

# Chiral sculptured thin films

SIR — We have observed optical activity in thin solid films composed of nanometre-scale helical columns. These films rotate the plane of polarization of light in a manner analogous to cholesteric liquid crystals and other structurally chiral media. This rotation demonstrates the optical activity of the helical structured films and indicates that these films possess other significant optical properties such as circular dichroism (the effect currently exploited in cholesteric liquid-crystal displays). Our measurements demonstrate the value of a new thin-film deposition technique<sup>1,2</sup> called glancing angle deposition (GLAD), which allows three-dimensional control of film structure on a scale of less than 10 nm.

In structurally chiral media, a helical structure creates optical activity. For example, in cholesteric liquid crystals (CLCs), the helical structure of the stacked layers of molecules alters the vibration ellipse of plane-polarized light<sup>3</sup>. Electromagnetic properties of chiral media have been investigated with light in

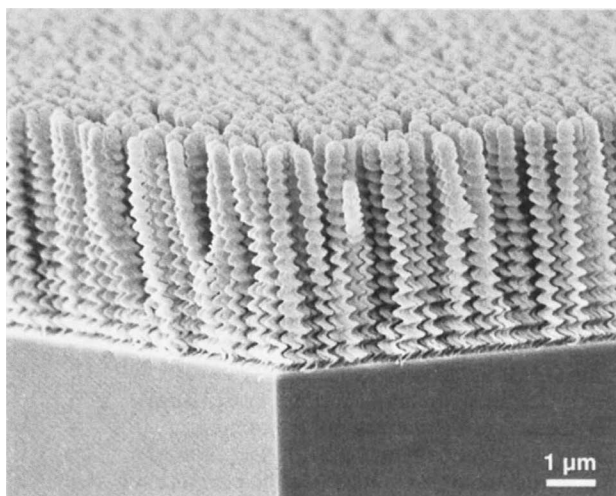


FIG. 1 Scanning electron micrograph of a magnesium fluoride sculptured thin film on a glass substrate. The film has 17.3 helical turns of pitch 360 nm.

CLCs, with microwaves in wire spirals<sup>4</sup> and with suitable wavelength radiation in other helically structured materials. We have previously described the use of a new fabrication technique to produce helical electromagnetic properties in thin solid films of inorganic compounds. These 'sculptured' thin films are characterized by helical columns with pitches comparable to the wavelengths of visible light<sup>5</sup>.

We fabricated the films with a deposition system using oblique incidence flux and substrate motion (GLAD)<sup>1,2</sup>. We evaporated source material in a vacuum chamber with a pressure of  $1 \times 10^{-6}$  torr ( $\sim 1 \times 10^{14}$  Pa). By tilting the substrate, the evaporant flux was incident at

an angle  $\theta$  of  $85^\circ$  measured from the substrate normal. Under conditions of almost grazing incidence ( $\theta > 75^\circ$ ), local film-growth variations lead to strong shadowing effects and competition between nucleating grains. The high points of the film intercept most of the flux, and the low points become shadowed and do not grow further. This leads to a porous film with isolated columns of material inclined towards the source of the flux.

We have taken advantage of this behaviour and incorporated a rotation of the substrate about an axis normal to the surface, to 'sculpt' the columns into helices, as shown in Fig. 1. Using feedback from a deposition rate monitor, the rotation speed of the substrate can be controlled to produce helices of a predetermined pitch. We have fabricated helices of similar form with pitches ranging from 50 to 2,000 nm, and in films composed of  $\text{MgF}_2$ ,  $\text{SiO}_2$ ,  $\text{CaF}_2$ , chromium, manganese and copper.

When linearly polarized light is incident on a helical sculptured thin film along the film's helical axis, the transmitted light exhibits a rotation of the plane of polarization. This optical rotation is a function of the incident light wavelength in a vacuum  $\lambda_{\text{vac}}$ , and the phenomenon is called optical rotatory dispersion<sup>5</sup>. The optical rotatory dispersion of the 17.3-turn  $\text{MgF}_2$  helical thin film (Fig. 1) was determined for a range of wavelengths,  $560 \text{ nm} \leq \lambda_{\text{vac}} \leq 633 \text{ nm}$ , in the visible spectrum (Fig. 2). From comparison with CLCs, we expect that optical rotation will be largest when the pitch ( $P$ ) equals some 'average' wavelength of light in the film  $\lambda_{\text{vac}}$  divided by a suitably averaged refractive index  $n_{\text{avg}}$  of the film. To estimate  $n_{\text{avg}}$  of the  $\text{MgF}_2$  chiral thin film, we used density measurements and a simple mixing rule<sup>6</sup>. With  $n_{\text{avg}} = 1.1$  and  $P = 360 \text{ nm}$ , we expect the  $\text{MgF}_2$  thin film to show very large optical rotation when  $\lambda_{\text{vac}} \approx 400 \text{ nm}$ . In the same regime, we expect strong circular dichroism (depolarization of linearly polarized light).

We measured optical rotations for enantiomeric pairs of sculptured thin films (an identical pair where one has exclusively left-handed helices and the other has exclusively right-handed

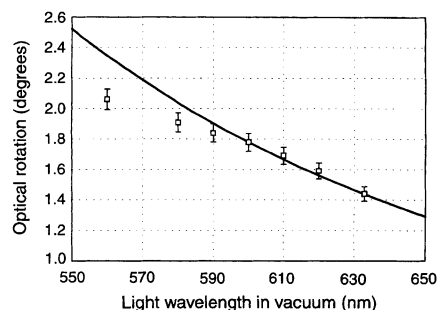


FIG. 2 Optical rotation as a function of wavelength (optical rotatory dispersion) of the magnesium fluoride chiral thin film shown in Fig. 1. Maximum optical rotation is expected when  $\lambda_{\text{vac}} \approx 400 \text{ nm}$ . The solid line shows the  $\lambda_{\text{vac}}^{-4}$  behaviour predicted for CLCs by the de Vries formula at high values of  $\lambda_{\text{vac}}$ .

helices). We found measured values to be anticlockwise for the right-handed member and clockwise for the left-handed member of the enantiomeric pair, the magnitudes of the two optical rotations being identical. In addition, we observed no optical rotation for a glass substrate without a film.

Measurements of optical rotatory dispersion of helical sculptured thin films demonstrate their optical activity. With the widespread use of organic chiral materials, these artificially produced chiral structures of inorganic materials seem to be a promising new optically active medium.

**K. Robbie**

**M. J. Brett**

Department of Electrical Engineering and  
Alberta Microelectronic Centre,  
University of Alberta,  
Edmonton, Alberta T6G 2G7,  
Canada

e-mail: robbie@ee.ualberta.ca

**A. Lakhtakia**

Department of Engineering Science and  
Mechanics,  
Pennsylvania State University,  
University Park,  
Pennsylvania 16802-1401, USA

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