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The influence of direct laser writing in polyimides on the alignment of organic liquid crystals was investigated. Laser writing was performed below the ablation threshold, which resulted in local melting of the polyimide. A surface relief structure was obtained as a result of the fast heating and cooling cycle during laser writing. No alignment of organic liquid crystals in the vicinity of the surface relief structure was observed as a direct result of the laser writing process. However, it appeared to be possible to wipe out the alignment originating from the rubbing process. This property proved to be useful to generate complex patterns in twisted nematic liquid crystal cells with locally uniaxial alignment. The contrast between the nonpatterned and patterned areas ranged between 40 and 50, which illustrates that the earlier described phenomena are potentially useful in, for instance, personalized security features. © *2002 American Institute of Physics.*
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I. INTRODUCTION

The molecular alignment of liquid crystals in contact with polymeric and nonpolymeric substrates was investigated extensively in the past.[1–3] Especially the alignment of organic liquid crystals by rubbed polyimide layers was studied in detail, which is related to its technological relevance for liquid crystal display (LCD) applications. A variety of other alignment techniques were also developed, based on, for instance, surface relief structures[4] and photoaligned polymers.[5] In comparison to rubbed polyimides, these alternative orientation methods have certain advantages. For instance they avoid the buildup of electrostatic charges during rubbing and the subsequent damage of the thin film transistors at the active plate of the LCD. They also avoid the generation of dust, which interfere with the manufacturing of LCDs under extreme clean conditions. More recently, the micropatterning of these orientation layers has attracted worldwide attention, which originates predominantly from the possibility to produce wide viewing angle liquid crystal displays.[6,7] This subscribes the need for patterning techniques for alignment layers for liquid crystals used in displays. But also other applications of liquid crystals may make use of alignment techniques with a higher control over the local order, such as future generations of advanced and personalized security features.[8] These security features operate on the principle of a reflective twisted nematic (TN) display filled with a LC layer (e.g., curable liquid crystal polymers), which has a fixed orientation above a patterned alignment layer. Contrast occurs due to alignment differences inside and outside the patterns. By using a single polarizer the image can be made visible.

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In this article we describe the patterning of polyimides by direct, focused laser writing and the influence of these patterns on LC alignment. It is known from literature that relief structures can induce LC alignment[4] and this effect can be used to construct TN LCD cells by writing these relief structures using a laser.[9] However, these patterns were formed by ablation, using a pulsed high energy laser, while in this article we report on laser writing in the melting regime at intensities below the ablation threshold and no material is removed from the substrate.

Polyimides are selected as a model material due to their extensive use as alignment layers and due to their excellent transparency in the visible light region. Laser writing potentially offers the possibility towards computer controlled generation of patterns with high speed and large design flexibility. The process and mechanism of laser writing and the surface modification of the polyimide is studied in detail. The resulting liquid crystal orientation is studied in transmissive-mode LCD cells and polarization microscopy.

II. EXPERIMENT

A. Materials

The precursor for the polyimide orientation layer AL1051 was obtained from JSR Electronics. Indium tin oxide (ITO) coated glass was obtained from Merck (type 327 735 PO). The polyimide precursor was spincoated (5 s at 1000 rpm, 40 s at 5000 rpm) on the ITO side of 2.5×2.5 cm glass/ITO substrates. After a prebake at 100 °C, the coating was placed in a vacuum oven at 170 °C for 90 min to produce the final polyimide coating. The thickness of the polyimide coating was 200 nm.

The LC material used was E7 ($T_{N-I}=59.8\,^{\circ}C$, $\epsilon\perp=5.2$, and $\epsilon=19$, $\Delta n=0.2246$), a mixture of one cyanoterphenyl and three cyanobiphenyl components, obtained from Merck Ltd.

B. Laser writing

Laser writing was performed using a continuous wave argon ion laser (Spectra-Physics Beamlok 2050), operating at 351 nm. The beam was focused using a single lens to a diameter of approximately 10 μm. Ultraprecision, computer controlled translation stages (Newport PM-500) supported the sample holder to position the sample through the laser beam. A manual translation stage was used to position the sample in the focal point of the lens. The laser power (measured just before the focusing lens) was set to 300 mW. The writing speed was 1 mm/s. With these settings the laser intensity remained below the ablation threshold and processing occurred in the melting regime.

C. Cell design

Electro-optical cells were constructed with several configurations: (i) two nonrubbed polyimide layers with a laser melted pattern on one side, (ii) one-side written TN, (iii) one-side written parallel, (iv) one side written rubbed/nonrubbed, and (v) two sides written TN. Rubbed orientation was induced by rubbing the polyimide coated substrates uniaxially with a velvet cloth. Two 2.5×2.5 cm plates of (patterned or nonpatterned) polyimide on glass/ITO attached to each other using an UV curable glue (Norland UV Sealant 91), provided with 6 μm cylindrical glass spacer particles. The cells were capillary filled with LC material at 80 °C, 20 °C above the nematic-isotropic transition temperature of E7.

D. Characterization

Coating thickness was determined using a Tencor P-10 Profilometer. Light absorption of the polyimide layer was determined by UV-visible (VIS)-near-infrared scanning spectroscopy (Shimadzu UV-3102 PC). The dimensions of the lines were studied by light microscopy (Zeiss Universal), environmental scanning electron microscopy (Philips XL30 FEG-ESEM) and atomic force microscopy (Digital Instruments Dimension 3100). The optical properties of the cells were examined by placing them between crossed and parallel polarizers. Macroscopic effects were studied by visual inspection and a digital photo camera. Microscopic effects were studied by polarizerized light microscopy (Zeiss Universal, mounted with a photocamera). Contrasts between the written and non-written sections of the cell between crossed polarizers were measured using a HeNe laser (Melles Griot, model 05-LHP-991, 30 mW, 632.8 nm), an integrating sphere (Newport, model 819) and a power meter and detector (Newport, models 1815 C and 818-UV). To investigate the switching characteristics, the cells were electrically switched at varying currents and examined by polarized visual inspection.

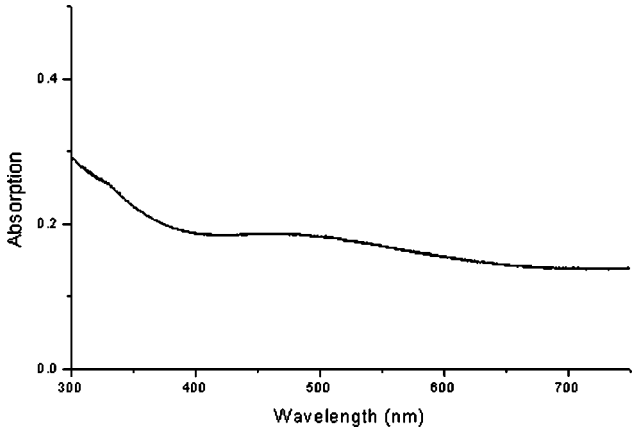

FIG. 1. UV–VIS spectrograph of a thin polyimide JSR AL 1051 coating on glass/ITO (reference: glass/ITO).

III. RESULTS AND DISCUSSION

For use in most (electro-)optical applications, the polyimide layer needs to be transparent in the visible wavelength range. Therefore, laser writing should preferably be performed in the UV-wavelength range where there is sufficient absorption (Fig. 1).

Laser processing can be done in several thermal and/or processing regimes, depending on the intensity of the absorbed, focused laser beam. In the case of polyimide AL1051, we found a heating regime at low intensities (<300 mW), a melting regime at moderate intensities (300–500 mW) and pyrolysis and ablation at higher intensities (>500 mW). In this article the processing is performed in the melting regime.

The induced temperature rise of the polyimide layer in the laser melting regime lies between the glass transition temperature and the decomposition temperature of the polyimide. This means that the melting occurs in a temperature window from 400 to 500 °C.

Local laser melting of polyimide coatings with a scanning laser spot from a continuous wave argon ion laser and the settings, as described in Sec. II, resulted in irregular relief structures. The laser melting induces material flow and subsequent resolidification.[10] Figure 2 shows atomic force microscope images of a typical laser melted line. The holes and humps had an irregular shape over the width and length of the lines. The relief structures have a width of circa 20 μm. The maximum depth and height of the holes is ranges between approximately 50 and 100 μm (the thickness of the polyimide layer itself is 200 μm).

Several LCD cell configurations were constructed to investigate the effect of the laser melted lines on the LC aligning properties of the polyimide.

Because the formation of the lines during laser writing involves flow of the polyimide, and subsequent molecular orientation of the macromolecules, it could be anticipated that the lines could induce alignment of liquid crystals that are brought on top. To examine this, a cell was constructed using two nonrubbed polyimide orientation layers. Figure 3 shows an optical micrograph of this cell. Because the polyimide was not rubbed, the LC molecules do not have a pre-

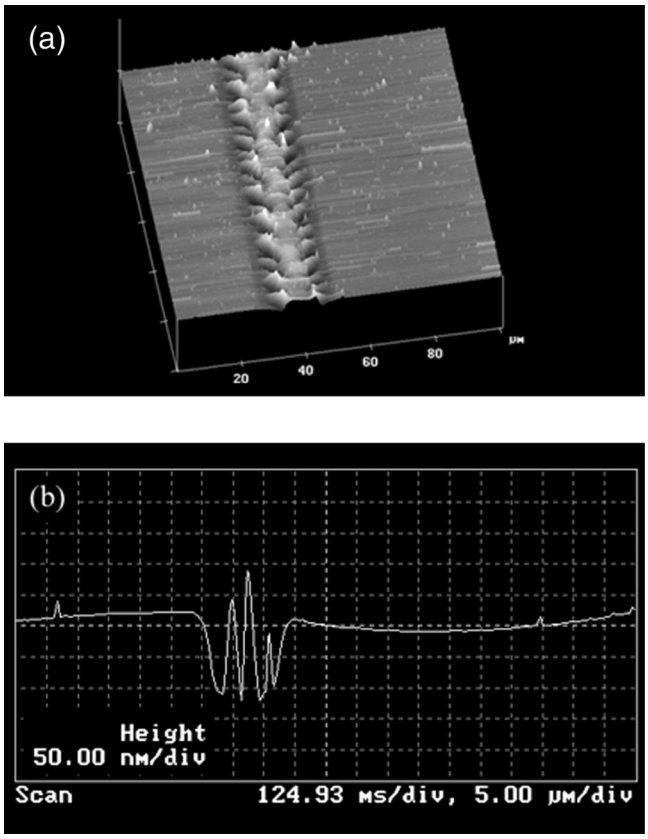

FIG. 2. Laser melted line, written at an intensity of 300 mW and a speed of 1 mm/s. (a) Three-dimensional AFM micrograph. (b) Height profile.

ferred orientation, as can be seen by the disclination lines throughout the sample. Above the laser melted lines the disclinations are not disturbed, indicating that the lines do not induce a preferred orientation direction to the LC molecules. Apparently there is no uniform molecular alignment of the polyimide in the vicinity of the written lines.

The second configuration was a TN LCD cell consisting of two glass substrates provided with oppositely rubbed polyimide coatings. Laser written patterns were present on one of the two polyimide orientation layers. Figure 4 shows photographs of this configuration. Figure 4(a) shows that the

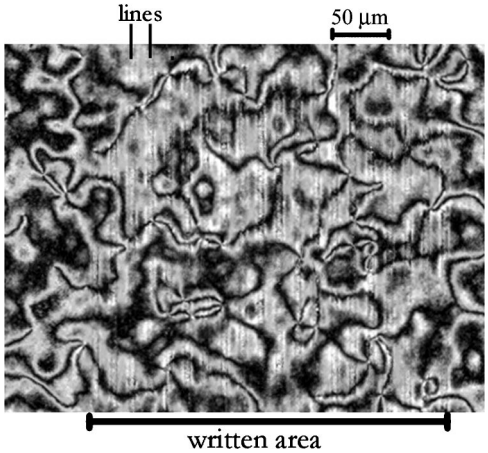

FIG. 3. Optical micrograph of a cell consisting of two nonrubbed polyimide layers with laser melted patterns on one layer.

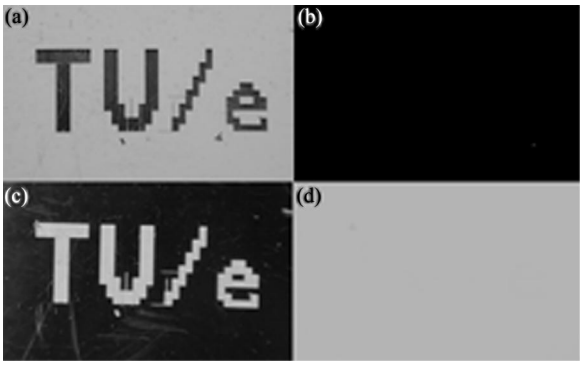

FIG. 4. Photographs of a TN–LCD with a laser written pattern on one orientation layer. (a) Crossed polarizers, $V=0$ V. (b) Crossed polarizers, $V=5$ V. (c) Parallel polarizers, $V=0$ V. (d) Parallel polarizers, $V=5$ V.

nonwritten sections of the cell show normal TN–LCD behavior: transparent between crossed polarizers in the absence of voltage (normally white). However, the written sections (the TU/e logo) are dark. The contrast between the patterned and nonpatterned sections of the cell ranged between 40 and 50. In Fig. 4(c) it can be seen that between parallel polarizers and no voltage exactly the opposite occurs, the patterns are transparent, while the nonwritten sections are dark (normally black). Figure 4(b) shows the cell when a voltage of 5 V is applied: the LC molecules are switched to a homeotropic state in both the patterned and nonpatterned areas (Frederiks transition), resulting in a completely dark cell between crossed polarizers. In Fig. 4(d) the result can be seen when a voltage is applied to a cell between parallel polarizers: the cell switches to a fully transparent state.

Figure 5 shows a schematic representation of the LC molecules within the hybrid cell inside and outside the patterns in the case when there is no voltage applied [Fig. 5(a)] and the homeotropic state when a voltage is applied [Fig. 5(b)].

When these hybrid cells electrically switched, it was observed that the LC molecules above the laser-melted patterns needed a higher voltage to switch to a homeotropic state. This indicates a parallel orientation at these sections because the surplus of elastic energy stored in the twisted configuration drives the liquid crystals to undergo the Frederiks transition at lower voltages. The absence of twist above the laser written lines points to a disruption of the alignment properties of the rubbed polyimide. The liquid crystals only experience strong anchoring at the rubbed polyimide at the opposite side while at the laser lines the anchoring is broken. Because of the elastic energy the liquid crystal tends to align uniaxial and parallel to the rubbing direction of the nonwrit-

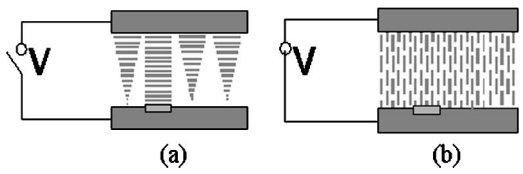

FIG. 5. Sketches of a cross section of a laser written TN–LCD cell. (a) $V=0$ V. (b) $V=5$ V.

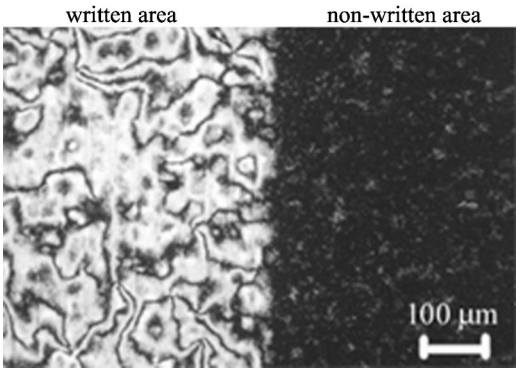

FIG. 6. Optical micrographs of a LCD cell with a rubbed/nonrubbed configuration (between crossed polarizers). A laser melted pattern was written on the rubbed polyimide layer (left side of the image).

ten polyimide. It should be noted here that the cells were constructed using liquid crystals without the presence of a chiral dopant.

Although the width of the individual lines in the patterns is only 20 μm, the influence of the lines on the liquid crystal alignment extents to approximately 50 μm. The Gaussian shape of the laser beam explains this. The highest intensities of the beam are in the center and therefore the largest volume effects take place there. Outside the relief structures there is an area that is still affected by the laser beam, although the intensity is not high enough to deform the material, while still the alignment properties of the polyimide are changed. The writing direction of the lines with respect to the rubbing direction does not have an influence. No difference in the LC alignment was observed above lines that were written perpendicular and parallel to the rubbing.

The next cell that was studied was constructed from two glass plates with parallelly rubbed polyimide coatings and locally laser written at one side. In this parallel cell the laser written patterns showed the same orientation as the surrounding nonpatterned areas. No disclinations were observed on the borders of the laser-melted pattern, the LC alignment was homogeneously parallel throughout the cell.

According to the earlier mentioned hypothesis, the LC material should orient itself according to the opposite, nonwritten orientation layer, resulting in a parallel orientation, but since the nonwritten sections of the cell also have a planar orientation, the cell should appear homogeneously planar. This is indeed what was observed. Patterns were written parallel and perpendicular to the rubbing direction of the orientation layers. No microscopic and macroscopic differences were observed between the two patterns, which again indicates that the written lines themselves do not influence the LC orientation induced by the nonwritten opposite orientation layer.

The fourth cell that was constructed had on one side a rubbed and on the other side a nonrubbed polyimide orientation layer. A laser-melted pattern was written at the rubbed side. The nonwritten sections of the cell macroscopically behaved like a planar cell, although between crossed polarizers the transmission through the cell was 20% more than a parallel cell with two rubbed polyimide layers (determined using the contrast measurement setup). Small domains with other orientations could be observed by microscope (Fig. 6).

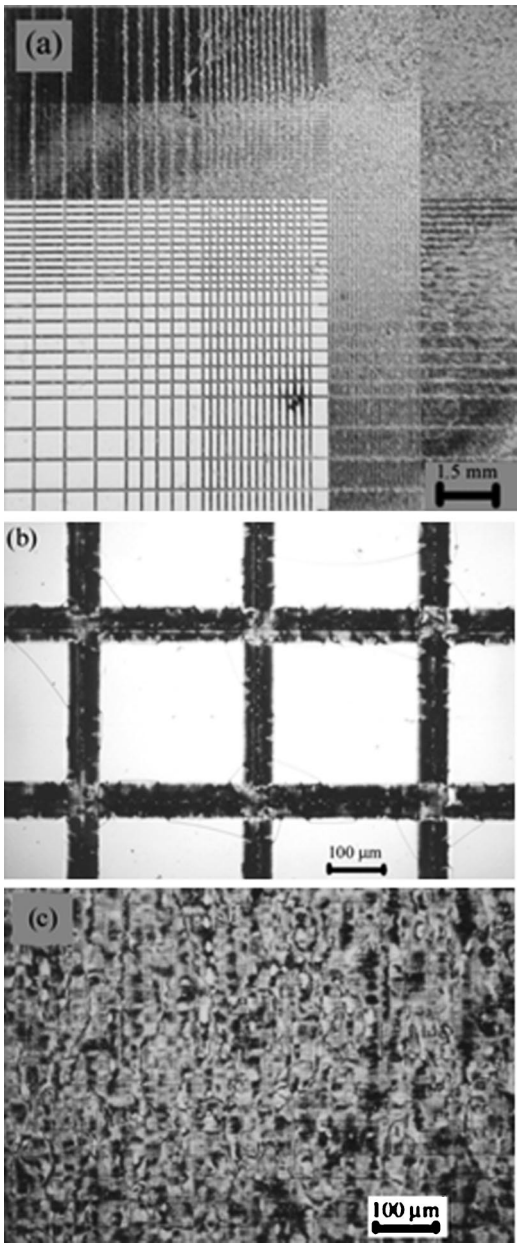

FIG. 7. TN–LCD cell with patterns written on both orientation layers between parallel polarizers. (a) Overall photograph of the two overlapping patterns. (b) Optical micrograph of 400 μm spaced grid. (c) Optical micrograph of 50 μm spaced grid.

Between crossed polarizers the pattern written on the rubbed polyimide appeared much lighter than its nonwritten surroundings (Fig. 6). A contrast of 5 was measured between crossed polarizers between the patterned and nonpatterned regions. As with the cells described before, the LC material effectively is oriented by the nonwritten, opposite side. In this case that side has no preferred LC aligning direction, since it was not rubbed, therefore the LC itself also has no preferred direction. This is indeed the case, as can be seen in the optical micrograph (Fig. 6) by the many dislocations present above the written patterns.

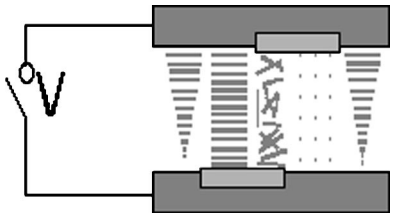

FIG. 8. Sketch of a cross section of a laser written TN–LCD cell with overlapping patterns of both orientation layers.

The fifth configuration was a TN cell with perpendicularly rubbed polyimide alignment layers and patterns written on both orientation layers. Both patterns were identical: a series of parallel lines. Several series of lines with a different spacing between the lines were constructed. During the cell construction the two patterned orientation layers were placed to form a grid structure with the two patterns exactly perpendicular to each other [Fig. 7(a)].

In this cell three regions can be distinguished: sections where there are no written patterns on both sides, sections with on one side a written pattern and sections where there are two overlapping written patterns (the cross sections).

In the sections without any patterns the cell behaves like a normal TN cell. In the regions with on one side a laser melted line, the LC molecules have a planar orientation, as with the second cell described in this article. The regions where the patterns overlap show a random orientation of the LC molecules, which is what could be expected from the previous results. The orientation of the LC molecules is determined by the opposite nonwritten orientation layer, but in this case the opposite layer also does not induce an orientation, similar to when there would be a non-rubbed polyimide. Figure 7(b) clearly shows all three regions.

Figure 7(c) shows an area of the cell where the written lines on both sides have a spacing of 50 μm, which means the whole area consists of overlapping lines and disclinations are present in the whole section. Figure 8 shows a sketch of the LC alignment within the cell in all three regions.

IV. CONCLUSIONS

From the five cells described earlier it can be concluded that with laser melted lines on polyimide orientation layers it is possible to permanently pattern LCD cells by local direct laser melting and generate contrast between the patterned and non-patterned areas. By breaking the azimuthal anchoring strength of one orientation layer, local areas with a different configuration are created. The LC material aligns itself according to the opposite nonwritten orientation layer, because the anchoring strength of this layer will overpower the written orientation layer. If the opposite orientation layer itself does not induce an orientation (e.g., because it was not rubbed or there are laser melted patterns on the opposite side), the LC material does not show homogeneous alignment.

ACKNOWLEDGMENT

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