Dual-layer ultrathin film optics II: experimental studies and designs

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Abstract
This paper presents an experimental study of using dual-layer ultrathin films with a high refractive index and low refractive index to approximate a single-layer thin film with an equivalent intermediate refractive index, which is the basis of the functional graded refractive index thin film stack using dual-layer ultrathin films. Using ion beam deposition, five sets of ultrathin films of titanium dioxide (TiO$_2$) and aluminium oxide (Al$_2$O$_3$) are deposited on silicon with different volume fractions and characterized by spectroscopic ellipsometer for the ordinary/extraordinary refractive index and by spectrophotometer for the reflectance. By designing the sequence of TiO$_2$ and Al$_2$O$_3$ ultrathin films, the measured results show a good agreement between the experiments and simulation of the equivalent birefringent thin film. An application example of using the TiO$_2$ and Al$_2$O$_3$ dual-layer ultrathin films to approximate a single-layer antireflection coating for silicon is presented.

Keywords: dual-layer ultrathin film, ion-beam assisted deposition, antireflection

1. Introduction

Today, most optical thin films for e.g., antireflection (AR) coating, high-reflection or wavelength filtering are based on the optimization of quarter-wavelength ($\lambda/4$) film stack by adjusting the layer thickness and adding film layers, while restricting to the existing available refractive index of materials. Alternative to this approach, thin films with "continuous" refractive index profile are considered attractive and for material systems in integrated photonic circuits, solar cells, light emitting diodes, lens coupler and other optoelectronic devices [1-4]. Recent progress in the graded refractive index (GRIN) thin film technology has led to encouraging achievement to approximate the desired
refractive index such as the use of composite films [5], nanostructured arrays such as nanorods or nanocylinders [6-8] and dual-layer ultrathin films [9, 10].

Out of all the aforementioned approaches, the most straightforward method to achieve the desired refractive index is the use of dual-layer ultrathin film of high \((n_H)\) and low index \((n_L)\) materials. According to the Herpin equivalent method [11], this ultrathin alternate layer structure can exhibit a similar spectral response to that of a single optical thickness of \(\lambda/4\) coating layer when the thickness of each layer is much smaller than the wavelength of interest. By simply changing the relative thickness of these index layers, any desired refractive index in between \((n_L<n<n_H)\) can be obtained [12]. At present, theoretical studies employing effective medium theory [13, 14] have suggested that dual-layer ultrathin film can approximate an effective birefringent material with the effective refractive index dependent on the volume fraction of the \(n_H\) material but without revealing the influence of thickness of dual-layer thin films, the incidence angle and desired refractive index of the birefringent film on the approximation. In our companion theoretical work, we further derive the detailed formulations of using dual-layer ultrathin films to approximate a single thin film layer for s-polarized and p-polarized light under arbitrary incidence angle. A comprehensive analysis of the effect of film thickness and the incidence angle for both s-polarized light and p-polarized light on the equivalence approximation is also given [15]. Unlike any other work, in this paper, we conduct the experimental study of dual-layer ultrathin film optics. As both \(\text{TiO}_2\) and \(\text{Al}_2\text{O}_3\) materials are finding an increasing use in the nanophotonic devices due to their good thermal and mechanical stability, the dual-layer ultrathin films based on \(\text{TiO}_2\) and \(\text{Al}_2\text{O}_3\) deposited by ion beam deposition (IBD) are thus chosen in this work to approximate a single-layer birefringent film.

IBD is a thin film deposition technique that combines the concurrent use of a low energy assisted ion beam source with the physical sputtering of material targets by a primary ion beam source in order to improve the properties of the deposited coating. Such difference from other ultrathin film deposition techniques such as chemical vapour deposition and atomic layer deposition permits control over film adhesion, intrinsic stress of the film and morphology. Applying such ion-assisted beam processes thus offers the ability to grow very dense, high quality and stable films with minimum
moisture absorption. Characterization tools such as ellipsometry and spectrophotometry are used to extract the effective refractive index of the ultrathin discrete bilayers with its equivalent birefringent thin film. The measured results show a good agreement with the simulated results of the equivalent birefringent thin film.

Building from the dual-layer thin films’ concept, we further demonstrate a design example of a simple three-layer TiO$_2$/Al$_2$O$_3$/TiO$_2$ ultrathin film to approximate a single layer for silicon (Si) antireflection coating. The flexibility in designing the dual-layer ultrathin film stack is demonstrated. Our work requires only three layers while retaining an excellent agreement indicated by both the theoretical and experimental results, instead of using 60 layers of Al$_2$O$_3$ and TiO$_2$ films by atomic layer deposition (ALD) for Si AR coating [16, 17]. The present experimental work can be further extended to a functional GRIN thin-film stack such as broadband omnidirectional antireflection coating, wavelength bandpass filter and integrated GRIN lens for the light coupling into a nanowaveguide.

2. Ultrathin TiO$_2$/Al$_2$O$_3$ layers: Experimental details

The growth of TiO$_2$/Al$_2$O$_3$ ultrathin films is carried out using IBD (Oxford Instrument Optofab3000) at room temperature with low background pressure of ~6 x 10$^{-6}$ Torr. This two-material thin film stack deposition is achieved by rotating and sputtering at the respective 4” dielectric target materials of TiO$_2$ and Al$_2$O$_3$ installed in the chamber. A mixture of argon and oxygen ions is used to provide a stable assist which helps to densify the films at reduced substrate temperature. We prepared five different sets of dual-layer ultrathin TiO$_2$/Al$_2$O$_3$ films on Si substrate. The total thickness of the dual-layer thin films is chosen to be 50 nm. The volume fractions of the TiO$_2$ layer, $f_H = \frac{h_H}{h_L + h_H}$, where $h_H$ and $h_L$ is the thickness of TiO$_2$ and Al$_2$O$_3$ film, respectively, for these five sets samples are 0.18, 0.32, 0.5, 0.6 and 0.8.
2.1 Characterization by ellipsometer: Effective Refractive index of single equivalent anisotropic film

For the deposited films, a variable angle spectroscopic ellipsometer (VASE) is employed to give the refractive index with dispersion over the wavelength range and thickness. Ellipsometry is known to measure the change in polarization of light reflected or transmitted from the surface of a sample. The change in polarization is represented by both an amplitude ratio, Ψ, and phase difference, Δ. These values are related to the ratio of Fresnel reflection coefficient $R_p$ and $R_s$ for p-polarized and s-polarized light, respectively and are written as $\frac{R_p}{R_s} = \tan(\psi) e^{i\Delta}$. Hence the spectral acquisition range and the variable angles of incidence in the VASE can be optimized for the determination of layer thickness or the optical constants of the film. Each single TiO$_2$ layer film and Al$_2$O$_3$ layer film and the dual-layer thin film are first characterized using the isotropic Cauchy model. The dual-layer thin film is then characterized incorporating the anisotropic Bruggeman effective medium approximation (EMA) model which treat both layers as an optical continuum to fit the measured (Ψ, Δ) curves [18]. We note that this model is valid for only ultrathin films (one tenth of the optical wavelength). The model mixes the isotropic optical constants of the measured single layer TiO$_2$ and Al$_2$O$_3$ and the void volume fractions in the anisotropic EMA model are assumed from the varying thickness of the two-layer TiO$_2$ and Al$_2$O$_3$.

We use one of the film sets with a volume fraction $f_{H}=0.18$ where the thickness of TiO$_2$ film is 9 nm and Al$_2$O$_3$ film is 41 nm as an example. Figure 1(a) and figure 1(b) compared the fitting results of Ψ and Δ parameters from the anisotropic Bruggeman EMA model against the measured homogeneous dual-layer films at three incident angles, 65, 70 and 75°. The results indicate a reasonable quality fit indicating for both the isotropic dual-layer model and single equivalent anisotropic film model. The mean squared error (MSE) which is used to quantify the difference between these curves is ~25. Figure 2 shows the resultant $n_{xx}$ and $n_{yy}$ and $n_{zz}$ of the single birefringent anisotropic film and the refractive index of the dual-layer TiO$_2$/Al$_2$O$_3$ film. The single anisotropic film has a refractive index in between the refractive index of single TiO$_2$ film and single Al$_2$O$_3$ film.
Figure 1. The comparison of the ellipsometric parameter (a) $\Psi$ and (b) $\Delta$ of the anisotropic Bruggeman EMA with the dual-layer model for 9nm TiO$_2$/41nm Al$_2$O$_3$ two-layer film at three incident angles, 65, 70 and 75$^\circ$. 
Figure 2. Plot of the resultant $n_{xx}$ and $n_{yy}$ and $n_{zz}$ of the single birefringent anisotropic film and the refractive index of the dual-layer TiO$_2$/Al$_2$O$_3$ film.

Figure 3. Plot of the corresponding effective $n_{xx}$ and $n_{yy}$ and $n_{zz}$ calculated and measured at 1000 nm wavelength against the volume fraction $f_H$.
2.2 Characterization by spectrophotometer: Comparison of dual-layer structure and birefringent film

For the TiO$_2$/Al$_2$O$_3$ dual-layer thin films, Figure 3 gives the corresponding effective $n_{xx}$ and $n_{yy}$ and $n_{zz}$ calculated and measured at 1000 nm wavelength against the volume fraction $f_H$ (different thickness of TiO$_2$ film) where $n_{xx} = n_{yy} = \sqrt{\frac{n_H^2 h_H + n_L^2 h_L}{n_H + n_L}}$ and $\frac{1}{n_{zz}} = \sqrt{\frac{1}{n_H^2 h_H + n_L^2 h_L}}$, $n_H$ and $n_L$ is the refractive index of TiO$_2$ and Al$_2$O$_3$, respectively. The circle and triangle marks are the respective ordinary and extraordinary refractive index measured via the spectroscopic ellipsometer. Open circles represent the measured results in $n_{xx}$ direction whereas the closed triangles represent the measured results in $n_{zz}$ direction. The MSE for these five film sets is ~25, 38, 47, 43 and 29. The measured data show a good agreement with the theoretical calculation. The measured results agree well with the calculated results except for the sample with $f_H = 0.8$ (40 nm TiO$_2$/10 nm Al$_2$O$_3$). This may be contributed by the high porosity of the 10 nm deposited layer Al$_2$O$_3$ which has a measured low refractive index of ~1.53 since thicker Al$_2$O$_3$ layer exhibits higher refractive index of ~1.64. This “effective” birefringence is an inherent property of dual-layer ultrathin film stack. Therefore, in our numerical calculation and design of dual-layer ultrathin film based devices, we take account of this “effective” birefringence using the equivalent anisotropic thin film modal for the accuracy of the design. The comparison between the isotropic and anisotropic equivalent thin-film models shows that there is some difference in terms of the device’s performance but it is not significant due to the orientation of extraordinary axis. However, when using this dual layer ultrathin film stack as graded refractive indexes lens for nanowaveguide collimating as proposed recently, this birefringent property introduces different focusing length between the s-polarized and p-polarized light [19].

Following the refractive index characterization of these dual-layer thin films, we seek to study the reflectance results. The reflectance measurement is conducted and compared with the numerical simulations based on the real dual-layer thin films structure and equivalent birefringent film. A UV-VIS-NIR spectrophotometer (UV-3600) with the integrating sphere compartment (MPC-3100) is used to carry out the reflectance measurement. The spectrophotometer is equipped with three detectors such as a PMT (photomultiplier tube), InGaAs (indium gallium arsenide), and PbS (lead sulfide).
detector which ensures high sensitivity across the entire measured wavelength range from 240 to 2600 nm. In addition, the compartment can accommodate large samples and allows the installation of absolute specular reflectance attachment of 5 and 45 degrees. Using the TiO$_2$/Al$_2$O$_3$ set with a volume fraction of $f_0=0.18$ where the thickness of TiO$_2$ film is 9 nm and Al$_2$O$_3$ film is 41 nm as an example, figure 4 compared the measured and simulated reflectance spectra with a reflection angle of 5°. Except for the bumps at around 720 and 850 nm which are due to the wavelength grating switch during the reflectance analysis, the experimental results agreed well with the calculated results based on the original dual-layer thin films (the dashed line). However the simulation results based on the usual one effective birefringent layer vary away from the two layers and it is more severe at the short wavelength end. As pointed out in our theoretical paper, the thickness of the dual-layer film is required to be less than 1/10 wavelength in the media in order for a good agreement between the equivalent birefringent film and dual-layer thin film. However, the ellipsometer measurement above still gives a good approximation. This is because the ellipsometer measurement used a much larger incident angles (65 to 75°) than the presented spectrophotometer results in this section and it was pointed out in our theoretical paper, that a large incidence angle has a better tolerance to the thin film thickness as compared to the case of small incidence angle.
Figure 4. Comparison of the measured and simulated reflectance spectra of dual-layer film with a reflection angle of 5°.

Figure 5. Division of a single Al₂O₃ layer to two thinner layers to form a top birefringent TiO₂/Al₂O₃ layer.

Figure 6. Comparison of the measured and simulated reflectance spectra of the hybrid thin film with a reflection angle of 5°.
To improve the approximation accuracy, we sub-divide the Al₂O₃ layer into two layers artificially as shown in figure 5. The top Al₂O₃ layer is combined with the TiO₂ layer to form the dual-layer ultrathin films and the bottom Al₂O₃ layer is retained. Therefore, the original dual-layer thin films now turns into a ultrathin isotropic Al₂O₃ layer with a birefringent layer on top and the birefringent layer has a corresponding \( n_{xx} = n_{yy} \) and \( n_{zz} \) of 1.76 and 1.69 respectively. For such hybrid thin films, the reflectance for this new approximated thin film layers is shown in figure 6. As compared to the results of single equivalent birefringent layer, this design of thin films gives a significant better agreement with the experimental data. This also implies that we can apply such hybrid thin-film stack, i.e., a combination of ultra-thin films based birefringent films with the isotropic thin film structure in practical coating applications as shown in the next paragraph.

3. Demonstration of TiO₂/Al₂O₃ ultrathin films as one single layer antireflection coating

Here, using the above concept of the hybrid dual-layer TiO₂ and Al₂O₃ ultrathin films, we demonstrate the use of such thin films to experimentally approximate a single antireflection coating for Si. This choice is made only for simplicity and is not limited to any applications. In Reference [16], the authors demonstrated using 60 layers of Al₂O₃ and TiO₂ films by ALD for Si AR coating. However for comparison, our dual-layer AR coating presented in this paper only requires three layers as shown below while retaining an excellent agreement with the desired single layer.
Figure 7 illustrates the design procedure starting from (a) to (d). Figure 7(a) is the original single layer antireflection film. Using the refractive index of silicon at 500 nm measured as design example, the corresponding refractive index and thickness of the single-layer antireflection film are 2.072 and 60.32 nm. According to the above example, the individual thickness of the film will be quite thick if we use just a single pair of TiO$_2$ and Al$_2$O$_3$ films directly to approximate the antireflection film. Therefore, in our design, we first split the antireflection layer film into two thinner layers and thickness of each layer is now 30.16 nm (dashed box in figure 7(a)). Next, two pairs of TiO$_2$/Al$_2$O$_3$ films is used to approximate them as shown in figure 7(b) and the thickness of the TiO$_2$ and Al$_2$O$_3$ is 16.9 nm and 13.25 nm, respectively.

A useful property for such dual-layer ultrathin films is that its performance is independence of the sequence of the two thin films. Hence it is possible to switch the sequence of the bottom TiO$_2$/Al$_2$O$_3$ films from figure 7(b) to figure 7(c) and the two Al$_2$O$_3$ thin films can be simply merged into one single thicker layer as shown in figure 7(d). Based on this new design, a three layer of thin TiO$_2$/ thicker Al$_2$O$_3$/ thin TiO$_2$ is formed to approximate the single antireflection layer and the thickness of the three layers is 16.9 nm, 26.7 nm and 16.9 nm, respectively. This three layer sequence has lesser number of steps in the fabrication process. In the fabrication process, the first layer of TiO$_2$ thin film is deposited on the Si substrate using IBD with 850 W of RF power to the 4 inch TiO$_2$ target
at 1.5 SCCM (standard cubic centimetre per minute) of Ar gas and 0.9 SCCM of O₂ gas for ~7 minutes. The second layer of Al₂O₃ is also deposited using 880 W of RF power to the 4 inch Al₂O₃ target at 3 SCCM of Ar gas and with 0.2 SCCM of O₂ flowing into the chamber for ~8 minutes. The growth process is then completed with the final deposition of TiO₂ layer for 7 minutes.

Optical measurement is then carried for three cases: 1) light with incidence angle of 5° (no obvious difference between s-polarized and p-polarized light at this small angle); 2) s-polarized light with an incidence angle of 45° and 3) p-polarized light under an incidence angle of 45°. The measured reflectance from bare silicon substrate is also presented in each figure. To have a comparison between the experimental data and theoretical design, the calculated reflectance from the single antireflection layer and TiO₂/Al₂O₃/TiO₂ three-layer thin film stack for these three cases are presented. The corresponding results for these three cases are given in figure 8(a), figure 8(b) and figure 8(c), respectively. The considered wavelength range is from 400 nm to 1100 nm. First, the results of the three cases show the significant reflection reduction as compared to bare Si due to the effect of the TiO₂/Al₂O₃/TiO₂ film stack and also the calculation has a very good agreement with the measured data, which means the designed TiO₂/Al₂O₃/TiO₂ has a very good approximation to the single-layer thin film for either s-polarized or p-polarized light under various incidence angles. Hence our current work requires only three layers to approximate a Si AR coating while retaining an excellent agreement indicated by both the theoretical and experimental results.
Reflectance vs. Wavelength (nm)

(a) Incidence light angle 5°

(b) S-polarized incidence light angle 45°
Figure 8. Measured and simulated reflectance spectra of TiO2/Al2O3/TiO2 stack at (a) s-polarized light with incident angle of 5° (b) s-polarized light with incidence angle of 45° (c) p-polarized light with incidence angle of 45°.

4. Conclusion

We have demonstrated the use of dual-layer ultrathin films with a high refractive index $n_H$ and low refractive index $n_L$ to approximate a single-layer thin film. With IBD deposition, a set of ultrathin films of TiO$_2$ and Al$_2$O$_3$ have been deposited on Si with different volume fractions and characterized by spectroscopic ellipsometer for the ordinary/extraordinary refractive index and by spectrophotometer for the reflectance, respectively. The measured results have shown a good agreement between the experiments and simulation of the equivalent birefringent thin film by designing the sequence of TiO$_2$ and Al$_2$O$_3$ layers. As an application example, our design and experimental demonstration of using TiO$_2$ and Al$_2$O$_3$ to approximate a single-layer antireflection for silicon agrees very well with the theoretical simulations. This experimental study of the dual-layer ultrathin films is useful for the development of graded-refractive index thin film stack based devices.
References


