Dielectric Multilayer Films Fabricated by Magnetron Sputtering: How Far Can the Iridescence Be Tuned?

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Periodic dielectric multilayer structures can generate interferential colours from optically transparent basic materials. Their iridescence property, i.e. the change of colour with the illumination or viewing angle, is exploited in the industry to produce structurally coloured coatings and paints. Magnetron sputtering is an efficient technique for producing multilayer films owing to its ability to deposit films on large surfaces with excellent uniformity and reproducibility in both the film thickness and composition. Based on a theoretical model of the optical response, we investigated the iridescence tuning range of the technologically important SiO_2/TiO_2 material system. Radically different iridescent behaviours were predicted theoretically and demonstrated experimentally by selecting appropriate combinations of period and layer thickness ratio.

Introduction

Iridescence is the property that structural materials have to display vivid, metallic colours which change with the angle of illumination or viewing. These colours have a physical origin lying in the interference of light waves within the material structure, hence so-called "structural colours".[1] To exhibit this property, the material's refractive index must be structured at the scale of visible light wavelengths (400–700 nm). Many iridescent materials can be found in nature, where a single biological dielectric material (usually chitin) embedded with air or water-filled regions (taking the form of layers or cavities) exhibit the refractive index contrast required to produce light interference.[1]

Plasma processes, such as magnetron sputtering, are suitable for the mass production of iridescent coatings on various substrates. These coatings may take the form of dielectric multilayer films, made by depositing alternatively thin layers of two different materials in a periodic way. Advantages of magnetron sputtering processes are the ability to deposit any kind of dielectric materials, the excellent uniformity and reproducibility of the deposited films on large areas, the precise control of both the film thickness and its composition.

The colour of the coating is determined by the wavelength at which the reflectance of the multilayer film is maximal. This wavelength, so-called the dominant reflected wavelength, can be predicted theoretically using a semi-infinite one-dimensional (1D) photonic crystal model of the multilayer film.[2] For a given incidence angle, the dominant reflected wavelength depends on the refractive indexes and the thicknesses of the two constitutive layers and, as the angle is increased, it shifts towards shorter wavelengths, producing iridescence.

The point of this article is: given two dielectric materials, how far the iridescence of the multilayer film can be tuned? In other words, how far can we change the visual aspect of the coating by only adjusting the layer thicknesses? To answer this question, we use an original approach for predicting the colour of periodic dielectric multilayer films, whose theoretical concept comes from our studies of the iridescence in various living organisms.[2] On the basis of

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Plasma Process. Polym. **2009**, *6*, S746–S750

DOI: 10.1002/ppap.200931801

this concept, we predict that radically different iridescent behaviours can be obtained by selecting the appropriate combinations of period and layer thickness ratio. This prediction is validated by measurements of the reflectance of SiO_2/TiO_2 multilayer films fabricated by magnetron sputtering.

Theoretical Model

The multilayer film is first regarded as a 1D photonic crystal of period $a = d_1 + d_2$, where d_1 and d_2 are the thicknesses of the two layers which form the unit cell. By convention, the most (less) refringent material is labelled #2 (#1). The dielectric materials are assumed to be non-absorbing (in the wavelength range of interest) and are characterised by a dielectric constant equal to $\varepsilon_{1,2} = (n_{1,2})^2$ ($n_{1,2}$: refractive index of material 1 or 2). The high-index to low-index layer thickness ratio is defined by $r = d_2/d_1$. The refractive index contrast is defined by $c = n_2/n_1$. The unit cell is repeated N times to form the multilayer film and the whole structure lies on top of a substrate.

Let us now consider the theoretical case of a *semi-infinite* 1D photonic crystal (i.e. $N \to \infty$) and compare it with the practical case of a multilayer film (N finite). The reflectance spectrum of the latter is characterized by narrow bands whose peak wavelengths are integer sub-multiples of the Bragg wavelength.[3] The shape of these bands depends on the number of unit cells in the periodic structure, N. Provided that N is sufficiently large, however, the spectral shape is practically unchanged by taking the limit $N \to \infty$. Starting from small values of N, the peak wavelength of the reflectance tends rapidly to the asymptotic ($N \to \infty$) value as N is increased whereas the peak intensity and the bandwidth of the reflectance evolve more slowly to their asymptotic values. The hue, saturation (purity) and brightness of a colour are related to the peak wavelength, spectral bandwidth and peak intensity of the reflectance, respectively (assuming that one single reflectance band is present in the visible range). The hue of a multilayer film can therefore be well estimated by assuming $N \to \infty$.

In the theoretical model, the following assumptions are made: $N \to \infty$, $c = n_2/n_1$ is small, λ is large compared with d_1 and d_2. The latter assumption (long-wavelength approximation) allows us to define an average refractive index for the unit cell. For transverse-electric (TE) light waves, at any angle of incidence, the average index, $\tilde{n}$, is given by:

$$\tilde{n} = n_1 \left(\frac{1 + rc^2}{1 + r} \right)^{1/2} \tag{1}$$

and the fundamental Bragg wavelength is given by:

$$\lambda_B(\theta) = 2a\sqrt{\tilde{n}^2 - sin^2\theta} \tag{2}$$

where θ is the angle of incidence of the light.[2] Based on Equation (2), we define $\lambda_B = \lambda_B(\theta = 0)$ and $\delta\lambda = \lambda_B(\theta = 0) - \lambda_B(\theta = \theta^*)$ as the Bragg wavelength at normal incidence and its shift as the angle is increased from 0 to θ^*, respectively.

Sample Fabrication and Characterisation Methods

Two SiO_2/TiO_2 multilayer ($N = 12$) films with different periods and layer thickness ratios were fabricated using the AJA magnetron sputtering system. Titanium target (2 in., 99.99% purity) and silicon oxide target (2 in., 99.9% purity) were used for dc sputtering in a reactive O_2 atmosphere and radio-frequency (RF) sputtering, respectively. For the deposition of TiO_2 layers, the O_2 flow rate was selected in order to operate beyond the transition region of the cathode voltage versus oxygen flow curve where the deposition fully works in the oxide mode. Fully automated deposition processes were carried out under argon gas flow (12 sccm), at room temperature and with a rotating substrate (microscope glass slides, $24 \times 76\ mm^2$) to increase the deposition uniformity. The experimental conditions are summarised in Table 1. In the present conditions, titanium oxide and silicon oxide were deposited in the amorphous phase. The TiO_2 and SiO_2 deposition rates were calibrated by

Table 1. Experimental conditions for the fabrication of strongly iridescent (SI) and weakly iridescent (WI) dielectric multilayer films made of 2×12 alternating layers of TiO_2 and SiO_2.

Sample	Coating thickness divided by the number of periods	TiO_2 (SiO_2) deposition time	TiO_2 (SiO_2) deposition rate	dc power	RF power	Pressure
	nm	min	$nm \cdot min^{-1}$	W	W	mTorr
SI	227.9 ± 1.2	60 (2)	5.0 (3.4)	300	270	3
WI	90.6 ± 0.3	2 (35)	2.5 (4.5)	300	270	3

dc and RF powers are relative to dc magnetron sputtering of titanium target in O_2 reactive atmosphere and to RF magnetron sputtering of silica target, respectively.

depositing a single layer of the corresponding oxide on a glass substrate and measuring its thicknesses with a DEKTAK surface profilometer (the deposition rate being equal to the measured thickness divided by the deposition time).

A strongly iridescent (SI) coating and a weakly iridescent (WI) coating were fabricated by depositing 2×12 layers of TiO_2 and SiO_2 on glass substrates. The TiO_2 and SiO_2 deposition times were chosen in such a way that the resulting period and layer thickness ratios gave either red or blue colour to the coating at normal incidence which shifts to either green or violet with the incidence angle. By fitting the sample transmittance spectrum measured at normal incidence (not shown) to a multilayer thin-film-on-thick-slab model, we were able to retrieve the thickness values of TiO_2 and SiO_2 layers.[4] For the SI (WI) sample, the TiO_2 and SiO_2 thicknesses were equal to 9 and 218 nm (84 and 10 nm), respectively. The retrieved values of the period (227 and 94 nm) were found to be in good agreement with the coating thickness (measured by DEKTAK surface profilometer) divided by the number of periods (Table 1). The retrieved values of d_1 and d_2 were used to spot the (a,r) coordinates of the SI and WI samples (crosses in Figure 1, see Theoretical Predictions).

Reflectance measurements were performed on the two coatings at various incidence angles using a CARY 500 UV–Vis–NIR spectrophotometer (VARIAN) equipped with a Variable Angle Specular Reflectance Accessory. The incident light beam was TE-polarised by inserting a Glan Taylor polariser between the monochromator and the sample and the reflected light was measured in the specular direction at angles of 20, 40 and 60°. A high-reflectivity specular reflectance standard mirror (STAN-SSH, OCEAN OPTICS) was used as a reference for the normalisation of the reflectance data. In theory, the reflectance cannot exceed 100%. In practice, the measured reflectance may exceed a little bit 100% due to experimental factors (modelling of the reference mirror reflectance, degradation with time of the reference mirror surface, etc.).

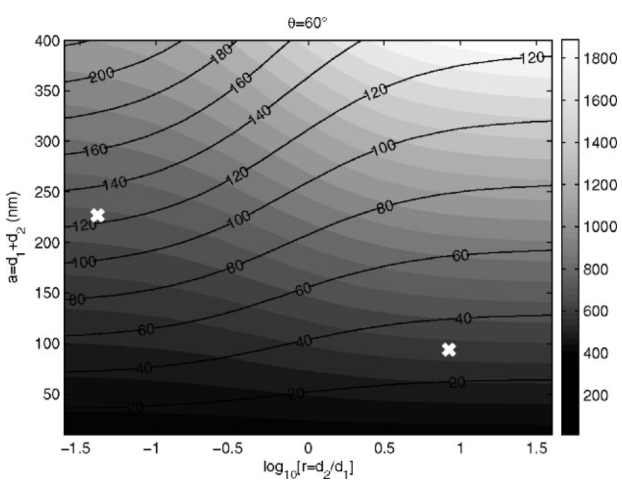

Figure 1. Maps of the dominant reflected wavelength at normal incidence (gray scale – values in nm) and its shift as the angle is increased from 0 to 60° (black lines – values in nm are indicated along the lines). The abscissa is the layer thickness ratio and the ordinate is the period of the multilayer structure. The maps were drawn for refractive index values of $n_1 = 1.45$ and $n_2 = 2.5$. Crosses correspond to actual layer thickness values of two SiO_2/TiO_2 multilayer films (SI and WI samples) which were designed to display strong (cross on the left) or weak (cross on the right) iridescence.

Theoretical Predictions

The iridescence of the multilayer film can be predicted on the basis of Equation (1 and 2). For this purpose, we draw the maps of λ_B and $\delta\lambda$ in the Cartesian coordinate system defined by a and r, the geometrical parameters of the multilayer film (Figure 1). The constitutive materials are considered to be given and therefore n_1 and $c = n_2/n_1$ are fixed in Equation (1). The maps of λ_B and $\delta\lambda$ give, respectively, the range of dominant reflected wavelengths (hues) at normal incidence and the range of dominant reflected wavelength shifts (iridescence) at a given angle, which are achievable by tuning the layer thicknesses independently. A point on the map gives the hue and the iridescence of a multilayer film whose layer thickness are related to the coordinates of the point by: $d_1 = a/(1 + r)$, $d_2 = r \times d_1$. If we want to design a coating which has *this* red hue (e.g. 630 nm) at normal incidence and turns to *that* green hue (e.g. 550 nm) at the angle of precisely 60°, we just have to pick up the coordinates of the intersection of the $\lambda_B = 630$ nm curve with the $\delta\lambda = 80$ nm curve in the map drawn for $\theta^* = 60°$. SI coatings are located in the north–west region of the map (small r, large a) whereas WI coatings are located in the south–east region of the map (large r, small a).

The maps of Figure 1 were drawn for $n_1 = 1.45$ and $n_2 = 2.5$. These refractive index values are typical of amorphous silica (SiO_2) and amorphous titanium oxide (TiO_2) in the visible part of the electromagnetic spectrum. The a-axis and r-axis ranges were calculated using a realistic range of layer thicknesses. The minimum thickness was taken equal to 5 nm, which was about the resolution limit of our thickness measurements. The maximum thickness was taken equal to 200 nm from practical considerations on the sample fabrication time (depending on the deposition rate, a layer of 200 nm could be deposited in 40–80 min, cf. Table 1). Our theoretical analysis shows that, by selecting appropriate values of the layer thicknesses within this range, one can tune considerably the iridescence of SiO_2/TiO_2 multilayer films. As a proof-of-principle, two different multilayer films were fabricated whose geometrical para-

Plasma Process. Polym. **2009**, *6*, S746–S750

DOI: 10.1002/ppap.200931801

meters are indicated by crosses in Figure 1. One is representative of SI coatings whereas the other is representative of WI coatings.

Experimental Results

The reflectance spectra measured in the visible range at variable angles on SI and WI coatings are shown in Figure 2 and 3, respectively. The spectra exhibit the expected Bragg reflection peak (with typical oscillations on both sides of the peak), which shifts toward shorter wavelengths as the angle is increased (cf. Equation 2). The latter property, i.e., the iridescence, is much less pronounced in the WI sample than in the SI sample, in agreement with the coating design. The WI coating looks more or less blue at all angles whereas the SI coating turns from red to green as the angle is increased from normal to grazing incidence. These results give a good example of how far the iridescence of multilayer film coatings can be tuned by playing with the layer thicknesses only, for a given pair of constitutive materials.

Using the retrieved layer thickness values, the dominant reflected wavelengths were predicted at the angles used for the measurements (vertical dashed lines in Figure 2 and 3). To improve the prediction, we have adapted the refractive index values to the wavelength range where the coating was designed to operate. Typical refractive index dispersion laws for amorphous silicon oxide and amorphous titanium oxide led to the following choices for the SI (WI) sample: $n_1 = 1.45$ (1.47) and $n_1 = 2.5$ (2.6). For both samples, the predicted dominant reflected wavelengths are in good agreement with the measured reflectance spectra. These results show the usefulness of the proposed theoretical approach for designing iridescent coatings.

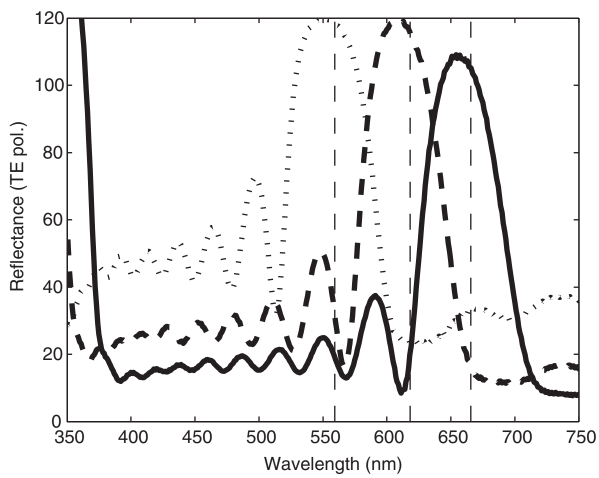

Figure 2. Reflectance spectra of SI sample measured at 20° (solid curve), 40° (dashed curve) and 60° (dotted curve) incidence angle. The polarisation state of the incident light was transverse-electric (TE). Vertical dashed lines indicate the positions of the dominant reflected wavelength as predicted by theory.

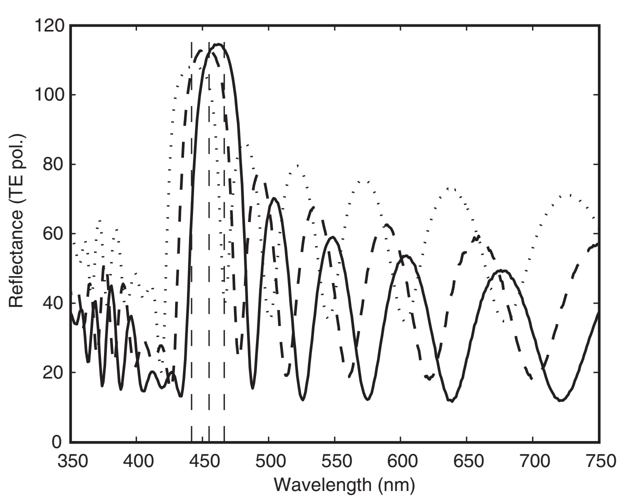

Figure 3. Reflectance spectra of WI sample measured at 20° (solid curve), 40° (dashed curve) and 60° (dotted curve) incidence angle. The polarisation state of the incident light was transverse-electric (TE). Vertical dashed lines indicate the positions of the dominant reflected wavelength as predicted by theory.

Conclusion

Two different dielectric SiO_2/TiO_2 multilayer films were fabricated on glass substrates by magnetron sputtering. Based on a theoretical model of the optical response, the layer thicknesses were chosen in such a way that the first design led to a SI coating whereas the second design led to a WI coating. Radically different visual aspects under variable incidence angles were achieved by this way: reddish-to-greenish changing hue for the first coating, stable bluish hue for the second coating. Theoretical predictions of the dominant reflected wavelength were found to be in very good agreement with measured reflectance spectra. The theoretical model proved to be a useful tool for exploring the iridescence tuning range of a given multilayer system, here SiO_2/TiO_2.

Acknowledgements: This work was supported by the *EU* through *FP6 BIOPHOT (NEST/Pathfinder)* 012915 project. M.R. was supported as Ph.D. student by the *Belgian Fund for Industrial and Agricultural Research (FRIA)*. C.V. was supported as research fellow by the *Belgian National Fund for Scientific Research (FNRS)*. V.W. was supported as scientific collaborator by the *FNRS*. *Aurélien Nonet* (LARN, FUNDP) is acknowledged for his technical support in using the PVD machine.

Received: September 12, 2008; Accepted: April 5, 2009; DOI: 10.1002/ppap.200931801

Keywords: magnetron; multilayers; optical coatings; optical properties; sputtering

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DOI: 10.1002/ppap.200931801