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Fumin Huang

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Optical Contrast of Atomically Thin Films

*Fumin Huang**

School of Mathematics and Physics, Queen’s University Belfast, Belfast, United Kingdom, BT7
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ABSTRACT: Here we provide a comprehensive description of the optical contrast of atomically-thin films, based on rigorous analytical solutions. The effects of thin film, substrate and light illumination conditions are fully revealed. The role of substrate is found to be completely represented by a single complex reflectivity, regardless of the structural details. High contrast is realized on low-reflection substrates; however, the phase of the complex reflectivity is critically important. Every thin film has specific reflectivity-phase conditions to achieve optimal contrast, which are uniquely defined by the optical properties of the thin film. Extraordinarily high optical contrast can be achieved on any thin film of any thickness, if the reflectivity of substrates matches the optimal phase conditions. We provide a universal phase map which can be used to determine the optimal phases of any given film. For example, the optimal phase of hexagonal boron nitride (hBN) films is found to be -90° , which paves the way towards designing high-contrast substrates to visualize this highly transparent 2D material. We also provide detailed discussions on the effects of a range of other factors, including polarizations, incident angles, and the numerical aperture of objectives.

I. INTRODUCTION

Visualizing and accurately determining the thickness of atomically-thin films is central in research and applications of two-dimensional (2D) materials, such as graphene,¹⁻³ hexagonal boron nitride (hBN),⁴ black phosphorous (BP),⁵ and a wide variety of transition metal dichalcogenides (TMDs).^{6,7} Many bulk 2D materials have layer-by-layer crystal structures bonded by weak van der Waals forces, hence monolayers or few-layer films can be exfoliated with mechanical or chemical methods,⁷⁻⁹ producing extremely thin 2D crystals with thickness between one atom and a few nanometers. These 2D films possess extraordinary properties not attainable in their bulk counterparts. One prominent example is graphene, a single-atom graphite layer, which however has better electrical and thermal conductivities than silver and is mechanically stronger than steel.¹⁰ Another example is TMDs. They are often indirect-bandgap semiconductors as bulk materials, but transferring to direct-bandgap semiconductors in monolayer forms, making them wonderful candidates for photonic devices.¹¹ Till date, several hundreds of species of 2D materials have been discovered.¹¹⁻¹³ The vast variety of 2D materials provide a plethora of fascinating properties, making promising materials for revolutionary applications in many industrial sectors, such as optoelectronics, sensors and energy.¹⁰⁻¹³ As the functionalities of 2D films are critically dependent on the number of layers, developing facile technologies to visualize and to rapidly and accurately determine the thickness of atomically-thin films is instrumentally important for the field of 2D materials.

Conventionally the thickness of thin films can be characterized with a variety of scanning probe microscopies, such as atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), but these methods are time-consuming and costly, requiring expensive equipment. In comparison, optical contrast spectroscopy (OCS) is a facile technique with many advantages, which can characterize film thickness non-invasively with minimal time, little cost and high accuracy. As such, it has become one of the most important thin-film characterization tools widely adopted in the determination of 2D materials thickness.¹⁻⁶

Despite much research has been carried out on OCS, a comprehensive description of the technique from fundamental optic principles has not been provided and there are a number of outstanding issues to be solved. For example, many measurements were taken with objectives of large numerical apertures (NA) spanning a broad range of incident angles, however quite often Fresnel reflection formulae at normal incidence were used to model the results, leading to notable discrepancy between theory and experiments.^{1,14} A second imminent issue is, although OCS has been successfully demonstrated on a number of materials,¹⁻⁶ it is still challenging on some extremely transparent materials, such as hBN. Till date, hBN is one of most difficult materials to visualize, with recorded maximum contrast only about 2.5% for a monolayer film.⁴ Most optical characterizations of hBN have been limited to multilayers.^{15,16} Finding the optimal conditions to achieve high contrast of hBN is central to the further development of this intriguing nanomaterial.^{17,18} As will be shown in this paper, even for films that are highly visible on some substrates, they could be invisible on different substrates. For instance, graphene is readily visible on SiO₂-coated Si,^{1,14} but hard to see on highly reflective metal surface.^{2,3} The rapid advance of

the field of 2D materials has empowered research and applications on a broad variety of materials, as the functionalities of 2D material devices are critically dependent on the underlying substrate material which the 2D materials are directly in contact, which could impact the electronic, optical, catalytic and electrochemical properties of 2D films through doping, strain and energy transfer processes.^{19,20} Currently contrast-enhancing substrates are mainly limited to oxidized Si and a few metallic structures. It is therefore desirable to develop high-contrast substrates with wide options of top-surface materials. To accomplish all these, a deep understanding of the fundamentals of the optical contrast of thin films is essential.

Here we provide a comprehensive description of the optical contrast of ultrathin films. The effects of thin film, substrate, and light illumination conditions (wavelength, incident angle, and polarization) are fully investigated. It is shown, the role of substrates is completely represented by a single complex reflectivity, regardless of the structural details of the substrate, *i.e.*, two substrates of different structures will produce same optical contrast for a given thin film, if they produce same complex reflectivity. In general, contrast increases with decreasing reflectivity of substrates, therefore optimal contrast will be achieved on substrates of minimum reflection. However, the phase of substrate reflectivity is crucially important. For any thin film, optimal contrast is only achievable at specific reflectivity phases uniquely decided by the optical properties of the thin film. Apart from substrates and thin films, optical contrast also depends on the illumination conditions of light, including wavelength, incident angles, and polarizations. To correctly interpret experimental results, all these effects need to be properly taken into account. The results in this paper demonstrate that, with appropriately designed substrates, extremely high optical contrast can be achieved on any film of any thickness.

II. THEORY

Optical contrast is induced by the reflectance difference of light on a substrate with and without a thin film (Fig.1), which is defined as

$$C = 1 - \frac{R'}{R} \quad (1)$$

$R' = |r'|^2$ and $R = |r|^2$, with r' and r being the complex reflectivity with and without the thin film, respectively. A positive contrast is achieved for $R' < R$, which means less light is reflected on the area covered with thin films in comparison to the bare substrate. Conversely a negative contrast is achieved for $R' > R$, corresponding to more light is reflected on the area covered with thin films. With this definition, the upper limit of positive contrast is unity (when $R' = 0$), whereas the negative contrast is unbounded, up to $-\infty$ (when $R = 0$).

Figure 1 Schematic of light reflection on a stratified substrate with and without a thin film. The substrate is composed of M layers of homogeneous planar films with optical properties denoted by ϵ_j , μ_j , and thickness by h_j , j is the layer number.

It is convenient to introduce a quantity denoting the relative change in reflectivity, $\chi = 1 - \frac{r'}{r} \equiv \chi_0 e^{i\psi}$. The contrast then is obtained as

$$C = 2\chi_0 \cos \psi - \chi_0^2 \quad (2)$$

which is related to both the magnitude and phase of χ .

For a stratified substrate composed of multilayer homogeneous planar films (the multilayer structure allows to generate desired complex reflectivity r by tuning the optical properties and thickness of the constituent layers³) as schematically depicted in Fig.1, r' is uniquely determined by r and the thin film. χ can be analytically expressed as (see Supplementary Information for derivation),

$$\chi = \frac{\frac{1+r}{r}[\eta^2 - (\frac{1-r}{1+r})^2] \tanh(-i\beta)}{\frac{2\eta}{1+r} + [\frac{1-r}{1+r} + \eta^2] \tanh(-i\beta)} \quad (3)$$

$\beta = nk_0 h \cos \theta_f$. n , h , θ_f are the refractive index (RI), thickness and refraction angle inside the thin film, as depicted in Fig.1. $k_0 = \frac{2\pi}{\lambda}$, λ is the wavelength of light in free space. For TM-

polarization $\eta = \frac{n_0 \cos \theta_f}{n \cos \theta} \equiv \xi$ and for TE-polarization $\eta = \frac{n \cos \theta_f}{n_0 \cos \theta} \equiv \zeta$, n_0 is the RI of the

surrounding medium and θ the incident angle. In the following, we focus discussions mainly on TE-polarization. The results of TM-polarization can be obtained straightforwardly by replacing ζ with ξ . The above formulae are exact without any approximation, which are applicable to any homogeneous thin film, any stratified substrate and arbitrary light illumination conditions.

In the case of ultrathin films like 2D materials, $k_0 h \ll 1$, so that $\beta \ll 1$, $\tanh(-i\beta) \approx -i\beta$. The second term in the denominator of Eq.3 is negligible comparing to the first term, so Eq.3 can be simplified as

$$\chi \approx -i\beta \frac{\frac{1+r}{r}[\eta^2 - (\frac{1-r}{1+r})^2]}{\frac{2\eta}{1+r}} \quad (4a)$$

By multiplying $r(1+r)$ on both the numerator and denominator of Eq.4a, we obtain

$$\chi \approx -i\beta \frac{(1+r)^2 \eta^2 - (1-r)^2}{2\eta r} \quad (4b)$$

For TE-polarization, replacing η with $\zeta = \frac{n \cos \theta_f}{n_0 \cos \theta}$ and applying the Snell's law of reflection, we have

$$\chi = -i \frac{k_0 h}{2r \cos \theta} \delta \quad (5a)$$

$$\delta = (1+r)^2 (n^2 - \sin^2 \theta) - \cos^2 \theta (1-r)^2 \quad (5b)$$

Let $\delta \equiv \delta_0 e^{i\phi}$, $r \equiv r_0 e^{i\varphi}$, from Eq.5a it is inferred

$$\chi_0 = \frac{k_0 h \delta_0}{2r_0 \cos \theta} \quad (6a)$$

$$\psi = \phi - \varphi - \frac{\pi}{2} \pm 2m\pi \quad (6b)$$

m is an integer so that $0 \leq \psi < 2\pi$. For simplicity, we assume $n_0 = 1$ in obtaining the above results. If the surrounding medium is not air, n should be considered as a reduced RI normalized to surrounding medium.

The above formulae apply excellently on few-layer 2D materials, as the condition $k_0 h \ll 1$ is well matched, *e.g.*, let $h = 1$ nm and $\lambda = 500$ nm, then $k_0 h \approx 0.012$.

III. RESULTS

Effects of substrate

As seen from Eq.6a, χ_0 is inversely proportional to r_0 , so in general a low-reflection substrate will provide a high contrast. However, the phase of χ (hence the phase φ of r , according to Eq.6b) is also important, as indicated in Eq.2. The effect of φ can be explicitly illustrated by keeping χ_0 constant. Based on Eq.2, maximum positive (negative) contrast will be achieved at $\psi = 0$ (π). This leads to the optimal phases $\varphi^\pm$ and optimal contrasts $C^\pm$ as following

$$\varphi^\pm = \phi \mp \frac{\pi}{2} \pm 2m\pi \quad (7a)$$

$$C^\pm = \pm 2\chi_0 - \chi_0^2 \quad (7b)$$

φ^+ and φ^- differ by a factor of π , which are decided only by ϕ (the phase of δ). In the case of $r_0 \ll 1$ (a necessary condition for high-contrast substrates), the r terms in Eq.5b are negligible, therefore

$$\delta \approx n^2 - 1 \quad (8)$$

Eq.8 indicates that ϕ is solely determined by n and independent on the incident angle. Eqs.(7, 8) suggest, every thin film has specific optimal phases ($\varphi^\pm$) for high contrast, which are uniquely determined by the optical properties (n) of the thin film. Ideally a high-contrast substrate should have a low reflectivity with the optimal phases given in Eq.7a. This is universal for any thin film.

Figure 2 Contrast map of graphene. (a) Calculated contrast of monolayer graphene on

substrates of complex reflectivity $r = r_0 e^{i\varphi}$. Numbers on contour plots indicate the contrast.

Traces of optimal phases $\varphi^\pm$ are indicated with dashed lines. The dotted line indicates the track of zero contrast. A few commonly-used substrates are marked by symbols. $\lambda = 560\text{ nm}$, $\theta = 0^\circ$, TE-polarization. Thickness of graphene is $h = 0.34\text{ nm}$ and $n = 2.6 + 1.3i$. (b) The maximum contrast $C^\pm$ and the corresponding phase $\varphi^\pm$ along the dashed lines in a.

As the effect of substrate is completely represented by a single complex reflectivity r , the contrast of a thin film can be fully evaluated based on r . Figure 2 shows the calculated contrast map (normal incidence, $\lambda = 560\text{ nm}$) of a monolayer graphene with regard to the magnitude and phase of the complex reflectivity r of substrates. Generally contrast increases with decreasing r_0 , consistent with the discussions above. However, the phase of r is also critically important. As seen from Fig.2a, no matter how small r_0 is, there always exist phases at which the contrast is zero (dotted lines). Optimal contrasts are localized in two distinct phase regions (blue and red areas). The maximum positive/negative contrasts are marked by dashed lines and plotted in Fig.

2b, both increasing with diminished reflectivity r_0 . For substrates of small reflectivity ($r_0 \ll 1$), optimal phases are nearly constant, *e.g.*, for graphene, $\varphi^+ \approx 328^\circ$ and $\varphi^- \approx 148^\circ$.

With the contrast map, the visibility of graphene on any substrate can be assessed. The contrasts of a few commonly-used substrates are highlighted on the map of Fig.2a, including 90 nm SiO₂/Si, 290 nm SiO₂/Si, SiO₂, Si and Au. Oxidized Si substrates provide ~14% contrast for a monolayer graphene, while Si and Au only provide a few percentages, which are consistent with experimental results.¹⁻³ This indicates that contrast critically relies on substrates. A film highly visible on one substrate could be invisible on another. Conversely, a film extremely transparent on conventional substrates can be made highly visible on appropriately-designed contrast-boosting substrates.

Optimal phases

According to Eq.8, the optimal phases of a thin film are solely decided by the complex refractive index of the thin film, $n = n_1 + in_2$. Figure 3 shows the map of φ^+ (φ^- is 180° difference) with regard to n . It is seen that φ^+ shifts clockwise with increasing n_2 when n_1 is fixed and anti-clockwise with increasing n_1 when n_2 is fixed. All the contour lines converge to a singular point at $n = 1$ (a virtual film of free space), where the phase is undefined as the contrast is zero. With this universal map, the optimal phases of any given thin film can be determined if the refractive index is known. To give examples, the optimal phases of a number of 2D materials are highlighted on the map, based on the refractive indices listed in Table 1.

Figure 3 Map of optimal phases. Calculated optimal phase (φ^+) with regard to the complex refractive index of thin film $n = n_1 + in_2$. The optimal phases of a number of 2D materials are highlighted. The refractive indices of 2D materials are shown in Table 1.

Table 1 Optimal phases of 2D materials. Refractive indices are adopted from the annotated refs. For TMDs, all n is for $\lambda = 520$ nm.

2D materials	n	$\varphi^+(\text{°})$
Graphene (Gr)	$2.6 + 1.3i^1$	-31
Graphene oxide (GO)	$1.65 + 0.2i^3$	-67
hBN	2.2^{14}	-90
Black phosphorous (BP)	$2.64 + 0.6i^{21}$	-60
MoS ₂	$4.98 + 1.1i^{22}$	-64
WS ₂	$4.74 + 1.31i^{22}$	-57
WSe ₂	$4.57 + 1.47i^{22}$	-53
MoSe ₂	$5.08 + 2.1i^{22}$	-43

Optimal phases are key information necessary for designing high-contrast substrates. It is seen from Fig.3, to achieve high contrast of hBN, the reflectivity of substrates needs to have a phase around -90° , *i.e.*, $r = -ir_0$, a pure imaginary reflectivity. The phases of most conventional substrates like those shown in Fig.2a are considerably away from -90° (270°), which is why these substrates fail to produce high visibility for hBN. With custom-designed substrates of pure imaginary reflectivity, extraordinarily high contrast can be achieved on monolayer hBN (the results will be presented in future publications).

Figure 4 Contrast vs number of layers. (a) Contrast of 1-11 layer graphene films on 90 nm SiO₂/Si (squares) showing a quadratic dependency on the number of layers, while that on Au substrates (triangles) is linear. $\lambda = 560$ nm. (b) Contrast spectra of 1-11 layer (from low to high contrast) hBN films on 290 nm SiO₂/Si substrates. The spectra strictly intersect at point A (429 nm) of zero contrast. Point B (574 nm) is a pseudo intersecting point. Contrast data extracted at

610 nm (dashed line) are presented in **a** (circles), showing a weak quadratic dependence on the number of layers. All the results are calculated with TE-polarization and at normal incidence.

Effects of film thickness

As shown in Eq.6a, χ_0 is linearly proportional to h . Inputting Eq.6a into Eq.2, we get

$$C = \frac{k_0 \delta_0 \cos \psi}{r_0 \cos \theta} h - \left(\frac{k_0 \delta_0}{2r_0 \cos \theta} \right)^2 h^2 \quad (9)$$

Generally contrast is a quadratic function of h . In some circumstances the second term in Eq.9 could be much smaller than the first term and is negligible so that the contrast becomes linear to the thickness, as often reported in literature.^{2,3} This corresponds to the condition of

$$k_0 h \ll \frac{4r_0 \cos \theta |\cos \psi|}{\delta_0} \quad (10)$$

The above condition can be matched when r_0 is not too small and $\cos \psi \neq 0$. For substrates of low reflectivity, the linear dependence is only applicable to a few layers. Figure 4a presents calculated contrasts for 1-11 layer graphene films on 90 nm SiO₂/Si (squares) and Au substrates (triangles), at $\lambda = 560$ nm and normal incidence. The contrast is linear to the layer number on high-reflectivity Au substrates (the condition of Eq.10 is well matched). In contrast, the dependence of contrast on thickness is quadratic on low-reflectivity 90 nm SiO₂/Si substrate, where linear relationship is only up to a few layers. These are consistent with Eq.9 and have been observed in experiments.^{2,3,14,23}

As the contrast function (Eq.9) is an inverted parabolic curve, it has a maximal value,

$$C_{max} = \cos^2 \psi \quad (11)$$

when

$$h = \frac{2r_0 \cos \theta \cos \psi}{k_0 \delta_0} \equiv h_0 \quad (12)$$

Eq.11 sets the upper limit of the maximally achievable positive contrast for a film, when the substrate and light illumination conditions are fixed. As the film thickness increases, the contrast initially increases until reaching the maximum at $h = h_0$, it then starts to decline after $h > h_0$. Cautions need to be taken when characterizing the thickness of 2D materials based on positive contrast, especially for high-visibility films such as TMDs. A low-contrast image may not necessarily be a thin film. It could be a thick film beyond the optimal thickness h_0 . In this case, OCS needs to be used in conjunction with other characterization techniques such as AFM or Raman for accurate results. Working with negative contrast will not have this problem, as negative contrast is unbounded, as shown in Eq.1.

Zero contrast

Under specific conditions, contrast can be zero. According to Eq.2, this corresponds to either

$$\chi_0 = 0 \quad (13a)$$

or

$$\cos \psi = \frac{\chi_0}{2} \quad (13b)$$

Based on Eq.5a, the condition of Eq.13a can only be met when $\delta = 0$, which indicates $\chi = 0$, regardless of film thickness h . This condition can be matched at a specific wavelength λ_o , so that $\delta(\lambda_o) = 0$. Since it is independent of film thickness, the contrast of multilayer films will all be zero at λ_o , therefore the contrast spectra of multilayer films will intersect at the point of λ_o . Zero

contrast could also be reached at a different wavelength when the condition of Eq.13b is matched, however, as χ_0 is proportional to h , this wavelength is dependent on film thickness, therefore it is a pseudo intersecting point which can be distinguished from the true zero-contrast intersecting point. To give an example, Figure 4b shows the calculated contrast spectra of 1-11 layers of hBN films on 290 nm SiO₂/Si substrates (normal incidence, TE-polarization). All the spectra meet at the zero-contrast point A ($\lambda = 429$ nm). Point B ($\lambda = 574$ nm) looks like a similar intersecting point, but actually is a pseudo one, as described above. The contrast data at $\lambda = 610$ nm is extracted and plotted in Fig.4a (circles), indicating a weak quadratic dependence on the number of hBN layers. The calculated spectra well resemble those measured in experiments.⁴

Effects of light illumination

Optical contrast also significantly depends on the conditions of light illumination, including wavelength, polarizations and incident angles. As χ_0 is inversely proportional to λ , contrast spectrum generally has a diminishing tail at long wavelengths,¹⁻⁶ as shown in Fig.4b. For highly dispersive thin films, refractive index n is strongly dependent on wavelength λ . This is often manifested as distinct features in the optical contrast spectra, as demonstrated in some TMDs.^{5,6,22} For stratified substrates, r is sensitive to λ . As discussed above, contrast usually increases with decreasing reflectivity, therefore the maximum positive/negative contrast points in a contrast spectrum are often linked to the reflectance minima of a substrate, as shown on 90 nm and 290 nm SiO₂/Si substrates.^{1,14,23} The spectral position of reflectance minima can be

shifted with varying thickness of SiO₂ films, hence the contrast maxima/minima can be tuned to desirable working wavelengths.

Figure 5 demonstrates how the contrast of a monolayer graphene depends on the incident angles and polarizations. The contrasts of TE- and TM- polarizations are notably different, but both are significantly dependent on the incident angle. For TE-polarization (Fig.5a), the maximum contrast increases with incident angle (Fig.5c), whereas for TM-polarization it decreases (Fig.5d). The wavelengths of maximum contrast blueshift with incident angle for both polarizations. For TE-polarization, it shifts from 550 nm at $\theta = 0^\circ$ to 408 nm at $\theta = 74^\circ$, and the contrast correspondingly increases from 14.3% to 97%. For TM-polarization, the wavelength of maximum contrast shifts from 550 nm at $\theta = 0^\circ$ to 400 nm at $\theta = 60^\circ$ (for $\theta > 60^\circ$, the wavelength is below 400 nm and out of the spectral range), and accordingly the maximum contrast drops from 14.3% to 7.4%.

In experiments, light is often incident from a range of angles with a spanning cone of θ_0 defined by the NA of an objective ($NA = \sin \theta_0$). For high numerical-aperture objectives, θ_0 is considerably large, so the impacts of polarization and incident angles are pronounced, which need to be properly taken into account for accurately interpreting experimental results.² Apart from polarization and incident angles, there is another important issue which however is often mistreated in theoretical modelling. From simple geometric optics configurations, it is obvious that light incident at different angles will have different proportions of power: those incident through the outer sector of the input aperture (corresponding to large incident angle) has higher portions of power than that incident through the center (small incident angle) of the input

aperture.^{2,26} The reflectance of light needs to be averaged with a weight-function of power with regard to the incident angle, which can be computed as,^{2,26}

$$\bar{R} = \frac{2 \int_0^{\theta_0} R(\theta) \tan \theta (\sec \theta)^2 d\theta}{(\tan \theta_0)^2} \quad (14)$$

where $R(\theta) = |r(\theta)|^2$ is the reflectance at incident angle θ . θ_0 is the spanning angle defined by the NA of objective, $NA = \sin \theta_0$. The results of Eq.14 have been demonstrated matching experimental results excellently.^{2,3} In literature, a variety of weight-functions of power has been used, most of them are Gaussian functions of various forms.^{4,23-25} The profile of Gaussian function means light incident at $\theta = 0^\circ$ contains the maximum portion of power, which contradicts the results in Eq.14 where most light is incident at large angles and minimum at $\theta = 0^\circ$. This suggests that Gaussian functions are inappropriate weight-functions to calculate the average light reflectance measured by high-magnification objectives, which may be one of the reasons contributing to the notable discrepancy between experimental and theoretical results.^{4,23-}

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Figure 5 Effects of light illumination. (a-b) Contrast maps of a monolayer graphene on 90 nm SiO₂/Si substrate, as functions of incident angles, wavelengths and polarizations, (c-d) The dependence of the maximum contrast and wavelength on the incident angle for TE- and TM-polarizations.

CONCLUSION

In summary, here we provide a comprehensive theoretical description of the optical contrast of atomically-thin films. The effects of substrate, thin film and light illumination conditions are fully

investigated. It is shown that for any thin film, high contrast can be achieved on low-reflectivity substrates with optimal phases uniquely decided by the optical properties of the thin film. A universal phase map is provided, which can be used to determine the optimal phases of any given film. With the key information of optimal phases, high-contrast substrates can be designed for any thin film. It is shown that high visibility for monolayer hBN can be achieved on substrates with an optimal phase of -90° . We also provide detailed discussions on a number of potential issues in OCS technology, such as the limitations of positive contrast, the dependence of contrast on film thickness, the zero-contrast intersecting points, and how to calculate the averaged optical reflectance measured by high-magnification objectives. The presented theoretical model is general, applicable to any planar thin films. It shows, with appropriate substrates, extraordinarily high optical contrast can be achieved on any film of any thickness.

AUTHOR INFORMATION

Corresponding Author

*Email: f.huang@qub.ac.uk

ORCID

Fumin Huang: 0000-0001-6489-9818

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