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Enhanced visibility of graphene: the effect of the Brewster angle

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Visibility and simple optical diagnostics possibilities of graphene layers on dielectric and semiconductor substrates at the Brewster angle are analyzed. The analysis is based on a numerical simulation. Several oxide semiconductors (ITO, ZnO, TiO_2), weakly absorbing Si, and strongly absorbing GaAs are considered. It is shown that at the Brewster angle the optical contrast of graphene flakes on a bare semiconductor substrate is actually strong enough to see them under an optical microscope and there is really no need to create an additional interference film on the substrate.

Keywords: optical characterization, two-dimensional materials, graphene, Brewster angle, differential reflectance.

1. Introduction

The most common method for the visualization of graphene [1] or graphene-like two-dimensional materials [2] is the optical contrast method (or optical imaging) [3–9], which is a very simple and inexpensive technique. However, in the case of semiconductor substrates this method is strongly dependent on the implementation of specially designed Fabry–Pérot type substrates to enhance the visibility of graphene flakes. For example, a thin dielectric film can be coated on the semiconductor substrate to meet a destructive interference condition to suppress reflectivity of a bare substrate (the most common substrate is SiO_2 (300 nm)/Si) that is easily destroyed by the graphene layer: a distinctive contrast under an optical microscope comes from the difference between the reflectivity of the area with graphene on top and the rest of the substrate without graphene.

It must be emphasized that the relative simplicity and accessibility of the optical contrast method played a major role in the rapid development of graphene-related research because to scan macroscopically large areas to find a micrometer-sized graphene flake is a practically impossible task for classical atomic force microscopy or scanning electron microscopy [1]. In addition, the optical contrast technique does not need a single layer graphene (SLG) as a reference (as in Raman), and it does not have an instrumental offset problem (as in atomic force microscopy). However, the generation of Fabry–Pérot type semiconductor substrates is, generally, not easy (except the case of silicon) and, which is even more important, we often need to transfer graphene immediately to a bare semiconductor surface.

On the other hand, it is well known that no reflection occurs also in the case when a p-polarized light beam is incident on a transparent bare substrate under the Brewster angle. At the same time, formation of an ultrathin film at this substrate leads to a measurable reflectivity depending on various film properties. A microscope based on this principle had been constructed already in the early 1990s (the so-called Brewster-angle microscopy (BAM)) as a direct and non-invasive method to study the micrometric morphology of Langmuir and Langmuir–Blodgett monolayers [10, 11]. Nowadays the BAM has become one of the most attractive and powerful techniques for the *in situ* real-time monitoring of such structures on air–water interfaces [12, 13].

However, for classical semiconductor materials (*e.g.*, Si, GaAs), the situation is radically different. In the visible region of the optical spectrum they are absorbing materials for which, in fact, exists the so-called pseudo-Brewster angle where the reflectance does not approach zero but has already a considerably different value from zero. If this value is not small enough, then the contrast of graphene flakes or the relative change of the reflectance produced by a graphene sheet are not large enough to ensure the visibility of graphene. Thus, at first glance there is an impression that graphene samples are not visible on the surface of such semiconductor materials at the Brewster angle.

The purpose of this work is to demonstrate that the BAM is applicable to the detection of graphene layers on semiconductor materials (the contrast required (at least 10%–15%) can be achieved). We consider several oxide semiconductors (ITO, ZnO, TiO_2), weakly absorbing Si, and strongly absorbing GaAs. We also show that surface differential reflectance (SDR) [14–18] at the Brewster angle is a highly sensitive surface probe for graphene-like materials and can be successfully implemented for counting of graphene layers.

2. Optical contrast of graphene at the Brewster angle

Assuming that all the media are nonmagnetic, we consider the reflection of p-polarized time-harmonic electromagnetic plane waves with wavelength λ in the ambient medium with real refractive index n_a from an absorbing ultrathin film of thickness $d_f \ll \lambda$ and with complex refractive index $n_f = n_f' + in_f''$ that is located on semi-infinite absorbing substrate with complex refractive index $n_s = n_s' + in_s''$ or on transparent substrate ($n_s'' = 0$). The analysis is based on the classical electromagnetic theory for a simple Fresnel-law-based slab model [19].

We analyze the reflectance R of p-polarized light from a substrate with graphene on it and compare this to the reflectance R_0 of p-polarized light from the bare (graphene

-free) substrate. The optical visibility of a graphene flake is then determined as the relative optical contrast C (or normalized difference in reflectance) between two such parts of the sample studied using a monochromatic light source

$$C = \frac{I - I_0}{I_0} = \frac{R I_a - R_0 I_a}{R_0 I_a} = \frac{R - R_0}{R_0} \equiv \frac{\Delta R}{R_0}$$

where I and I_0 are the intensities of the reflected light from the graphene and the bare substrate, respectively, and I_a is the intensity of incoming light. In practice, it is important to keep in mind that the diameter of a graphene flake must be larger than the spot of light.

In relation to fully transparent substrates ($n_s'' \to 0$) the following should be noted: real physical interfaces do not represent perfectly flat surfaces but between two media always a transition layer exists that is usually caused by the microscopic roughness of surfaces, adsorption (*e.g.*, water), or the presence of the native oxide layer. However, as it turns out, the results of specific calculations for slightly rough transparent substrates contrast values are still very large in the immediate vicinity of the Brewster angle (Fig. 1).

Moreover, they are large enough for even a few degrees away from the Brewster angle. Note that surface roughness is modeled using an effective medium approximation (EMA) [20, 21]. This model assumes that the physical roughness is represented

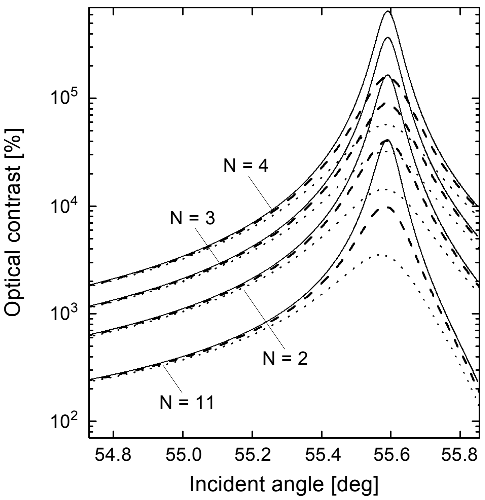

Fig. 1. Optical contrast (λ = 630 nm) as a function of the incident angle for different number N of graphene layers with $d_f = N \cdot 0.34$ nm and $n_f = 2.7 + 1.4i$ on silica substrates ($n_s = 1.46$, $\varphi_B = \mathrm{atan}(1.46) = 55.6°$) with different thicknesses of the roughness surface layer d_p = 0.6 nm (solid lines), 1.2 nm (dashed lines), and 2.0 nm (dotted lines) if the EMA refractive index of roughness layers n_p = 1.22 (50% silica and 50% voids with n_a = 1).

by a flat layer (with the thickness d_p and the refractive index n_p) which is composed of a random mixture of solid material (the hills of roughness) and voids (the empty space between the hills), *i.e.*, optical properties are a volume-weighted average of two media. In addition, it is important that the characteristic size of the homogeneous regions must be much smaller than the wavelength of radiation.

Calculations also show that graphene sheets with different number of the graphene layers have clearly different contrast values (Fig. 1). Therefore, measuring photometrically the value of the optical contrast (the differential reflectance $\Delta R/R_0$), we can successfully determine on the basis of this quantity the number of the graphene layers. Nevertheless, one should pay attention to the following fact: we do not always know exactly whether we have any graphenes on the substrate – maybe some other material accumulates on the substrate during the course of the technological process (for example, there is only water without graphene). Indeed, calculations show that for transparent substrates the value of the differential reflectance caused only by the water layer is also very large at the Brewster angle (*e.g.*, $C \sim 10^3$ for 3 nm water layer on a silica substrate). So, at first glance, it seems that this method is unable to discriminate between a graphene flake and an arbitrary dielectric material. But here comes to the rescue another important aspect of the angle dependence of the differential reflectance. Namely, for graphene and dielectric layers the sign of the contrast is different for incidence angles which are less or greater than the Brewster angle of incidence: for graphene layers $C > 0$ if $\varphi < \varphi_B$ (φ is the angle of incidence) and $C < 0$ if $\varphi > \varphi_B$ but for dielectric layers the contrary is true: $C < 0$ if $\varphi < \varphi_B$ and $C > 0$ if $\varphi > \varphi_B$ (strictly speaking, at large angles of incidence ($\varphi \to 90°$) the quantity C can become negative again, but its value is very small).

Thus, at the Brewster angle contrast values are especially high for transparent substrates, for example, various glassy materials with low refractive index. On the other hand, for such materials, in fact, there is no special need for the measurements at the Brewster angle because sufficient contrast is also achieved at the normal incidence (*e.g.*, if $n_s \le 1.5$, then $C > 10\%$ at $\varphi = 0°$ and $\lambda = 500$ nm). However, if the real part of the refractive index of the substrate increases ($n_s' > 1.5$), then the optical contrast for the normal incidence decreases very rapidly ($C < 10\%$ at $\varphi = 0°$) and graphene flakes distinction under an optical microscope becomes very difficult or even impossible. Note that the absorption in the substrate material ($n_s'' > 0$) further reduces the optical contrast at the normal incidence. For example, higher refractive index substrates ($n_s' \ge 3...4$) include such important semiconductors as Si or GaAs where the refractive index becomes complex when the quantum energy of radiation approaches (or is greater than) the bandgap energy – this leads to a very low contrast at the normal incidence. Because of this, directly onto the semiconductor substrate, the transferred graphene is not seen under a conventional optical microscope (normal incidence of light). In order that graphene would become visible, it is necessary to generate a specific dielectric film onto the semiconductor surface, which reduces the substrate reflectivity at normal incidence by means of destructive interference (the simplest example is the 300 nm (or 100 nm) SiO_2 layer generation on Si substrate).

On the other hand, it is clear that much easier it is to change the incident angle – go to the Brewster angle of incidence – more exactly to the pseudo-Brewster angle φ_{pB} since due to the absorption in semiconductor materials, the angle where the reflectance is minimal, is, generally, different from the value of $\varphi_B = \operatorname{atan}(n_s'/n_a)$ ($\varphi_{pB} > \varphi_B$). Nevertheless, calculations show that if the imaginary part of the refractive index of a semiconductor substrate is significantly lower than the real part of the refractive index, then the reflectance at the Brewster angle is still very small (the angle φ_{pB} also differs little from the angle φ_B) and the value of the contrast is mainly determined by the surface quality of the substrate. In addition to usual roughness of the surface, there is often a problem in the water adsorbed at the surface. Of course, the natural oxidation of the substrate material also reduces the contrast. At the same time, it should be noted that the surface quality effect appears particularly acute only in the immediate vicinity of the Brewster angle.

Addressing semiconductors, it should first be noted that Brewster's method is of particular interest for oxide semiconductors because their refractive index is smaller than the value of the refractive index of classical semiconductors (*e.g.*, Si, Ge, $A^{III}B^{V}$) and, therefore, the corresponding Brewster angle is not much greater than the Brewster angle for the air–water interface in the conventional BAM. Notice that large Brewster angles ($\varphi_{pB} \geq 70°$) may lead to additional experimental problems. Calculations of optical contrast for graphene on such well-known oxide semiconductor substrates as ITO,

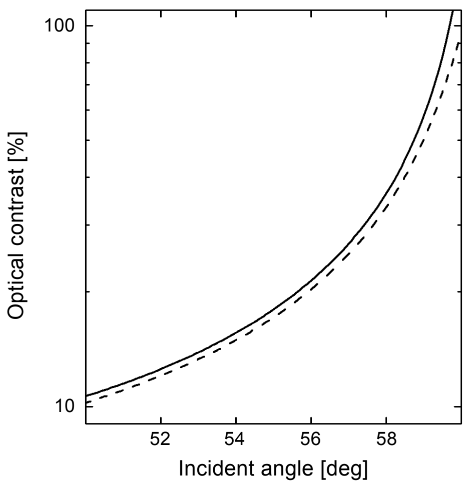

Fig. 2. Optical contrast ($\lambda = 630$ nm) as a function of the incident angle for monolayer graphene with $d_f = 0.34$ nm and $n_f = 2.7 + 1.4i$ on ITO (In_2O_3-SnO_2, $n_s = 1.78 + 0.0032i$, $\varphi_B = 60.7°$) bare substrate (solid line) and on ITO with water surface layer ($n_w = 1.33$, $d_w = 4$ nm) between graphene and substrate (dashed line).

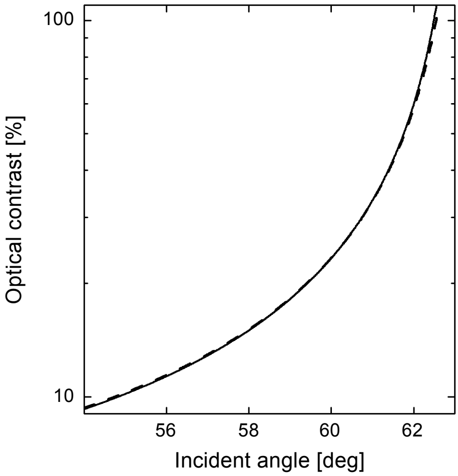

Fig. 3. Optical contrast ($\lambda = 630$ nm) as a function of the incident angle for monolayer graphene with $d_f = 0.34$ nm and $n_f = 2.7 + 1.4i$ on ZnO substrates ($n_s = 1.99$, $\varphi_B = 63.3°$) with different thicknesses of the roughness surface layer $d_p = 0.5$ nm (solid line) and 3.0 nm (dashed line) if the EMA refractive index of roughness layers $n_p = 2.16$ (50% ZnO and 50% voids with $n_a = 1$).

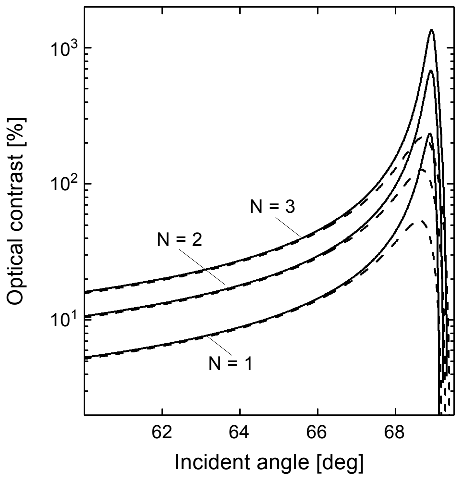

Fig. 4. Optical contrast ($\lambda = 630$ nm) as a function of the incident angle for different number N of graphene layers with $d_f = N \cdot 0.34$ nm and $n_f = 2.7 + 1.4i$ on TiO_2 substrate ($n_s = 2.6$, $\varphi_B = 68.85°$) with different water layers ($n_s = 1.33$; $d_w = 1$ nm (solid lines) and $d_w = 3$ nm (dashed lines)) between graphene and substrate.

ZnO, and TiO_2 are shown in Figs. 2, 3, and 4, respectively. As we can see, the values of optical contrast at the incident angles close to the Brewster value are large enough to ensure good visibility of graphene by using BAM instead of usual optical microscopy.

As follows, we discuss the traditional semiconductors such as Si and GaAs. For example, for the crystalline silicon the optical contrast in the vicinity of φ_{pB} is demon-

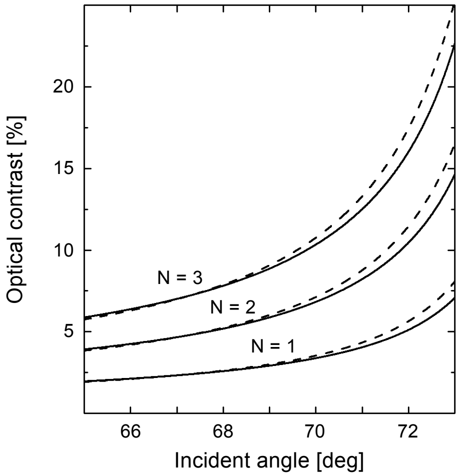

Fig. 5. Optical contrast (λ = 630 nm) as a function of the incident angle for different number N of graphene layers with $d_f = N \cdot 0.34$ nm and $n_f = 2.7 + 1.4i$ on crystalline silicon ($n_s = 3.9 + 0.016i$) with SiO_2 (n_{ox} = 1.46) surface layers with different thicknesses: d_{ox} = 0.3 nm (solid lines) and 3.0 nm (dashed lines) [22].

strated in Fig. 5. Thus, close to the Brewster angle the graphene flakes are well visible on the bare surface of conventional silicon (without a special interference film), however, the problem is the relatively high incident angle (greater than 70°).

As the number of the graphene layers increases, the contrast also increases. A few degrees away from the pseudo-Brewster angle, where the contrast values are smaller than exactly at the pseudo-Brewster angle, the dependence of the contrast on the surface quality of the substrate (roughness, oxide or water layers) is considerably smaller and curves for different thicknesses of graphene sheets separate clearly and do not overlap. Consequently, in this region it is quite possible on the basis of photometric measurements of $\Delta R/R_0$ to determine the number of graphene layers (as in the case of transparent substrates).

Next, we consider another semiconductor – GaAs, which is of great interest for optoelectronics. In this semiconductor the absorption of light is stronger (the imaginary part of the refractive index of GaAs is greater than the corresponding value for Si), therefore, the reflectance at the Brewster angle is already significantly different from zero, *e.g.*, at λ = 450 nm, $n_s = 4.84 - 0.861i$, $R(\varphi_{pB}) = 7.2 \times 10^{-3}$, φ_B = atan(4.84) = 78.3° and C = 19.2% (we did not take into account the effect of a surface oxide on GaAs because its typical thickness is only ~2 nm). Of course, such a contrast is still perfectly adequate that the graphene flakes would be clearly visible at the Brewster angle. However, in the short-wave part of the visible region ($\lambda \leq 400$ nm) the optical contrast for a GaAs substrate is already so low (Fig. 6) that graphene flakes are no longer visible under an optical microscope even at the Brewster angle.

As in the case of transparent substrates, we often do not know whether a test object is not the graphene flake. Maybe there is some other material in place of the graphene, *e.g.*, the ubiquitous water, which at the Brewster angle has a sufficiently large value

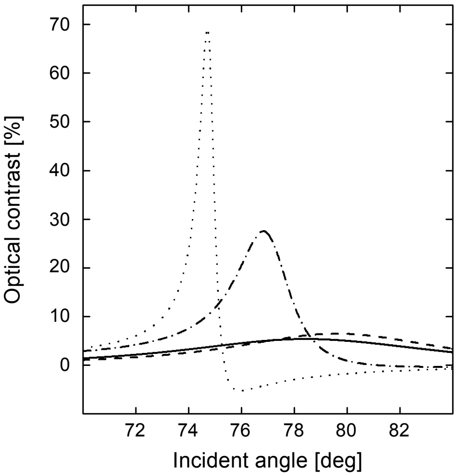

Fig. 6. Optical contrast as a function of the incident angle for monolayer graphene with $d_f = 0.34$ nm and $n_f = 2.7 + 1.4i$ on GaAs [23] at different values of $\lambda = 800$ nm (dotted line, $n_s = 3.68 + 0.0857i$), 500 nm (dash-dotted line, $n_s = 4.31 + 0.427i$), 400 nm (dashed line, $n_s = 4.37 + 2.14i$), and 300 nm (solid line, $n_s = 3.73 + 2.0i$).

for the optical contrast on a semiconductor substrate as well. However, it turns out that for semiconductor substrates this problem can also be easily solved by changing just the angle of incidence: close to normal incidence the sign of the optical contrast is different for graphene layers and dielectric surface layers.

3. Conclusions

The Brewster-angle microscopy/reflectometry is a powerful technique for optical diagnostics of graphene-like two-dimensional materials on dielectric and semiconductor substrates. The essential property of the Brewster angle microscopy is that it allows to see directly the graphene flakes on a bare semiconductor material – this means that to suppress the reflection from the semiconductor substrate it is not necessary to use a special interference film on the surface of the semiconductor as it is a commercial system Si/SiO_2 (300 nm). The latter feature is currently of first importance in microscopy of two-dimensional materials on other types of semiconductors (different from silicon) where the generation of an interference structure is not always so easy (at the same time, a prerequisite for handling graphene is its easy visibility). A surface differential reflectance method at the Brewster angle is very sensitive surface probe and can be successfully implemented for counting of graphene layers.

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