Optical performance of porous TiO₂ chiral thin films

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Optical performance of porous TiO₂ chiral thin films

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ABSTRACT

Porous thin film structures have been fabricated by physical vapor deposition at an incident flux angle that was typically greater than 80°. This deposition technique, often called glancing angle deposition (GLAD), was used to create thin films composed of isolated helical columns. Modification of the deposition parameters was used to control the porosity, the handedness, and the pitch of the helical structure. The high porosity of the GLAD film (>50%) permits fluids, and in particular liquid crystals (LC), to be incorporated into the voids of the nanostructure. We present the results of a study assessing the effect of film material, chiral morphology, and liquid crystalline material on the optical performance of helical GLAD films. Films fabricated from TiO₂, a high refractive index material, exhibited strong optical rotation of linearly polarized light and selective reflection of circularly polarized light. By increasing the number of turns of the helix the chiral optical response was enhanced, and by tailoring the pitch of the helical columns, the wavelength-dependence of the reflection band was tuned to preferentially reflect red, green, or blue light.

Keywords: selective reflectivity, liquid crystals, optical activity, chiral thin film, glancing angle deposition

1. INTRODUCTION

1.1 Background

The use of absorbing elements in a conventional twisted nematic liquid crystal display (LCD), including the polarizers positioned along the top and bottom of the LC cell and the colour filters present in a colour LCD, dramatically reduces device efficiency. Even in the theoretical best case, due to the polarizers and colour filters alone, less than 17% of the transmitted backlight ever reaches the viewer's eye. In reality, due to absorption by the transparent conductors, waveguide losses, scattering, and the limited aperture size of each pixel, the actual efficiency is often less than 3%. A superior LCD would employ a configuration of polarizers and colour filters that are constructed from non-absorbing materials. An example of such a material is a cholesteric liquid crystal (CLC). CLCs are capable of selectively reflecting circularly polarized light at wavelengths where $pn_o \leq \lambda \leq pn_e$ (p is the pitch of the CLC, and n_o and n_e are the local ordinary and extraordinary refractive indices). By stacking several layers of CLCs in series, with the pitch of each layer designed to reflect light at a different wavelength, a high efficiency reflective-LCD can be created.¹ However, difficulties inherent to CLCs include loss of alignment in thicker CLC layers and irreversible switching.²

The ability to control the alignment of LCs is often essential to device operation and performance. Conventional substrate processing techniques, such as rubbing,³ chemical treatments,⁴ oblique thin film deposition,⁵ and photoalignment,⁶ are used to anchor the position of those LC molecules that are the nearest to the substrate interface. But because these techniques are only applied to the substrate, alignment control tends to degrade towards the center of the LC cell. By embedding LCs within the void regions of a porous thin film matrix, whose nanostructure is carefully tailored by an advanced deposition technique known as glancing angle deposition (GLAD), the alignment of LCs can be controlled throughout the cell.⁷⁻⁹

In this report, we review how the GLAD process can be used to fabricate thin films composed of individual helical columns, which exhibit a chiral optical response and how, by impregnating the voids of the porous film nanostructure with LCs, the optical activity of the composite material can be enhanced. We demonstrate that both the selectivity reflectivity and the optical activity of the GLAD film can be improved by using TiO₂; a material that has both a high refractive index and low absorption within the visible regime. We also show that by tailoring the pitch of the helical columns, the wavelength-dependence of the reflection band may be tuned to preferentially reflect red, green, or blue light, a promising characteristic for display applications.

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1.2 Glancing angle deposition

Young and Kowal first measured optical activity in inorganic thin films in 1959.¹⁰ These fluorite films were deposited by physical vapor deposition (PVD) onto rotating substrates at oblique angles ($<70^\circ$). After theoretical studies by Lakhtakia and Weiglhofer¹¹ and Azzam¹², Robbie and Brett were the first to fabricate highly porous chiral thin films by increasing the deposition angle to $>80^\circ$ while rotating the substrate at a constant rate.¹³⁻¹⁵

At GLAD angles, thin film growth dynamics are dominated by self-shadowing and limited adatom diffusion. Nucleation sites present during the initial stages of film growth shadow regions of the substrate (Fig. 1) and lead to the formation of individual columns that grow towards the incident vapor flux. By using two stepper motors to control the position of the substrate (Fig. 2) and a crystal thickness monitor to obtain feedback regarding the deposition rate, the GLAD film's columnar microstructure can be modified to produce helices, chevrons, vertical posts, or more advanced structures.^{16,17} Helical films (Fig. 3), in particular, are formed by rotating the substrate at a constant rate about the ϕ -axis. The speed of rotation, relative to the deposition rate, controls the pitch of the helix and the direction of rotation governs the handedness of the film. A wide variety of GLAD film materials can be deposited using evaporation, pulsed laser deposition,¹⁸ and sputtering.¹⁹

Figure 1: Self-shadowing at GLAD angles.

Figure 2: The GLAD scheme.

When nematic LCs are incorporated into the voids of dielectric helical GLAD films, including magnesium fluoride, alumina, and silicon dioxide, the resultant composite material exhibits a number of superior optical properties:⁷⁻⁹

- Diffuse scattering is reduced due to a lower refractive index contrast between the film and the void regions.
- The selective reflectivity of the GLAD film – liquid crystal hybrid material is amplified, suggesting that the GLAD film acts as an alignment backbone that imposes a chiral-like orientation of the nematic LC molecules.
- In a similar fashion, the optical activity (the rotation of linearly polarized light) of the GLAD film is improved when impregnated with nematic LCs.
- When the refractive index of the thin film is approximately equal to that of the LCs, the chiral optical response can be reversibly switched off by applying a voltage across the cell.

The optical rotation exhibited by a series of SiO₂ helical GLAD films is shown in Fig. 4. The pitch of each film was held constant (450 ± 10 nm) while the number of turns (or thickness) of the film was varied. Also plotted is the optical rotation for the same set of films after impregnation with Merck ZLI 4792 NLCs. Upon adding LCs, the average effective rotatory power per micron doubled, from $0.67^\circ/\mu\text{m}$ to $1.34^\circ/\mu\text{m}$.

Figure 3: SEM image of a helical SiO₂ GLAD film.

Figure 4: Peak optical rotation versus film thickness for both LC-filled and unfilled SiO₂ GLAD films.

2. METHODOLOGY

By comparing the chiral optical response of helical GLAD films fabricated from dielectric materials, it is apparent that the magnitude of the response is proportional to the film's bulk refractive index.⁸ To exploit this relationship, a series of helical TiO₂ GLAD films were fabricated to take advantage of titanium oxide's high refractive index. This approach has also been taken by Hodgkinson *et al.* when fabricating thin-film helicoidal bianisotropic mediums (TFHBM), which also exhibit strong optical activity but are deposited at less oblique angles ($\leq 70^\circ$).²⁰

TiO₂ GLAD films were deposited by electron beam evaporation onto glass (Corning 7059) substrates at an incident flux angle of $\alpha = 85^\circ$. The source material consisted of 3-6mm pieces of 99.9% pure TiO₂ (Cerac Inc.), and a sufficient flow of O₂(g) was added to the vacuum chamber to keep deposition pressure above 5×10^{-5} Torr. Film morphology was investigated by scanning electron microscopy (SEM) and optical characterization was completed using both a spectrophotometer and a spectroscopic ellipsometer. Table 1 is a summary of the various TiO₂ films that were fabricated, where RH denotes a right-handed helix and LH denotes a left-handed helix. Samples A through D and samples E through L form two sets of films with a constant pitch and variable thickness. Samples B, I, M form a set of films of a constant number of turns and a variable pitch, and samples N and O form an enantiomorphic pair. Both samples N and O were fabricated without the addition of O₂(g) during the deposition. Samples F and N form a pair of GLAD films, deposited with and without the addition oxygen. Fig. 5 is a SEM image of a helical TiO₂ film; compared to other helical GLAD films, TiO₂ films tend to exhibit a larger column diameter and a steeper rise angle of the helix.

Table 1: Helical TiO₂ GLAD film samples

Sample	Handedness	Turns	Pitch [nm]	Thickness [μm]
A	RH	3	275	0.83
B	RH	5	275	1.38
C	RH	7	275	1.93
D	RH	12	275	3.30
E	RH	2	330	0.66
F	RH	3	330	0.99
G	RH	4	330	1.32
H	RH	4.9	330	1.62
I	RH	5	330	1.65
J	RH	5.4	330	1.77
K	RH	5.8	330	1.90
L	RH	7	330	2.31
M	RH	4.5	420	1.89
N	RH	3	330	0.99
O	LH	3	330	0.99

Figure 5: A helical TiO₂ GLAD film.

2.1 Spectrophotometer measurements

To gauge the chiral optical response of helical GLAD films, there are two important properties that can be measured: optical activity and selective reflectivity. A Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer was used to measure the rotation of linearly polarized light over a broad range of wavelengths. A linear polarizer, the sample, and a second linear polarizer were placed in the beam path; the transmission axis of one polarizer was fixed and the transmission axis of the other polarizer (the analyzer) was varied. By rotating the analyzer to find positions of minimum transmittance at each wavelength, the optical rotatory dispersion (ORD) attributed to the sample could be measured. A significant improvement to the measurement was made by fitting a $\cos^2 \theta$ function to the $\%T(\theta)$ data at each wavelength, (where θ is the angle of the transmission axis of the analyzer) as illustrated in Fig. 6.

Figure 6: (a) $\%T(\theta)$ fit to a $\cos^2 \theta$ function; (b) ORD without curve fitting; (c) ORD with curve fitting.

Rather than directly measure the selective reflectivity, a much simpler approach is to measure the difference in the transmission spectrum of left-circularly polarized light (LCP) and right-circularly polarized light (RCP) since a right-handed chiral GLAD film will preferentially transmit LCP light while scattering RCP light, and a left-handed chiral GLAD film will preferentially transmit RCP light while scattering LCP light. Circularly polarized light was generated by placing a linear polarizer and a quarter-wave plate in series, with the fast axis of the quarter-wave plate oriented at $\pm 45^\circ$ with respect to the transmission axis of the polarizer.

2.2 Ellipsometer measurements

The measure of optical activity and selective reflectivity was repeated using a second instrument – a variable angle spectroscopic ellipsometer (VASE) (model V-VASE from J. A. Woollam Co., Inc.), operated in transmission mode. Without inserting additional optics into the beam path, the V-VASE is capable of measuring the first 3 rows of the Mueller matrix,^{21,22} normalized so that the m_{11} coefficient is unity at each wavelength. To determine the non-normalized elements of the Mueller matrix, m_{11} is calculated by measuring the transmittance of randomly polarized light or by measuring the average transmittance of two mutually orthogonal polarization states. For instance,

$$m_{11}(\lambda) = \frac{1}{2} [T_s(\lambda) + T_p(\lambda)] \quad (1)$$

where $T_s(\lambda)$ is the transmittance of s-polarized light and $T_p(\lambda)$ is the transmittance of p-polarized light. Optical rotation is calculated using equation 2

$$OR = \frac{1}{2} \arctan \left(\frac{m_{31} + m_{32} \cos 2\alpha + m_{33} \sin 2\alpha}{m_{21} + m_{22} \cos 2\alpha + m_{23} \sin 2\alpha} \right) - \alpha \quad (2)$$

where α in this case is the angle of the linearly polarized light before propagation through the sample. The difference in the transmittance of LCP and RCP light is calculated using the m_{14} coefficient of the Mueller matrix:

$$T_{LCP-RCP}(\lambda) = -2 m_{14}(\lambda). \quad (3)$$

All of the optical measurements, those made by both the VASE system and the spectrophotometer, were done with the substrate surface perpendicular to the beam path so that incident light was parallel to the helical axis of each film. A comparison of the measurements made by the VASE system and those made by the spectrophotometer appears in Sec. 3.4; in the rest of this report the data presented was measured by the spectrophotometer.

3. RESULTS

3.1 Selective reflectivity

The difference between the transmittance of LCP and RCP light for a series of right-handed TiO_2 GLAD films is shown in Fig. 7. By increasing the pitch of the helix, the reflection band could be shifted towards lower frequencies, from blue to green to red, and even to infrared frequencies provided that the film material and substrate are non-absorbing.

Figure 7: Selective reflectivity in helical TiO_2 GLAD films at red, green, and blue wavelengths (samples A, J, M).

Increasing the thickness of a GLAD film by adding more turns to the helix also increased the selective reflectivity. Fig. 8 illustrates the increase in peak selective reflectivity for a series of TiO_2 films grown at a constant pitch of 330 nm. From 2 turns to 5 turns, the peak value of $\%T_{LCP-RCP}(\lambda)$ nearly doubles, from 6.7% to 12.8%. The response of thicker films was not included in Fig. 8 because beyond approximately 5 turns, the helical structure of TiO_2 tends to degrade, resulting in a significant rise in diffuse scattering and a reduction in selective reflectivity.

Figure 8: Peak values of $\%T_{LCP-RCP}(\lambda)$ as a function of film thickness (sample E through sample I).

3.2 Optical activity

Two typical ORD curves are shown in Fig. 9 and Fig. 10. The $\%T_{LCP-RCP}$ spectrum has been plotted on the same graph in each figure to illustrate the presence of the reflection band. In both cases, the TiO_2 film rotated the plane of vibration in a counterclockwise direction (levorotatory) when looking back towards the light source, which is consistent with the fact that they were both right-handed films. However, unlike CLCs, the optical rotation does not experience anomalous rotatory dispersion (a change in sign) around the reflection band; a property that was consistent in every TiO_2 sample that was measured.

A second interesting characteristic is the shape of the ORD curve as a function of the helical pitch. TiO_2 GLAD films fabricated with a relatively small pitch produced ORD curves with local maxima and minima within the reflection band, as shown in Fig. 9. When the helical pitch was relatively large, the features of the ORD curve degenerated into a simple monotonic function, as shown in Fig. 10. This behavior has also been observed in TFHBMs.²⁰

Figure 9: ORD exhibited by a relatively small pitch helical TiO_2 GLAD film (sample J);
(♦) – optical rotation; (solid line) – $\%T_{LCP-RCP}$.

Figure 10: ORD exhibited by a relatively large pitch helical TiO_2 GLAD film (sample M);
(♦) – optical rotation; (solid line) – $\%T_{LCP-RCP}$.

Fig. 11 is a plot of the peak optical rotation for samples E through L as a function film thickness. The average effective rotatory power per micron for samples E through L was $3.4^\circ/\mu\text{m}$. Other TiO_2 films exhibited rotatory powers per micron as high as $6^\circ/\mu\text{m}$ – $7^\circ/\mu\text{m}$ at high frequencies, which is significantly greater than the rotatory power exhibited by crystalline quartz ($0.022^\circ/\mu\text{m}$),²³ fluorite films ($0.155^\circ/\mu\text{m}$),¹⁰ and CLCs ($\sim 1^\circ/\mu\text{m}$).²⁴

Figure 11: Peak optical rotation in helical TiO_2 GLAD films as a function of film thickness (sample E through sample L).

3.3 Enantiomorphism

Samples N and O are an enantiomorphic pair of GLAD films, fabricated without the addition of $O_2(g)$ during the deposition. The deposition pressure simply decreased continuously as oxygen in the melt was depleted. Without the addition of oxygen, the chamber pressure at any particular time during the deposition relies strongly on the condition and history of the melt, a variable that is often difficult to control. This implies that TiO_2 films fabricated without oxygen are more difficult to reproduce. With this in mind, the correspondence of both the selective reflectivity (Fig. 12) and the ORD (Fig. 13) observed in sample N and sample O proves that chiral GLAD films exhibit enantiomorphism and that the GLAD process is highly reproducible.

Figure 12: Selective reflectivity in an enantiomorphic pair of 3 turn, 330 nm pitch, helical TiO_2 GLAD films; (o) – sample N; (•) – sample O.

Figure 13: Optical rotatory dispersion in an enantiomorphic pair of 3 turn, 330 nm pitch, helical TiO_2 GLAD films; (dotted line) – sample N; (solid line) – sample O.

Initial experiments have shown that TiO_2 GLAD films fabricated without the addition of $O_2(g)$ during the deposition improves the chiral optic response. Fig. 14 highlights the 15% (relative) enhancement to the selective reflectivity between sample F and sample N. Future studies will investigate this phenomenon further.

Figure 14: Enhancement of the selective reflectivity in TiO_2 fabricated without the addition of $O_2(g)$ during the deposition. (open circles) – sample F; (solid line) – sample N.

3.4 VASE Measurements

By measuring the appropriate elements of the Mueller matrix using transmission ellipsometry, both the selective reflectivity and the optical activity of sample B were calculated. Fig. 15 and Fig. 16 illustrate how well the VASE measurements correspond with those made by the spectrophotometer.

Figure 15: $\%T_{LCP-RCP}(\lambda)$ of sample B as measured by the (open circles) – spectrophotometer; (solid line) – VASE.

Figure 16: ORD of sample B as measured by the (open circles) – spectrophotometer; (solid line) – VASE.

3.5 Impregnating TiO_2 GLAD films with LCs

Impregnation of TiO_2 films involved heating the substrate to $\sim 70^\circ\text{C}$ to drive off condensation, dropping a small quantity of LCs onto the surface of the film, and spinning the substrate to distribute the LCs and to remove any excess liquid. The filled thin film – LC composites were heated to above the clearing point temperature of the particular LC for 10 minutes and then cooled to room temperature in an attempt to discourage domain formation and improve LC alignment. Optical measurements were taken both before and after heating the composite to above the clearing point. It has been our experience that a layer of poorly oriented LCs can form on the top of the GLAD film. To reduce depolarization effects due to this misaligned layer, optical characterization was also performed with the air/film/substrate configuration reversed so that the substrate appeared foremost in the beam path. The average refractive index and the clearing point temperature for the two types of nematic LCs used to impregnate the TiO_2 GLAD films are listed in Table 2. In none of the configurations outlined above did the addition of these nematic LCs to the porous TiO_2 GLAD films produce an enhancement in the chiral optical response of the helical film. Fig. 17 is an example of the reduction in selective reflectivity caused by adding Merck ZLI 4792 NLCs to sample N.

Table 2: LCs used to impregnated TiO_2 GLAD film.

Nematic LC	n_e	n_o	Δn	$T_{N-I} (^\circ\text{C})$
ZLI 4792	1.576	1.479	0.097	60.5
E7	1.746	1.522	0.225	92.0

Insufficient filling of the voids regions may have caused the attenuation of the chiral optical response despite the hydrophilic properties witnessed in alternative GLAD film materials.^{25,26} Future experiments will investigate the use of surface treatments to encourage LC absorption. Conversely, the reduction of the chiral optical response may have been due to the various refractive indices involved. In previous experiments, the bulk refractive index of the GLAD film was approximately equal to that of the embedded LCs.⁹ In the case of TiO_2 , the bulk refractive index of the GLAD film is significantly higher than that of the LCs. Further study of the GLAD thin film – LC composite as an effective medium will be pursued.

Figure 17: Reduction in the selective reflectivity of a TiO_2 GLAD film upon impregnation with ZLI 4792 NLCs; (dotted line) – TiO_2 film; (solid line) – TiO_2 film – LC hybrid.

4. CONCLUSION

We have demonstrated that the GLAD technique can be used to deposit highly porous thin films composed of individual helical columns. By using TiO_2 , a dielectric with a large index of refraction, to fabricate helical GLAD films, a large chiral optical response was produced. Both the selective reflectivity and the optical rotation increase with respect to the thickness of the film, and by tailoring the pitch of the helix, the wavelength-dependence of the optical response was tuned to preferentially reflect light at red, green, or blue wavelengths. Impregnating the pores of MgF_2 , Si_2O_2 and Al_2O_3 GLAD films with nematic LCs reduces diffuse scattering and enhances the chiral optical response, which can be reversibly switched off by applying a voltage across the thin film – LC cell. To date, adding nematic LCs to TiO_2 GLAD films has not produced an enhancement of the chiral optical response; future studies will focus on resolving the composite nature of the GLAD thin film – LC material using effective medium theory, and on improving the hydrophilic properties of TiO_2 GLAD films.

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