Influence of light on self-diffraction process in liquid crystal cells with photoconducting polymeric layers

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In this paper we present experimental results on the influence of an external light on phase grating recording process in nematic liquid crystal cell with a photoconducting polymeric layer (PVK doped with TNF). Depending on voltage applied to the cell, the external light can amplify or attenuate the diffracted, into first order light power measured in degenerate two-wave mixing experiment. From the time delay between the opening of the external light and the moment of diffraction signal change, we deduce information about the effective charge carriers mobilities in PVK:TNF polymeric layer. We also discuss and present simple explanation of the observed effect.

Keywords: nematic liquid crystal panel, self-diffraction, charge carrier mobility, photoconducting polymer.

1. Introduction

Light can induce reversible or permanent changes of dielectric properties of almost any material. The subject of great interest is the design of materials in which light induced changes are dynamic (i. e. reversible) and occur already at low laser intensities, at least at ~mW/cm². One can mention many groups of materials in which such a process, frequently called photorefraction, is possible. Generally speaking, photorefractive materials are those in which spatially modulated light can induce refractive index modulation mapping the light pattern incident on the medium. In classic photorefractive materials, (either crystals or polymers) light generates a distribution of charge carriers via photoconductivity of the material and the spatial modulation of electric field resulting form the charge density distribution produces a corresponding modulation of material's refractive index via linear electrooptic effect [$\Delta n(x) \propto n^3 r E_{sc}(x)$], where r is the component of Pockels tensor, n is the refractive index of the material and E_{sc} is the space charge field. Periodic or nonperiodic refractive index modulation can form a diffraction grating or hologram in a material then store information. Incident laser light upon diffraction on the hologram can read the information stored optically in the material.

Recently liquid crystal panels have been found to exhibit very attractive photorefractive properties mostly due to the fact of easy reorientation of their molecules in the optical or electrical field. Photorefraction can be realised either by doping liquid crystal with photochromic molecules, photoconductivity sensitisers or by placing liquid crystal adjacent to photoconducting polymeric layers serving both as alignment as well as space charge field creating ones upon light excitation. It is important to realise that the liquid crystal must not be noncentrosymmetric in order to show photorefraction. In liquid crystals, the whole mechanism of photorefractivity is based on director reorientation and not due to the Pockels effect as is the case in photorefractive crystals and polymers.

Nematic liquid crystal panel with photoconducting polymeric layer is an excellent optical material used in the domain of real-time holography, light amplification, optical correlation or phase conjugation etc. The mechanism of light induced refractive index changes in such a panel is well known and was described in several papers [1,2]. Performance characteristics of hybrid polymer liquid crystal (HPLC) panels depend generally on many parameters both external: bias voltage, optical configuration, geometry as well as on LC parameters (birefringence, rotational viscosity, dielectric anisotropy) and properties of polymeric layers (their resistivity, photosensitivity, charge carriers mobility, photogeneration efficiency) to mention just the most important ones.

In this paper, we focus our attention to the processes taking place in a thin polymeric layer upon incidence of periodically modulated in space light intensity pattern (interference fringes form crossed laser beams) and changes imposed by another light (laser or UV lamp) not carrying any spatial information. Both light sources have the wavelengths which are sufficient to induce photogeneration of charge carriers in polymer layer. The photogeneration and charge transport in polymer is here probed by the observation of light self-diffraction on the refractive index grating

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formed in nematic liquid crystal layer. Measuring diffraction efficiency

$$\eta = \frac{I_{diff}}{I_0} = \sin^2\left(\frac{\pi d \Delta n_{e,K}^{eff}}{\lambda}\right), \qquad (1)$$

where I_0 is the intensity of incident beam, I_{diff} is the intensity of first order diffracted beam, d is the thickness of LC layer, λ is the wavelength of the incoming light and $\Delta n_{e,K}^{eff}$ is the averaged over LC thickness amplitude of the extraordinary refractive index of the grating one can probe $\Delta n_{e,K}^{eff}$ which is sensitive of the space charge field formed in the system. Then, any changes in photogeneration efficiency, photodetrapping, charge carrier drift and diffusion will be reflected by changes of this amplitude and consequently by observed diffraction efficiency changes. The temporal behaviour of the space charge field formed in the polymeric layer can be studied by the mentioned technique providing the dynamics of the changes do not exceed reorientational ability of liquid crystal itself. In the present paper, we analyse conditions for which external light can amplify the existing grating and introduce non direct holographic method for evaluation of charge carriers mobility in very thin (~100 nm) polymeric layer constituting the liquid crystal panel.

2. Experimental

Experimental set-up used by us is composed of classic degenerate two-wave mixing (DTWM) system supplemented by the optical system delivering light into an area of formation of diffraction grating as is shown in Fig. 1(a).

Two beams from the He-Ne laser ($P = 25$ mW, $\lambda = 632.8$ nm, Spectra Physics) cross each other at the angle $2\theta = 3.5°$ and incident onto the HPLC panel tilted at $\alpha = 40°$ with respect to the bisectrice of the 2θ angle. For the external light source we used an Ar$^+$ ion laser (cw, $P = 4$ W, $\lambda = 514.5$ nm, Innova 90, Coherent). Power of diffracted light was measured with a fast photodiode coupled with a two-channel digital oscilloscope and computer. Measurements of diffraction efficiency were done with the two-head laser power meter Labmaster Ultima, Coherent. For the measurements of charge carrier mobility it was necessary to exactly measure the time of opening of the Ar$^+$ laser beam with respect to the diffraction intensity changes, so we have used the another photodiode for triggering the oscilloscope.

Liquid crystal panel with photoconducting polymeric layer is schematically shown in Fig. 1(b). Liquid crystal panel is symmetrical and composed of two ITO covered glass plates with inner parts covered by spin-coated thin layers (~100 nm) of photoconducting polymer. We have used poly(N-vinyl carbazole) (PVK) sensitised with trinitrofluorenone (TNF) at the ratio 10:1 dissolved in chloroform. Then the polymeric layers were rubbed in order to get the planar configuration of the LC panel. After assembling the panel of 10 μm in thickness was filled with the nematic liquid crystal mixture E7 (Merck, Darmstadt, Germany) characterised at room temperature by positive dielectric anisotropy $\Delta\varepsilon = +13.8$, birefringence $\Delta n = 0.2253$ at 589 nm with $n_e = 1.7464$ and $n_o = 1.5211$) and viscosity $\gamma = 39$ mm^{2}s^{-1}.

3. Description of the physics underlying DTWM experiment

Illumination of the LC panel with the two He-Ne laser beams polarised along the rubbing direction (~10 mW each, diameter ~3 mm) generates the light interference pattern $I(x) = I_o[1 + m\cos(Kx)]$ where $K = 2\pi/\Lambda$ is the grating wavevector, $\Lambda = \lambda/2n\sin\theta$ and m is the light intensity modulation factor (here $m \approx 1$). As the PVK sensitised with TNF
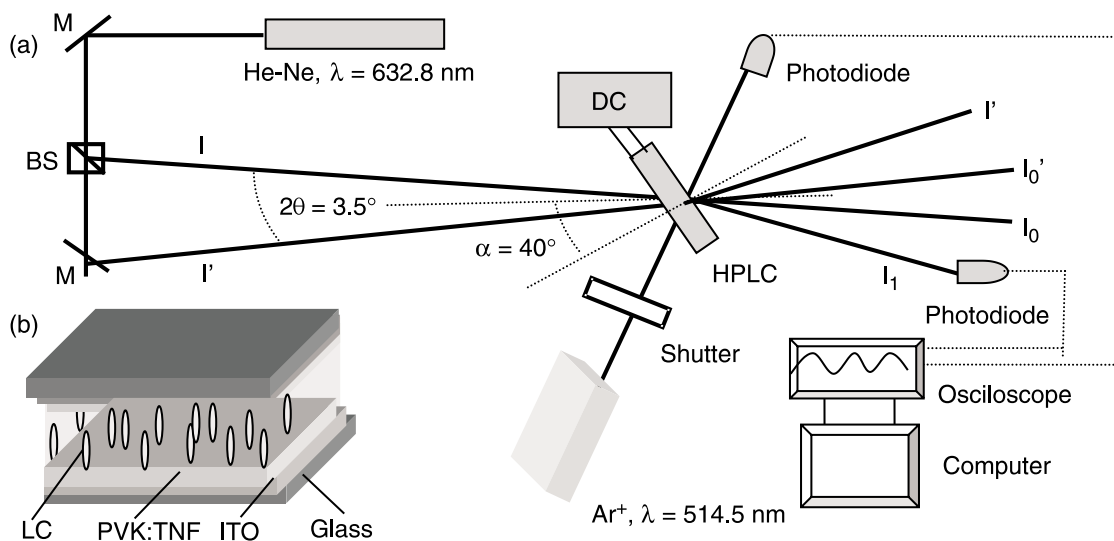

Fig. 1. Scheme of the degenerate two-wave mixing setup used in the experiment (a), simplified schematic structure of the hybrid polymeric liquid crystal panel (b).

is photoconducting in almost whole visible range, we can safely assume that in the bright regions of the fringe pattern there is a photogeneration of the electrons and holes which depend on the photon absorption probability by the complex PVK:TNF and the effective electric field strength in the photogeneration place. As a result of drift and diffusion charge carriers move from the place of their photogeneration with the velocity given by the product $\mu_\pm$ E, where $\mu_\pm$ is the mobility of the holes and electrons in the polymer and E stands for the local electric field. Under steady-state illumination conditions a periodic distribution of space charge is build-up which creates the space charge field E_{sc} which in turn effectively modulates the externally applied electric field E_a. Superposition of the two fields E_a and E_{sc} forms a complex electric field pattern in which molecules of nematic liquid crystal are reoriented. The electric field torque acting on molecules is given by

$$\Gamma_{el} = \varepsilon_o \Delta\varepsilon(\hat{n}(E_{sc} + E_a))(\hat{n}(E_{sc} + E_a)) \qquad (2)$$

where $\hat{n}$ is the director of the liquid crystal. As a result the modulation of molecular reorientation is set-up across the LC layer and along the direction r. The grating, in the simplest case, can be described by a modulation of the dielectric permittivity tensor of the liquid crystal at the operation wavelength

$$\hat{\varepsilon} = <n_e^{eff}>^2 + \hat{\varepsilon}_0^{(1)} + \hat{\varepsilon}_K^{(1)}\left[\frac{E'E^*}{I_0 + I_b}\exp(-iKr) + c.c\right] \qquad (3)$$

where $\hat{\varepsilon}_0^{(1)}$ is the spatially homogenous change in permittivity; $\hat{\varepsilon}_K^{(1)}$ is the change in permittivity with the spatial frequency K; E', E are the complex-field amplitudes of the writing beams, $I_0 = I'(z = 0) + I(z = 0)$ is the total incident light intensity, and I_b is the background (incoherent) light intensity. The refractive index modulation, as was shown before [3], is not uniform along the LC layer thickness and the phase shift ξ exists between the index grating

and the light fringe pattern. In order to see the light self-diffraction in such LC panels they should be tilted at about 45° with respect to the bisectrice of the grating writing laser beams [4]. So, induced diffraction grating efficiently diffracts the light and many diffractions orders are clearly visible. Moreover, depending on the phase shift ξ in such a structure, the transfer of energy between the incoming beams is possible as it depends on exponential gain coefficient $\tilde{\Gamma}$ given by

$$\tilde{\Gamma} = \frac{k_0\Delta n_{e,K}\sin\xi I_0}{(I_0 + I_b)} \qquad (4)$$

where $\Delta n_{e,K}$ is the effective refractive index grating amplitude seen by the reading wave of wavevector k_0.

In the present work we analyse the influence of external light incident at the area of light induced grating by monitoring a temporal behaviour of the first order diffracted beam I_1 [cf. Fig. 1(a)]. By changing the intensity of the incoming not bearing any spatial information light (from Ar+ laser) we could study the dynamics of grating erasure or as observed for some external bias an apparent grating amplification process. The illumination time was set to 25 s for the observation of grating erasure/amplification process or to 0.5 s for the measurements of charge carriers mobility in the polymeric layer.

4. Results

4.1. Change of diffraction efficiency in response to external illumination

In Fig. 2, we present examples of the oscilloscope traces of diffraction power measurements in a sample biased with $U = 11$ V as a function of 514.5 nm laser beam intensity. The moment at which the Ar+ laser beam was opened is indicated by an arrow.
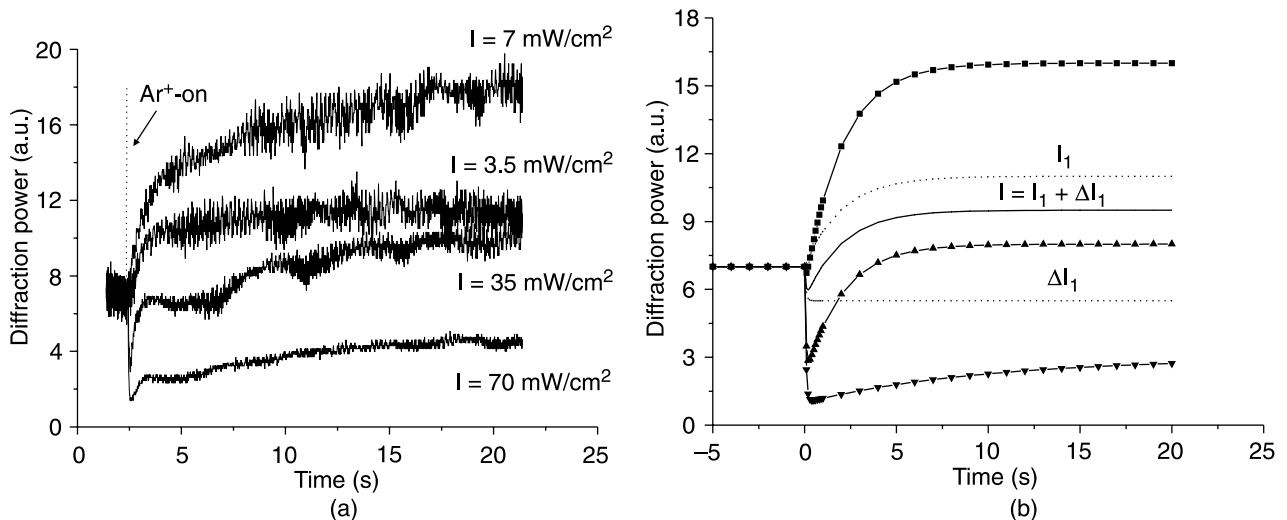

Fig. 2. Changes of diffraction power in time vs. intensity of argon laser with U = 11 V (a) experiment, (b) simulation results.

One can notice that we deal with two distinct type of responses. For low laser light intensities (1–10 mW/cm^2) a slow increase of diffraction efficiency is observed. The time constant of the signal rise is $\tau_R = 3$ s. For higher Ar$^+$ laser beam intensities (10–40 mW/cm^2) the fast decrease in diffracted power is observed followed by its slow rise. In both cases after 15 seconds the saturation of the diffraction is observed. Behaviour, shown in Fig. 2, was well repeatable within the same sample and only details were different on other samples studied, so we may safely say that it is general in this type of HPLC panels. The intriguing feature was the grating reinforcement in the presence of the external Ar$^+$ light. Initially we supposed that we deal with the photoinduction of phase shift ξ between light interference pattern and refractive index grating which can rise the intensity of the zero order beam in DTWM experiment at the cost of depletion of the other. This could be seen as the first order diffraction I_1 increase (e.g. stronger beam diffracted on the grating of a given amplitude $\Delta n_{e,K}$ will give more power into the first diffraction order). However, this requires that the I_1' first order diffracted beam loses its power at the same time. In order to exclude this possibility we performed the DTWM experiment and placed detectors at both sides of the zero order beams. The result which is shown in Fig. 3 is clear: both first order beams I_1 and I_1' are influenced by the same way by the opening of the Ar$^+$ light, i.e., exhibiting small rise. Supposition of the energy transfer should give in such an experiment a clear increase of I_1 accompanied by a clear decrease of I_1' beam power. So, we reject this mechanism of diffraction power increase and propose another one.

In Fig. 4, the plot of diffraction efficiency measured in HPLC panel biased with $U = 11$ V in function of intensity of 514.5 nm laser light is given. As is seen for small light intensities there is an increase in saturated diffraction efficiency followed by its decrease starting at $I = 10$ mW/cm^2. For intensities higher than $I = 40$ mW/cm^2 one can only observe the decrease in saturation diffraction efficiency. It is evident that the process of grating amplitude increase or
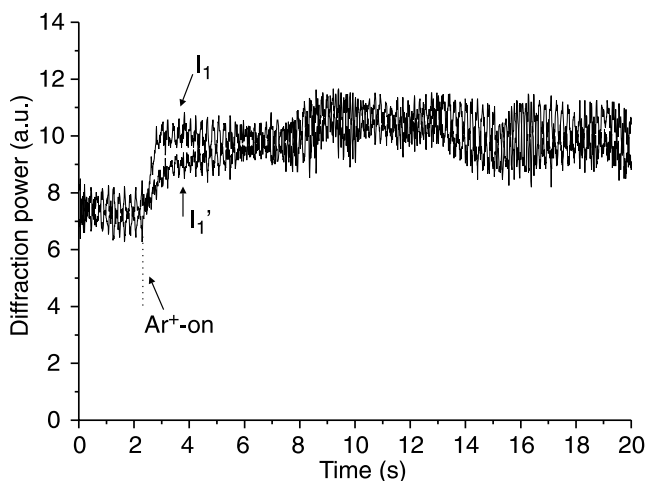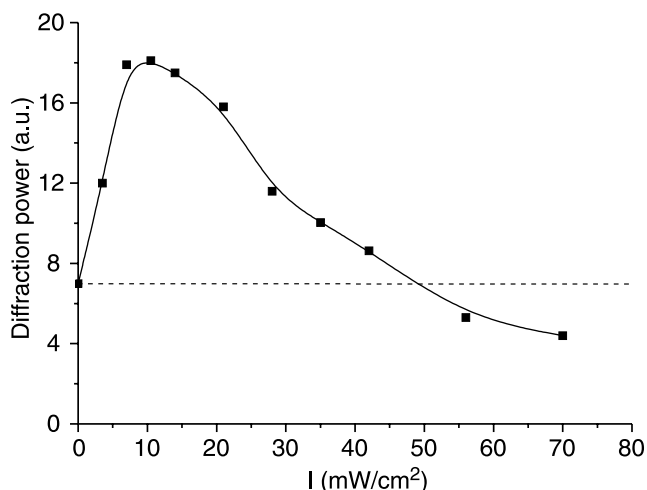

Fig. 4. Changes of diffraction power vs. intensity of 514.5 nm laser light.

decrease is linked with charge carrier generation and transport in the polymeric layer. We have measured the dependence of diffraction efficiency in HPLC panel in function of voltage applied to the 10 μm thick panel and present in Fig. 5.

From this dependence peaking at 17 V ($\eta_{max} = 22\%$) we can see that depending on voltage applied to the sample one can observe at least two processes when a small positive value of voltage ΔU is added (here $\Delta U = 4$ V). When the voltage is set at 11 V and one adds $\Delta U = 4$ V, the increase in diffraction efficiency will be from 7% to 15%. On the other hand, if the same voltage is added to the sample biased initially with 21 V one will observe the qualitatively different behaviour, namely the decrease in diffraction efficiency from 19% to 17%. Now, assuming that the uniform illumination of HPLC panel by an Ar$^+$ laser light is capable to induce the noncompensated by current flow positive photovoltage ΔU_{ph} then explanation of the effect observed at 11 V is obvious. It is sufficient to assume that the external light is absorbed in the polymeric layers and produces an increase in effective voltage acting on the LC layer. This
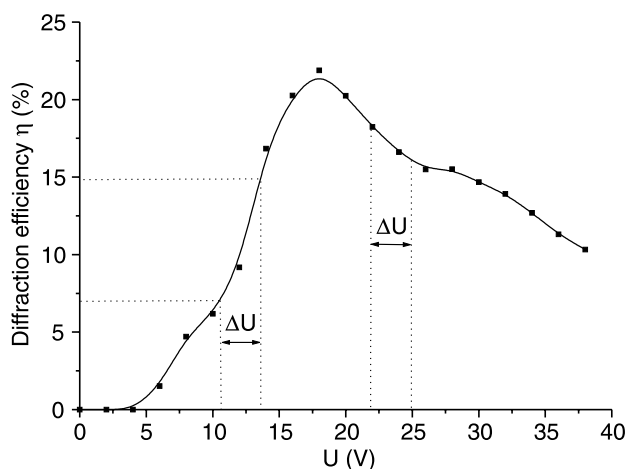

Fig. 3. Changes of diffraction power for I_1 and I_1' first order beams.

Fig. 5. Diffraction efficiency η measured for a LC sample in function of an externally applied voltage U, $\Lambda = 6.5$ μm.

voltage builds up with the characteristic time constant depending on light intensity level and resistivity of the whole system. So, even for the same grating amplitude an increase in diffraction efficiency is possible because the molecules in the whole LC layers assume more efficient orientation for grating recording. For the voltage higher than 20 V, applied to the HPLC panel, we could never observe the diffraction efficiency increase for any laser light illumination level. The voltage build-up is a relatively slow process and we will describe it with the single exponential growth function

$$I_1(t, I_b) = I_1(0) + I_{1,sat}(I_b)\left[1 - \exp\left(-\frac{t}{\tau(I_b)}\right)\right] \quad (5)$$

where the $I_1(0)$ is the diffraction beam intensity with no external light incident on the panel, $I_{1,sat}(I_b)$ is the value of the equilibrium diffraction beam intensity possible to achieve in the system at time $t = \infty$. We suppose that the time constant of the process is also dependent on the background illumination level I_b. In order to properly describe the observed signals (cf. Fig. 2) we must add also the second important mechanism namely action of I_b on existing distribution of space charge in the polymeric layer. Such a light is strongly absorbed by the carbazole-TNF CT complex so, it induces the photogeneration of charge carriers in the whole illuminated region. By production of charge carriers also in dark fringe places the amplitude of the space charge field E_{sc} must decrease also one should consider a photodetrapping process. The light of 514.5 nm is far more energetic than 632.8 nm light then it can remove some trapped carriers, forming space charge, from their places. Both mentioned processes are much faster than the photovoltage buildup process. The grating smearing out process we can approximate with a function

$$\Delta I(t, I_b) = -I_{1,sm}(I_b)\left[1 - \exp\left(-\frac{t}{\tau_{sm}(I_b)}\right)\right] \quad (6)$$

where $\tau_{sm}(I_b)$ is the time constants describing process of photodetrapping and photogeneration of charges by I_b light intensity, $I_{1,sm}$ can be regarded as the amplitude of the mentioned process. Summation of these two functions given by Eqs (5) and (6) will resemble observed experimentally curves after proper choice of parameters. For example the $\tau_{sm}(I_b)$ time constant is always much shorter than the τ the time constant of photovoltage build-up.

Examples of few curves generated by this way are shown in Fig. 2(b). Their parameters are: $I_{1,sat}$:10, 4, 6, 2, $I_{1,sm}$:1, 2, 8, 10, τ_{sat}-2, τ_{sm}-0.07. It is worth to notice that increase in the external light source intensity leads to both an increase in photovoltage and increase in space charge smearing out process. The latter process for high enough light intensities dominates over the first one (cf. Fig. 2).

4.2. Charge carrier mobility evaluation

In any photorefractive material the knowledge of charge carrier mobility is an important issue [5]. Effective carrier mobilities determine the response time of the device and it its possible to measure them using a holographic time of flight method as proposed by Biaggio *et al*. [6].

In our measurements of light induced grating erasure in HPLC panels we observed the substantial time delay between the onset of Ar+ light and start of the diffracted power changes. We think that this might be connected with the time which is necessary for the photogenerated charge carriers to arrive at the place where the space charge is situated, i.e., across the polymer layer thickness.
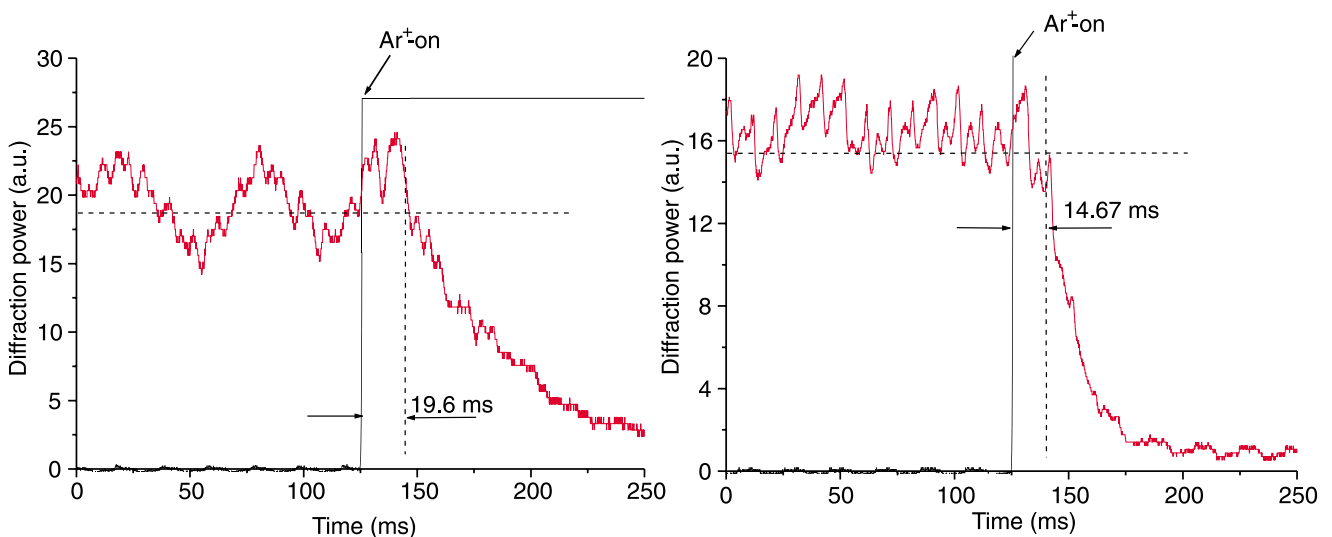

Fig. 6. Examples of oscilloscope traces of grating erasure by opening of 514.5 nm light. (a) $U = 15$ V, $t_d = 19.6$ ms, (b) $U = 25$ V, $t_d = 14.67$ ms.
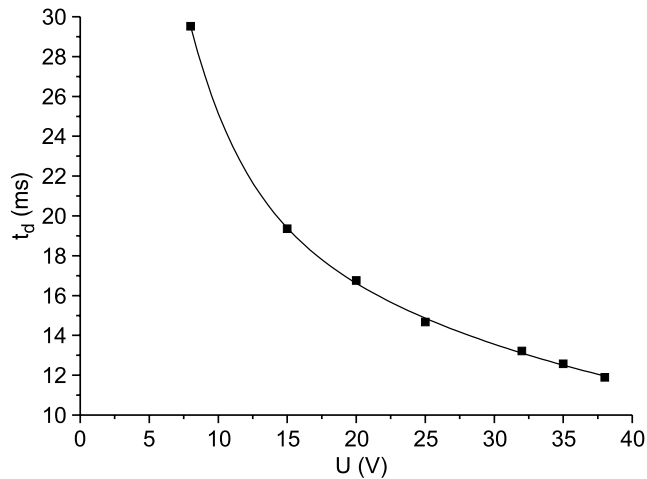
Fig. 7. Delay time between Ar⁺ light opening and start of diffraction efficiency decrease vs. applied field.

Fig. 8. Hole mobility vs. externally applied electric field in PVK:TNF (10:1) polymeric film.

As it is well known that the holes are much more mobile than the electrons [7] in PVK:TNF polymer, we assume that we can estimate the hole mobility measuring the delay time in function of applied voltage. In Fig. 6, we show two examples of oscilloscope tracing of grating erasure measurements for $I = 70$ mW/cm^2 at 15 and 25 V applied to the HPLC panel with delay times td equal to 19.6 ms and 14.7 ms, respectively. In Fig. 7, we plotted the measured delay time in function of voltage applied to the sample observing the expected typical behaviour $\tau_d \sim U^{-1}$ and in Fig. 8 the hole mobility in function of externally applied electric field to the layer. We estimated the hole mobility in the PVK:TNF polymer to the amount $\mu_h = 2.8 \times 10^{-6}$ cm^2/Vs at $E = 2.5 \times 10^{-6}$ cm^2/Vs which lies in the range of values determined by usual time of flight technique [5]. However, the weak point in the mobility determination lies in the difficulty of estimation of the effective charge carrier drift length (we used here the polymer thickness $l = 100$ nm) and the value of electric field within the polymeric film which depends also on resistivity of the adjacent LC layer.

5. Conclusions

We have demonstrated how the external light can influence the diffraction efficiency of *in-situ* written holographic grating in hybrid photoconducting polymer nematic liquid crystal panel. We proposed a simple model explaining both the grating reinforcement mechanism and erasure. We propose the holographic method of estimation of hole drift mobility in thin polymeric PVK:TNF layer.
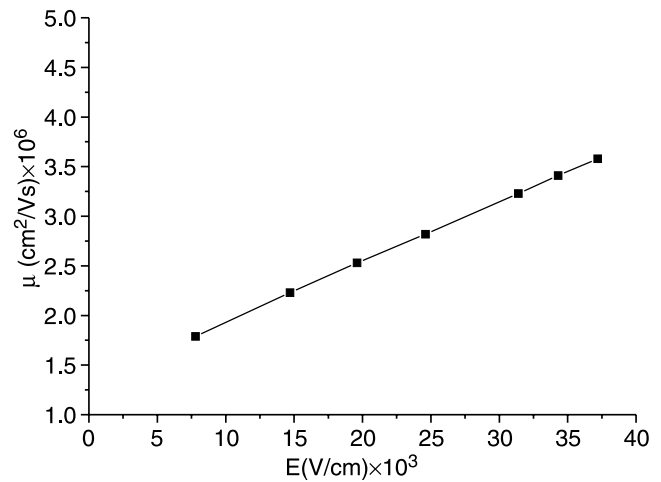
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