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Optical activity of chiral thin film and liquid crystal hybrids

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Using the glancing angle deposition (GLAD) technique, we have fabricated porous, chiral thin films with optically anisotropic helical microstructures that exhibit optical phenomena such as wavelength specific rotation of linearly polarized light. Initial research has shown that the porosity of the films allows for the addition of nematic liquid crystals (NLCs) to the films for promising applications in dynamically switchable devices, while simultaneously enhancing the optical properties of the film. This study describes the fundamental optical behaviour of LC-filled chiral thin films in relation to material, porosity, structure and thickness. It was found that for SiO_2 films, the addition of NLCs increased the effective rotatory power by two-fold when compared with results from the film without added LCs. The rotatory power of Al_2O_3 and MgF_2 films, while being similarly increased by the addition of LCs, exhibited a reversal in sign, or direction of rotation, for the visible wavelength spectrum investigated. The effects of film porosity and structure were studied by varying the angle of incidence from 83° to 86°; it was found that the greater porosity of the films deposited at larger angles allowed for more filling by the LCs and thus a larger increase in rotatory power. Finally, the addition of LCs was observed to shift the wavelength of peak rotation towards smaller values.

1. Introduction

The manufacture of liquid crystal (LC) devices relies heavily on the ability to control the orientation of the anisotropic molecules. Substrate processing techniques such as rubbing [1], oblique thin film deposition [2, 3] and photoalignment [4] impose LC alignment at the surface which is useful for thin cells. However, for thicker cells, orientation control degrades as the distance from the substrate interface increases. The use of porous films prepared by glancing angle deposition (GLAD) with controllable microstructure allows for long range orientation control over the entire thickness of the cell.

The GLAD technique of thin film growth uses physical vapour deposition at extreme angles of incidence ($>80°$ from normal) to produce highly porous films with porosities of greater than 50% [5, 6]. Automated control of substrate orientation and rotation, with deposition rate feedback from a crystal thickness monitor, allows for the films to be created with chiral structure and specified dimensions such as helical pitch (defined as the vertical distance between each helical turn), helical radius and handedness. As can be seen in figure 1, both the structure and porosity can be controlled by this advanced deposition technique. Ultimately, we are able to create chiral films with sub-micron features that are optically anisotropic with respect to incident circularly polarized light.

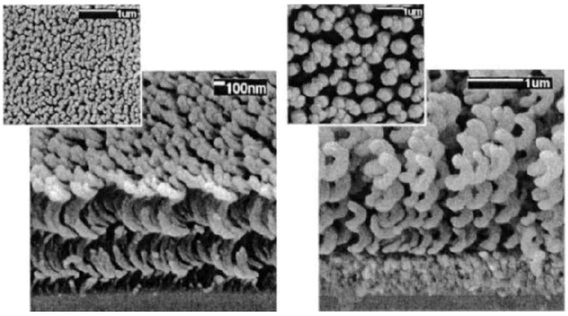

Figure 1. Example of two helical SiO_2 GLAD films; on the left is a film deposited at 83°, while on the right is a film deposited at 85°. The insets show the difference in porosity from a top view.

The first observation of optical activity and circular Bragg reflection in obliquely deposited thin films was with fluorite films by Young and Kowal in 1959 [7]. These films were deposited at more conservative oblique angles ($<70°$) and the resulting semiporous films exhibited rotatory powers up to $0.155° \mu m^{-1}$ (amount of rotation

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per thickness of film). Following theoretical work by Lahktakia and Weiglhofer [8] and Azzam [9], Robbie *et al.* fabricated highly porous chiral thin films using the GLAD technique [10–12]. These films exhibited optical activity derived from circular birefringence resulting from the index of refraction difference between the helical structures of the film and the air gaps surrounding them.

In addition to the inherent optical activity of chiral GLAD films, their high porosity allows for the introduction of liquids such as nematic liquid crystals (NLCs) to fill the voids in the film and modify the effective circular birefringence. Using as motivation the knowledge that structured surfaces can be used as alignment devices for LC molecules, Robbie *et al.* were first to combine GLAD films with NLCs and show that the optical properties of the composite cell were enhanced [13]. The addition of LCs to the GLAD film provides a backbone of the GLAD helical structure for anchoring of the LC molecules. As a result, a chial order is given to the non-chiral NLCs over the entire thickness of the film.

There are several benefits to the addition of NLCs to GLAD films. First, the high porosity of the films in combination with the optical materials used to fabricate them creates a hydrophilic structure whose optical properties may be influenced by environmental conditions. By filling the film with LCs and preventing the water due to ambient humidity from entering the structure, we expect to reduce the sensitivity to humidity observed in unfilled porous films [14]. Second, the contrasts of high/low index of fraction at the many film–air interfaces of the unfilled cells produce a large amount of scattering, reducing overall transmission. By reducing the difference in the index of refraction across these interfaces by the addition of liquid crystals, the appearance of the films changes from a frosty white characteristic of scattering light (unfilled), to nearly transparent (filled). Finally, and most important, the anisotropy of the NLC molecules can be ordered by the structure of the film, aligning the LC molecules to create cells with larger rotatory powers and even allow for dynamic devices capable of electro-optic switching, as reported in work by Sit *et al.* [15].

It is important to note here that helical, highly porous GLAD films deposited at extreme angles are not, by themselves, ideal polarization rotators. Denser films with inherent helical structure deposited at lower angles have been shown by Hodgkinson *et al.* to have greater effective rotatory powers than more porous films [16]; however, the interest in highly porous GLAD films lies in their versatility. By allowing the addition of nematic liquid crystals to the films, the above-mentioned benefits of producing dynamic, active devices can be exploited.

2. Method

Chiral GLAD films were fabricated on glass substrates with SiO_2 ($n = 1.47$) and Al_2O_3 ($n = 1.66$) using electron beam evaporation, and with MgF_2 ($n = 1.38$) using thermal evaporation. The films were created in sets of varying thickness, helical pitch, and deposition angle for all materials. The handedness of the films was also varied to ensure that enantiomeric pairs exhibited mirrored results. The films were each characterized optically as deposited and after filling with Merck ZLI 4792 NLC. The filling process entailed placing a sample of the film heated to 65°C on a photoresist spinner, dropping a small amount of the LC onto the sample, starting the spinner at low rpm to distribute the LCs, and finally spinning at higher speed to remove any excess liquid from the top of the film. Heating the film before the addition of the LC was an attempt to drive off any humidity that had condensed within the fine structure of the film and which would otherwise affect the results by preventing complete filling by the LC molecules. Because the films are hydrophilic, the LCs were easily introduced into the microstructure once any moisture was removed, enabling thorough filling.

Rotatory dispersion (optical activity as a function of wavelength) was investigated at 20°C to compare the effects of adding NLCs to the various GLAD films. To measure the optical activity, a standard polarimetry apparatus was used comprising a high intensity, broadband light source, two chromatic linear polarizers mounted in graduated rotary mounts, and the sample, which was placed between the polarizers. A control measurement was taken without a sample in place and the minimum intensity was taken as the reference angle. Measurements were then taken with the sample in place and the change in angle of minimum intensity from the reference angle for each wavelength was defined as the rotation due to the sample. For all measurements, the sample was held with the substrate perpendicular to the incoming beam so that incident light was parallel to the helical axes.

3. Results

3.1. *Effect of deposition angle*

The deposition angle at which incidence flux impinges on the substrate surface is critically important to the resulting structure of the film. It is through the mechanism of self-shadowing, caused by oblique deposition, that we are able to produce these unique nano-scale shapes, and the dependence of the films' optical properties on this parameter was tested to determine the optimal angle at which to produce our films. Films of SiO_2 and Al_2O_3 were grown at angles varying from 83° to 86°, and the effective rotatory powers of the films, defined as the maximum rotation normalized by the thickness of the film, were plotted against these angles. It is important to note that in an anisotropic chiral medium, effective rotatory power is not exclusive and independent of the film thickness. However in the short wavelength regime it has been shown to be a valid means of comparison with other types of material [16]. This range of deposition angles is typical, as at smaller angles the films are either too dense for the addition of LCs, one of the main foci of this experiment, or at higher angles the relative deposition rate is much too slow due to the cosine dependence of flux on the tilted substrate.

From the graph of figure 2, it is possible to see the importance of structure and hence deposition angle on the efficiency of the film/LC devices. For the unfilled films the more distinct structures grown at higher angles resulted in greater rotatory powers; this is especially obvious for the Al_2O_3 films. Even more notable is the increase in the rotatory powers for the LC-filled films deposited at higher angles. The greater porosity of these films means that larger amounts of active LC molecules can be incorporated into the structure, while the more distinct helical structure may enable a better chiral nematic phase to be induced in the LC molecular order due to the backbone effect of the film. Inconclusive measurements were obtained from the Al_2O_3 film deposited at 86° and as such are not included in the results. From these results it can be seen that films deposited at 85° will result in good overall efficiency for both unfilled and LC filled variations.

3.2. *Effect of LC filling on rotatory power*

Polarization rotation measurements were performed on sets of MgF_2, Al_2O_3 and SiO_2 films deposited at 85° with a varying number of helical turns and a constant pitch of 450 ± 10 nm. The results, shown in figure 3 and summarized in the table, indicate that for the films without embedded LCs, there is an increasing dependence of maximum rotation on the number of turns (thickness). Note that the rotation was taken to be positive if the

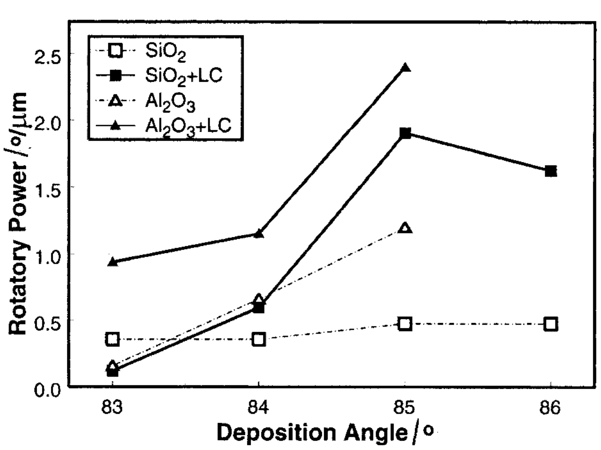

Figure 2. Average effective rotatory power plotted as a function of angle of incidence of flux during deposition for both unfilled and LC-filled Al_2O_3 and SiO_2 films.

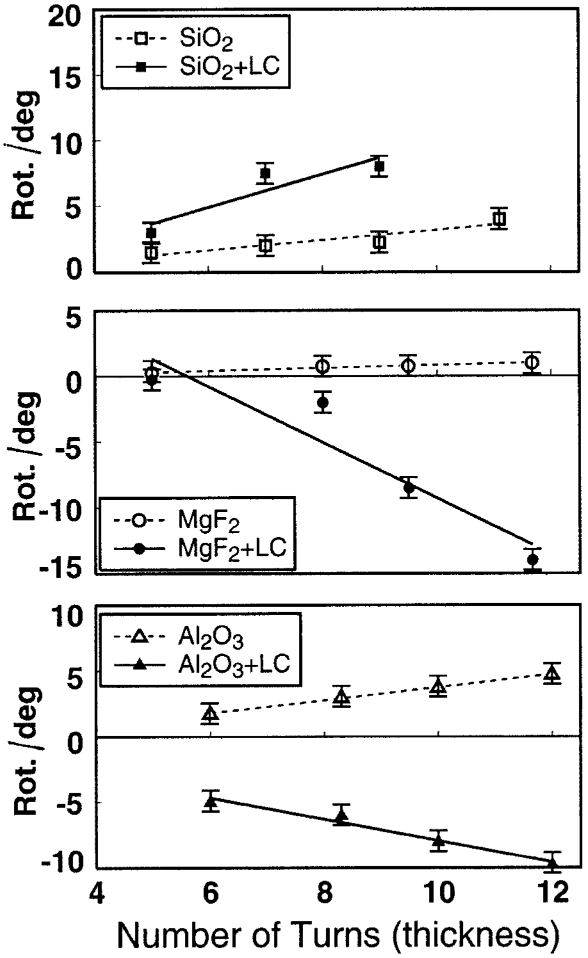

Figure 3. Peak optical activity measurements as a function of film thickness for both LC-filled and unfilled, MgF_2, SiO_2 and Al_2O_3 films. The addition of LCs results in an overall increase in rotation for all film materials, while there is a reversal in direction of rotation for the LC-filled MgF_2 and Al_2O_3 films.

Table. Calculated average effective rotatory powers for both unfilled and LC filled MgF_2, SiO_2, and Al_2O_3 films. Note that the reversal in sign for the filled films represents a rotation in the opposite direction from the convention.

	Calculated average effective rotatory power/deg μm^{-1}	
Material	Film	Film + LC
MgF_2	0.16	−0.96
SiO_2	0.67	1.34
Al_2O_3	1.05	−2.3

direction of the rotation was opposite the handedness of the film (i.e. for a left-handed film a right-handed rotation would be taken as positive). The index of refraction of the film materials can be seen to play an important part in the magnitude of rotation through its effect on circular birefringence. The greater rotation exhibited by the SiO_2 over the MgF_2 films, and even more by the Al_2O_3 films, was as expected due to the higher bulk index of refraction of the materials resulting in greater anisotropy as seen by incident circular polarizations of light.

When the NLCs were added to the films, several important results were observed. First, the magnitude of the rotation for all sets of filled films was considerably greater, as seen from the graphs in figure 3. This increase in optical activity supports the theory that there is a chiral nematic phase induced in the LCs by the chiral backbone of the GLAD film. A second important observation was that the MgF_2 and Al_2O_3 films with embedded LCs rotated the plane of polarization in the opposite direction from the unfilled film, while the SiO_2 films maintained the same rotational direction. The general trend of gradually decreasing rotation with increasing wavelengh was observed in all measurements, implying that the visible spectrum under investigation lay to the right of the Bragg resonance wavelength for all films, with and without LCs, and that the change in rotational direction was not simply characteristic of a wavelength shift to the opposite side of the resonance peak. An example of the change in both magnitude and direction can be seen in figure 4. This behaviour may have its basis in a potentially complex combination of liquid crystal molecule/film surface interactions and/or LC domain interactions, and further study is required to determine its exact origin.

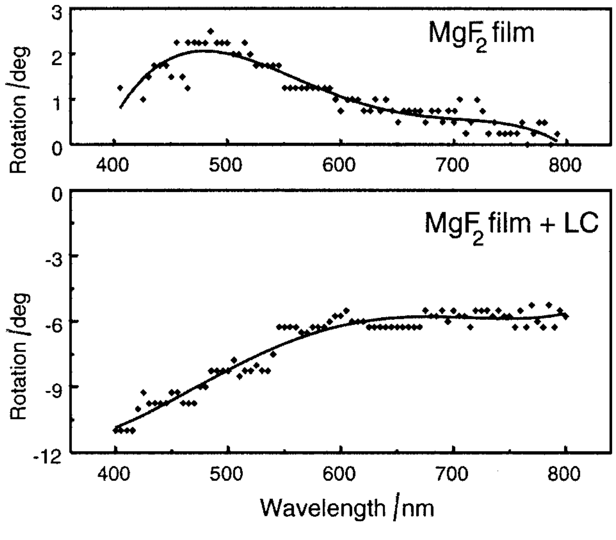

Figure 4. Rotation measurements for a 6 µm MgF_2 film on glass, without the addition of LCs (top), and with the addition of LCs (bottom). The hybrid device gives almost six times the rotation of the film alone. Note the reversal in rotational direction along with the shift in wavelength of peak rotation to lower values after the addition of the LCs.

3.3. *Effect of LC filling on wavelength response*

A final result observed for the addition of LCs to these chiral porous films was the change in wavelength dependence of the rotatory dispersion. The shift in peak wavelength due to the addition of LCs is shown in the example results of figure 4. (Note that the precision of the measurements was limited to $\pm 0.25°$, and a 4th order curve was fit to the data.) In general, maximum coupling of incident light into the film should occur at a critical wavelength given by $\lambda_c = n_{\mathrm{eff}} p$, where p is the helical pitch and n_{eff} is the effective index of refraction of the film due to its structure and material [17]. At this critical wavelength, resonance should occur when the rotation is a maximum (ideally infinite) or, for transmission measurements of the films, where there is the largest difference between transmission of left and right circular polarizations of incident light. In an ideal model of optical activity, the rotation should change from $+\infty$ to $-\infty$ as one proceeds to lower wavelengths from the critical value; however our results showed a finite rotation at the resonanace peak due largely to the finite thickness of the film.

From the relationship $\lambda_c = n_{\mathrm{eff}} p$, the critical wavelength is related to the effective rotatory power through the effective index of refraction, n_{eff}. A higher n_{eff} would typically result in a film with greater rotatory power because of the greater phase difference introduced between the two circularly polarized modes. By adding LCs to the film and increasing the effective rotatory power of the structure, the values of n_{eff} and the critical wavelength λ_c should increase. This is not the case however, as can be seen in figure 4. Although the transmission window of the glass and film does not include the resonance point at the critical wavelength, it is possible to see from the shift of the peak rotation from approximately 480 nm to below 400 nm, upon the addition of LCs, that there is a decrease in the value of λ_c. In this case the rotation spectrum is shown for an MgF_2 film where the bottom half of the figure also shows the reversal in direction of rotation. This behaviour is the second unexpected result from these tests and requires further study better to comprehend the phenomenon.

4. Conclusions

In summary, we have shown that the addition of nematic LCs to porous, helical GLAD films improves the optical properties of the film, specifically in relation to optical activity. The results suggest further confirmation that this enhancement is due primarily to the chiral backbone that the film structure provides for the LCs, although the exact mechanism has still to be determined. It was found that a deposition angle of 85° yielded the optimal structure for LC/GLAD film hybrid devices due to the increased pore size associated with the larger incidence angles. Increasing the interest in this study were the two unpredicted results that accompanied the addition of LCs to the porous thin films, specifically that MgF_2 and Al_2O_3 films had a reversal in rotational direction, while there also occurred a shift in the resonance point toward shorter wavelengths. This study was motivated primarily because the composite structure of the porous film filled with LCs is desirable not only because of the enhanced properties and more versatile devices, but also because it allows for increased overall transmission from index matching and potentially less dependence of the optical properties on environmental effects.

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References

[1] Zocher, V. H., 1925, *Naturwissenschaften*, **13,** 1015.

[2] Janning, J. L., 1972, *Appl. Phys. Lett.*, **21,** 173.

[3] Urbach, W., Boix, M., and Guyon, E., 1974, *Appl. Phys. Lett.*, **25,** 479.

[4] Gibbons, W. M., Shannon, P. J., Sun, S. T., and Swetlin, B. J., 1991, *Nature*, **351,** 49.

[5] Robbie, K., and Brett, M. J., 1997, *J. vac. sci. Technol.*, **A15,** 1460.

[6] Robbie, K., and Brett, M. J., 1999, US Patent 5 866 204.

[7] Young, N. O., and Kowal, J., 1959, *Nature*, **183,** 104.

[8] Lakhtakia, A., and Weiglhofer, W. S., 1995, *Proc. r. Soc. Lond.*, **A448,** 419.

[9] Azzam, R., 1992, *Appl. Phys. Lett.*, **61,** 3118.

[10] Robbie, K., Brett, M. J., and Lakhtakia, A., 1995, *J. vac. sci. Technol.*, **A13,** 1991.

[11] Robbie, K., Brett, M. J., and Lakhtakia, A., 1996, *Nature*, **384,** 616.

[12] Rovira, P. I., Yarussi, R. A., Collins, R. W., Venugopal, V. C., Lakhtakia, A., Messier, R., Robbie, K., and Brett, M. J., 1998, *Thin solid Films*, **313-314,** 373.

[13] Robbie, K., Broer, D. J., and Brett, M. J., 1999, *Nature*, **399,** 764.

[14] Hodgkinson, I. J., Wu, Q. H., and McGrath, K. M., 1999, *Proc. SPIE*, **3790,** 184.

[15] Sit, J. C., Broer, D. J., and Brett, M. J., 2000, *Liq. Cryst.*, **27,** 387.

[16] Hodgkinson, I., Wu, Q., Lakhtakia, A., and Robbie, K., 2000, *Appl. Opt.*, **39,** 642.

[17] Oseen, C. W., 1933, *Trans. Faraday Soc.*, **29,** 883.