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Microchannel-flowed-plasma modification of octadecyltrichlorosilane self-assembled-monolayers for liquid crystal alignment

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ABSTRACT

We report that a chemical patterning technique based on local plasma modification of self-assembled monolayers has been utilized to fabricate surfaces for domain liquid crystal alignment. Highly hydrophobic octadecyltrichlorosilane monolayers deposited on glass substrates coated with Indium-Tin-Oxide were brought into contact with elastomeric stamps comprising trenches on a micro scale, and then exposed to an oxygen plasma. In the regions exposed to the plasma the monolayer was etched away leaving a patterned surface that exhibited surface energy differences between surface domains. The surfaces that bear the micropatterns have been shown to be capable of producing patterned alignment of nematic liquid crystal.

1. Introduction

The Liquid Crystal Display (LCD) is currently the dominant technology in modern flat-panel-display products. The use of liquid crystals in display technology relies entirely upon the ability to precisely control the orientational order of the liquid crystal molecules over a large area. The local average orientation of the molecular long-axis is described by the unit vector director and conventionally denoted by $\mathbf{n}(\mathbf{r})$. In a liquid crystal cell or device, a domain is defined as a localized region of the liquid crystal in which $\mathbf{n}(\mathbf{r})$ is constant. The use of liquid crystals in electro-optic and photonic devices is coming to rely increasingly on liquid crystals with patterned orientational structures [1–4]. Therefore, the various means of applying a pattern to a surface – in order to produce multi-domain liquid crystal alignment – have attracted much attention. The traditional surface process of rubbing polymer thin films cannot satisfy the demands because fine patterning is not readily achievable. Over the last two decades a variety of primarily physical techniques including laser ablation [5], electron-beam writing [6], and microrubbing [7], have been developed to produce spatially topographical inhomogeneous surfaces for domain liquid crystal alignment. However, these techniques are typically not well suited to a volume-manufacturing environment.

An alternative approach is to chemically pattern the surface and thereby impose a physicochemical inhomogeneity on the substrate in order to achieve locally orientational order in the liquid crystal [8]. Our attention was drawn to the Micro-Channel-Flowed-Plasma (μCFP) modification [9] for its ability to selectively pattern of Self-Assembled-Monolayers (SAMs) and to impart a patterned template of surface energy on to a variety of substrates. The μCFP method, which is a soft lithographic method combining the chemical modification of SAMs [10,11] and the elastomeric-stamp-based micro-contact printing technique [12], was initially developed for micro-patterning of silicon wafers for the fabrication of semiconductor devices. We utilized μCFP to modify SAMs and to transfer surface patterns into the SAMs coated on patterned substrates. The modified surfaces were found to bear micropatterns that exhibited a surface free energy difference between adjacent surface domains. So they can be used as command surfaces to align liquid crystals. We report herein some preliminary results that demonstrate the performance of the modified surface in domain liquid crystal alignment.

2. Experimental details

The SAMs utilized here comprised monolayers of octadecyltrichlorosilane (OTS, $H_3C(CH_2)_{17}SiCl_3$) formed on Indium-Tin-Oxide (ITO) coated glass substrates through a self-assembly mechanism. OTS (purchased from Alfa Aesar) was selected because of its low surface energy (ca. 20 mJ/m^2), which is about half that of polyimide films typically used for the planar alignment of liquid crystals and with the capability of homeotropic alignment of liquid crystals. OTS was dissolved in hexadecane to make a 1.0 mM solution. ITO glass plates (12 × 12 mm^2) were sonicated first in neutracon for 30 min, next in acetone for 3 min, then thoroughly rinsed with deionized (DI) water. After surface cleaning, the substrates were activated by exposure to an O_2 plasma in a 0.16 kPa chamber for 10 min. The plasma was produced using a microwave plasma generator (PVA Tepla, PS400) with 18 W 2.45 GHz microwave. The activated substrates were immersed into the OTS/hexadecane solution

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at room temperature (26 °C). A highly-organized, covalently-bonded OTS molecular monolayer spontaneously assembled on to the surface through a combined process of adsorption and hydrolysis. The samples were further sonicated in turn in toluene, ethanol followed by DI water, then finally dried in a stream of filtered nitrogen gas. The effective surface coverage ζ of OTS-SAM over a substrate can be estimated using the following equation [13],

$$\zeta = \frac{1 - \cos\alpha}{1 - \cos\alpha_{\mathrm{m}}}, \tag{1}$$

where α is the contact angle of DI water measured from the sample and α_{m} is the maximum contact angle of DI water achieved for the OTS-SAM.

Contact angle measurements of sessile water drops were performed using a drop shape analysis system (KRÜSS, DSA100). For each sample, the surface was divided into 25 regions arranged in 5 rows by 5 columns. A DI water drop was placed at each of these 25 small regions and the contact angle was measured. A contact angle for the sample was obtained from an average of the 25 measured values. Soaking time was found to have a significant impact on the contact angle. Initially, the contact angle, as illustrated in Fig. 1, increased with soaking period, and exhibited a wide variation. The contact angle was found to become saturated and the standard deviation was lower when the substrate was soaked for longer than 40 min (Fig. 1). The average contact angle of the DI water drop set on the surface of the sample prepared by soaking the substrate for 1 h was 111.6° with a notional standard deviation of ±0.6°. Therefore, all of the OTS-SAMs used in the present study were produced by immersing the substrates in the OTS solution for 1 h or longer to guarantee good coverage.

For the purpose of patterning the OTS-SAM, poly(dimethylsiloxane) (PDMS) based elastomeric stamps were fabricated using a replica-molding technique [14,15]. In this technique, the Sylgard 184 silicone elastomer kit (Dow Corning), a mixture of 10:1 w/w base to cross-linker, was poured over lithographically-created masters having the desired patterns on their surfaces, then cured at 130 °C for 1 h and peeled off. The masters were produced using standard photolithographic fabrication procedures. A negative photoresist SU8 (Gersteltech Sarl, product code: GM1060) was spun onto an optical-flat glass slide that was then exposed to UV light at 365 nm following soft baking at 65 °C. The photoresist layer was patterned to create the desired topographic pattern using a mask. Although patterns with complex features can be easily produced on SAMs, stamps comprising parallel microtrenches with 50% duty cycle were utilized in the present study to demonstrate the feasibility of using μCFP to manipulate the domain structure on a single substrate.

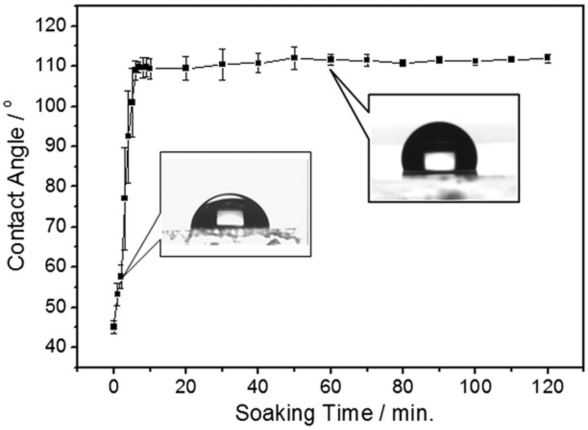

Fig. 1. Contact angle of deionized water drop vs. duration of soaking ITO glass substrates in OTS solution. Inserted images display the profiles of the water drops on the substrate surface before and after being covered by OTS monolayer, respectively.

The molecular alignment of the liquid crystal on the OTS-SAM was examined using a polarizing optical microscope (POM) (ZEISS, Axioskop40). The liquid crystal used was the nematic mixture E49 (Merck), whose nematic-to-isotropic phase transition temperature is 100 °C.

3. Results and discussion

In the present study, the contact angle for each sample was calculated as the average of the values acquired over the different positions on the surface of the sample. The value of the standard deviation for a sample is a measure of the range of the wettability across the surface of the sample, and reflects the degree of the non-uniformity of the OTS thin film on the surface of the sample. According to its nature as a monomolecular-layer, the uniformity of the OTS-SAM on a solid substrate can be described by the surface coverage. Therefore, the variation of contact angle with soaking time shown in Fig. 1 can be attributed to the degree of the coverage of the OTS-SAM on the substrate. Practically, it is difficult to determine directly whether a surface is completely covered. The values of the contact angles reported in the literature for sessile water drops on OTS-SAMs formed on silicon wafers are between 109° and 114° [16–19]. Assuming that $\alpha_{\mathrm{m}} = 114°$ and using Eq. (1), we can estimate an average coverage of 97.2% for the OTS-SAMs formed on our substrates. A well-grown OTS monolayer on an ITO plate is highly hydrophobic, with a surface free energy of 20.3 mJ/m^2.

Fig. 2a shows a POM image of E49 sandwiched between OTS-SAMs. In the POM, the sample appeared completely dark, and the black appearance was unchanged on rotating the sample indicating that the director **n** of the liquid crystal is parallel to the optical axis of the POM. Conoscopic observation of the sample showed that the center of the isogyre corresponding to the director **n**, as illustrated in the insert in the top right corner of Fig. 2a, was in the center of the conoscopic image which confirms that the director **n** is coincident with the optical axis of the POM. Based on these observations, the liquid crystal layer is identified to be in homeotropic alignment on the OTS-SAM.

Exposure of the OTS-SAM to an O_2 plasma leads to conversion of the surface functional groups and etching of the alkyl chain of the OTS molecules. The mechanism of chemical conversion of the plasma modification of OTS has been well documented. The plasma-induced chemical conversion of OTS is attributed to surface hydroxylation of the terminal methyl groups and sequential oxidation of the resulting hydroxyl groups [10,12]. This plasma modification causes a drastic increase in the surface free energy (Fig. 2b). At a higher energetic state (66.8 ± 0.6 mJ/m^2), the surfaces can no longer support vertical anchoring of the liquid crystal molecules, and as a result, the molecules adopt a planar anchoring configuration. The appearance of a schlieren texture (Fig. 2b) in the sample indicates that the planar alignment of the liquid crystal is degenerate, i.e., the molecules orient randomly in any azimuthal direction.

To carry out the μCFP process, a PDMS stamp was brought into contact with the OTS-covered substrate, and the microtrenches (~6 μm deep) on the stamp formed the microchannels for an O_2 plasma (Fig. 3). The sample was exposed to an O_2 plasma generated with an 18 W 2.45 GHz microwave for 30 min. Local conversion of the terminal functional groups occurred on the OTS monolayer regions that were exposed to the plasma. The plasma treatment produced a grating pattern, comprising alternating parallel OTS-SAM and ITO stripes, and simultaneously created a surface template with alternating energetic states on the substrate.

The domain liquid crystal alignment effect of the patterned OTS-SAM was studied by examining POM images of liquid crystal layers in cells that were constructed with the plasma treated substrates used as back-plates, and cover-plates whose surface were coated with OTS-SAMs. The cell-gap was maintained at 3.1 μm, with a standard deviation of 0.1 μm, using glass spacers. The cells were filled with E49. Fig. 4 shows a POM image of a sample whose back-plate comprises 300 μm wide OTS-SAM stripes. In the POM, the sample exhibited alternating stripes. In the stripe regions where both the back-plate and the cover-