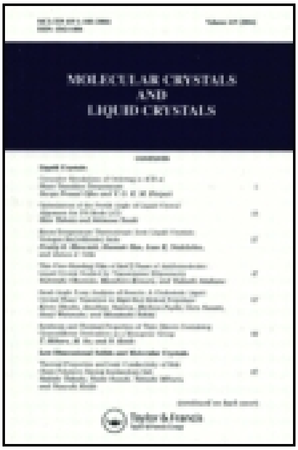

Molecular Crystals and Liquid Crystals

Asymmetric Response to Electric Field in Nematic Liquid Crystal Cells Containing Vanadium Oxide Thin Films Prepared by Sol-Gel Synthesis

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Asymmetric Response to Electric Field in Nematic Liquid Crystal Cells Containing Vanadium Oxide Thin Films Prepared by Sol-Gel Synthesis

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The asymmetric insertion of oxide layers having mixed conduction properties (ionic and electronic) in liquid crystal cells induces various kinds of electro-optical response of the liquid crystals, and this behaviour has been related to the structural differences of the inserted films. In this work, it is reported a structural study of such oxide films deposited on indium tin oxide (ITO) covered glasses. To have further confirmations of the model and a better understanding of the basic mechanism underlying the rectification effect and the connections with the structural and electrical properties of the films, Vanadium oxide layers have been studied before and after thermal treatment. Moreover the gelification via spin coating has been implemented and the optimisation tests of various relevant parameters have been performed. The chemical, structural and optical evolution has been extensively investigated as a function of the thermal annealing treatment, by performing vibrational spectroscopy analysis (micro-Raman and IR) and impedance spectroscopy characterization, before testing the films into the NLC cells.

Keywords: electro-optical response; nematic liquid crystal; vanadium oxide; vibrational spectroscopy

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1. INTRODUCTION

The optical properties of liquid crystal–oxide film systems are of great interest both from the technological point of view and that of fundamental science, providing a suitable model to investigate phenomena involving interface formations in many research fields: physics, biophysics, chemistry, biology, and so on.

Moreover, taking into account that both the components of the liquid crystal-oxides interface are very sensitive to the external influences, it is reasonable to believe that these systems will be very perspective for the different applications.

Electro-optical effects in liquid crystals are either odd (mainly linear) or even (mainly quadratic) with respect to the external electric field [1]. Generally speaking, the materials showing the odd (linear) effect are more preferable since they are sensitive to the field polarity and keep rather high sensitivity at low electric fields.

In general, nematic liquid crystals (NLC) have been largely used in many devices like displays, spatial light modulators, light valves, etc., because the NLC's internal order is very sensitive both to external fields as well as to the properties of boundary surfaces. In fact, applied electric fields can change the orientation of a NLC induced by a particular surface, so that the nematic director **n** is changed by the 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 axes, respectively). This electrically controlled birefringence results in the variation of the transmitted light between crossed polarizers (optical switching).

NLC widely used in the display technology manifest the quadratic effect. Conventionally, they may be switched ON by a voltage but have to relax back to the OFF state without applied field. Such a relaxation is rather slow. A serious advantage of any polarity sensitive material is a possibility to force it to switche between the two states and by-pass a free relaxation process. When one controls both the ON and OFF state by an external field E(of opposite polarity) the response time is considerably reduced ($\tau \sim 1/E$ or $1/E^2$ for the linear and quadratic effects, respectively). A similar effect is known, for instance, for NLC with inversion of the dielectric anisotropy sign on the frequency scale [1], however, in that case, high frequency addressing requires for high power due to strong dielectric losses.

The nematic cells with symmetric boundary conditions as well as the NLC themselves are centrosymmetric. Such cells manifest only the quadratic-in-field electro-optical effects (an exception is a chiral nematic, i.e., cholesteric phase that may show a linear response, especially strong in the pretransitional range adjacent to the smectic C^* phase [2]).

Few years ago a new method has been developed to achieve the polarity sensitive electro-optical response in nematic [3,4] and ferroelectric [5] liquid crystal cells. It consists of the insertion of a mixed conductor film as electrode, deposited using different techniques such as evaporation, sputtering, sol-gel coating, etc. The first material checked for such devices has been the tungsten trioxide (WO_3) [3,4]. Its electrochemical properties are well known and it is widely used in electrochromic devices. A quantitative model has been developed [6] to explain the interaction between the WO_3 oxide film and the liquid crystal at the interface. The basis of polarity- sensitive electro-optic response is related to the different results of the ionic diffusion process, which takes place in the WO_3 electrode during the anodic and cathodic polarization (for a better understanding of the matter, it's convenient, for the following discussion, to define the electric polarization with respect to the electrode made of the mixed conductor film; i.e., the phase of the applied voltage is always connected to the vanadium electrode). For instance, in case of anodic polarization, under the action of a low-frequency external electric field, the free charge carrier (H^+), always present in these films [7], migrates towards the oxide-liquid crystals interface, giving rise to a reverse internal electric field, which counteracts the reorientation of NLC molecules. The same model has been qualitatively applied to more complex systems, based on mixed films of different oxides such as titania/vanadia with variable atomic ratios, obtained via sol-gel route. NLC cells assembled with a thin titania-vanadia film (prepared at $pH = 1$) on one electrode show a polarity-sensitive electro-optic response similar to the one reported for WO_3 cells, with the reorientation of NLC molecules inhibited by an internal electric field during the anodic polarization [8].

For these aims, many efforts have been made in recent years in order to find materials with electro-optic response qualitatively opposite to the WO_3 one. Mixtures of V_2O_5 with NiO, TiO_2, Bi_2O_3, SbO_3, and InO_3 have been investigated and some results were reported in literature very recently [9]. Unfortunately the optical contrasts provided by such devices were low and no model was reported to explain the new effect.

However, many experimental evidences collected in the course of such investigations suggest the importance of chemical details during the sol gel route to determine the structural and conductive properties of the films: in particular both the pH values in the hydrolysis step and the thermal annealing seem to be quite critical. In the present work, we report about inverted polarity-sensitive electro-optic response of NLC asymmetric cell when the vanadia films used as electrodes are synthesized in the same condition but with different thermal history of the films.

Finally, qualitative models are presented, in order to explain the surface charge distribution in the liquid crystals cell and thereafter the inverted effect.

2. EXPERIMENTAL

2.1. Material Synthesis and Film Deposition

Vanadium Pentoxide xerogel has been prepared by using the sol-gel proton exchange resin route: 0.5 M sodium metavanadate solution is passed through a proton exchange resin (Dowex 50W-X2, 50-100 mesh) to obtain a polyvanadic acid solution, which spontaneously forms polymeric networks through an autocatalytic process. After some time, this solution becomes dark red and the viscosity increases, resulting in a vanadium pentoxide sol-gel [10–14].

The gel has been deposited on ITO (indium tin oxide)-glass (sheet resistivity $\rho_s = 20\,\Omega^2$, Unaxis GmbH) substrate. Before the spin-coating deposition the ITO glasses have been ultrasonically cleaned in acetone, bidistilled water and isopropanol and then dried with warm air (50 degrees) [15,16].

The deposition has been made by spin-coating technique [17,18] with SC10 CaLCTec s.r.l. spin coater. Different spin rate velocities have been used to obtain homogenous films. Here are shown the results regarding the films obtained at 2400 rpm. The time of the spinning was 25 s and the time to go from 0 to 2400 rpm and to go from 2400 to 0 rpm was 4 s. Some samples, made in this way, have been heated at 100°C, some 300°C and some 600°C for one hour.

2.2. Vibrational Spectroscopies

For the spectroscopic characterizations of the films a Raman microprobe Jobin-Yvon Labram was used, equipped with a Charge Coupled Device (CCD) detector and a He-Ne laser (632.8 nm emission). In all the experiments a 100× Mplan Olympus objective was used. The power of the laser out of the objective was about 5 mW and the laser spot had a nearly circular shape of 2–3 μm apparent diameter. To avoid unwanted laser induced crystallizations, proper neutral filters were used with different optical densities: i.e., OD 0.3, OD 0.6, OD 1, OD 2 and OD 3, corresponding to light transmission fraction of 0.5, 0.25, 0.1, 0.01 and 0.001, respectively.

Infrared spectra have been collected with an FT-IR spectrometer, model NEXUS EZ Omnic Nicolet, equipped with a MID-IR detector (range 400–4000 cm^{-1}). IR measures have been performed on the film by using the grazing angle option.

Some spectral contribution due to ITO layer appears, because of the very small thickness of the films. The background to be subtracted has been collected both by using the standard gold-coated glass, and also by collecting the reflectivity spectrum of an ITO-coated glass, treated at the same temperature as the measured film. The spectral differences between these two cases are not significant, except for the different ITO contribute appearing in the final spectrum.

2.3. Electric Properties of Films

The bulk electrical conductivity of these oxides is usually quite low and they act as insulators. In general, the electric properties of thin films deposited by sol-gel dip coating can strongly depend on several factors: the thickness of the film, the initial structure, and the eventual structural changes due to thermal treatments. The electric properties of the films have been investigated by using an impedance analyzer (EG&G 273 A).

The distance between the samples connectors pointed on the film was ~5 mm. One connector acts as working electrode, while the counter electrode has been short-circuited with the reference one.

A schematic drawing of the experiment is shown in Figure 1. The thin oxide film (d ~ 500 nm) was deposited onto the ITO electrode.

Owing to the wide distance between the connectors, compared to the thickness of the oxide film, we can simplify the electric scheme as shown in Figure 1. The longitudinal resistance R^{L}_{ox} is many orders of magnitude greater than R^{L}_{ITO} and the current flow through it can be neglected. The resistance R^{L}_{ITO} is even much lower than transversal resistance R^{T}_{ox}, so what the impedentiometer effectively measures is two times R^{T}_{ox}.

2.4. Liquid Crystal Cell Assembling

The liquid crystal is enclosed between two glass plates in the standard sandwich configuration by using metallic clamps. The thickness of the cells was ensured by stripes of Mylar (8 μm), and the final value was deduced by analyzing the interference patterns in the transmittance spectrum of the empty cell, measured by a spectrophotometer. Both glasses are covered by ITO acting as electrodes but only one of them is also covered with vanadium pentoxide.

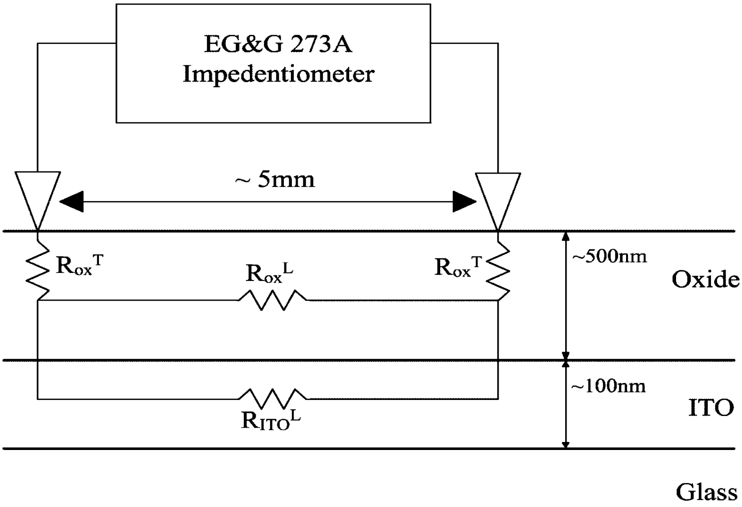


FIGURE 1 The electric scheme used to check the electric properties of the vanadia oxide films. R_{ox}^{L} and R_{ox}^{T} represent the longitudinal and the transversal resistances of the oxide, respectively. R_{ITO}^{L} represents the resistance of the ITO electrode.

The other one was covered with polyimide after a careful cleaning in chromic mixture and repeated cleansing with acetone, and underwent a rubbing process, to insure a better planar alignment of the NLC molecules. For the electrodes covered by the oxide, on the contrary, no surface treatment has been performed because the rectification effect is supposed to be related to the ionic charge distribution and motion at the oxide-liquid crystals interface. Thus, the insertion of an alignment layer could strongly modify the wanted phenomena. Moreover, the vanadia layer induced a homogeneously planar alignment of the liquid crystal molecules (**n** parallel to the boundary surfaces) in all the prepared cells.

The introduction of the liquid crystal in the space enclosed between the asymmetric glass plates was made very slowly to prevent any orientational alignment induced by the flow. The cell was filled with a NLC called *BL001* by Merck (former E7). The temperature range of existence for the nematic mesophase is from 20°C up to 61°C and the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} = +13.8$ (at 20°C).

2.5. Electro-optical Response of the NLC Cells

Observations of the electro-optical response of the cells, between crossed polarizers, were made by a polarizing microscope Axioskop

Pol (Zeiss). 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. Video microscopy was performed by a 3CCD color camera TCM 112 (GDS Elettronica) connected to a PC equipped to visualize and to capture 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 7254) and saved in digital form for the subsequent processing. We have used both monochromatic light (He-Ne laser) and "white" light (the bulb of the microscope). Although the best fringes can be seen with monochromatic light, all the records discussed in this paper have been obtained using white light. From an applicative point of view, one is interested in that the effects presented in the following can be obtained with white light irradiation.

3. RESULTS AND DISCUSSION

The structural changes occurring in the vanadia films because of the thermal treatments can be easily monitored by using the micro-Raman spectroscopy, non-destructive technique, quite sensitive to the degree of order in the film and to the chemical changes and segregations, even in the case of amorphous structures. In Figure 2 are reported representative Raman spectra of the various film samples, collected at room temperature after the thermal treatments, with proper filters to decrease the local heating effect of the impinging laser beam.

The spectra collected on the "as deposited" sample are quite close to that obtained from the gel solution and this confirms that the spin-coating deposition does not change the structure of the gel.

The 300°C heating treatment induces the formation of the band at $\sim 780\,\text{cm}^{-1}$ and the decreasing of the band at $\sim 352\,\text{cm}^{-1}$. All these transformations are consistent with the process of progressive dehydration, with the formation of $V_2O_5 \cdot n\ H_2O$ with $n < 0.5$. However, the band at $\sim 780\,\text{cm}^{-1}$ has been assigned to the presence of tetrahedral vanadate (IV) [19]. This could suggest that in these films vanadium is present in two different oxidation states (V^{+4} and V^{+5}) and that the elimination of the water from the films increases the presence of tetrahedral vanadate.

The most remarkable features of the spectra (d) are the sharp Raman peaks at ~ 431, ~ 888, ~ 911 and $\sim 946\,\text{cm}^{-1}$. In the other kind of spectra (e), collected on the 600°C annealed films, some weak

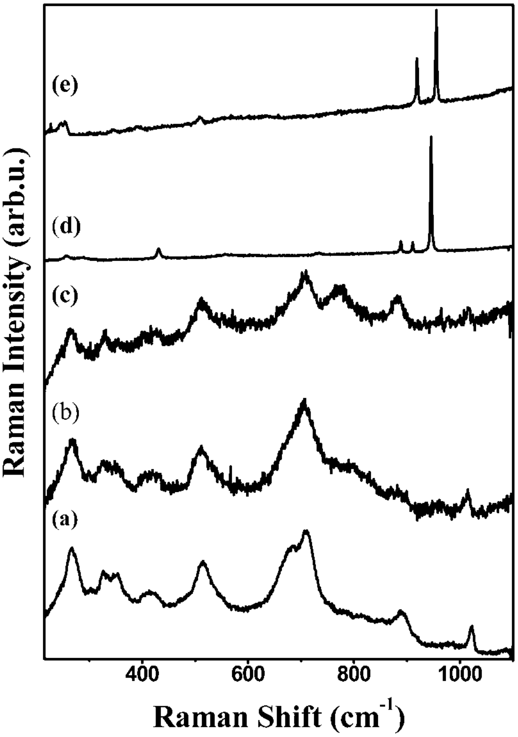


FIGURE 2 Raman spectra collected on vanadium oxide films: (a) not annealed, (b) annealed at 100°C, (c) annealed at 300°C, (d) annealed at 600°C, film center and (e) annealed at 600°C, off center.

Raman bands occur at ~346, ~388, ~552, ~630 cm^{-1} and the sharper peaks at ~227, ~247, ~253, ~509, ~919, ~956 cm^{-1}. The sharp spectral features observed in these last samples annealed at 600°C show the polycrystalline character of such films, against the amorphous disordered character of the films "as deposited" or undergoing moderate thermal treatments.

The exact nature of this crystal structure is not easily determined, also because more phases can coexist. However, its spectrum is clearly different from that of single crystal [20] and from the ones collected on standard polycrystalline films of V_2O_5 obtained by various techniques [21–24], by using hot substrates or after thermal treatments. In fact, similar spectra with so well defined peaks, indicative of the polycrystalline nature of the films, have been found on lithium-intercalated vanadium pentoxide films [25,26]. One of the most remarkable difference concerns the absence in those spectra there of Raman band due to the shortest multiple V–O bond that appears usually at frequency higher than 980 cm^{-1} [23,24,27] in the standard polycrystalline V_2O_5. It has been already seen that octahedrally coordinated vanadium oxide compounds show the highest Raman bands at 954 and 887 cm^{-1} [28] while the band between 920–945 cm^{-1} and the band at 890 cm^{-1} have been assigned to polyvanadate chains bonded to the support [29].

All these factors can support the hypothesis that the spectra d) and e) shown in Figure 2 are representative of a mixed valence (V^{+5}/V^{+4}) vanadium oxide films. These thin films are made of polyvanadate chains, with octahedrally coordinated units of vanadium oxide where some tetragonal vanadium oxide can be found, maybe on the surface of these structures.

Finally, the high temperature of the last annealing makes possible some solid state reaction between elements of the glass substrate and the deposited films, so that it cannot be discarded the hypothesis of the formation of an interlayer of $NaVO_3$, between vanadium oxide film and ITO layer due to the increased mobility of the sodium ion (Na^+) from the glass, due to the highest thermal treatments.

With regard to this problem, ellipsometric spectroscopy investigations could be useful in order to confirm the presence of $NaVO_3$ as interlayer (between vanadium oxide film and ITO layer) thin film.

In any case, the basic result of the spectroscopic monitoring of the structural changes of the vanadia films is the strong change between a disordered, amorphous structure, basically unchanged for thermal treatments up to 300°C, and the occurrence of well crystallized films after the fast annealing at a nominal temperature of 600°C. A further experimental evidence of such change is given by the comparison of IR reflectance spectra, collected in the grazing angle configuration.

In Figure 3 are shown three spectra corresponding to moderate annealing and to the highest treatment at 600°C. The comparative analysis reveals that no appreciable spectral change occurs between the film annealed at 100°C and the one annealed at 300°C (spectra a and b, respectively). On the contrary, a more remarkable change with the appearance of new spectral features below 900 cm^{-1} is well evident for the 600°C annealed sample (spectrum c).

The strong structural change occurring at the highest temperature must be responsible for the radical modification of the electric conduction properties of the films, i.e. from a dominant ionic conductivity for the amorphous films, supported mainly by the protons always present in sol-gel derived materials, toward a mainly electronic conductivity, allowed by the strong increase of the long range crystalline order. However, the details of such electric properties change are better

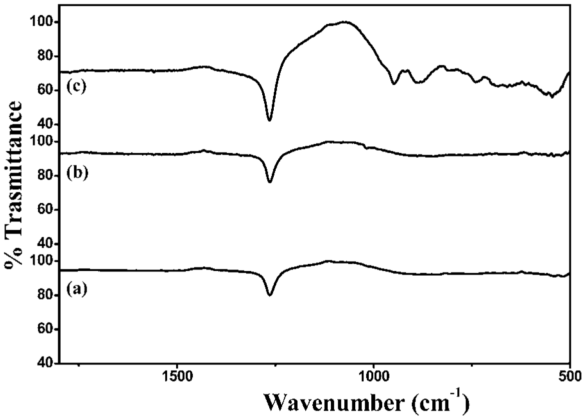


FIGURE 3 Infrared spectra collected on vanadium oxide films: (a) annealed at 100°C, (b) annealed at 300°C and (c) annealed at 600°C.

investigated by other kind of measurements, while the vibrational spectroscopy control certifies only the structural and chemical changes.

The electro-optical response of NLC cells containing "as deposited," 300°C and 600°C annealed oxide films has been collected.

Usually NLC cells with no special films inserted onto the electrodes exhibit a symmetric, impulsive-like, pattern of transmitted light signal through the cell. That behavior is basically similar to the one shown by NLC cell containing a not annealed oxide film (Fig. 4). The small asymmetry present in the optical response is due to transient phenomena in the liquid crystals reorientation, and is not significant compared with transient peaks.

The optical response of the cell changes after each annealing process of the vanadia film inserted into the cell as shown in Figure 5 (annealing at 300°C) and Figure 6 (annealing at 600°C). In both cases we have an asymmetric response but with two different behaviors. For the cells containing 300°C annealed film the reorientation of NLC molecules was inhibited by an internal electric field during the anodic polarization. That results in an almost square wave-like electro-optical response in phase with the voltage applied to the cell. This behavior is similar to the previously reported one for WO3 [3] and Ti-V [8] films. The effect can be qualitatively explained with the same model [6] developed for NLC cells containing WO3 films.

The electro-optical response of the NLC cell containing a vanadia film annealed at 600°C is opposite to the previous one. The

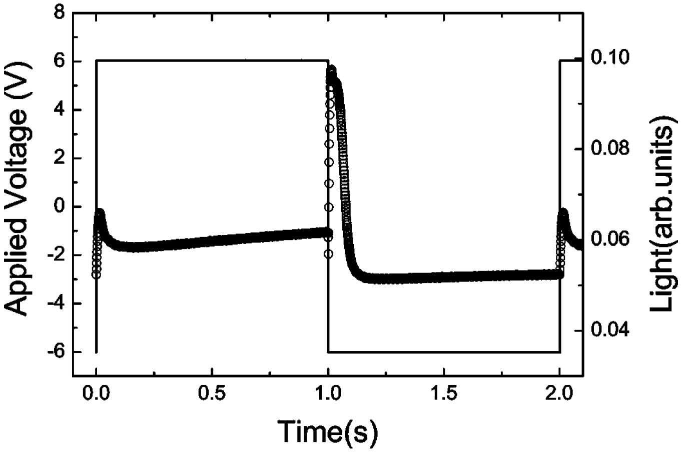


FIGURE 4 Transmitted light through a nematic liquid crystal cell between two crossed polarizers, having one electrode coated with a sol-gel deposited not annealed vanadia film. The behavior is basically similar to the one of usually NLC cells with no special films inserted onto the electrodes. The phase of the applied voltage is always connected to the vanadium electrode.

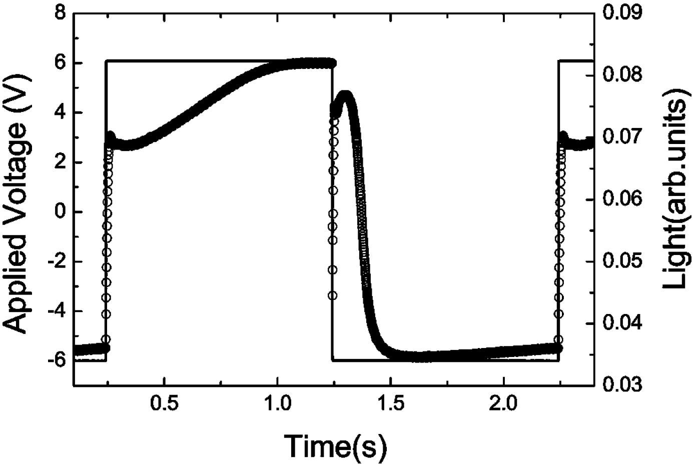


FIGURE 5 Transmitted light through a nematic liquid crystal cell between two crossed polarizers, having one electrode coated with a sol-gel deposited vanadia film undergone an annealing process at 300°C after sol-gel deposition. The optical response is in phase with respect to the external applied voltage. The electrical ground in all the measurements is on the electrode without vanadium.

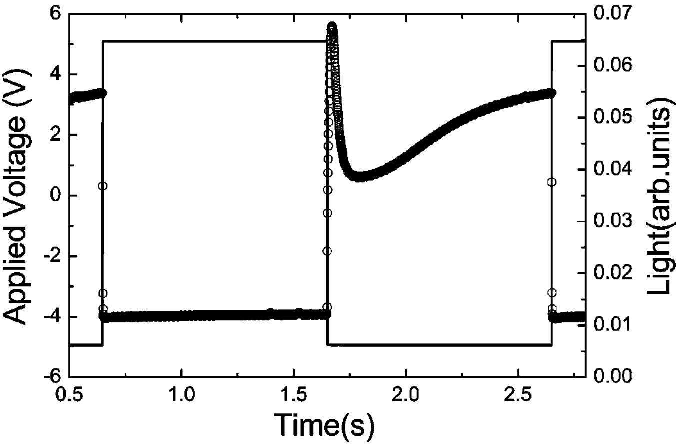


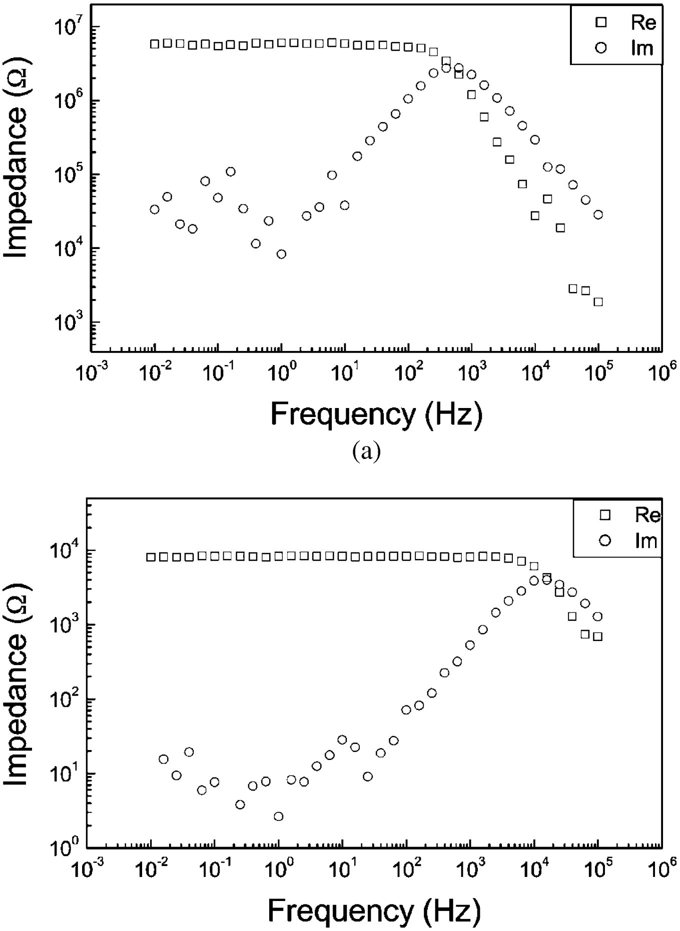
FIGURE 6 Transmitted light through a nematic liquid crystal cell between two crossed polarizers, having one electrode coated with a sol-gel deposited vanadia film undergone an annealing process at 600°C after sol-gel deposition. The optical response is in opposition of phase with respect to the external applied voltage.

reorientation of NLC molecules is now inhibited by an internal electric field during the cathodic polarization resulting in an optical response in opposition of phase with respect to the external applied voltage.

The electrical properties of oxide vanadia films have been investigated to determine its electrochemical properties. The conductivity of these films plays an important role in the electro-optical behavior of the liquid crystals asymmetric cells.

Measurements of the electric impedance have been performed after each annealing step at 300°C and 600°C. The most remarkable finding for the vanadia film is the dramatic decrease of the impedance of the films as the temperature increases (see Fig. 7a and 7b).

The measurement on the 300°C annealed films reveals very high impedance, with its real part of the order of $10^7\,\Omega$ at 1 Hz, while the imaginary part of the impedance is of the order of $10^4 - 10^5\,\Omega$. The real part of the impedance of the film is reduced of three orders of magnitude after the annealing at 600°C, while the shape of the curve remains almost flat up to 10^4 Hz. The decrease of four orders of magnitude is due to a strong reduction of the out of phase component of the current flow through the oxide film. The cut-off frequency probably occurs for higher frequency, above our measuring range, as suggested by the behavior of the imaginary part. This is the typical behavior of a pure electronic conductor. This transformation can be explained by a



(a)

(b)

FIGURE 7 (a) Real and imaginary parts of the impedance for the 300°C annealed vanadia film; (b) Real and imaginary parts of the impedance for the 600°C annealed vanadia film.

decrease, inside the film, of water molecules concentration and related ions, due to crystallization of the oxide, which is complete at 600°C as shown by the Raman spectra.

The electric properties of the films change after the 600°C annealing, passing from being insulator to conductor. In fact these oxide films have an ohmic resistance reduced of three orders of magnitude, while the capacitive reactance actually vanishes.

The experimental results shown in this work render evident the important role played by the thermal history of the oxide films, with an increasing role of conduction electrons for the annealed films. On such basis, a phenomenological model of the effect can be proposed, taking into account the effects of thermal annealing upon ionic and electronic conductivity of the oxide.

The electric conductivity properties of the inserted films play an important role in the rectifying behavior of the optical response of the LC cells, because of a diffusion-controlled charge redistribution process, which is mainly responsible of the asymmetric effective electric field. Experiments on asymmetric cells containing 300°C thermally annealed vanadia films demonstrate that the relevant process involved in the considered device are related to the differences in the protons conductivity, surely strongly enhanced by the water content of the films.

The analysis of the measurements reveals significant differences of the electrochemical processes involving the protons in 300°C thermally annealed vanadia films for the two opposite field polarizations. More precisely, during the anodic charge of the vanadia thin film a H^+ diffusion process occurs toward the oxide-LC interface and no recombination occurs at ITO-ionic conductive oxide interface. The consequence of this displacement of charge is a reverse internal electric field, which counteracts unipolarly the external perturbation; in such a way that a greater modulus of the external applied field is needed to reach the Frédericksz transition threshold.

On the contrary for the cathodic charge the same applied voltage is sufficient to trigger the optical switching, and that implies the absence or a strongly reduced density of any double layer creating an inner counterfield.

The creation of a proper charge distribution at the interfaces is responsible for the inner fields, which modify the electro-optical responses of the nematic LC layer. This effect depends on the diffusion rate of all the mobile charges in the oxide as well as on the recombination rate.

Moreover, the experimental results shown by 600°C thermally annealed vanadia films, compared with the 300°C thermally annealed one, render evident the important roles played by the thermal history of the oxide films. By changing the temperature of annealing, we obtained a brand new electro-optical effect, opposite to that previously reported.

This opposite effect could be explained, in principle, using the same model created for WO_3 [6] and applied also to the 300°C thermally annealed vanadia films: it should be enough to invert the sign of ions moving into the oxide and responsible of the counter field created inside the cell.

Unfortunately, there is no experimental evidence of significant current of negative ions inside these films, nor conduction of negative ions has been reported in literature about these materials. The present experimental studies suggest, on the contrary, an increasing role of conduction electrons for the 600°C annealed films. On such basis, a phenomenological model of the effect can be proposed, taking into account the effects of thermal annealing upon ionic and electronic conductivity of the oxide.

In the model created for the WO_3 films the ions H^+ play the main role in the creation of a counter field due to their abundance and to the columnar morphology of such oxide, promoting ionic intercalation and deintercalation. In the present case, the annealing process at 600°C eliminates completely water and the associated H^+ ions from the film, and no appreciable re-intercalation of water can occur after the crystallization process. The measurements of AC conductivity performed on the 600°C annealed films unambiguously showed that the dominant conduction is almost electronic, and no frequency dependence is observed in the wide range investigated.

Assuming this starting hypothesis, the electrons coming from ITO during the cathodic polarization can go through the mixed oxide and accumulate at the oxide-liquid crystals interface, for an amount depending on the chemical potential barrier of such specific interface [3].

Moreover, the role played by the liquid crystal layer must be accounted for. If the liquid crystal were a perfect dielectric, when applying a voltage across the cell, the potential would vary linearly with distance and the electric field would be constant. On the contrary, if the liquid crystal contains a certain amount of free ions, there will be a build-up of positive charge to the cathodic side of the cell and a similar build-up of negative charge on the other side. The electric potential will no longer have a linear dependence and the electric field will not be constant. It will present a lower value in the bulk of the liquid crystal layer and higher values close to the surfaces [6]. The larger are the boundary charges the higher are the values of the field near the surface and the lower is the field in the bulk of the liquid crystal layer. These two boundary charges on the liquid crystals tend to screen the charges on mixed oxide–liquid crystal or ITO–liquid crystal interfaces. The consequence of this displacement of charge is a reverse internal electric field, which counteracts unipolarly the external perturbation, in such a way that a greater modulus of the external applied field is needed to reach the threshold for the reorientation of NLC molecules.

On the contrary, for the anodic polarization, the same applied voltage is sufficient to trigger the optical switching, and that implies the absence or a strongly reduced density of any double layer creating an inner counter field. In fact, it has to be emphasized that the free ion concentration in good liquid crystals is quite low. With the cathodic polarizations, it is the negative charge of electrons injected at the oxide–liquid crystal interface that is rapidly diffused into the bulk and eventually form the negative charge in front of the polymer coated ITO interface. Because of the high chemical potential of polymer–liquid crystal interface electrons cannot traverse to the positively charged ITO electrode. It has been reported [30] that the conductivity across the director of cyanobiphenyls is larger than that along it. With the anodic polarization, the electrons cannot be injected from the polymer-covered side; neither there is a charge of positive ions free to be injected at the oxide covered electrode so that at the two boundaries only the few free ions normally present in the liquid crystal are collected.

4. CONCLUSIONS

In the present work the authors report a complete study on NLC cells containing vanadia oxide films with different thermal history. Two opposite electro-optical effects of the NLC cells are observed, passing from an "in phase" to an "in opposition of phase" optical signal after a complete crystallization of the vanadia annealed at 600°C.

The difference in the structure of the oxide is responsible of the two effects. The experiments here reported suggest that in partially crystallized films the relevant processes involved in the NLC device are still related to the proton conductivity [8], surviving in the basically amorphous structure of the films. The electronic conductivity of the oxide is prevalent after a complete crystallization of the film and it plays an important role in the inverted rectifying behavior of the liquid crystal cells. The inverted effect is due to the charge redistribution process controlled by the differences of chemical potential of electrons.

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