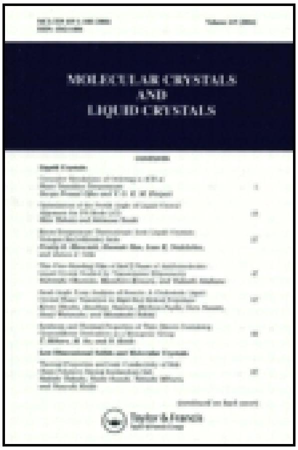

Molecular Crystals and Liquid Crystals

Photoalignment of Liquid Crystals on Chalcogenide Glassy Films

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Photoalignment of Liquid Crystals on Chalcogenide Glassy Films

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First observation of photoaligning of nematic liquid crystals (LC) on inorganic films, namely on a chalcogenide glassy films is reported. We found that irradiation of chalcogenide surfaces by visible laser beam of low-power (~30 mW) results in efficient reorientation of the director in the irradiated areas. The anchoring energy associated with the light-induced easy orientation axis is of the order $10^{-6}\,J*m^{-2}$ *that is typical for standard organic polymer photoaligning materials. The surprise is that the direction of the reorientation depended on the time of the exposure. For short exposures director reoriented toward the polarization of light and longer exposures resulted in the reorientation away from the light polarization. The effect of light-induced alignment was used for recording of the surface-mediated electrically controlled holograms in the LC cell.*

Keywords: Anisotropy; chalcogenide glassy; liquid crystal; photoalignment

INTRODUCTION

Alignment of a liquid crystal in a cell by irradiation of photosensitive polymer aligning layers with polarized light was found in the end of

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80s, and it brought forth a lot of expectations for astonishing applications for LCD technology [1–5]. Photoalignment effect caused by producing of light-induced anisotropy on polymer surface allowed hoping for development of advanced aligning technology. Unlike rubbing, photoalignment is non-contact technique and gives a possibility of easy controlling of the director orientation, pretilt angle and anchoring energy. Besides, there are no principle limitations to get homogeneous alignment on large substrates that make the method very promising for fabrication of the LCDs of last generations. At the same time, the method can be effectively used for the alignment of LC in tiny telecommunication devices where the rubbing technique is very difficult to apply.

Despite evident advantages of photoalignment technology, insufficient photosensitivity, relatively low anchoring energy and sufficient sticking effect prevent a wide application of photoalignment in LCD industry, and this technique is used so far just in scientific laboratories. Therefore, a search and development of new photoalignment materials are an issue of great present importance. Till now observation of photoalignment effect and development of photoaligning materials were limited by organic polymers materials. At the same time strong effects of light-induced anisotropy are inhered not just for polymers and can be observed in inorganic materials. Therefore it looks reasonable to extend a search of photo-orientants on this kind of materials.

Chalcogenide glasses are among the most promising inorganic materials that reveal light-induced anisotropy. The effect of light-induced anisotropy in these materials is known since the end of 70s when Zhdanov *et al.* [6,7] as well as Hajto and Ewen [8] reported that a linearly polarised laser beam could produce optical anisotropy in chalcogenide glassy films. The following studies of many scientific teams showed rich physics behind and variety of mechanisms leading to light-induced anisotropy in chalcogenides (see Review Articles [9,10]).

It was shown that irradiation of chalcogenide glasses and glassy films with polarized light resulted not only in optical anisotropy but also in appearance of many polarization-dependent phenomena. Examples of such phenomena are anisotropic optomechanical effect [11], polarization-dependent photocrystallization [12], photoinduced anisotropy of photoconductivity and mobility of charge carriers [13], anisotropic surface deformation [14] and anisotropic expansion that may results in producing of a surface relief on the chalcogenide surface in the case of irradiation with two interfering beams [15,16].

In early publications, photo-induced anisotropy in chalcogenide films was explained by interaction of polarized light with some optically anisotropic structural elements whose optical axes are oriented randomly [8,9]. According to this assumption, linearly polarized light interacts especially strongly with structural elements with optical axis parallel to the electrical vector of the light and destroys these elements, resulting in appearance of optical anisotropy. Later, more detailed models of photo-induced anisotropy in thin chalcogenide films were proposed in [17] but in most cases these models developed the initial idea proposed in [8,9]. So, Fritzsche in his model [18] discussed the photoinduced redistribution of anisotropic microvolumes in the glass, when the microvolumes with axis parallel to the electric vector of exciting light are transformed into ones having axis orthogonal to this vector. Tikhomirov and Elliott [19] considered the photoinduced orientation of randomly oriented valence alteration pairs–the charged defects with negative correlation energy, characteristic for chalcogenide glasses [20]. In the other models different kinds of possible micro-anisotropic structural elements of glassy films were considered, and all of them were discussed in the detailed revue paper of Tanaka [9].

The main features of phenomenon of light-induced anisotropy in chalcogenide glasses are: (1) Linearly polarized light induces dichroism and birefringence of a certain sign that is usually saturated during tens of seconds or several minutes of irradiation depending on the light intensity. (2) The anisotropy can be destroyed after heating the anisotropic sample to a temperature somewhat lower than the glass transition temperature and can be created repeatedly by subsequent irradiation of the cooled sample with linearly polarized light. (3) The anisotropy is erased with irradiation with nonpolarized light. (4) The anisotropy axis can be reoriented repeatedly by means of irradiation with linearly polarized light with an orthogonally oriented electrical vector without any fatigue effect. These features, especially reversibility of the anisotropy make chalcogenide glasses rather effective materials for photoalignment of LCs.

Here we report on first observation of photoaligning of nematic LC on an inorganic films, namely on chalcogenide glassy films.

MATERIALS, SAMPLES AND EXPERIMENTAL RESULTS

In this research we used thin films of two chalcogenide glasses $As_{50}Se_{50}$ and As_2S_3. Films were fabricated by thermal evaporation of starting glassy materials from quartz crucibles onto suitably cleaned Corning glass substrates in vacuum ($p \sim 10^{-6}$ Torr).

Both kinds of the films possess effect of photoinduced anisotropy. For illustration, we show in Figure 1 the process of photoinduced dichroism generation and reorientation of the axis of the dichroism maximum under action of He-Ne laser beam for the $As_{50}Se_{50}$ film of

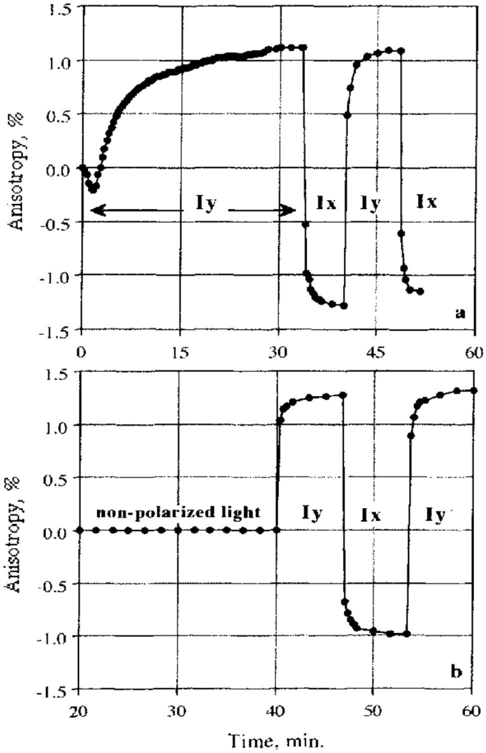

FIGURE 1 Kinetics of dichroism producing in an $As_{50}Se_{50}$ film under action of linearly polarized beam with two orthogonal polarizations directions ($\vec{y}$ and $\vec{x}$) for initially not-treated film (a) and for the film initially irradiated with unpolarized light (b).

1.2 μm thickness [21]. We used linearly polarized light with two orthogonal directions of electrical vector (**y** and **x**). It is seen from Figure 1a that the initial dichroism growth in the non-treated film is rather prolonged (10–20 min), while the dichroism reorientation happens much faster ($<$ 1 min). In the case of long film irradiation with the unpolarized light, the following irradiation with linearly polarized light results in the rapid appearance of dichroism (Fig. 1b) [10]. Similar processes are characteristic for the dichroism generation and reorientation for the As_2S_3 films excited by Ar^+ laser light. These results are explained by light-induced formation of valence alteration pairs (VAPs) in chalcogenide film [10,21]. Exposure with polarized light leads to producing and rapid orientating of VAPs perpendicular to the polarization of the absorbed light that causes photoinduced dichroism in the film. Previous irradiation of the film with unpolarized light results in producing of randomly angular distributed VAPs ready to be reoriented during consequent irradiation with polarized light.

To test photoaligning properties of chalcogenide glasses we utilized a classic nematic liquid crystal pentyl-cianobiphenyl (5CB) from Merck. The experiments were carried out in combined LC cells consisting of reference and tested substrates separated by spacers with thickness $L = 20\,\mu\text{m}$. Reference substrate was covered with a rubbed polyimide layer that provided strong unidirectional planar alignment of LC director with a small pretilt ($\sim 1^\circ$). The tested substrate was covered with the chalcogenide film. The cells were filled with the LC 5CB at elevated temperature above the clearing point, $T_c \approx 34.5^\circ\text{C}$ and slowly cooled down to the room temperature in magnetic field $\sim 3\,\text{kGs}$. During the cooling the cell was disposed on aluminum plate faced by the test substrate to the surface of the plate. The temperature of the plate was about 50°C. This arrangement provided starting of the nematic phase from the reference substrate, and resulted in a satisfactory uniform planar alignment of the LC over the cell parallel to the direction of the rubbing of the reference surface $\vec{e}_{ref}$.

To test if the chalcogenide glass may serve as photoaligning material we irradiated the As_2S_3 film with linear polarized beam from diode-pumped solid state laser (power, $P \approx 30\,\text{mW}$, beam diameter, $d \approx 0.5\,\text{mm}$, intensity, $I_{pump} \approx 16\,\text{W/cm}^2$, wavelength, $\lambda = 0.473\,\mu\text{m}$). The polarization of the pump beam, $\vec{E}_{pump}$ made an angle $\vartheta_0 = 45^\circ$ to the initial direction of the director in the cell, $\vec{n} \parallel \vec{e}_{ref}$.

The irradiated areas were examined in a polarized microscope and compared with the surrounding non-irradiated areas. Irradiation of the chalcogenide surface during up to 120 min before making and filling of the cell did not allow us to determine if there are any changes of the alignment in the irradiated areas in compare with non-irradiated one. It seems that magnetically mediated alignment that occurred during the cooling of the cell in the magnetic field [22,23] masked a photoalignment, if any. Irradiation of the filled cell from the side of the tested substrate also did not caused any reliable photoalignment effect due to strong absorption ($> 80\%$) of the pump beam in the chalcogenide layer and intensive light scattering in it. Therefore, we irradiated the chalcogenide surface from the side of the reference substrate keeping the LC in the isotropic phase. In this case we avoided a change of the light polarization during propagation of the beam through birefringent LC media. A strong scattering caused by director fluctuation was also diminished in this case.

Observation in a polarizing microscope showed in this case the evident changes of the director orientation in the irradiated spots.

Namely, we found a twist structures in the irradiated areas that was the result of reorientation of the director on the tested surface. It signified a producing of a light-induced easy orientation axis on the chalcogenide surfaces.

Under experimental conditions the Mauguin regime was realized, that is the vector $\vec{E}_{test}$ followed the director through the whole cell [24]. Therefore the value of the twist angle φ_{test} in the irradiated area coincided with the angle of deviation the director on the tested surface from initial position.

The dependence of the orientation of the director on the tested As_2S_3 surface, i.e. of the light-induced twist angle φ_{test} on the exposure time t_{test} is presented in Figure 2. We counted the angle φ_{test} counterclockwise from the initial direction of the director, $\vec{d}_{test,0}$ (see insertion in Fig. 2). A homogeneous planar alignment was observed in the not-irradiated areas of the tested surface, e.g. $\varphi_{test} = 0$ at $t_{exp} = 0$. The irradiation resulted in the twist structure in which the light-induced twist angle $\varphi_{test} > 0$. Increase of the exposure till $t_{exp} \approx 30$ min led to the gradual increase of twist angle, i.e. direction $\vec{d}_{test}$ approached to the polarization $\vec{E}$. Longer exposure $t_{exp} \approx (30-60)$ min caused the deterioration of the light induced alignment; we observed a polydomain structure in the irradiated areas. Further exposure brought

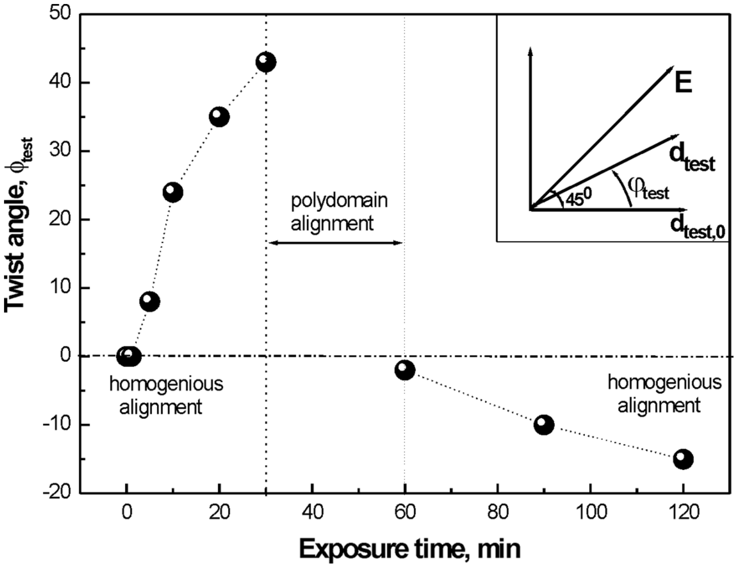

FIGURE 2 Dependence of director orientation on exposure time. The geometry of the experiment is shown in the inset.

to the change of the sign of the angle φ_{test} i.e. the director began to move away from the vector $\vec{E}$.

Such behavior of the light-induced twist structures is typical for a case of the change of the easy axis direction with the exposure. In Ref. [25] it was found that the change of the sign of the light-induced twist $\vec{E}_{test}$ in the LC cell doped with azo-dye molecules was caused by the change of the easy axis from the direction perpendicular $\vec{E}_{test}$ to the direction parallel to $\vec{E}_{test}$. In that system the producing of the easy orientation axis and its direction change were determined by competition of light-induced desorption and adsorption of dye molecules on/from the surface, which efficiencies depended on the light irradiation dose. The change of the easy axis direction from perpendicular $\vec{E}_{test}$ to parallel to $\vec{E}_{test}$ was also observed in the LC cell with photoaligning layer where two mechanisms of photoinduced anisotropy had different exposure dependencies [26]. Therefore, one may suggest that the observed $\varphi_{test}(t_{exp})$ dependence is also caused by change of the easy axis direction from the position being parallel to $\vec{E}_{test}$ in the short exposure range to the direction parallel to $\vec{E}_{test}$ in the long exposure range.

We cannot explain now why the direction of the director orientation and easy axis in the As_2S_3 film depends on the light irradiation dose. As we described in the introduction, irradiation of chalcogenide glassy films with polarized light causes many polarization-dependent phenomena. For instance, besides of photo-induced anisotropy due to VAPs reorientation that does not change the macroscopic morphology of the glass surface, there are a number of the effects that causes a formation of a surface relief on a chalcogenide surface [11,13,14]. The direction of the light-induced relief can be both parallel and perpendicular to the polarisation of the light, and its characteristics depend on the irradiation dose. This relief can contribute to the LC orientation due to Berreman mechanism [24]. Therefore, one can suggest that the observed alternation of LC orientation on the chalcogenide films is a result of competition of different mechanisms of light-induced anisotropy in these films.

In the suggestion that the dependence $\varphi_{test}(t_{exp})$ is caused by change of the easy axis from the position parallel to $\vec{E}_{test}$ to the direction parallel to $\vec{E}_{test}$, the value of the twist angle is unambiguously connected with the value of the anchoring energy W_{test} of the liquid crystal with the aligning surface [25]:

$$\frac{\sin 2(\phi_{ref} - \varphi_{test})}{\varphi_{test}} = \frac{2K_{22}}{W_{test}L} \tag{1}$$

Here φ_{test} is the direction of the light induced easy axis, $\varphi_{test} = 45^\circ$ for $t_{exp} \leq 30\,\text{min}$; $\varphi_{test} = -45^\circ$ for $t_{exp} \geq 60\,\text{min}$, K_{22} is a Frank constant for twist deformation, W_{test} is an anchoring energy of LC in the Rapini-Popullar approximation, $W_{test} = 1/2\ W_0 \cos^2 \varphi_{test}$, W_0 is the surface potential. Substituting the measured values $\varphi_{test}(t_{exp})$ and the values of the experimental parameters, $L = 20\,\mu\text{m}$ and $K_{22} = 3.6 \times 10^{-12}\,\text{N}$ in (1) we can get the dependence of the anchoring energy on exposure time, $W_{test}(t_{exp})$ depicted in Figure 3.

The experiments described above were also performed by utilizing the LC cells with chalcogenide films $As_{50}Se_{50}$. We used the pump beam from diode-pumped YAG laser in these experiments ($I_{pump} \approx 16\,\text{W/cm}^2$). The wavelength of the laser, $\lambda = 530\,\text{nm}$ corresponded the red wing of the adsorption band of the chalcogenide. In opposite to the case of As_2S_3 film, the reorientation toward $\vec{E}_{test}$ began just after $t_{exp} \approx 30\,\text{min}$ of exposure and achieved $\varphi_{test} \approx 8-10^\circ$ after $t_{exp} \approx 120\,\text{min}$ and there was no change of the reorientation sign in the exposure region.

The observed effect of light-induced alignment was used for recording of surface-mediated holograms in the LC cell. To record the hologram two laser beams with polarizations parallel to $\vec{e}_{ref}$ were crossed in the plane of the cell. The irradiation was performed in the isotropic phase of the LC and the beams were directed from the side of the reference surface. The cooling of the cell after the exposure resulted

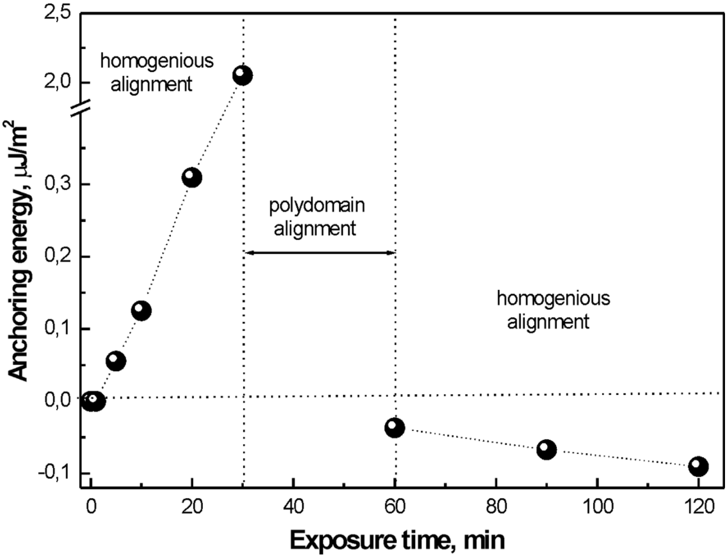

FIGURE 3 Dependence of anchoring energy on exposure time.

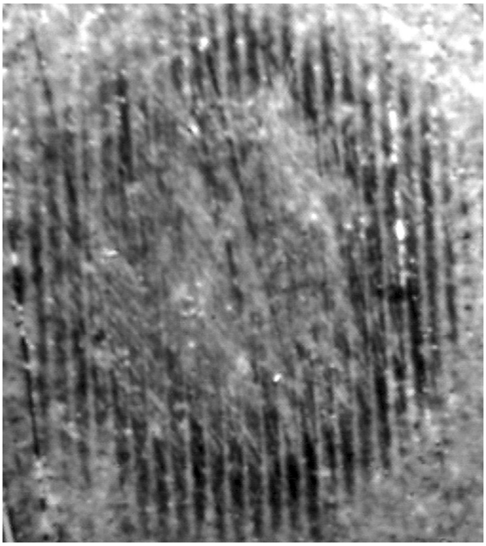

FIGURE 4 Photo of the spatial light-induced modulation of the director (polarization diffraction grating) in polarization microscope.

in producing of spatial modulation of the director on the chalcogenide surface that was extended to the bulk of liquid crystal. The photo of the resulted periodic structure with the spatial frequency $40\,\mathrm{mm}^{-1}$ in $5\,\mu\mathrm{m}$ LC cell between crossed polarizers is shown in Figure 4. The spatial modulation of the director in the azimuthal plane of the cell resulted in a spatial modulation of the polarization state of the tested beam on the exit of the cell that is in formation of a polarization diffraction grating and appearance of the diffracted beams of several orders in a far optical zone. The efficiency of the first order diffraction achieved several percents. Efficiency of the diffraction could be controlled by application of ac electric field ($0 < \mathrm{U} < 10\,\mathrm{V}$, $\mathrm{f} = 1\,\mathrm{kHz}$) which reoriented the director from initial planar position to the homeotropic one, and by this means changed the phase retardation of the pump beam.

CONCLUSION

First observation of photoaligning of nematic LC on inorganic films, namely on chalcogenide glassy films is reported. We found that irradiation of chalcogenide surfaces by visible laser beam of low-power ($\sim 30\,\mathrm{mW}$) results in efficient reorientation of the director in the irradiated areas. The anchoring energy associated with the light-induced easy orientation axis is of the order $10^{-6}\,J^{*}m^{-2}$ that is typical for standard organic polymer photoaligning materials. The surprise is that the direction of the reorientation depended on the light irradiation dose. For low doses director reoriented toward the polarization of light and higher doses resulted in the reorientation away from the light polarization. The effect of light-induced alignment was used for recording of the surface-mediated electrically controlled holograms in the LC cell.

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