2$ heterostructures as a function of varying substrate and underlayer thicknesses. It must be mentioned here that the calculations in figures 2(a) and (c) incorporated the spectrum of the LEDs in order to corroborate the results of the visibility experiment while the calculations in figures 2(b) and (d) have been performed...
assuming a typical $\alpha_{\text{NA}}$ of 0.9 and integrating over the spectrum of an incandescent light source of blackbody temperature 3100 K, the most common light source used in optical microscopes employed for the searching of suitable flakes of van der Waal materials for device fabrication. Although we have assumed the spectral sensitivity of our camera (SONY ICX252AQ CCD image sensor) in our calculations, it does not differ widely across different cameras [41]. Such a model gives us three values of visibility (one for each colour channel). In these figures, we have plotted the maximum of the absolute values of the three visibilities arising from red, green and blue channels. From our experiments, we have arrived at an absolute visibility threshold value of 2.5% above which the graphene would be visible. In this way, the phase space of BN-SiO2 thicknesses in figure 2(b) can be divided into ‘islands of visibility’ (bounded by dashed white lines in the figure), where graphene would be visible if the BN and SiO2 thicknesses lie within such an island. The same has been done in figure 2(d) for graphene-MoS2 heterostructure. In these figures, we see that using lower thicknesses of SiO2 substrate results in higher visibility for graphene in both graphene-BN and graphene-MoS2 heterostructures. Figure 2(b) also indicates that in a graphene-BN heterostructure on SiO2 (with a typical thickness of 300 nm), the visibility of graphene reduces with increasing BN thickness. For BN thicknesses above $\approx 42$ nm, graphene is visible only at low SiO2 thicknesses and in the supplementary information (figure S2), we have shown that a 380 nm double layer of polymethyl methacrylate (PMMA) spin-coated on the heterostructure improves the visibility significantly for thicker BN on 285 nm SiO2.

Figure 3(a) shows the experimental results and theoretical calculations for graphene-BN-MoS2 heterostructure (the right panels show the corresponding optical images under the illumination of various LEDs). We see good agreement between the theory and experiment even in a three-layer heterostructure. The insets in figures 2(a), (c) and 3(a) show that a model that considers only normal incidence is
inadequate in explaining the experimental results and therefore, one must resort to an oblique incidence model to make reliable predictions. Figures 3(b) and (c) show visibility calculations for graphene-BN-MoS$_2$ and graphene-MoS$_2$-BN heterostructures as a function of SiO$_2$ and BN thicknesses and assuming MoS$_2$ to be a monolayer. We observe that this figure looks similar to the graphene-BN graph. This is because of the similarity between the refractive indices of MoS$_2$ and BN especially in the red and green wavelength ranges and because we are only considering monolayer MoS$_2$. Similar to the graphene-BN heterostructure, lower SiO$_2$ thickness is recommended for better visibility of graphene.

Figure 4 shows the maximum absolute visibility for various heterostructure configurations on 285 nm of SiO$_2$ along with the peak wavelengths. It also suggests various thicknesses of van der Waals materials that can be used for viewing graphene on 285 nm SiO$_2$. These values tend to lie in the green wavelengths which our eyes are most sensitive to. This is not a coincidence but a result of choosing SiO$_2$ thickness to be 285 nm. From our calculations, we can conclude that effects of van der Waals materials under graphene are fundamentally no different when compared to a regular dielectric. Although the effect of the substrate dominates over non-metallic van der Waals materials, using an SiO$_2$ substrate of an arbitrary thickness to improve the visibility is often neither desirable nor practical. Instead, our aim in this paper is to provide a general framework and codes to allow the readers to calculate the visibility of any crystal within a heterostructure. In case of poor visibility, the readers may consider choosing an underlayer (say, BN) of appropriate thickness, if the calculations predict that this improves the visibility. From the figure, we also note that graphene-Bi$_2$Se$_3$ has very poor visibility. This is attributed to the high extinction coefficient of Bi$_2$Se$_3$ [42], due to the existence of its metallic surface states. Hence, we expect graphene’s visibility to be adversely affected by metallic single- to few-layers. A similar reduction

Figure 3. (a) Visibility as a function of wavelength for graphene-BN-MoS$_2$ heterostructure showing experimental and theoretical plots. The panels to the right of (a) are optical micrographs under the illumination of LEDs of different wavelengths (namely 465, 535, 590 and 635 nm) converted to greyscale. The scale bar at the bottom right is 2 μm. Colour plots of the maximum of absolute visibilities of (b) graphene-BN-MoS$_2$ and (c) graphene-MoS$_2$-BN heterostructures. White dashed lines are contours drawn at 2.5% absolute visibility.
in contrast was already observed for graphene on gold substrates [22, 23].

In the supplementary information (figure S2), we have computed the visibility for other common heterostructure configurations such as BN-graphene-BN, PMMA-graphene-BN, PMMA-graphene-MoS2 and a recently proposed photocatalyst, graphene-ZrS2 [43] using the same method and have identified optimal thicknesses of different layers for maximum visibility.

In conclusion, we have studied the conditions for the optimal visibility of graphene in van der Waals heterostructures. We have also performed experiments to demonstrate the accuracy of our predictions. Our methods and codes may be directly employed to calculate the visibility of a van der Waals material in a heterostructure.

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Figure 4. Maximum absolute visibilities and their peak wavelengths for various heterostructures. BN thickness is assumed to be 11 nm and MoS2 thickness is assumed to be monolayer in all heterostructures. Bi2Se3 is assumed to be monolayer in all heterostructures. BN, PMMA-graphene-MoS2 and a recently proposed photo-catalyst, graphene-ZrS2 [43] using the same method and have identified optimal thicknesses of different layers for maximum visibility.

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