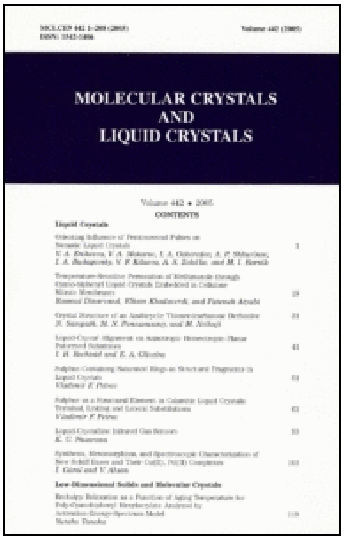

Molecular Crystals and Liquid Crystals

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Liquid Crystal Mono- and Nano-Layers Covalently Bonded to Silicon and Silica Surface for Alignment of LC Layers

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We synthesized two types of liquid crystalline nano-layers covalently bonded to Si and Si/SiO$_2$ wafers. Monolayers of terminal and lateral low molecular weight mesogens exhibit spontaneous homeotropic orientation, while planar orientation is obtained by means of rubbing process. On the other hand a novel polymer liquid crystal nano-layer, obtained via atom transfer radical polymerization (ATRP) of acrylate monomer from Si/SiO$_2$ surface, exhibits planar orientation of liquid crystalline side chain moieties. Structure of such novel composites was confirmed by optical studies as well as spectroscopic methods, including ellipsometry. The goal was to obtain low molecular weight liquid crystals alignment just from the mentioned above, modified surfaces.

Keywords Atom transfer radical polymerization; functional interfaces; liquid crystals; self-assembled monolayers and nanolayers; surface organometallic chemistry

Introduction

There is a significant interest in modification of silicon and silica via surface organometallic chemistry (SOMC) [1,2]. Functional interfaces play nowadays increasingly important role in micro- and nano-structuring technology, since the time when the pathway of chemical reactions with solid silicon substrate was presented by Chidsey [3,4] (alkenes/Si, alkynes/Si) and Whitesides [5,6] (alkanethiols/Au).

This developing trend of the search for novel self assembled monolayers (SAM's) is fueled by potential application of such organic/inorganic composites, ranging from surfaces of controlled wettability [7], surface passivation of solar cells [8], molecular recognition systems [9], molecular bioelectronics [10] and DNA chips [11], to surface grafted molecular motors [12]. Our interest, in this respect, focuses on

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application of silicon wafers with LC modified surfaces as photoconducting and orienting substrates in photonic devices [13].

Several synthetic methods have been developed for preparation of covalently bonded organic mono- and nano-layers on silicon. In general, they lead to formation of either Si–C or Si–O–Si bonds between organic moieties and surface silicon atoms [1,2]. The latter ones are generated, once organic layers are grown from silica or quartz [14].

A recent work by Ferringa [12] illustrates well the Si-O-Si bond formation as an alternative pathway to hydrosilylation reaction (leading to Si-C bond between organic group and the surface atoms [5,6]). Piranha solution generates Si-OH bonds on the surface, which can be then condensed with an appropriate chloro- or alkoxysilane to give the organic moiety covalently bonded to the substrate (Si or silica).

The purpose of this study is formation of liquid crystalline (LC) mono- and nano-layers having a stable chemical linkage with semiconductor (Si) and semiconductror/insulator (Si/SiO_2) surfaces. Such the modified wafers could find application as alignment devices for opto-electronic elements, e.g., wave-guide couplers (Fig. 1), splitters or sensors.

A similar approach has been presented in the past [15], concerning a liquid crystalline film designed for LC flat panel displays. However, no details concerning synthesis have been presented at that time and only formation an idealized, cross-linked nanolayer structure has been claimed (Fig. 2).

Our present generic research concentrates on development of the most effective methods of surface organometallic chemistry (SOMC), leading to novel organic (LC)/inorganic hybrid materials and orientation studies of the LC layers deposited

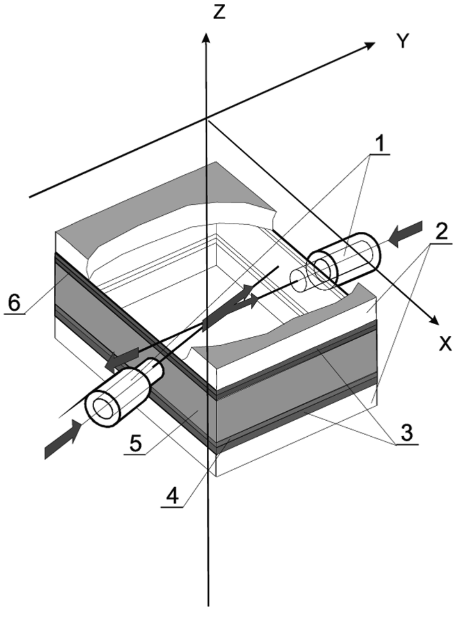

Figure 1. Wave-guides coupler: 1 – wave-guides, 2 – glass (upper) and silicon (lower) plates, 3 – electrodes (layers of ITO), 4 – nanolayer of covalently bonded liquid crystal, 5 – nematic mixture of low molecular liquid crystals, 6 – polyimide layer.

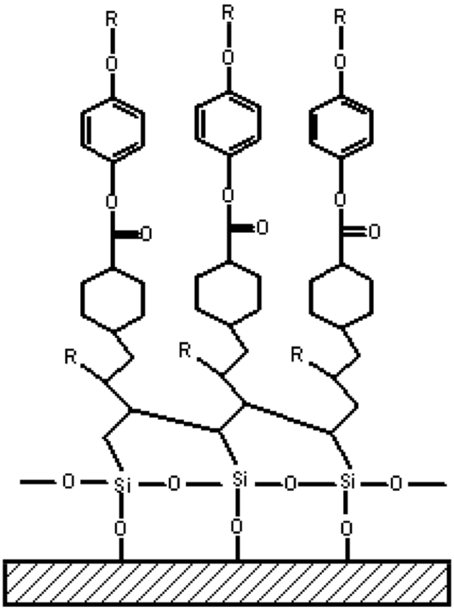

Figure 2. An example of liquid crystal system network bonded via triethoxysilane.

over surfaces of such materials. We have synthesized three types of monolayers, having covalently bonded liquid crystalline moieties of cyanobiphenyl, methoxyphenyl benzoate and bis(methoxybenzoyl) type as well as acrylic polymer layer, having cyanobiphenyl liquid crystalline core in the side chain. Orientation studies of LC moieties, relative to the inorganic surfaces, were performed in order to evaluate potential application of such materials in opto-electronic devices.

Experimental

Materials

Silicon wafers Si (100), and Si (100) with 300 nm layer of SiO_2 were purchased from Aldrich and Si-Mat Silicon Materials. Their surface was modified to generate Si-OH and Si-H reactive groups, as described elsewhere [1,16]. Toluene and THF were dried according to reported procedures [17] and stored under nitrogen. Copper(I) bromide, copper(II) bromide, pentamethyldiethyltriamine (PMDTA), allyl 2-bromobutyrate, triethoxysilane and chlorodimethylsilane were purchased from Aldrich and used as received. 3-Chlorodimethylsilylpropyl 2-bromoisobutyrate was prepared by hydrosilylation of allyl 2-bromoisobutyrate and chlorodimethylsilane as described in [18]. Tris[2-diethylaminoethyl]-amine (Me_6TREN) was made according to [19] and acrylate monomer-4′-(7-undecenyloxy)-4-cyano-biphenyl acrylate (5), according to [20].

Mesogenic alkenes (Fig. 3) were made as follows: 4′-*cyano-4-(7-octenyloxy) biphenyl (1)* and *4′-methoxyphenyl-4-(10-undecenyloxy)-benzoate (2)* were prepared by literature methods described, respectively, in [21] and [22].

5-[[[2′-[[4″-methoxybenzoyl]oxy]-methylene]-4′-[(4″methoxybenzoyl)-phenyl] oxy]carbonyl]dec-9-ene (3a) and *5-[[[2′-[[4″-methoxybenzoyl]oxy]-methylene]-4′-[(4″methoxybenzoyl)-phenyl]oxy]-carbonyl]but-3-ene (3b)* were made by

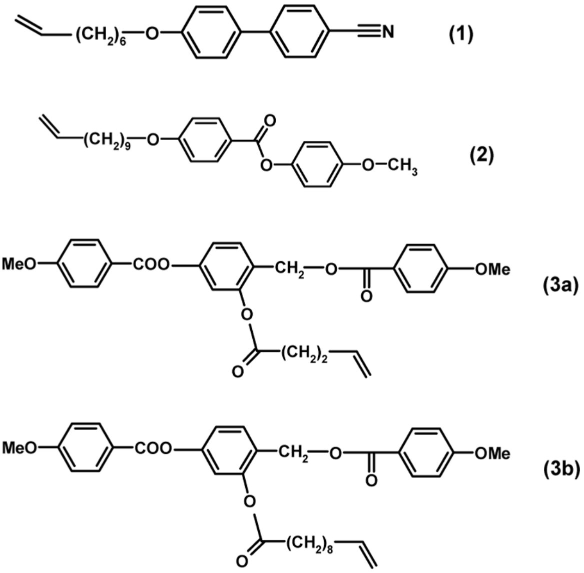

Figure 3. Structures of terminal and lateral liquid crystalline alkenes.

esterification of the substituted phenol 2-[[(4′-methoxybezoyl)oxo]methylene]-4-[(4″-methoxybezoyl) oxy]phenol (4) [23] with 10-undecenoyl chloride (Aldrich) and 4-pentenoyl chloride (Aldrich) (Fig. 4). Thus, 2-[[(4′-methoxybezoyl)-oxo]-methylene]-4-[(4″-methoxybezoyl) oxy]phenol (2.76 g, 6.7 mmol) in 55 ml of dry THF was stirred in a two-neck flask at room temperature, while solutions of 4-pentenoyl chloride (1.42 g, 8.2 mmol) in THF (5 ml) and triethylamine (1.09 g, 8.2 mmol) in THF (5 ml) were simultaneously added drop-wise to the solution. Once the addition was completed the reaction mixture was stirred for 18 hours and a white deposit of triethylammonium chloride precipitated. Then, the reaction mixture was poured into 250 ml of cold water. The separated oil was crystallized from a mixture of ethanol (120 ml) and toluene (20 ml) yielding 0.8 g (24.4%) of 5-[[[2′-[[4″-methoxybenzoyl]oxy]methylene]-4′-[(4″methoxybenzoyl)-phenyl]oxy]carbonyl]-but-2-ene (3a) as white crystals.

Anal. Found: C, 68.7; H, 5.4. $C_{28}H_{28}O_8$ Calc.: C, 68.6; H, 5.3.

^{1}H NMR ($CDCl_3$) δ ppm: 2.4 (m, 2H, a, $\underline{CH_2}CH{=}CH_2$), 2.6 (m, 2H, b, $CH_2\underline{CH_2}COO$), 3.8 (s, 3H, c, OCH_3), 3.9 (s, 3H, d, OCH_3), 5.0–5.2 (m, 2H, e, $\underline{CH_2}{=}CH$), 5.3 (s, 2H, f, $Ar\underline{CH_2}O$), 5.7–5.9 (m, 1H, g, $\underline{CH}{=}CH_2$), 6.9 (d, 4 aromatic H, h, ortho to OCH_3), 7.0 (d, 2 aromatic H, i, ortho to OOC), 7.1 (s, 1 aromatic H, j, ortho to CH_2OOC), 8.0 (d, 4 aromatic H, k, meta to OCH_3).

5-[[[2′-[[4″-Methoxybenzoyl]oxy]-methylene]-4′-[(4″methoxybenzoyl)phenyl]oxy]-carbonyl]dec-9-ene (**3b**) was made by the above procedure, using 10-undecenoyl chloride, to give 0.85 g (40%) of the acrylate (**3b**) as white crystals.

Anal. Found: C, 72.3; H, 6.9. $C_{38}H_{28}O_8$ Calc.: C, 71.0; H 6.7.

^{1}H NMR ($CDCl_3$) δ ppm: 1.2 (m, 10H, L, $CH_2CH_2\underline{(CH_2)_5}CH_2CH{=}CH_2$), 1.5 (m, 2H, m, $CH_2\underline{CH_2}(CH_2)_5CH_2CH{=}CH_2$), 2.0 (m, 2H, n, $\underline{CH_2}CH{=}CH_2$), 2.2 (m, 2H, o, $OOC\underline{CH_2}CH_2$) 3.9 (s, 6H, p, OCH_3), 4.9 (m, 2H, q, $\underline{CH_2}{=}CH$), 5.1 (s, 2H, r, $Ar\underline{CH_2}O$), 5.8 (m, 1H, s, $\underline{CH}{=}CH_2$), 7.0 (d, 4 aromatic H, t, ortho to OCH_3),

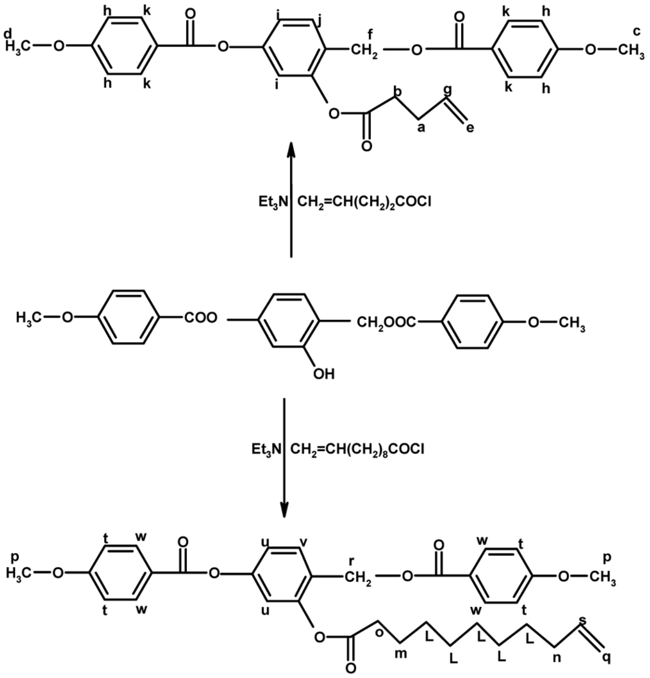

Figure 4. Synthesis of lateral mesogenic alkenes.

7.3 (d, 2 aromatic H, u, ortho to OOC), 7.4 (s, 1 aromatic H, v, ortho to CH_2OOC), 8.1 (d, 4 aromatic H, w, meta to OCH_3).

Monolayer LC Films Formation

Hydrogen terminated flat silicon wafers ~10 × 10 mm were etched chemically [1] and subsequently reacted with toluene solutions (8 ml, 10 wt% of terminal alkenes – {4′-cyano-4-(7-octenyloxy) biphenyl (1), 4′-methoxyphenyl-4-(10-undecenyloxy)-benzoate (2) and the lateral 5-[[[2′-[[4″-methoxybenzoyl]oxy]-methylene]-4′-[(4″methoxybenzoyl)phenyl]oxy]-carbonyl]dec-9-ene (3b)}. The heterogeneous hydrosilylation process was carried out at 100°C for 48 hours [16].

Hydroxy-terminated Si/SiO_2 wafers were made in a CVD reactor at moist nitrogen flow (p = 300 Pa, T = 350°C, t = 10 min, I = 0.2 A, P = 80 W). Then ~10 × 10 mm shards were reacted with $(EtO)_3SiH$, followed by hydrosilylation of lateral mesogen – 5-[[[2′-[[4″-methoxybenzoyl]-oxy]methylene]-4′-[(4″-methoxybenzoyl)phenyl]oxy]carbonyl] but-3-ene (3a) [16].

The monolayers were characterized by goniometric and ellipsometric measurements, ESCA, and AFM.

LC Polymer Layer Formation. ATRP from Si/SiO₂ Surface

Atom transfer radical polymerization initiator – 3-chlorodimethylsilylpropyl 2-bromoisobutyrate was anchored on hydroxy-terminated Si/SiO_2 shards [14] and such the system was used for polymerization of LC monomer – 4′-(7-undecenyloxy)-4-cyano-biphenyl acrylate (5) (Fig. 5), from such the modified surface. Thus, silicon

(100) wafer shard, covered with 300 nm of SiO_2 and functionalized with ATRP initiator (dimethylsiloxylpropyl 2-bromoisobutyric group), was placed in a Schlenk flask, in a toluene (5 ml) solution containing 4′-(7-undecenyloxy)-4-cyano-biphenyl acrylate (5) (0.5 g, 1.19×10^{-3} mol), CuBr (3.2×10^{-3} g, 2.3×10^{-5} mol), $CuBr_2$ (0.5×10^{-3} g, 2.3×10^{-6}) and PMDTA (2.1×10^{-3}, 1.2×10^{-5} mol). The reaction was carried out at 60°C, under argon. At time intervals (1, 2, 3 and 22 hours) the shard was withdrawn, washed, dried and the thickness of the generated layer was controlled by ellipsometric spectroscopy. Analogous conditions were applied when Me6TREN was used as the ATRP ligand. The growth of polymer was controlled after 1, 2, 20 and 23 hours (Fig. 7).

Orientation of liquid crystalline moieties against the surface, in nano- and mono-layers was determined using experimental set-up shown in Figure 6.

Characterization

^1H NMR was carried out with a Bruker DRX-500 MHz spectrometer using $CDCl_3$ as the solvent. Phase transition temperatures were determined by DSC 2920 (TA Instruments) and optical microscopic measurements. Surface morphology of LC

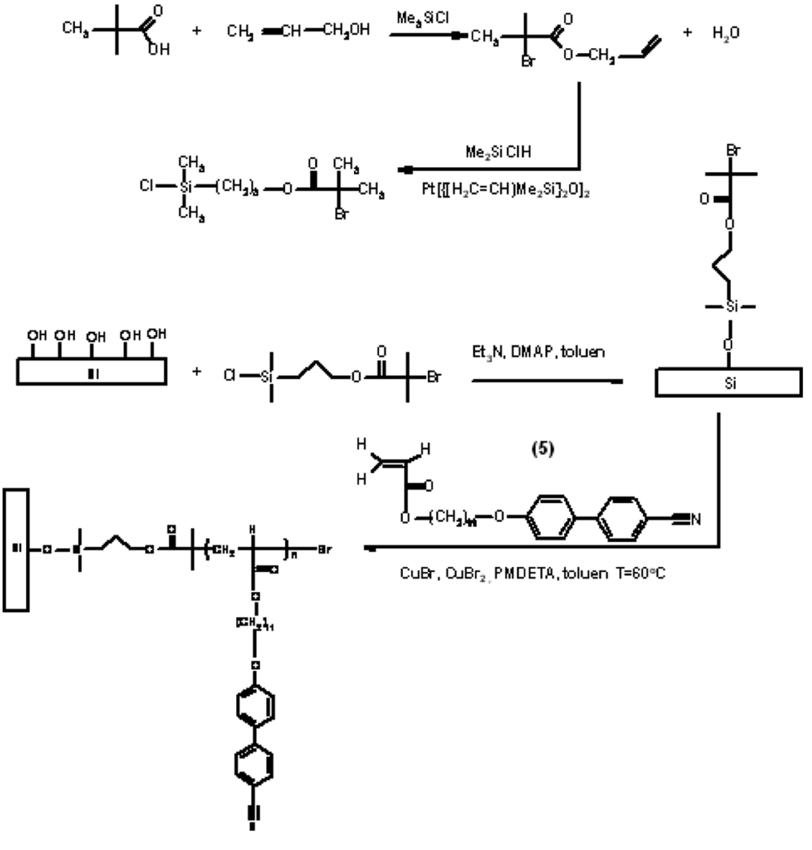

Figure 5. Synthesis of mesogenic acrylate monomer and its ATRP polymerization from Si/SiO_2 surface.

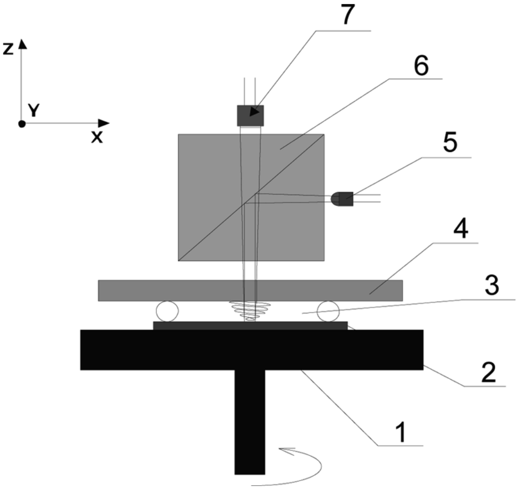

Figure 6. Experimental set-up for orientation studies: 1 – rotating table; 2 – silicon wafer; 3 – liquid crystal layer; 4 – glass reference plate; 5 – LED; 6 – broadband polarizing cube beamsplitter; 7 – photodetector.

layers was followed using AFM (Nanoscope IIA, Digital Instruments) and their elemental analysis by ESCA (Vega-Tescan Instrument). The layers were also characterized by ellipsometry (V-VASE, J. A. Wollam Co. Inc.,) and contact angle measurements (F70B Goniometer), using "DROP" program. The effect of LC modified silicon surface on orientation of nematic liquid crystal mixture was studied in a sandwich cells of the experimental set-up, presented in Figure 6. The cells consisted of the investigated silicon wafers, with covalently bonded low molecular weight LC moieties, a standard mixture of low molecular weight LC's nematics [24] and a reference glass plates providing unidirectional planar or homeotropic orientation.

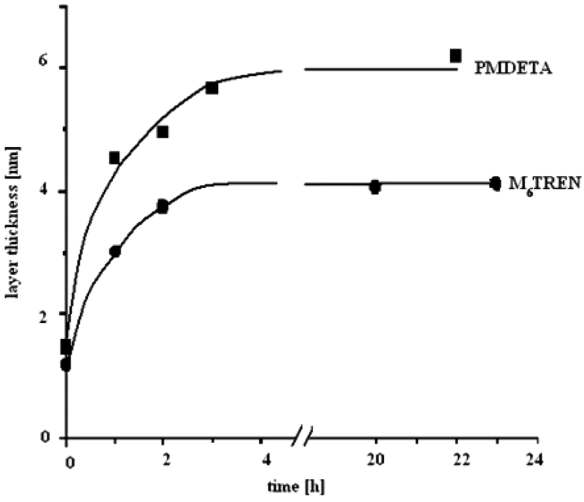

Figure 7. Progress of atom transfer radical polymerization followed by ellipsometric measurements of the thickness of liquid crystalline nano-layer.

The orienting layer on reference plates were prepared by spin coating with commercially available polyimides SE 130 and SE 1211 (Nissan Chemical Industries), respectively, for planar and homeotropic alignment, followed by heating for 30 min at 80°C and then for 60 min at 180°C. Unidirectional planar orientation was generated by rubbing, using rubbing cloth for liquid crystal panels YA-19R (Yoshikawa Chemical Company). The liquid crystal layer thickness was fixed by glass spacers PF-100 (Nippon Electric Glass).

Results and Discussion

Syntheses

We have synthesized two types of liquid crystalline layers covalently bound to silicon (or silicon/silica) surface. The first group of liquid crystalline monolayers (with low molecular weight liquid crystals) were made by hydrosilylation of terminal mesogenic alkenes (1), (2), (3a, 3b), bearing respectively, cyanobiphenyl, methoxy benzoate as well as phenol butyrate and undecenoate moieties with Si-H modified silicon (100) wafers. Additionally, (3b) was also hydrosilylated on triethoxysilane modified Si/SiO_2 surface.

Another type of covalently anchored liquid crystalline layer was made by atom transfer radical polymerization of liquid crystalline acrylate (5) from the Si/SiO_2 surface.

The surface was modified with an ATRP initiator – 3-chlorodimethylsilylpropyl 2-bromoisobutyrate. ATRP gave the unique opportunity to obtain polymer layer made of chains having very low polydispersity index (PDI ~ 1.1). In this case the silane moiety with a single Si–Cl function was used for generation of Si−H on Si/SiO_2 surface. From our experience it appears that the typically used trifunctional systems, e.g., $(EtO)_3SiH$, being very reactive, leads to complicated monolayer structure. Apart from formation of the expected Si–O–Si bonds with hydrophilic surface (Si–OH groups), they generate as well an irregular polysiloxane network, as a result of hydrolytic condensation of ethoxy groups themselves. Thus, contrary to many earlier reports [15,25,26], the chemically uniform layers are never formed once multifunctional surface modifiers are used.

Orientation Studies

The sandwich cell made of silicon wafer and reference plate enclosed a liquid crystal layer acts as reflective one and the normalized reflectance $R_\perp$ for the cell with twist angle Φ can be solved by Jones matrix method. Under the crossed-polarizer configuration the reflectance of the cell can be described by the following Jones matrices as $R_\perp = |M|^2$, where:

$$M = \begin{bmatrix} \cos\beta & \sin\beta \end{bmatrix} \begin{bmatrix} \cos\overline{X} - i\frac{\Gamma}{2}\frac{\sin x}{x} & -\phi\frac{\sin\overline{X}}{X} \\ \phi\frac{\sin\overline{X}}{\overline{\overline{X}}} & \cos\overline{X} + i\frac{\Gamma}{2}\frac{\sin\overline{X}}{\overline{\overline{X}}} \end{bmatrix} \begin{bmatrix} \cos\overline{X} - i\frac{\Gamma}{2}\frac{\sin x}{x} & \phi\frac{\sin\overline{X}}{\overline{\overline{X}}} \\ -\phi\frac{\sin\overline{X}}{\overline{\overline{X}}} & \cos\overline{X} + i\frac{\Gamma}{2}\frac{\sin\overline{X}}{\overline{\overline{X}}} \end{bmatrix} \begin{bmatrix} -\sin\phi \\ \cos\phi \end{bmatrix}$$

β is the angle between the polarization axis and the front LC director, Φ is the twist angle, $X = [\Phi^2 + (\Gamma/2)^2]^{1/2}$ and $\Gamma = 2\pi d \cdot \Delta n/\lambda$, where d is the liquid layer thickness, Δn the liquid crystal birefringence and λ light wavelength in vacuum.

The analytical solution of this equation has the form [27]:

$$R_{\perp} = \left(\Gamma \frac{\sin X}{x}\right)^2 \left(\sin 2\beta \cos X - \frac{\phi}{X} \cos 2\beta \sin X\right)^2$$

This solution allowed us to differentiate the orientation which have been promoted by silicon wafer surface. For twisted or planar homogenous orientation, during cell rotation the reflectance is function β. Once no reflectance modulation was observed for the cell with homeotropicaly oriented reference substrate it led to conclusion that the silicon plates promote homeotropic alignment. We have been able to obtain the unidirectional planar orientation through standard rubbing process of the silicon surface.

Conclusions

Thus, we have shown, that both homeotropic and planar alignment of liquid crystals can be obtained on modified silicon or silicon/silica wafer surface. It can be reached either by simple chemical bonding of both terminal and lateral low molecular mesogenic moieties or by subsequent rubbing process. On the other hand, the liquid crystalline polymer grown from Si/SiO_2 surface generated planar arrangement of side chain mesogens. The plot (Fig. 7) showing the growth of thickness of the polymer layer against time demonstrated, that once PMDETA was used as a ligand for Cu salts, at least 30 acrylate LC monomeric units were attached. Me_6-TREN ligand was less effective and it was found that only 20 monomeric units formed the nano-layer. To our best knowledge it is the first case of the ATRP process initiated from silicon surface, applied to a liquid crystalline monomer. This polymerization method offers an unique opportunity of generating uniform macromolecular chains, chemically linked to the surface and capable of transferring orientation onto low molecular liquid crystals. The results of orientation studies were independently confirmed by ellipsometric measurements. In all cases the detrmined thickness of monolayers corresponded, within an experimental error, to the most extended conformation of the respective liquid crystal moieties. The presented studies open up a new way of creation semiconductor – liquid crystal structures, in which photoinduced reorientation of liquid crystal layer can be controlled more efficiently, compared to previously described system [13].

Acknowledgments

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