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Photoinduced Alignment of Liquid Crystals using Polyimide Irradiated with a Polarised Excimer Laser

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A linearly polarised excimer laser is used to photoinduce an anisotropy in polyimide liquid crystal alignment layers. Exposure with the laser using 10 shots of fluence 13 mJ cm^{-2} results in saturated alignment with an azimuthal anchoring energy greater than 10^{-5}J m^{-2}. The liquid crystal alignment direction is perpendicular to the polarisation direction of the incident beam. A model is presented to explain the observation of a small liquid crystal pretilt angle on oblique exposure of the excimer laser. This assumes an initial predominantly planar and symmetric polyimide chain distribution which is tilted by oblique irradiation.

Keywords: polyimide; liquid crystals; alignment; photoinduced; anisotropy; pretilt angle

INTRODUCTION

The excellent mechanical, thermal and optical stability of polyimide thin films result in their widespread use as liquid crystal alignment layers in commercial displays. The alignment direction and pretilt angle are chosen by rubbing the orientation layer but this process can generate dust and static electricity which affects the yield of active matrix liquid crystal displays. Furthermore, rubbing cannot provide the microscopic variations in director orientation required for multi-domain displays which give wide viewing angles. The anisotropic crosslinking of polymers with cinnamate or coumarin sidechains on

illumination with linearly polarised UV light was first explored as a non-contact alignment technology[1-4]. More recently it was found that prolonged exposure of polyimides to linearly polarised light from a UV lamp can also achieve liquid crystal orientation[5,6]. The alignment results from the anisotropic depolymerisation of the polyimide chains along the polarisation direction of the incident light. Therefore the alignment direction is usually perpendicular to that of the incident polarisation although parallel alignment has been found using some polyimides containing sidechains[7,8]. The threshold UV fluence required to achieve photoalignment is generally high (>10 J cm^{-2}) compared to that in polyvinyl cinnamate derivatives[4] ($\approx$ 50 mJ cm^{-2}) although a threshold of 0.72 J cm^{-2} was found for an oxydiphenylene polyimide[8]. Small pretilt angles have been reported with oblique exposure of some polyimides using nonpolarised light[9,10].

Recently, we reported an alternative non-contact alignment method of polyimide[11]. Gratings were etched using a nonpolarised excimer laser exposed through a phase mask and alignment along the groove direction was achieved because of minimisation of the elastic strain at the grating interface as explained by Berreman[12]. However, when polarised light was incident, a much stronger surface anchoring is observed suggesting that a photoinduced effect similar to that observed with continuous Mercury lamp illumination contributes to the alignment. In this paper, the anchoring energy produced by polarised laser irradiation of the alignment layer is investigated. A model is presented to explain the observation of a pretilt angle when exposure at oblique incidence is used.

EXPERIMENTS

Polyimide films (Nissan SE130) of thickness 2000 Å on InSnO coated glass were prepared by spin-casting followed by baking at 180° for 30 minutes. They were irradiated using a KrF excimer laser at 248 nm with a pulse duration of 25 ns and a polarisation ratio of $\approx$ 20:1. Twisted cells of thickness 17 μm filled with the nematic liquid crystal E7 (Merck) were constructed using one exposed alignment surface and one rubbed polyimide layer with perpendicular alignment directions. The twist angle, ϕ, of the cell was measured using a polarising microscope. The pretilt angle of antiparallel nematic cells, constructed with two photo-aligned surfaces exposed with equal UV fluence, was determined by the crystal rotation method[13].

EXPERIMENTAL RESULTS

The twist angle of 90° twisted nematic cells is normally less than 90° because of competition between the bulk twist energy and finite surface anchoring. Assuming infinite anchoring at the rubbed polyimide surface, the azimuthal anchoring energy can be found from the equation[14]

$$W_\phi = \frac{2K_{22}\phi}{d \sin 2\phi} \qquad (1),$$

where K_{22} is the twist elastic constant and d the cell spacing measured before filling using a spectrophotometer. Figure one shows the variation of the azimuthal anchoring energy with the number of laser shots for a cell constructed with an alignment layer exposed directly with polarised light at a fluence of 13 mJ cm^{-2} per shot. This is less than the threshold fluence for ablation (= 22 mJ cm^{-2}). The liquid crystal alignment direction is found to be perpendicular to the polarisation direction of the laser. No photoinduced alignment was observed when nonpolarised light was incident.

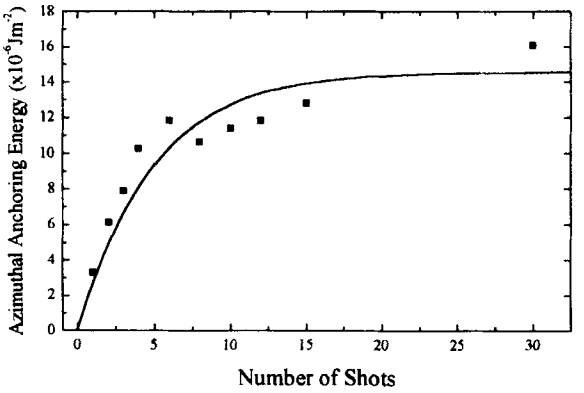

FIGURE 1 Variation of azimuthal anchoring energy with number of laser pulses of fluence 13 mJ cm^{-2}.

It can be seen that with an exposure of 10 shots (total exposure time ~250ns) or more, saturated alignment is achieved. This exposure is much smaller than that required when continuous illumination is used implying that non-linear effects are involved in the alignment process. Further measurements are in

progress to investigate whether alignment results from anisotropic depolymerisation as occurs during lamp exposure.

The azimuthal anchoring energies and liquid crystal pretilt angles obtained after oblique exposure of the alignment layers are shown for a range of incident angles in figure two. The incident light can be described as elliptically polarised and the intensity ratio of its s:p polarisation varies with the angle of incidence because the reflection at the air-polyimide interface is polarisation dependent. The substrate azimuthal plane is defined as the **x,y** plane and the sample is tilted in the **y,z** plane.

Angle of Incidence (°)	Azimuthal Anchoring Energy ($\times 10^{-6}$ J m^{-2})	Pretilt Angle (°)
60	7.4 ± 1.4	0.7 - 1.2
70	17.9 ± 3.2	0.7 - 1.0
75	2.7 ± 0.7	0.7 - 0.9.

TABLE 1 Variation of azimuthal anchoring energy and pretilt angle with incident angle for oblique exposure of alignment layers with the excimer laser.

Fairly strong anchoring ($\approx 10^{-5}$ J m^{-2}) is found but nonzero pretilt angles are only measured when the azimuthal alignment direction is parallel to **y**. This occurs when the direction of the linearly polarised component with greatest intensity is parallel to the **x** axis i.e. when the s:p intensity ratio is > 1. All the measured pretilt angles are small, with the lower limit of 0.7° for the pretilt angle obtained because no tilt disclinations are observed on switching.

DISCUSSION

Commercial twisted nematic displays require a pretilt angle to avoid tilt disclinations during switching. For photoinduced alignment, the pretilt angle is easily varied when the alignment direction is parallel to the polarisation direction of the UV light[3]: the polarisation axis can be tilted out of the substrate plane by exposure at non-normal incidence. Iimura et al.[15] succeeded in generating small pretilt angles ($\approx 0.3°$) in polyvinylcinnamate by means of a double exposure of the alignment layer even though the alignment direction was perpendicular to the polarisation direction. The first exposure was used to define the azimuthal alignment direction of the liquid crystal and the second exposure of p-polarised light was incident at an oblique angle to

generate a tilt asymmetry. No explanation was given why the generated pretilt angle was much less than the refraction angle of the second exposure.

Here, we propose a model, based on the anisotropic depolymerisation of polyimide chains, to account for the generation of a small pretilt angle on oblique incidence of elliptically polarised light. The model follows from the work of Chen et al.[16], and uses the assumption that the probability of a photochemical reaction is proportional to $\boldsymbol{m}.\boldsymbol{e}$ where $\boldsymbol{m}$ is the polarisation vector of a photosensitive bond, assumed parallel to the polyimide chain direction, and $\boldsymbol{e}$ the electric field direction of the optical wave. Hence the angular distribution of photosensitive bonds varies with time during a photochemical reaction according to

$$N(\theta,\phi) = N_0(\theta,\phi) \exp(-\alpha t \cos^2\theta \cos^2\phi) \quad (2)$$

where α is a constant, θ is the tilt angle and ϕ the azimuthal angle. N_0 indicates the density of photosensitive bonds at time $t = 0$. Depletion of the polyimide chains occurs preferentially in the direction of the electric field so that the predicted azimuthal alignment is perpendicular to the polarisation direction and parallel to the greatest density of undepleted chains.

As stated above, for exposure at oblique incidence, we define the substrate azimuthal plane as the **x,y** plane and the sample is tilted in the **y,z** plane. The generation of a pretilt angle requires an asymmetry in the latter plane. The elliptically polarised light can be divided into s- (parallel to **x** axis) and p- linearly polarised components with an s:p amplitude ratio of $\approx$ 11:1 when the incident angle is 70°. Because of its greater intensity, the s-polarisation component defines the azimuthal alignment direction to be parallel to the **y** axis. However, for exposure with s- polarised light, the depletion of bonds has cylindrical symmetry with respect to the **x**- axis: hence no asymmetry can be generated in the **y,z** plane. However, the smaller p-polarised component does give the required asymmetry for oblique incidence. Taking both s- and p- polarisation into account, the azimuthal (**x,y**) and polar (**y,z**) distribution of photosensitive bonds can be separated as follows:

$$N(\phi) = N_0(\phi) \exp(-\alpha_s t \cos^2\phi) \exp(-\alpha_p t \sin^2\phi) \quad (3)$$

and

$$N(\theta) = N_0(\theta) \exp(-\alpha_p t \cos^2(\theta + \theta_0)) \quad (4)$$

where $\phi = 0$ and $\theta = 0$ are parallel to the **x** and **y** axes respectively. The ratio α_s:α_p is related to the intensity ratio of the s:p polarisation. π-θ_0 is the alignment layer tilt angle, where θ_0 is the refraction angle of the incident UV light. Using equations 3 and 4, and assuming that the polymer chains are isotropically oriented before elliptically polarised UV exposure, the azimuthal

and polar distributions of remaining polyimide chains are calculated for an incident angle of 70° and an exposure time t corresponding to $\alpha_s t = 5.5$ and $\alpha_p t = 0.5$. Figure 2a shows that the azimuthal number density of the polymer is greatest along the y direction This predicts the liquid crystal alignment direction to be parallel to y which agrees with the experimental result.

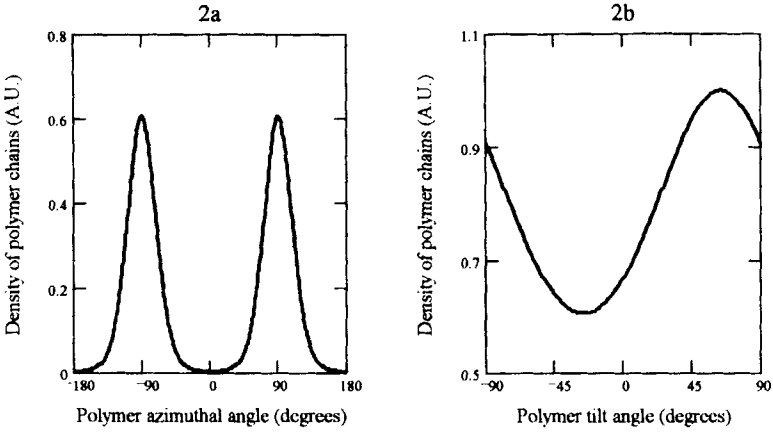

FIGURE 2 Number density of undepleted polyimide chains as a function of azimuthal angle (2a) and polar angle (2b)

The polar distribution of the polyimide, illustrated in figure 2b, shows a polymer inclination or tilt angle of 64°. This corresponds to the polar angle which gives the maximum density of undepleted chains. For nematic cells with rubbed polyimide layers, there is a complex relationship between the liquid crystal pretilt angle and the inclination angle of the aligning polymer: the two angles can differ by up to a factor of three[17,18]. However, in this work the calculated inclination angle corresponds to the much smaller experimental liquid crystal pretilt angle of $\approx 1.5°$. This discrepancy can be resolved by considering the initial polar distribution of the polyimide. Spin-cast polyimide has been shown to orient parallel to the substrate with a standard deviation (σ) of a few degrees[19]. Assuming such a Gaussian distribution, i.e.

$$N_0(\theta) = \exp(-(\theta^2/2\sigma^2)) \quad (5)$$

equation four is recalculated with $\sigma = 15°$ and a polymer tilt angle of 1.5° is found as illustrated in figure three.

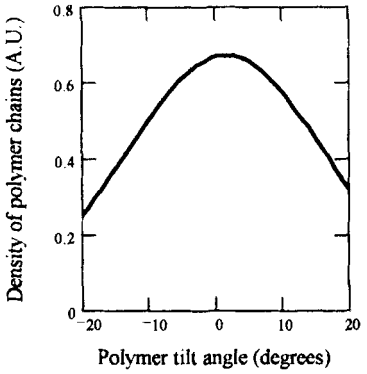

FIGURE 3 Polar distribution of undepleted polyimide chains on irradiation at an incident angle of 70°. The initial polar distribution is assumed to be Gaussian with a standard deviation of 15°.

We cannot quantitatively compare this value to the experimental measurement of the liquid crystal pretilt angle as neither the polar distribution of our unirradiated polyimide layer nor the relationship between the polymer inclination and liquid crystal pretilt angles are known. However, we believe that the measured liquid crystal pretilt angle can be accounted for by assuming an initial predominantly planar and symmetric polyimide chain distribution which is tilted by oblique irradiation with the excimer laser.

Our model also explains why no pretilt angle is generated when the intensity ratio of the s:p polarisation is < 1: the tilt of the sample during oblique exposure must be in the plane containing the liquid crystal alignment axis.

CONCLUSIONS

Exposure of a polyimide film with a polarised KrF excimer laser creates a photoinduced anisotropy which can be used to align nematic liquid crystals. Azimuthal anchoring energies > 10^{-5} J m^{-2} are measured and a fluence of 13mJ cm^{-2} with 10 shots is sufficient to create saturated alignment. Small pretilt angles can be generated by oblique exposure with the laser.

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