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Electrical and electro-optical investigations of liquid crystal cells containing WO_3 thin films

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An interesting application of the fast ion transport properties of tungsten trioxide is presented, when it is inserted as an electrode in nematic liquid crystal (NLC) cells. In a standard sandwichlike cell the nematic liquid crystal, confined between two transparent plane electrodes of purely electronic conductors [indium tin oxide (ITO)], undergoes a molecular reorientation under the action of an external electric field E. This electrically controlled birefringence (electro-optical switching) is proportional to E^2, thus polarity insensitive [L. M. Blinov and V. G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials* (Springer-Verlag, New York, 1994)]. When a thin film of tungsten trioxide is deposited by magnetron sputtering onto one of the transparent ITO electrodes, and a NLC cell is assembled with such asymmetry, the electro-optical response becomes polarity sensitive [G. Strangi *et al.*, Appl. Phys. Lett. **74**, 534 (1999)]. The analysis of this response suggests the occurrence of a reverse internal electric field, associated with the ionic diffusion process of protons always present in these sputtered WO_3 films [E. Cazzanelli *et al.*, Electrochim. Acta **44**, 3101 (1999)]. By using an opportune voltage waveform it is possible to evaluate such an internal field. Impedance and cyclic voltammetry measurements were carried out on these cells, comparing ''as-deposited'' and ''annealed'' tungsten trioxide electrodes. These studies confirm that an important ionic diffusion process is involved in the establishment of an internal electric field, which modifies the electro-optical response of the nematic liquid crystal cell.

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I. INTRODUCTION

In the last 30 years liquid crystalline materials have been largely exploited for many technological applications [1,2]: displays, smart windows, light valves, spatial light modulators, and so on.

Nematic liquid crystals (NLCs) are largely used in many of these devices. In particular, NLCs are used for modulation of the electro-optic response because they are very sensitive to external agents and in particular to surface forces, which depend on the alignment layers, surface charges, temperature, and so on [2]. In fact, a specific orientation order in the NLCs can be induced via specific treatments of the boundary surfaces that affect the behavior of the entire liquid crystal layer.

Electro-optical phenomena observed in uniform structures are purely orientational, i.e., molecular director **n** reorients in an electric field under the action of a dielectric torque, which is proportional to the dielectric anisotropy $\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$ ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ being the dielectric permittivities parallel and perpendicular to the optical axis, respectively). This effect is well known as electrically controlled birefringence (ECB) which results in the variation of the transmitted light between crossed polarizers (optical switching). In usual NLC cells the electro-optical effects are not dependent on the polarity of the external perturbation [1,2].

In this work further investigations are presented on the polarity-dependent optical response of NLC confined between two different electrodes (Fig. 1): one constituted by the usual indium tin oxide (ITO) transparent electronic conductor, the other by a thin film of tungsten trioxide (WO_3) deposited by magnetron sputtering on an ITO substrate.

The tungsten trioxide WO_3 is a compound well known for its electrochromic [3,4] and catalytic properties [5]. It is mostly used as an active electrode in the electrochromic devices, because of the mixed conduction properties (i.e., ionic and electronic), and for its peculiar electronic structure [3].

The processes of intercalation-deintercalation of small ions (H^+, Li^+, Na^+), occurring also in the bulk crystal, are greatly enhanced in the WO_3 films [6,7], because of many available paths for a fast ion diffusion along the grain borders. The insertion of foreign cations allows for a redistribution of additional balancing electrons among the electronic bands of the host compound, resulting in a change of the film coloration, from a pale yellow to a blue coloration (electrochromic effect) [4]. However, this effect induces strong changes in the optical transmission spectra only for appreciable amounts of cations entering in the host structure of the film. A well-operating electrochromic device requires, in fact, a layer of electrolyte, having purely ionic conduction, and a counterelectrode, having mixed ionic and electronic conductivity, whose electrochemical characteristics (charge-discharge capacity, in particular) matches those of the WO_3 active electrochromic layer [3].

In the NLC cell containing a WO_3 film, the electrochro-

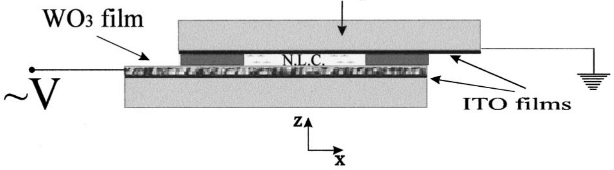

FIG. 1. Scheme of the asymmetric liquid crystal cell. The nematic liquid crystal (NLC) is E7 (BL001 provided by Merck).

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mic effect, if it even exists, is accidental and negligible with respect to the optical switching due to the ECB of the NLC layer.

The schematic picture of the asymmetric NLC cell discussed in the present work is clearly shown in Fig. 1. Besides the two support glasses, the sequence of the active layers is the following: (i) a transparent, purely electronic conductor (ITO); (ii) a NLC layer, having typical thickness of the order of 10 μm, behaving as a dielectric insulator; (iii) a transparent WO_3 film, about some hundred nm thick, having mixed ionic and electronic conductivity; (iv) another ITO transparent electronic conductor.

In the case of our asymmetric NLC cells the unipolar electro-optical response is strictly related to the ionic diffusion behavior in the WO_3 film, as will be discussed below.

The important ionic diffusion process in the tungsten-oxide film can be attributed to the H^+ ions always present in such WO_3 films, even grown by different methods [8–12].

A major role in the proton conductivity in tungsten trioxide films is played by the water molecules, always present in the films, donating protons to the system and also supporting the hopping of H^+ cations. Actually, very special care must be used to have water-free WO_3 films [13]; otherwise, the proton concentration and relative conductivity is appreciable and induces interference also in the measurement of other ion conductivities [14–17]. It is well known that after an annealing process, inducing dehydration of the film and the elimination of all the hydrogen containing species, the ionic conductivity strongly decreases.

The presence of water is strictly connected to the particular structural configuration of the films, extensively studied and described by Nanba [18]. The annealing changes the structure in a two-step process, well demonstrated by calorimetric measurements [19]: (i) elimination of water out of the film occurs at lower temperatures, but leaves a disordered structure in the film; (ii) at higher temperatures, a crystallization process starts, driving the film structure toward crystalline phases, of a distorted ReO_3-type, similar to those of the bulk crystal [20]. The temperature values for these transformations are strongly dependent on the particular deposition methods: for instance the crystallization is reported for different films between 300 °C [19] and 500 °C [11].

In the present work we make a comparative analysis of the complex impedance and cyclic voltammetry of complete NLC cells containing as-deposited and annealed WO_3 films.

Before that we will analyze the electrical behavior of the cell with as-deposited films, the ones giving a well reproducible, unipolar electro-optical switching of the device.

II. EXPERIMENT

Thin WO_3 films were deposited by radio frequency (r.f.) sputtering in a reactive atmosphere of Ar and O_2 gas, and the ratio oxygen/argon was maintained at a value of 10% during deposition. Sputtering parameters varied for r.f. power between 100 and 250 W and for deposition times between 10 and 30 min, in order to obtain a film thickness of some hundreds nm. The sheet resistance of the ITO layer was 20 $\Omega/\square$. The samples were made using different deposition times for tungsten trioxide, to investigate the influence of the film thickness on the electro-optical response of the liquid crystal.

The heating treatment on the film used for NLC cells has been carried out in air, by using a standard laboratory oven (Carbolite Furnaces, Mod. RMP14/3). The sample was heated with a rate of 6–7 °C/min up to 250 °C, kept at such temperature for 15 min, and underwent a further heating step up to 303 °C, with a rate of about 3 °C/min. After a permanence of 5 min at the maximum temperature, it was cooled down with the rate of 10 °C/min.

The conducting glass plates, without any surface treatment to induce preliminary alignment of liquid crystal, were closed in the standard sandwich configuration (see Fig. 1). The thickness of the cells was ensured by stripes of Mylar (8–36 μm). The introduction of the liquid crystal in the space enclosed between the asymmetric glass plates was made slowly to prevent any orientational alignment induced by the flow. The nematic liquid crystal inserted in the cell is known commercially as BL001 by Merck (former E7); it is an eutectic mixture of four different cyanobiphenyl compounds. The temperature range of existence for the nematic mesophase is between 20 and 61 °C. The dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} = +13.8$ (at 20 °C).

Observations of the electro-optical response of the cells, between crossed polarizers, were made by a polarizing microscope Axioskop Pol (Zeiss). Videomicroscopy was performed by a 3 charge-coupled device (CCD) color camera TCM 112 (GDS Elettronica) connected to a PC equipped to visualize the images of the samples. The investigation of the transmitted light intensities was carried out by a large area silicon photodiode (Hamamatsu) mounted on the polarizing microscope. The electrical signal proportional to the light intensity was collected by a digital oscilloscope (Tektronics, Mod. TDS 784).

For the comparative electrical measurements on liquid crystal cells containing as-deposited and annealed electrodes, glass plates coated by WO_3 were chosen in such a way to have sputtering parameters quite similar to each other, so that chemical and structural characters are quite comparable.

A preliminary electrochemical characterization for both the as-deposited and the annealed samples was carried out by a Potentiostat/Galvanostat/Impedentiometer EG&G Mod. 273 A. The impedance of the samples was investigated in the frequency range 1 mHz to 100 KHz. The amplitude of the applied voltage was chosen as 100 mV so as to avoid undesired electrically induced reorientation of the liquid crystal. Cyclic voltammetry measurements were also carried out to complete the comparative analysis of the electrochemical behavior. The interval of the applied voltage was -2 to 2 V and the scan rate was set to 50 mV/sec.

III. RESULTS AND DISCUSSION

As already reported [21,22], and also confirmed in the present work, the tungsten trioxide layer induces a homogeneously planar alignment of the liquid crystal molecules (**n** parallel to the boundary surfaces) along the *x*-axis (see Fig. 1).

The starting orientation of the NLC cell is set in such a way to have a maximum of the transmitted light, when placed on the stage of the microscope between crossed polarizers.

When a low-frequency voltage, above a certain threshold, is applied to our asymmetric NLC cell, we observe a decrease of transmittivity only for the cathodic polarization (from now on we will consider the electrical polarization with respect to the WO_3 side of the cell).

Given the above-mentioned initial conditions, $\phi=45°$ is the angle between the polarization vector of the incoming light and the initial undistorted direction of the director **n**, the NLC layers manifest birefringence $\Delta n=n_e-n_o=n_\parallel-n_\perp$, being n_e and n_o the extraordinary and ordinary refractive indexes, respectively. If the applied electric field, along the z-direction, exceeds its threshold value, the director deviates from its unperturbed direction. The angle θ between the director and the z-axis is a function of z, while in first approximation we can assume that **n** remains perpendicular to the y-axis. Therefore, the refractive index for the ordinary ray remains unchanged, $n_o=n_\perp$. At the same time the refractive index for the extraordinary ray (n_e) decreases, tending toward n_o, according to

$$n(z)=n(\theta)=\frac{n_o n_e}{(n_o^2\sin^2\theta+n_e^2\cos^2\theta)^{1/2}}. \tag{1}$$

The phase difference δ between the extraordinary and the ordinary ray for monochromatic light of wavelength λ is found by integrating over the layer depth d,

$$\delta=\frac{2\pi}{\lambda}\int_0^d[n_e(z)-n_o]dz=\frac{2\pi d\langle\Delta n(z)\rangle}{\lambda}. \tag{2}$$

The intensity of the light passing through the cell depends both on the angle ϕ and the phase difference δ,

$$I=I_0\sin^2(2\phi)\sin^2\left(\frac{\delta}{2}\right), \tag{3}$$

where I_0 is the intensity of the incident linearly polarized light. The external electric field changes the direction of **n**, so that $\theta=\theta(E,z)$, and consequently the values of δ and I change.

The effect of optical switching in a standard nematic cell is independent of the sign of the electric field, as reported in many works present in the literature [1,2]. The optical response of NLC becomes polarity dependent when we insert as electrode a WO_3 thin film. In Fig. 2 are shown the video-microscope images of the optical switching for the anodic [Fig. 2(a)] and the cathodic [Fig. 2(b)] polarization.

The application of a square-wave voltage in a wide frequency range (d.c.–300 Hz) emphasizes an electro-optical response discriminating the sign of the electric field [Fig. 3(a)]. In Fig. 3(b) is reported the usual quadratic behavior of the optical response during the application of a square-wave voltage for a standard cell confined between electrodes of purely electronic conductor (ITO). The comparison points out the rectificating power of the asymmetric cells, in which the unipolar response occurs on times of the order of milliseconds.

As reported in our previous work [22], above some frequency value (about 300 Hz) the electro-optical response approaches that of the usual cells (i.e., polarity independent). This fact indicates that the ionic diffusion characteristic time of WO_3, rather than the characteristic times of liquid crystals' reorientation, are relevant for the polarity sensitive electro-optical response.

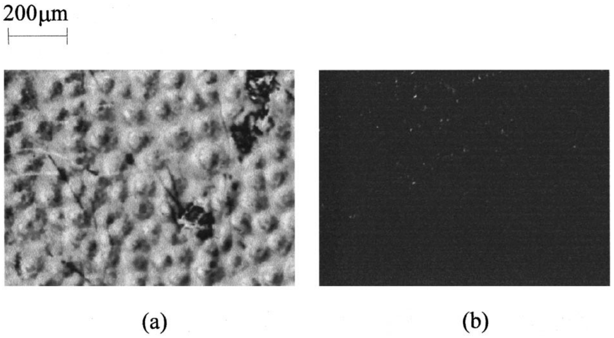

FIG. 2. Video-microscope images between crossed polarizers relative to the optical switching induced by a low-frequency voltage. (a) Anodic polarization of the WO_3 film. (b) Cathodic polarization of the WO_3 film.

In order to better explain the optical phenomena we carried out several measurements on the aforementioned asymmetric cells. The first step consisted of the measurement of the current flowing through the cells upon application of a voltage waveform composed of a rectangular pulse of finite amplitude (positive or negative) followed by a zero voltage

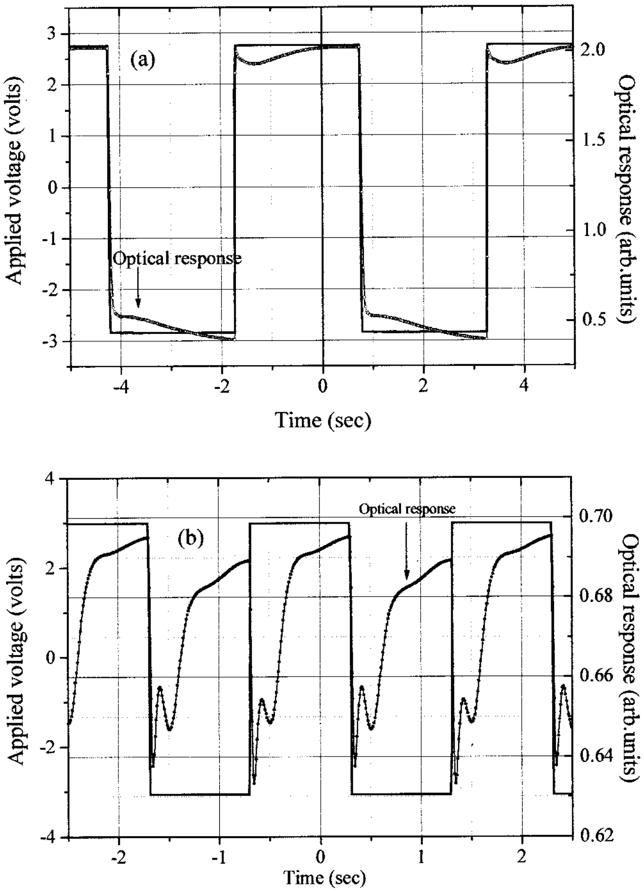

FIG. 3. The polarity-sensitive electro-optical response of the presented cell (a) is compared with the usual quadratic response of a customary LC cell (b) confined with electrodes of purely electronic conductors like ITO.

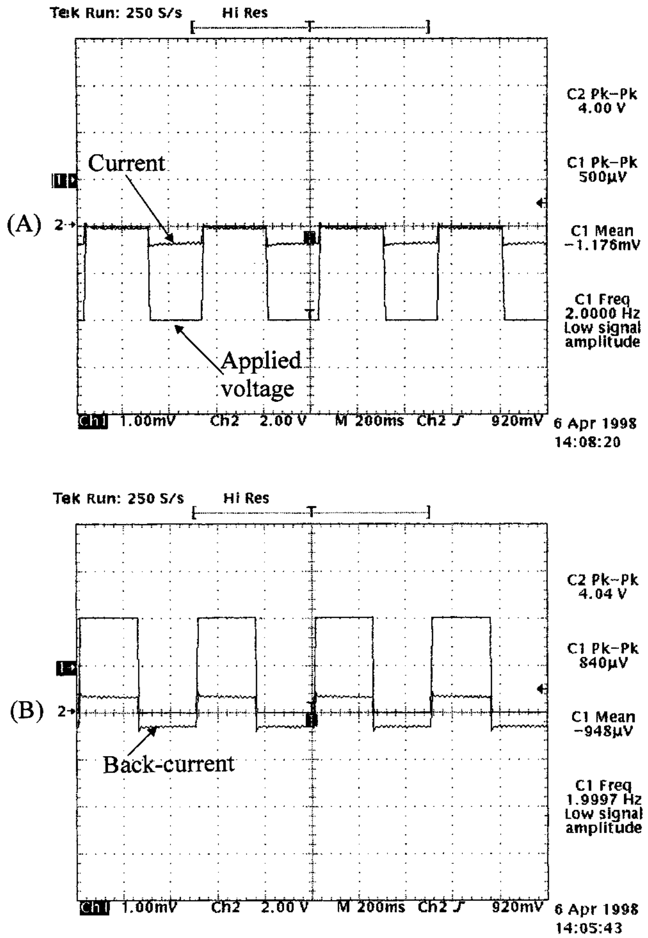

FIG. 4. The behavior of the current is reported during the application of a square-wave voltage. (a) Cathodic polarization. (b) Anodic polarization.

pulse of the same duration. Analyzing the current behavior during the cathodic polarization [Fig. 4(a)], a negative charging current is observed, which vanishes when the electric field is removed. For the anodic polarization [Fig. 4(b)], on the contrary, the current does not vanish when we remove the external electric field and a negative current (back-current) occurs.

The explanation is strictly related to the cross-link between purely electronic conductors (ITO), mixed conductors (WO_3), and dielectric materials (NLC). The role played by the different interfaces of the WO_3 layer with respect to the ionically blocking film (ITO) and the dielectric layer (NLC) become extremely relevant during the inversion of the polarity, which modifies the electrical potential profile in the sample. At the ITO-WO_3 interface, ITO has free electrons and they can diffuse in the porous WO_3, giving rise to a recombination process with the WO_3 protons, modifying the charge carriers' concentration profile in the oxide films. The recombination process becomes quite important when the cations are pushed at the ITO-WO_3 interface during the cathodic polarization, whereas it is strongly reduced during the anodic polarization, when the protons are pushed toward the WO_3-NLC interface. In this latter case, by removing the applied electric field a back-diffusion occurs (back-current) to restore the electrical equilibrium.

The cathodic recombination process ITO electrons–WO_3 protons insures a well-established electrical equilibrium that prevents any back-diffusion process. On the other hand, the modification of the concentration profile of the charge carriers results in a reverse internal electric field, when the WO_3 film undergoes the anodic polarization. In other words, the externally applied electric field controls the charge profile at both ITO-WO_3 and WO_3-NLC interfaces according to Nernst's law,

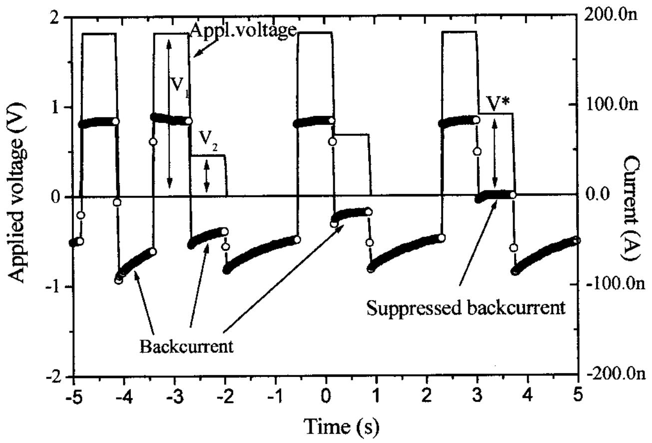

FIG. 5. The figure shows the current behavior during the application of a specific voltage waveform. The back current is suppressed in order to evaluate the internal electric field. Note in the current plot are reported 50 points/sec.

$$E = -\frac{1}{Zq}(\mu_r - \mu_l), \tag{4}$$

where r and l refer to WO_3-NLC and ITO-WO_3 interfaces, respectively. Z here is the number of the charges of the ions, μ is the chemical potential, and q is the elementary charge.

In order to evaluate the intensity of the internal electric field during the anodic polarization of the cell, we developed a specific voltage waveform to apply to the liquid crystal cells. This waveform consists of a succession of a first higher voltage rectangular pulse, of constant value V_1, followed by a subpulse of lower voltage V_2, with increasing height from zero up to a certain value V_2^* (Fig. 5). A zero voltage pulse separates each of these composite pulses. During the first anodic pulse ($V_{\text{appl}} = V_1$), the free ions of the WO_3 migrate toward the WO_3-NLC interface giving rise to an ionic current (positive). At the end of the first pulse, the ions are pushed at the interface and the following short circuit releases the ions, producing an evident back-current. The second voltage pulse ($V_{\text{appl}} = V_2$) keeps the accumulated charges at the WO_3-NLC interface (suppression of the back-current), when a proper voltage value V_2^* is reached. As it can be seen in Fig. 5, the increasing voltage V_2 corresponds to a progressive vanishing of the back-current until the voltage V_2^* is reached. In conclusion, the value V_2^* gives a good estimate of the internal electric field. The consequence of the internal field establishment is the modification of the effective electric field in the NLC sample, now polarity sensitive.

During our experiments we observed different cells, varying the thickness of both the NLC layer and the WO_3 film. In any case, the polarity-sensitive electro-optical response remains qualitatively the same, also after several weeks of ob-

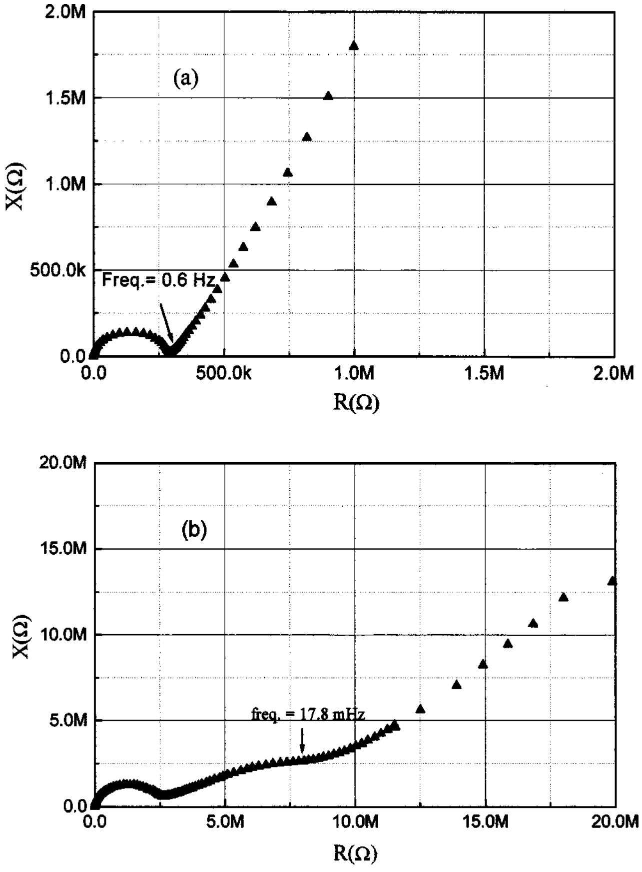

FIG. 6. Nyquist diagrams relative to the impedance measurement of the as-deposited sample (a); annealed sample (b).

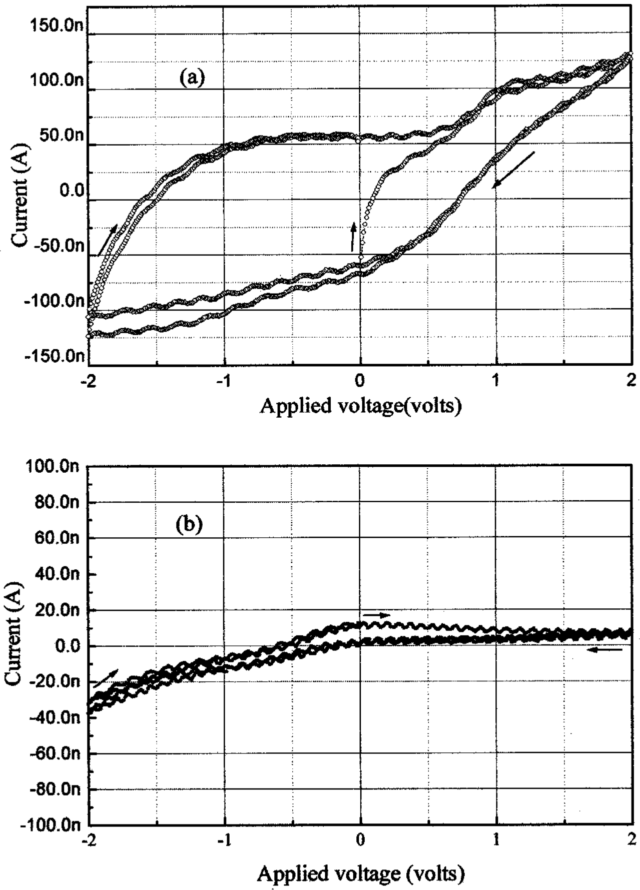

FIG. 7. Cyclic voltammetry of the as-deposited sample (a); annealed sample (b).

servation. Furthermore, the cells have to undergo cyclability tests, during which the applied voltage was swept for about 30 hours between −2.5 and 2.5 V, and the measured currents were found perfectly reproducible.

To check in another way the role of diffusing protons of tungsten trioxide in the peculiar electro-optical response of the NLC layer, a comparative investigation has been carried out on several cells, containing sputtered WO_3 thin films having different structures of water contents, as a consequence of different heat treatments. In fact thermal annealing induces dehydration reactions and crystallization of the film at higher temperatures [19]. Different experimental techniques (complex impedance measurements and cyclic voltammetry) have been used for such NLC cells. The thermal annealing of the opportunely chosen plates (WO_3+ITO+glass) was carried out to expel the adsorbed water molecules and to study, as the electrochemical processes at the boundary surface of the NLC cells depend on the hydrogen content of the films.

The analysis of the Nyquist diagrams (Fig. 6) has been performed both on the cells containing as-deposited WO_3 film [Fig. 6(a)] and on those with thermal annealed tungsten trioxide films [Fig. 6(b)]. As it is pointed out in the figures, the beginning of the region where the ionic diffusion process becomes dominant in the plot (Warburg impedance) shifts at lower frequency, when passing from the cell with as-deposited film to the cell containing annealed film.

A nearly perfect linear dependence of $X = \mathrm{Im}(Z)$ on $R = \mathrm{Re}(Z)$ (Z being the impedance of the cell) indicates a well-defined diffusion process in the former case (starting from about 0.5 Hz down to lower frequency), while in the latter case, a roughly linear dependence $X(R)$ starts at lower frequency, i.e., about 20 mHz. It is also important to note that the diameters of the semicircles in the Nyquist plots, related to the resistance of the cells, are quite different. In fact, the diameter of the semicircle is remarkably increased in the annealed sample [Fig. 6(b)]. The water molecules desorbed after heating of the surface do not contribute anymore to the diffusion process of protons toward the liquid crystal layer; therefore the observed behavior is quite reasonable.

The picture becomes even clearer by analyzing the cyclic voltammetry measurements performed on the same samples, at constant sweeping rate during all the measurements. In such a case the total transferred charge is represented by the area enclosed in the cycle.

By comparing the plot of the measurement relative to the sample without heat treatment [Fig. 7(a)] with that relative to the annealed sample [Fig. 7(b)], it is well evident that in the latter case the transferred charge is considerably reduced.

Therefore, quite relevant chemical transformations, strongly affecting the protonic conductivity, occur during the heating process up to 300 °C, even in the absence of the final step of crystallization of the film into a distorted ReO_3-type structure. This peculiar fact is revealed by the analysis of the Raman spectrum of the annealed film, which shows no dramatic changes with respect to the reported spectrum of the as-deposited film (see Fig. 3, Ref. [22]).

This current analysis on the cells containing WO_3 films undergoing different treatments supports the hypothesis that an important cationic diffusive process in the as-deposited film plays a specific role for the creation of an interfacial double layer by charge separation.

IV. CONCLUSIONS AND REMARKS

This paper has highlighted a new method to achieve the polarity-dependent optical response in a nematic liquid crystal cell. It consists of the asymmetrical insertion of mixed conductor film (WO_3) as electrode. Our attention has been focused on the liquid crystal behavior strongly influenced by the electrochemical process, which occurs at the different interfaces. The basis of the asymmetrical electro-optic response must be searched in the ionic diffusion process, which takes place in the WO_3 electrode during the anodic polarization. Under the action of a low-frequency external electric field, the protons (H^+) always present in these films [14,23], migrates towards the oxide-NLC interface, giving rise to an interface formation (reverse internal electric field) which counteracts the threshold phenomena of the molecular reorientation. The electrical measurements (current, complex impedance, cyclic voltammetry) carried out on the cells with ‘‘as-deposited’’ WO_3 electrodes pointed out a remarkable diffusive process, which vanishes for the thermally annealed WO_3 films. The interesting electrical and optical behavior of the presented device fits well within a simple model of a double layer formation at the WO_3–NLC interface depending on the polarity of the external perturbation.

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