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An analytical method to determine the complex refractive index of an ultra-thin film by ellipsometry

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ABSTRACT

We proposed a completely analytical method to determine the complex refractive index of an ultra-thin film on an arbitrary substrate by ellipsometry. The method is based on directly solving the polynomial equation derived from the 2nd-order Taylor expansion of ellipsometric functions without any prior knowledge about electronic transitions of the material. Numerical simulations demonstrate that the proposed method can be applied to deal with ultra-thin films with a wide thickness range from a single atomic layer to 5 nm over an ultra-broad spectral range from deep ultraviolet to infrared regions. With the proposed method, complex refractive indices of typical two-dimensional (2D) materials, including the monolayer graphene and 1–3 layer WSe_2, were experimentally investigated over an ultra-wide spectral range (193–1690 nm). The proposed method shows great potential in the accurate determination of complex refractive indices of ultra-thin films especially the emerging 2D materials.

1. Introduction

The complex refractive indices describe the propagation and loss of the electromagnetic wave in the medium, and they are basic optical constants of materials [1]. They reflect light–matter interactions, including reflection, refraction, absorption, and emission of light in materials. On one hand, the complex refractive index can not only help us to investigate basic optical phenomena, such as the photovoltaic (PV), photoluminescence (PL), optical scattering, and plasma, but also provide basic physical knowledge on the behind mechanisms, such as the bandgap, optical transitions, critical points, and band structure [2,3]. On the other hand, these optical constants are basis for optical analysis and optimal design of related devices [4,5]. Therefore, accurate determination of the complex refractive index is one of the major topics in the field of material characterization. It is of great importance for the design and control of novel materials and related devices.

Spectroscopic ellipsometry is the most commonly used and powerful technique to determine the optical constants of nanofilms [1–3,6–9]. Compared with other techniques, such as methods based on the transmission/reflection/absorption spectra [10–12], the ellipsometry detects the polarization state change of the light after reacting with the samples, and can provide enough information in one measurement to solve the complex refractive index without any additional functions, such as the Kramers-Kronig relation [1]. The traditional ellipsometric analysis contains two basic procedures, namely the forward modeling and the inverse data fitting [6]. There are two main problems in the traditional ellipsometric method to determine the optical constants of materials especially ultra-thin absorbing films. The first one is that one needs much prior knowledge about the material, such as the bandgap, the positions and types of the optical transitions, to establish an appropriate forward model and to obtain reliable initial parameters for the inverse fitting. The second issue is that there are too many parameters to be determined in an absorbing film, and mutual coupling between parameters will make the inverse fitting procedure time-consuming and easily falling into a local optimum or non-convergent. For an ultra-thin absorbing film, the optical index usually changes with the thickness of the film due to scaling effect [7–9,13], which enhances the coupling between the optical constants and the film thickness. For some emerging two-dimensional (2D) materials, which are typical ultra-thin films, the physical knowledge about the optical properties remains unknown. Bad initial parameters and high correlations between parameters make the fitting procedure time consuming and easily falling into a local optimum or non-convergent, and the accuracy even reliability of the final results will be significantly reduced. Therefore, the traditional ellipsometric methods based on iterative fitting have difficulties and limitations in evaluating the complex refractive indices of ultra-thin

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absorbing films.

To address the above issues, several techniques were developed to avoid the shortage of traditional ellipsometric methods based on inverse fitting. A classic point-by-point method can solve the complex refractive index directly from the complex ellipsometric ratio by applying the Fresnel equations [1]. However, this method can only deal with the pseudo optical constants of bulk materials. Many researchers used multi-incidence ellipsometry or combined the transmission or reflection with the ellipsometry to reduce the correlations between parameters in ellipsometry [14–17]. Urban *et al.* developed a new geometry of numerical ellipsometry named the *n-k* plane method, which can overcome the problem of multiple solutions and local solution in traditional ellipsometric methods based on least squares fitting [18–21]. Based on the determination of contours of the ellipsometric function and constrained splines, Gilliot *et al.* extracted the complex refractive index of absorbing films and investigated the correlations between the dielectric function, thickness and morphology of very thin films [22–24]. Although these above techniques find wide applications in accurate determination of optical constants of various thin films, they are still based on the iterative framework and not analytical. Some researchers developed semi-analytical solutions to determine the optical constants of thin films based on polynomial representation of the ellipsometric functions, such as the fifth-degree polynomial method for transparent films [25], and the sixth-degree polynomial method for absorbing films [26]. Recently, several analytical methods based on the approximation of the ellipsometric functions have been presented to deal with the ellipsometry for ultra-thin films [27–34]. Adamson demonstrated an analytical formula based on 1st-order approximate Taylor expansion to directly determine the optical constants of 2D ultra-thin films from the measured ellipsometric parameters [27–29]. However, Adamson only presented simulation results to verify his formula, which lacks experimental argumentation. Very recently, Jung *et al.* proposed a similar formula based 1st-order Taylor expansion, and then experimentally investigated the optical permittivity of 2D transitionmetal dichalcogenides (TMDCs) [30]. Due to the long-wave limit, the 1st-order approximate formula is only accurate for the visible and infrared spectral regions [28,30]. Nestler and Helm proposed a 2nd-order approximate formula, and they simultaneously determined the refractive index and thickness of ultra-thin polymer films using the formula [31]. However, their formula is suitable for transparent films with thickness greater than 5 nm.

In this paper, aiming to overcome the limitations of the existing techniques, we proposed a totally analytical method to deal with the inverse ellipsometry for ultra-thin films without prior knowledge of electronic transitions. A polynomial equation about the complex refractive index is derived from the 2nd-order Taylor expansion of the ellipsometric functions. The exact solution for the complex refractive index can be obtained by two steps: (1) solving the polynomial equation about the complex refractive index by using the Ferrari method; (2) filtering the false solutions by basic physical constraint. The proposed method can be applied to evaluate the complex refractive index of an ultra-thin absorbing film on an arbitrary substrate. The applicability and advantages have been discussed through numerical simulations. Results demonstrate that the proposed method can be applied for wider wavelength range (from deep ultraviolet to infrared regions) and thickness range (< 5nm) with much higher accuracy than the previous 1st-order Taylor approximate formula. With the proposed method, we experimentally investigate the complex refractive indices of typical 2D materials, including the monolayer graphene and 1–3 layer WSe_2 over an ultra-wide spectral range (193–1690 nm).

2. Principles and methods

As schematically illustrated in Fig. 1, the ellipsometry investigates the optical properties and the morphology of a thin film by detecting the polarization state change of the light reflected from the sample [1].

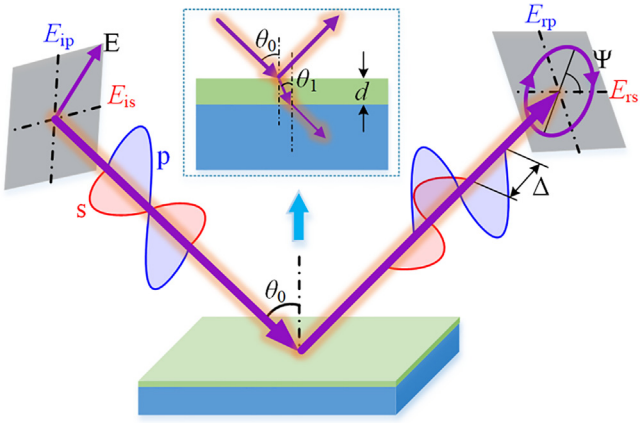

Fig. 1. Scheme of the ellipsometry for a thin film.

The polarization state change is usually described by two ellipsometric angles, i.e., the amplitude ratio angle Ψ and the phase difference Δ, which are defined by the reflection coefficients of the p- and s-component of the polarized light:

$$\rho = \tan\Psi exp(i\Delta) = \frac{r_p}{r_s}, \tag{1}$$

where, ρ is usually called the complex ellipsometric ratio, r_p and r_s refer to the reflection coefficient of the p-polarization light and that of the s-polarization light, respectively.

For an ultra-thin film sample, it consists of three parts, namely the surrounding medium (usually air), thin film, and supported substrate. The ellipsometry involves two interfaces, i.e., the air/film interface and the film/substrate interface as shown in Fig. 1. Drude's reflection coefficients can be calculated by the Fresnel equations:

$$r_p = \frac{N_s\cos\theta_0 - N_0\cos\theta_1 + i\frac{2\pi d_T}{\lambda}(N_T^2\cos\theta_0\cos\theta_1 - N_0N_s + N_0N_s^3\sin^2\theta_1/N_T^2)}{N_s\cos\theta_0 + N_0\cos\theta_1 + i\frac{2\pi d_T}{\lambda}(N_T^2\cos\theta_0\cos\theta_1 + N_0N_s - N_0N_s^3\sin^2\theta_1/N_T^2)}, \tag{2a}$$

$$r_s = \frac{N_0\cos\theta_0 - N_s\cos\theta_1 + i\frac{2\pi d_T}{\lambda}(N_0N_s\cos\theta_0\cos\theta_1 + N_s^2\sin^2\theta_1 - N_T^2)}{N_0\cos\theta_0 + N_s\cos\theta_1 + i\frac{2\pi d_T}{\lambda}(N_0N_s\cos\theta_0\cos\theta_1 - N_s^2\sin^2\theta_1 + N_T^2)}, \tag{2b}$$

where, θ_0 and θ_1 are the incident angle and the refractive angle on the air/film interface respectively, λ is vacuum wavelength of the polarized light, N_0 and N_s are the complex refractive index of the ambient medium and that of the substrate respectively, d_T and $N_T = n - ik$ are the thickness and complex refractive index of the film, n and k refer to the refractive index and the extinction coefficient respectively. According to Snell's law, we have $N_s\cdot\sin\theta_0 = N_0\cdot\sin\theta_1$.

Since the thickness of an ultra-thin film is of atomic level, it satisfies the condition of $2\pi d_T/\lambda \ll 1$ especially for the long-wavelength range. Then, ρ can be expressed analytically as a power series in the terms of $\phi = 2\pi d_T/\lambda$. Here, we approximate ρ by using the Taylor expansion at $d_T = 0$ to get the following 2nd-order approximate formula:

$$\rho(\phi) = \rho(0) + i\rho'(0)\phi + \frac{\rho''(0)}{2!}\phi^2. \tag{3}$$

Herein, $\rho(0) = r_p/r_s|_{\phi=0}$ represents the ellipsometric ratio of the bare substrate, and it can be calculated by Eq. (2) if we set $\phi = 0$. And it also can be obtained by ellipsometry on the bare substrate according to Eq. (1). The latter is preferred to eliminate the experimental errors.

In Eq. (3), the 1st-order and 2nd-order coefficients are given by

$$\rho'(0) = A\frac{(N_T^2 - N_0^2)\cdot(N_T^2 - N_s^2)}{N_T^2}, \tag{4}$$

$$\rho''(0) = \frac{(N_T^2 - N_0^2)^2(N_T^2 - N_s^2)}{N_T^4}\cdot[2B(N_T^2 - N_s^2) + 2C(N_s^4 + N_T^2N_0^2)], \tag{5}$$

where, the abbreviations A, B, and C have the following forms as given by

$$A = -2\frac{N_0}{N_s^2 - N_0^2}\cdot\frac{\sin^2\theta_0\cdot\cos\theta_0}{\cos^2(\theta_0 - \theta_1)}, \tag{6a}$$

$$B = -2\frac{N_0N_s}{(N_s^2 - N_0^2)^2}\cdot\frac{\sin^2\theta_0\cdot\cos^2\theta_0}{\cos^3(\theta_0 - \theta_1)}, \tag{6b}$$

$$C = -2\frac{N_0}{N_s}\frac{\cos\theta_0}{(N_s^2 - N_0^2)^2}\cdot\frac{\sin^2\theta_0\cdot\cos\theta_0}{\cos^2(\theta_0 - \theta_1)}. \tag{6c}$$

It can be seen that these coefficients as given by Eq. (6) are independent of the film, and they can be calculated by the incident angle and indices of the substrate and surrounding medium.

By inserting Eqs. (4) and (5) into Eq. (3), we can obtain

$$\rho(\phi) = \rho(0) + iA\phi\frac{(N_T^2 - N_0^2)\cdot(N_T^2 - N_S^2)}{N_T^2} + B\phi^2\left(\frac{(N_T^2 - N_0^2)(N_T^2 - N_S^2)}{N_T^2}\right)^2 + C\phi^2\left(\frac{(N_T^2 - N_S^2)(N_T^2 - N_0^2)}{N_T^2}\right)\frac{(N_T^2 - N_0^2)N_s^4 + (N_T^2 - N_0^2)N_T^2N_0^2}{N_T^2}. \tag{7}$$

Eq. (7) can be rewritten as a quartic equation about N_T^2:

$$a\cdot(N_T^2)^4 + b\cdot(N_T^2)^3 + c\cdot(N_T^2)^2 + d\cdot(N_T^2) + e = 0. \tag{8}$$

The coefficients in Eq. (8) are given by

$$a = B\phi^2 + C\phi^2N_0^2, \tag{9a}$$

$$b = iA\phi - 2B\phi^2(N_0^2 + N_s^2) - C\phi^2(N_0^4 + 2N_0^2N_s^2 - N_s^4), \tag{9b}$$

$$c = -iA\phi(N_0^2 + N_s^2) + B\phi^2(N_0^4 + 4N_0^2N_s^2 + N_s^4) + C\phi^2(2N_0^4N_s^2 - N_0^2N_s^4 - N_s^6) - \rho + \rho(0), \tag{9c}$$

$$d = iA\phi N_0^2N_s^2 - 2B\phi^2N_0^2N_s^2(N_0^2 + N_s^2) + 2C\phi^2N_0^2N_s^6, \tag{9d}$$

$$e = B\phi^2N_0^4N_s^4 - C\phi^2N_0^4N_s^6. \tag{9e}$$

If we know the thickness of the thin film in advance, we can calculate the complex refractive index of the film analytically from the measured ellipsometric angles (Ψ, Δ) at each wavelength. Here, we will give details about the process for obtaining the exact solution for the complex refractive index of the film. We can use Ferrari method to solve the quartic equation shown in Eq. (8), and the solution is given by

$$N_T^2 = -\frac{b}{4a} + \frac{1}{2}\left(\pm_s\sqrt{\alpha + 2y} \pm \sqrt{-\left(2\alpha + 2y \pm_s \frac{2\beta}{\sqrt{\alpha + 2y}}\right)}\right), \tag{10}$$

where in, the forms following ' $\pm_s$' should have the same sign. If $U = 0$, y is given by

$$y = -\frac{5}{6}\alpha - U, \tag{11a}$$

otherwise, y has the following form

$$y = -\frac{5}{6}\alpha - U + \frac{P}{3U}, \tag{11b}$$

where P, Q, and U are given by

$$P = -\frac{\alpha^2}{12} - \gamma, \tag{12a}$$

$$Q = -\frac{\alpha^3}{108} + \frac{\alpha\gamma}{3} - \frac{\beta^2}{8}, \tag{12b}$$

$$U = \left(\frac{Q}{2} \pm \sqrt{\frac{Q^2}{4} + \frac{P^3}{27}}\right)^{1/3}. \tag{12c}$$

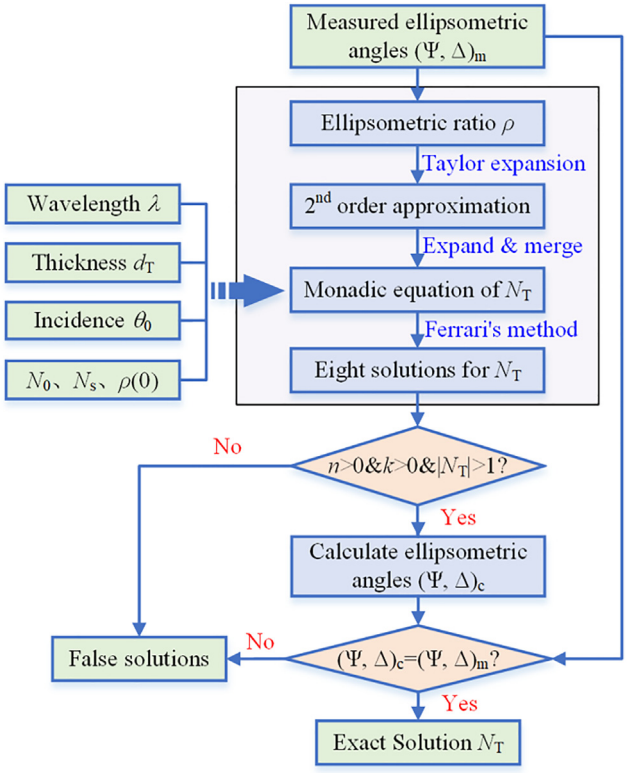

Fig. 2. Flow chart of the proposed analytical method to determine the complex refractive index of an ultra-thin absorbing film by ellipsometry.

Here, α, β, and γ can be calculated by a, b, c, d, and e as defined in Eq. (9)

$$\alpha = -\frac{3b^3}{8a^2} + \frac{c}{a}, \tag{13a}$$

$$\beta = \frac{b^3}{8a^3} - \frac{b\cdot c}{2a^2} + \frac{d}{a}, \tag{13b}$$

$$\gamma = -3\frac{b^4}{256a^4} + \frac{b^2c}{16a^3} - \frac{bd}{4a^2} + \frac{e}{a}. \tag{13c}$$

According to Eq. (10), there will be eight mathematical solutions for N_T, but only one of them is true. Two steps can help us to find the final exact solution for the complex refractive index of the film. Firstly, we can filter most of the false solutions by simply checking whether satisfies the basic physical constraint, i.e., $n = \text{real}(N_T) > 0$, $k = -\text{imag}(N_T) > 0$ and $|N_T| > 1$. Secondly, we can plug the remaining solutions into the ellipsometric functions as shown in Eqs. (1) and (2), and compare the calculated ellipsometric angles with measured ones to finally obtain the exact complex refractive index of the film. Fig. 2 shows the flow chart of the above procedures. By using the proposed method, one can analytically determine the optical constants (including the refractive index n and the extinction coefficient k) of an ultra-thin absorbing film by ellipsometry without any prior knowledge about the material, such as the bandgap and the electronic transitions.

3. Results and discussion

3.1. Numerical simulations

In this part, we will present the applicability and advantages of the proposed method in evaluating the complex refractive index of an ultra-thin absorbing film via numerical simulations. The proposed method is based on the 2nd-order Taylor expansion of the ellipsometric ratio into the terms of $\phi = 2\pi d_T/\lambda$ as shown in Eq. (7). Obviously, it is an

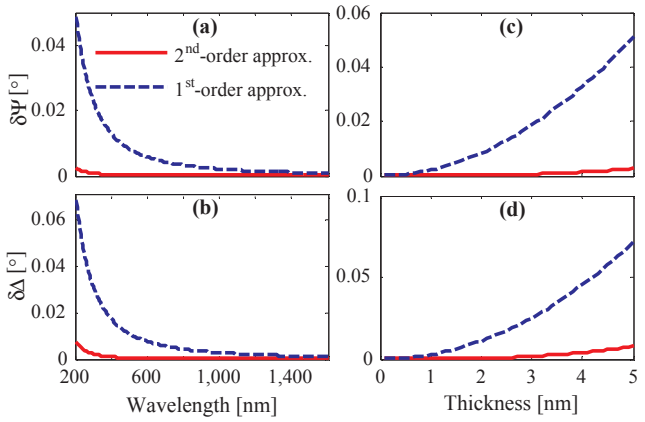

Fig. 3. Absolute errors of ellipsometric angles of a thin film (N_T = 3.8 − 1i) on a substrate (N_s = 4.2–1.3i) at 60° incident angle when utilizing the approximate Taylor expressions. (a), (b) (δΨ, δΔ) versus the wavelength over the range from 200 nm to 1600 nm with the film thickness set as d_T = 2 nm; (c), (d) (δΨ, δΔ) versus the film thickness within a range from 0.1 nm to 5 nm under a specific wavelength λ = 1000 nm. Red solid lines correspond to results of the proposed 2nd-order approximate method, and blue dashed lines refer to results by the 1st-order approximation formula. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

approximate formula, and its accuracy is significantly affected by parameters involving in the expression, including the film thickness d_T, the wavelength λ, the index of the substrate N_0, and the index of the target film material N_T. Here, we will discuss the influences of these parameters on the final accuracy of the proposed method.

Firstly, we make a comparison between the proposed 2nd-order approximation method and the most commonly used 1st-order approximation [30]. In the simulations, the indices of the substrate and the film are given with specific values (N_s = 4.2–1.3i and N_T = 3.8–1i), and the incidence is set as θ_0 = 60°. The film thickness d_T is within a range from 0.1 nm to 5 nm, and the wavelength λ is over a range from 200 nm to 1600 nm. The difference between the ellipsometric angles calculated by the Taylor expansion approximate formula and those calculated by the exact ellipsometric functions, and the ellipsometric angle difference is noted as (δΨ, δΔ). Fig. 3(a) and (b) demonstrate the simulated results (δΨ, δΔ) versus the wavelength with a specific thickness d_T = 2 nm, and Fig. 3(c) and (d) show simulated results (δΨ, δΔ) versus the film thickness under a specific wavelength λ = 1000 nm. The blue dashed lines and red solid lines represent results for the 1st-order approximation and the 2nd-order approximation, respectively. It can be seen from Fig. 3, the ellipsometric errors (δΨ, δΔ) become larger with the wavelength decreasing and with the thickness increasing for both the 1st-order and the 2nd-order approximations. This means the Taylor approximate methods are suitable to evaluate optical constants for thin films over long wavelengths. In addition, as expected, the proposed 2nd-order approximate method obviously shows much smaller errors (δΨ, δΔ), indicating that it has a higher accuracy than the 1st-order approximation especially for relatively thick films over short wavelengths. We can conclude that compared with the 1st-order approximation, the proposed 2nd-order approximate method can be applied to evaluate the complex refractive index of thin films with a much wider thickness range over a much broader wavelength range.

In the second simulations, we focus on investigating the influences of the indices of the film and the substrate on the accuracy of the proposed method. The absolute error in ellipsometric angles (δΨ, δΔ) is again taken as the evaluation criteria. In the simulations, the refractive index n of the target film ranges from 0.5 to 5, while the extinction coefficient k is from 0 to 5. The incidence and the wavelength are set at 60° and 1000 nm, respectively. To perform a comprehensive investigation, three different substrates, including the low-index sapphire (N_s = 1.76), high-index silicon (Si) (N_s = 3.8), and absorbing copper (Cu) (n_s = 0.343–6.789i), are taken into consideration. Fig. 4 shows the absolute errors of ellipsometric angles (δΨ, δΔ) as function of the refractive index n and extinction coefficient k of the film on different substrates. It can be observed from Fig. 4 that the ellipsometric errors (δΨ, δΔ) gradually become larger with the increase of both the refractive index n and the extinction coefficient k of the target film. This phenomenon tells us that it is better to use the approximate Taylor

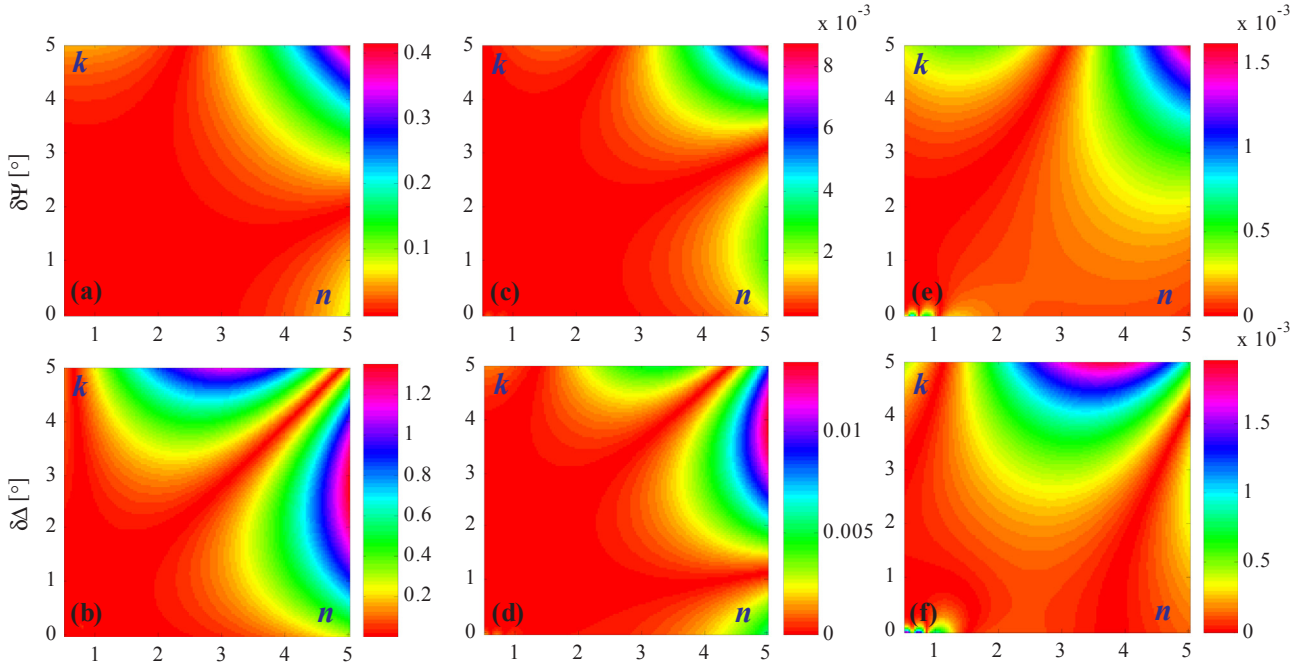

Fig. 4. Simulation results about absolute errors of ellipsometric angles (δΨ, δΔ) of a thin film with a specific thickness of 1 nm on different substrates: (a), (b) Sapphire; (c), (d) Si; (e), (f) Cu. The wavelength and incidence are 1000 nm and 60°, respectively. The refractive index n changes from 0.5 to 5.0, and the extinction coefficient k is from 0 to 5.0.

expression to deal with relatively low-index materials.

The proposed method exhibits significantly different accuracies when the film is on different substrates as shown in Fig. 4. The ellipsometric errors (δΨ, δΔ) are much larger for low-index substrate than those of high-index substrate whether it is transparent or not. For the Sapphire substrate, the deviations in ellipsometric angles can as large as the level of 1°. While for the Si and Cu substrates, the deviations in ellipsometric angles are of 10^{-3} degree, which is smaller than the measurement accuracy (~0.01°) of a general spectroscopic ellipsometry, and they can be neglected in practice. Simulation results in Fig. 4 tell us that the proposed method is more suitable to deal with low-index thin films on a high-index substrate. However, it should be noted that the low-index thin film and high-index substrate will extremely reduce the proportion of the effective optical response in the ellipsometry, namely the signal-to-noise-ratio (SNR) is reduced. Therefore, in practice, it is a compromise between the choice of substrate and the measurement SNR when we use the approximate Taylor formula to determine the optical constants of a thin film.

Finally, simulations on 2D MoS_2 films on Si substrate with thickness ranging from a monolayer to 7 layers are taken as examples to verify the proposed method in. In the simulations, the incidence is set as 60°, and wavelength range is from 193 nm to 1690 nm. Each layer of MoS_2 is assumed to have a nominal thickness 0.615 nm, and the complex index of 2D MoS_2 from a previous publication [7] is chosen as the reference N_{TR}. Using the N_{TR} and the above given parameters, we can calculate the exact ellipsometric angles of 2D MoS_2 with different layers according to the ellipsometric functions as given by Eqs. (1) and (2). Then we can resolve the complex index N_T from the ellipsometric angles by using the 2nd-order approximate formula. Fig. 5 illustrates the calculated N_T from ellipsometric angles of different layers compared with the reference index N_{RT}. It can be seen that the deviations (δn, δk) in the refractive index and the extinction coefficient from their reference values change significantly with the wavelength as well as the layer number (i.e., the thickness) of the 2D MoS_2 thin film. Overall, the deviations (δn, δk) are much smaller over the long wavelength range than those over the short wavelength range as expected. For the infrared range ($\lambda > 700$ nm), δn is less than 0.005 and δk is less than 0.01 for all the 1–7 layer 2D MoS_2 thin films, which is of a very high level for optical constant determined by ellipsometry. On the other hand, the deviations (δn, δk) monotonously increase with the layer number increase, again indicating that the proposed method is more accurate for thinner film. It can be observed that for the 2D MoS_2 below 5 layers, the maximum errors in both n and k are less than 0.1 over the ultra spectral range of 193–1690 nm, which is of an acceptable level. Thus, the proposed method can be expected to evaluate the optical constants of ultra-thin films especially 2D materials analytically from the measured ellipsometric angles with a rather high accuracy.

3.2. Experiments

In this section, experiments are performed on the analytical determination of the optical constants of two typical 2D materials, including a monolayer graphene and 1–3 layer WSe_2, to further verify the proposed method. The experimental setup is based on a Mueller matrix ellipsometer (ME-L, Wuhan Eoptics Technology Co., Wuhan, China) [35,36] whose applicable wavelength range covers 193–1690 nm. It should be clarified that since the proposed formula is based on Taylor expansion of the ellipsometric ratio, it can only be applied to solve one pair of optical constants of materials without optical anisotropy. Therefore, the Mueller matrix ellipsometer is not necessary, and researchers can also use a standard ellipsometer to perform the experimental investigation. For optically isotropic samples, the off-diagonal elements in the Mueller matrix are zero, and the diagonal elements determine ellipsometric angles, i.e., $\cos(2\Psi) = -(m_{12} + m_{21})/2$ and $\tan(\Delta) = (m_{34} - m_{43})/(m_{33} + m_{44})$, where m_{ij} is the normalized Mueller matrix elements in the i-th row and j-th coloum [1]. In the experiments, the ellipsometric angles (Ψ, Δ) of the 2D film samples as well as the bare substrate are obtained at the incident angle of 65° in air. All the 2D materials in this paper were prepared by the chemical vapor deposition (CVD) method, and the sapphire is chosen as the substrate. Figs. 6 and 7 demonstrate the experimental results of the graphene and 2D WSe_2, respectively.

The ellipsometric angles over 193–1690 nm measured by the ellipsometer are shown in Fig. 6(a) and (b). It can be seen that the measured ellipsometric angles contain instrument noises and they exhibit poor SNR due to the weak optical response of the monolayer graphene in the ellipsometry. The nominal thickness of the monolayer graphene is 0.335 nm, which has been widely known and accepted [37]. The complex index of the substrate has been determined separately by the ellipsometer in advance, and the index of the air is ideally assumed as 1. With these parameters, the complex refractive index of the monolayer graphene can be analytically resolved from the measured ellipsometric angles by the approximate Taylor expansions. Fig. 6(c) and (d) present the refractive index n and the extinction

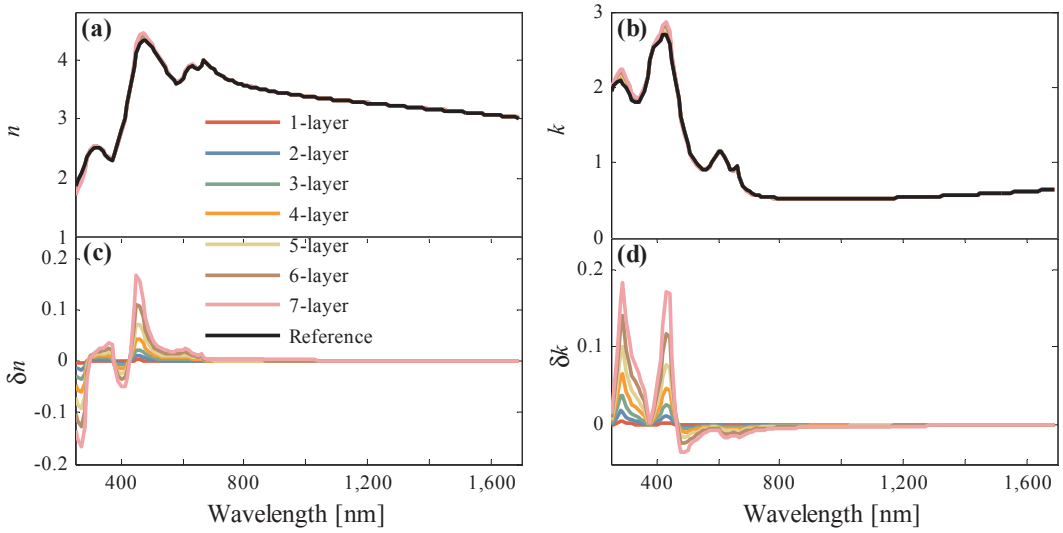

Fig. 5. Simulation results about calculating the optical constants of 2D MoS_2 films with different layers over the wavelength range from 193 nm to 1690 nm by using the proposed method compared with the reference results (black solid lines): (a) refractive index n; (b) extinction coefficient k; (c) errors in refractive index δn, and (d) errors in extinction coefficient δk.

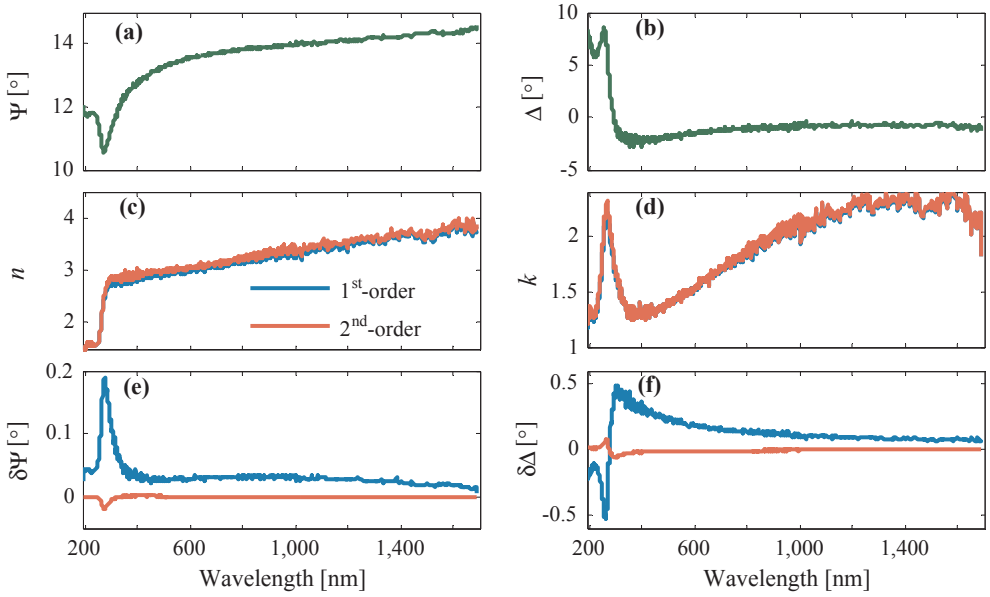

Fig. 6. Experimental results of the CVD monolayer graphene. Measured ellipsometric angles: (a) the amplitude ratio angle Ψ and (b) the phase difference angle Δ; Optical constants determined by the approximate formulas: (c) refractive index *n* and (d) extinction coefficient *k*. Absolute errors between the calculated and the measured ellipsometric angles: (e) δΨ and (f) δΔ.

coefficient *k* respectively determined by our 2nd-order method compared with results determined by the 1st-order formula. We can observe that the optical constant spectra contain obvious fluctuations over the concerned wavelength range. These fluctuations can be attributed to the measured noises in the ellipsometric angles. Both of the proposed 2nd-order or the previous 1st-order approximate formulas solve the optical constants point by point, therefore the random noises in ellipsometric angles are correspondingly reflected as fluctuations in the final results. Nevertheless, the optical constants are with high agreement with those in previous publications [6], and the major absorption peak due to the π-to-π* exciton transition in the graphene can be clearly distinguished at about 260 nm (4.75 eV). Fig. 6(e) and 6(f) give the absolute errors between the calculated and the measured ellipsometric angles. Without doubts, the ellipsometric errors (δΨ, δΔ) of our method are much smaller than those of the 1st-order approximate formula especially over the short wavelength range. These results indicate that the proposed method is more accurate than the published 1st-order approximate method in evaluating the optical constants of ultra-thin absorbing films.

It should be noted that the proposed method cannot deal with the optical anisotropy in materials. 2D layered films are optical anisotropic, and they have different optical constants in directions parallel and perpendicular to the measurement plane, i.e, the in-plane and out-of-plane directions. However, due to the limited thickness of a 2D film, the out-of-plane optical response is rather weak, and the ellipsometry mainly counts on the in-plane optical response [38]. Therefore, when

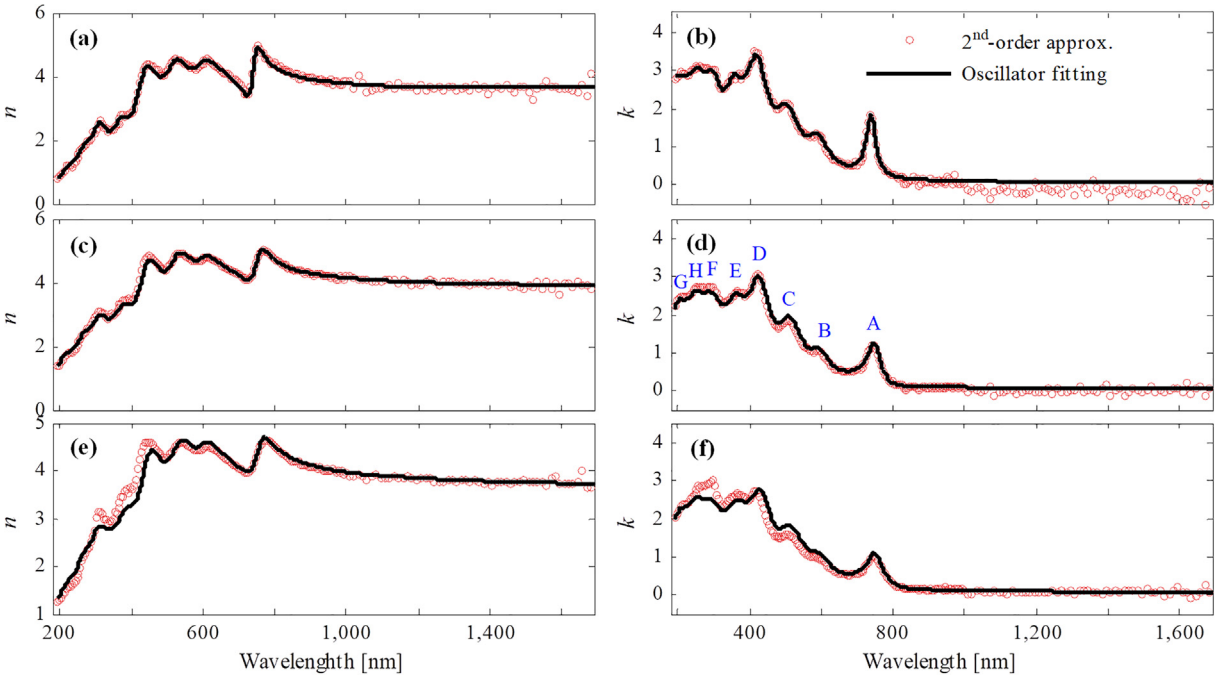

Fig. 7. Measured optical constants of 2D WSe_2 films. Subfigures in the left column are refractive index *n* and subfigures in the right column are extinction coefficient *k*. (a, b) Monolayer, (c, d) bilayer, and (e, f) trilayer. Red open circles and black solid lines correspond to results obtained by our method and those by the fitting method using classical oscillator model, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

using the proposed method to determine the in-plane optical constants of 2D materials (or other ultra-thin films), the ignorance of the optical anisotropy is reasonable.

Finally, we experimentally evaluate the optical constants of 2D WSe_2 with the thickness ranging from a monolayer to 3 layers. The 2D WSe_2 films were grown on gold foil by an ultrafast ambient-pressure CVD method using WO_3 powder and Se pellets as precursors, and then were transferred onto polished sapphire substrates. Details about the preparation and characterization of the 2D WSe_2 samples can be found in our previous publication [8]. The thicknesses of the 2D WSe_2 films can be determined by using atomic force microscope (AFM), and they are 0.661 nm, 1.123 nm, and 1.853 nm for the monolayer, the bilayer, and the trilayer WSe_2. Similar with the graphene, the complex index of the sapphire substrate has been determined separately by the ellipsometer in advance, and the index of the air is ideally assumed as 1. Then, the complex refractive index of the 2D WSe_2 films can be evaluated by the proposed 2nd-order Taylor approximate method. Since the optical constants including the refractive indices and the dielectric functions of 2D WSe_2 have been relatively widely investigated by spectroscopic ellipsometry [8,39,40], we have enough prior knowledge about the critical points and electronic transitions of 2D WSe_2, which can help us easily construct a reliable optical model for traditional ellipsometric analysis. Therefore, the measured ellipsometric spectra are also analyzed by the traditional method based on iterative fitting procedure to make a comparison and verify the proposed analytical formula. A classic stacking model containing the ambient air, the WSe_2 film layer, and the substrate, is used to embody the optical structure of the 2D WSe_2 film on the sapphire substrate. According to literatures [8], the dispersive properties of 2D WSe_2 over the concerned spectral range are described by a classical oscillator model, combining 3 Cody–Lorentz oscillators and 5 Lorentz oscillators. With the established optical model and parameterized oscillator model, theoretical ellipsometric spectra can be calculated by the transmission matrix method, and then they are fitted to the measured data by using the Levenberg-Marquardt (LM) algorithm.

Fig. 7 comparative presents the complex refractive indices of the 2D WSe_2 films determined by both of the proposed 2nd-order Taylor approximate method and the traditional inverse fitting method based on models. It can be observed that the two sets of results show extremely high agreement with each other over the whole spectral range. The optical constant curves determined by the oscillator fitting method are smooth and continuous, while results by the proposed method are obtained point by point and contain random fluctuations due to the measurement noises in the ellipsometric angles. All the feature absorption peaks (marked with uppercase letters A-G as shown in Fig. 7) can be unambiguously identified from the calculated extinction coefficient k of 2D WSe_2. The positions of these feature peaks agree well with the fitting results and those in previous publications [8]. These absorption peaks correspond to specific optical transitions in 2D WSe_2. In the traditional ellipsometric analysis, one must know lots of prior knowledge about the optical transitions, such as the bandgap, the positions and types of the transitions, etc., to successfully implement an appropriate model. Without the prior knowledge, the fitting procedure would suffer bad initial parameters, which will reduce the accuracy even reliability of the final results and cost more time. Our proposed method can analytically evaluate the optical constants directly from the measured ellipsometric angles, and it has the advantage of independency on any prior knowledge of the optical transitions of the material.

4. Conclusions

In summary, we proposed an analytical formula to deal with the inverse ellipsometry of an ultra-thin film on arbitrary substrates based on 2nd-order Taylor expansion of ellipsometric functions. Detailed derivations were presented to obtain a polynomial equation about the complex refractive index from the 2nd-order Taylor expansion. The exact solution for the complex refractive index can be obtained by two steps: (1) solving the polynomial equation by using the Ferrari method; (2) filtering the false solutions by basic physical constraints. Numerical simulations were performed to discuss the applicability and advantages of the proposed method compared with the previous 1st-order Taylor formula. Results demonstrate that the proposed method: (1) can be applied for ultra-thin films with wider thickness range from a single atomic layer to 5 nm; (2) can be applied for ultra-wide spectral range from deep ultraviolet to infrared regions; (3) has about an order of magnitude higher accuracy than the 1st-order Taylor formula. With the proposed method, we experimentally investigated the complex refractive indices of typical 2D materials, including the monolayer graphene and 1–3 layer WSe_2 over an ultra-wide spectral range (193–1690 nm). Results calculated by the proposed method show high agreement with those obtained by traditional ellipsometric analysis based on inverse fitting, which demonstrates the validity of the proposed method. The present work provides a new way to extend the ellipsometry to explore the optical properties of ultra-thin films especially novel 2D materials with complex and unknown electronic characteristics.

CRediT authorship contribution statement

Honggang Gu: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Funding acquisition. **Simin Zhu:** Methodology, Software, Investigation, Resources, Writing - original draft. **Baokun Song:** Investigation, Resources, Writing - review & editing. **Mingsheng Fang:** Investigation, Writing - review & editing. **Zhengfeng Guo:** Validation, Writing - review & editing. **Xiuguo Chen:** Writing - review & editing, Funding acquisition. **Chuanwei Zhang:** Writing - review & editing. **Hao Jiang:** Writing - review & editing, Funding acquisition. **Shiyuan Liu:** Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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