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Orientational control of liquid crystal molecules by reformed poly(dimethylsiloxane) alignment layer via ion-beam irradiation

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Abstract

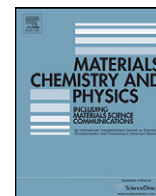
We introduce an alternative approach to making a reformed PDMS layer as a pretilt controllable alignment layer, which can be used in the vertical alignment (VA) and twisted nematic (TN) modes, by varying the ion beam (IB) energy. Depending on different the dielectric anisotropy of surfaces, PDMS layers have been demonstrated to align LC molecules homogeneously and homeotropically. The electro-optic characteristics of aligned VA and TN-LCD based on PDMS layer were comparable to those of VA and TN-LCD based on polyimide, showing good potential of PDMS film as an alignment layer.

Research highlights

► This paper introduces the fact that poly(dimethylsiloxane) alignment layers contain two liquid crystal molecular orientations, as follows: vertical orientation and homogeneous orientation via changing the intensity of ion-beam irradiation. ► We have demonstrated how an analysis of the proper ion beam intensity conditions for both alignment layers can be applied to two different LCD modes, the vertical alignment mode and twisted nematic mode. ► We show that IB irradiation on PDMS layers could be used to fit the different types of LCs, with control of the degree of chemical reformation by varying the IB energy. ► The mechanism of alignment for both cases would be depends on the dielectric anisotropy of the layer in which Si–C bonds are replaced by Si–O.

Keywords: Polydimethylsiloxane; Liquid crystal; Pretilt angle; Ion beam; Dielectric anisotropic

Article Outline



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ABSTRACT

We introduce an alternative approach to making a reformed PDMS layer as a pretilt controllable alignment layer, which can be used in the vertical alignment (VA) and twisted nematic (TN) modes, by varying the ion beam (IB) energy. Depending on different the dielectric anisotropy of surfaces, PDMS layers have been demonstrated to align LC molecules homogeneously and homeotropically. The electro-optic characteristics of aligned VA and TN-LCD based on PDMS layer were comparable to those of VA and TN-LCD based on polyimide, showing good potential of PDMS film as an alignment layer.

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1. Introduction

Modern liquid crystal display (LCD) technologies make strong demands for liquid crystal (LC) alignment: it should be highly uniform and stable, as well as possess very specific alignment parameters, such as controllability of the pretilt angles and electro optic (EO) characteristics [1]. These attributes would be highly desirable not only for future generations of displays, but also for current rapidly developing applications. Recently, inorganic materials have been studied intensively as an alternative alignment approach for various applications such as advanced LCDs, organic light emitting diodes (OLED), and flexible displays [2,3]. Additionally, numerous methods to achieve an intermediate pretilt angle, including mechanical rubbing [4], oblique deposition [5], ultraviolet alignment [6], plasma treatment [7], and IB bombardment [8], have been developed. However, despite the considerable effort that has been devoted to this, several technical challenges remain, such as stability, the high temperature process, the high cost of the manufacturing process, and problems with controlling the pretilt angle.

Polydimethylsiloxane (PDMS) materials are the most widely used silicon-based organic polymers, due to their primary advantages, which include ease of bonding, optical properties, insulator function, and low cost [9]. Here, we present an alternative approach to making a reformed PDMS layer as an alignment layer, which can

be used in two different kinds of alignment modes, by varying the ion beam energy without modifying the alignment material or changing the alignment process.

Numerous methods to obtain PDMS alignment layer have been proposed. Kim et al. proposed photoinduced silicon oxide film as a vertical alignment layer for VA mode LCDs [10]. Hwang et al. suggested PDMS thin layer for durable intermediated liquid crystal pretilt angles [11]. Although several methods have been shown potential for advanced LCD applications, the mechanism of orientational control of liquid crystal molecules by reformed poly(dimethylsiloxane) alignment layer is not entirely clear. In this paper, we suggest the possibilities reformed processes to make PDMS alignment layers, aligned both homogeneously and homeotropically, by controlling the intensity of IB irradiation used. Determining the suitability of a specific alignment requires taking into account various factors, such as the complex interactions between LC molecules and the molecular structure or dispersion and polar forces. We have demonstrated how an analysis of the proper ion beam intensity conditions for both alignment layers can be applied to two different LCD modes, the VA mode and twisted nematic TN mode. Furthermore, EO characteristics are presented to demonstrate the LC alignment property, as PDMS layers have generally suffered from making thin films, due to the high viscosity.

2. Experimental

As an alignment layer, we used Sylgard-184 poly(dimethylsiloxane) (PDMS; Dow Corning), and dichloromethane (Aldrich) and transparent substrates, such as a clean slide glass and ITO glass (1737 Corning glass substrate). PDMS was diluted with

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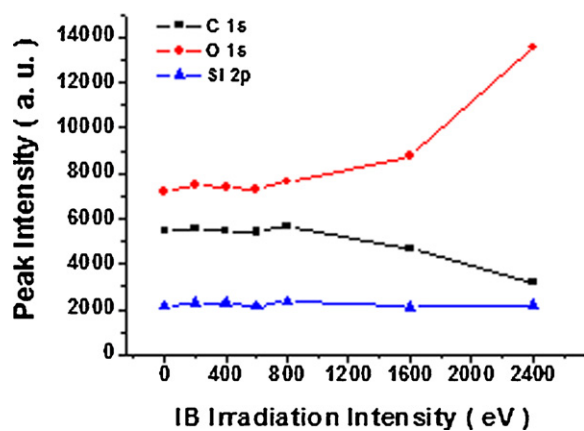


Fig. 1. Variation in the XPS spectra peak intensity of IB-irradiated PDMS surfaces as a function of IB intensity.

dichloromethane, which allowed the fabrication of membranes as thin as ~ 120 nm. The mixtures were coated on clean substrates using a spin coater at 6000 rpm for 60 s. The coated glass was then placed on a hot plate at 80°C for 60 min and then stored at room temperature for 4 h to remove any residual solvent.

After coating the polymer on the substrates, the 120-nm-thick films were irradiated for 60 s using a DuoPIGatron-type IB system. The working pressure of the IB irradiation chamber was approximately 0.1 m Torr, and the Ar gas flow rate was $1.1\text{ cm}^3\text{ min}^{-1}$ at standard temperature and pressure. To control the degree of reformation, the IB irradiation energy was changed by 200 eV, from 0 to 2800 eV.

Commercial LCs (Merck) with positive ($\Delta\epsilon = 2.1$) and negative ($\Delta\epsilon = -4$) dielectric anisotropy were used for LCD fabrication. The refractive indices in the ordinary axis and extraordinary axis were 1.4833, 1.5684 and 1.4742, 1.5512, respectively. The isotropic transition temperature was 75°C .

The ITO-coated glass substrates with PDMS on the ITO surfaces were assembled in an antiparallel configuration with a cell gap of $60\ \mu\text{m}$ to measure the pretilt angles, and the TN LCDs and VA LCDs were prepared with a cell gap of $5\ \mu\text{m}$ to examine the EO characteristics. The positive and negative LCs were then injected into the LCDs. For comparison purposes, TN LCDs and VA LCDs with homogeneous PI (SE 150) and homeotropic polymer (A JALS-696-R2) rubbed using a rubbing machine were fabricated, which were the favored conditions for stable LC alignment.

Each sample, irradiated by a different IB irradiation energy, was evaluated by X-ray photoelectron spectroscopy (XPS; ESCALAB 200i XL, VG Scientific Instruments). The measured binding referred to the C 1s signal at 284.4 eV, and then the composition of each sample was determined from a comparison of the normalized area intensities of C 1s peaks.

A real-time confocal microscope (MX50-CF, OLYMPUS, Japan) was used to examine the fabricated structures. Pretilt angles were measured by the crystal rotation method (TBA 107 tilt-bias angle evaluation device, Autronic). The V - T and R - T characteristics of the VPS LCDs were measured using a LCD evaluation system (LCD-700, Otsuka Electronics).

3. Results and discussion

The chemical formula of PDMS is $\text{CH}_3[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{Si}(\text{CH}_3)_3$, where the monomer units $[\text{Si}(\text{CH}_3)_2\text{O}]$ are repeated n times. We assume that PDMS is influenced by the IB irradiation, breaking the bonds of Si-CH₃, Si-O-Si, and the other polymer chain; it occurs as a co-reactant among silicon, the methyl group, and oxygen. After initially breaking the polymer chain Si-CH₃ by IB irradiation, there are anisotropic molecular interaction forces between LCs and the aligning layer. Irradiated PDMS monomolecular layers have been demonstrated to align LC molecules homogeneously and homeotropically, depending on the level of reformation among

Table 1
Binding energy and Si 2p proportion according to the number of oxygens.

		Si(-O) ₁ 101.5 eV	Si(-O) ₂ 102.1 eV	Si(-O) ₃ 102.8 eV	Si(-O) ₄ 103.4 eV
Proportion	None	35.17%	29.65%	19.48%	15.70%
of Si 2p	800 eV	33.68%	45.29%	11.41%	11.61%
peak (%)	2400 eV	16.72%	16.34%	32.45%	34.49%

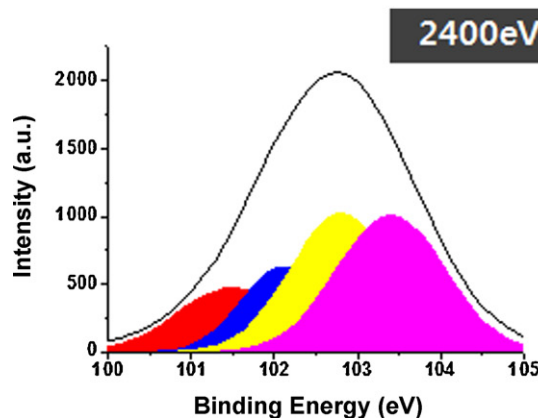
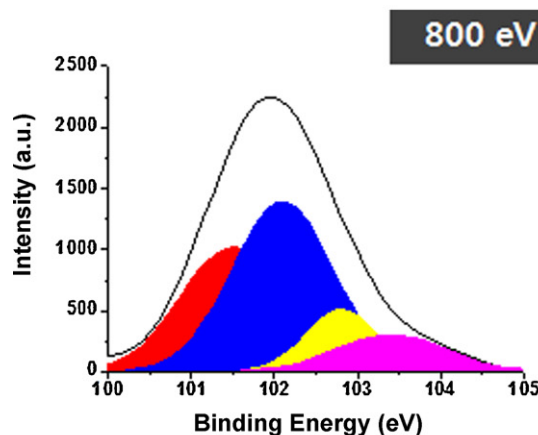
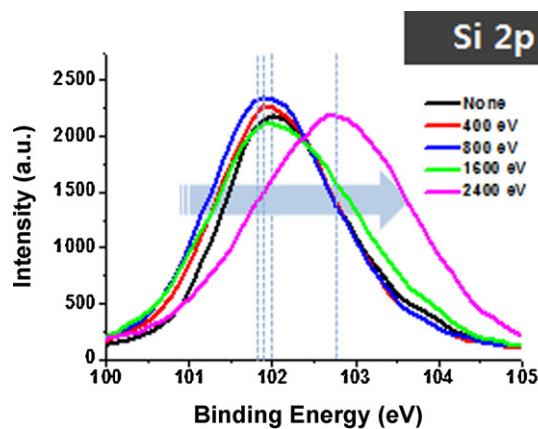


Fig. 2. Si 2p core level XPS spectra of the PDMS surfaces according to IB intensity.

co-reactants. The pretilt angles are controlled by the polarity of suitable functional groups introduced in the aligning molecules, as well by the effect of anisotropic chemical interactions. PDMS for LC with positive and negative dielectric anisotropy can be controlled by varying the chemical composition, through the use of IB irradiation.

Here, we describe a change in PDMS chemical composition, which could be available for the alignment of both dielectric LCs, depending on differences in the chemical composition. PDMS membranes analyzed by X-ray photoelectron spectrometry (XPS) of the C 1s, O 1s, and Si 2p core levels for verifying the changes in composition before and after IB irradiation are presented in Fig. 1. The full-width-at-half-maximum (FWHM) was kept below 1.6 eV to ensure accurate observations. The measured binding referred to the C 1s signal at 284.4 eV, and then the composition of each sample was determined from a comparison of the normalized area inten-

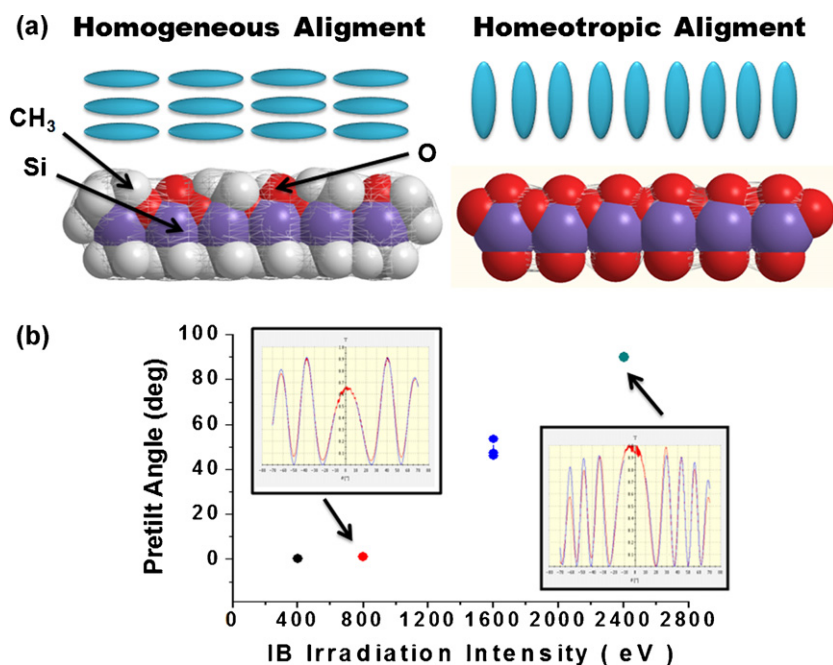


Fig. 3. (a) The LC alignment layer with positive and negative dielectric anisotropy on the IB-irradiated PDMS layers. (b) Pretilt angle of LC cell was measured with varying IB energy.

sities of C 1s peaks. As shown in Fig. 1, the intensity of the peak of C 1s decreased with increasing IB intensity. The major component, presented as C–Si in C 1s, changed slightly at IB intensities below 800 eV, but the position of the peak decreased at higher intensities of IB irradiation. On the other hand, the intensity of oxygen increased in O 1s with increasing IB intensity.

Applying IB irradiation to the PDMS layer increased the binding energy of the Si 2p peak by 0.887 eV as shown in Fig. 2(a). These changes in XPS spectra indicated the effect of IB irradiation on changing the complex chemical structure of the PDMS surface. The Si bonds in the main chain of PDMS are discussed in connection with investigating surface reformation, which affects the alignment layer direction. With increasing IB irradiation, there was a chemical shift of the Si 2p central axis to the right. Changing the silicon–oxygen composition was the most appropriate way for demonstrating alignment, by the Si 2p analysis.

The Si 2p peak was analyzed based on the supposition that there are only four component peaks within the Si 2p envelope, i.e., Si(–O)₁, Si(–O)₂, Si(–O)₃, and Si(–O)₄. The position of the Si 2p peak in PDMS (Si(–O)₂, BE = 102.1 eV) and quartz (Si(–O)₄, BE = 103.4 eV) were measured [12]. The other binding energies were estimated by assuming that the influence of introducing one oxygen is equal

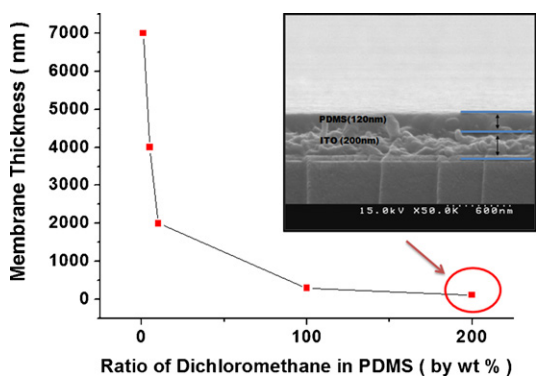


Fig. 4. Membrane thickness of PDMS according to the mixture ratio of dichloromethane.

to half the difference, as shown in Table 1 [13]. The evident difference in tendencies found in the Si 2p peak analysis is shown in Fig. 2. Silicon reformed with a different number of oxygens, according to increasing IB intensity. With an IB intensity of 800 eV, the

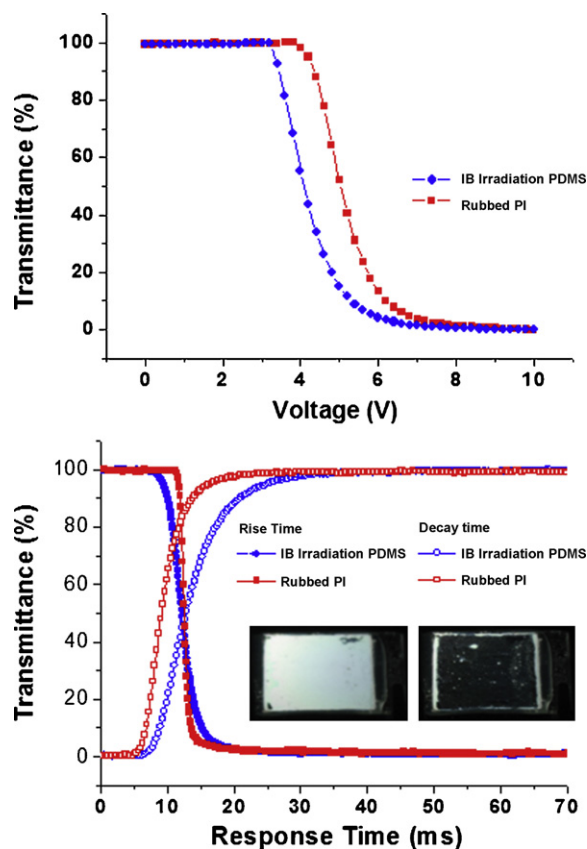


Fig. 5. V–T and R–T characteristics of the IB-irradiated TN-LCD using PDMS irradiated with an incident IB energy of 800 eV in comparison with rubbed PI. Photographs of symmetric LC cell ($d = 5 \mu\text{m}$) filled with positive LC, viewed between two crossed polarizers.

oxygen portions of Si were 35.17% Si(-O)₁, 45.29% Si(-O)₂, 11.41% Si(-O)₃, and 15.70% Si(-O)₄. With the breaking of the Si-CH₃ bonds, which are weaker than Si-O-Si bonds, by IB, the CH₃ was replaced by oxygen. This tendency comes into focus when increasing the IB intensity: at 2400 eV, the oxygen proportions of Si were 16.72% Si(-O)₁, 16.34% Si(-O)₂, 32.45% Si(-O)₃, and 34.49% Si(-O)₄.

These results indicate that the alignment comes into play when silicon has a certain number of oxygens that have polarity and anisotropy, depending on the bonding. Generally, many acceptable mechanisms have been proposed to explain the phenomenon of LC alignment, such as the surface chemical bonding mechanism including electron coupling, dipole-dipole interaction, and van der Waals forces. However, there are no electron couplings, because there are no electrons in PDMS layer. Mechanisms based on van der Waals forces and dipole-dipole interactions have been proposed for SiO_x films. According to a recent report, the single evaporation of SiO₂ can align LC homogeneously or homeotropically, depending on the dielectric anisotropy of the LC being positive or negative, respectively [5]. The van der Waals potential, taking into account the anisotropy of LC polarizabilities, has been used to explain the alignment mechanism.

Fig. 3(a) indicates that depending on the increasing number of covalent bonds with oxygen in the surrounding environment of silicon, the valence electron pair without sharing with silicon has an effect on the alignment due to polarity. At 800 eV, PDMS monomolecular layers have no orientation difference, but anisotropic properties come from the dielectric anisotropy. The induced dipole on the IB-irradiated PDMS layer is parallel to the substrate. However, when irradiated with an IB intensity of 2400 eV, most of the Si-CH₃ bonds break and co-react with Si-O; the effect of other isotropic chemical interactions can be considered to be independent of the angle between the direction of LC alignment, due to the stable symmetry. Strong van der Waals interactions between the silicon oxide layer and LC molecules induce a random planar alignment, and the weak interaction results in a vertical alignment, because of the maximization of the molecular interaction between LC molecules [10]. Fig. 3(b) demonstrates that the IB intensity leads to control of the pretilt angle of the LC cell. The described pretilt angle trend was confirmed for a number of oxygens having polarity.

IB-irradiated PDMS layers were fabricated by varying the IB energy with positive and negative dielectric LCs. The PDMS layer and LC molecules induced a random planar alignment that was affected by IB irradiation. When IB-irradiated at 800 eV, the LC cells showed uniform alignment with positive homogeneous LC. However, when IB-irradiated at 2400 eV, the LC molecules aligned homeotropically with negative dielectric LC, whereas positive dielectric LC molecules were not aligned uniformly.

We investigated the EO characteristic of two kinds of modes, the TN-LCD cell and the VA-LCD cell, with one kind of material layer, with varying irradiation intensity. To achieve an extremely thin and sensitive PDMS layer, such as is widely used in PI film, PDMS was diluted with dichloromethane (Aldrich) by varying the proportion and mixed curing agent ratio from 10:1. By increasing the mixture ratio of dichloromethane, the membrane thickness of PDMS declined rapidly (Fig. 4). It is critical to make a thin layer for it to be used as the LC alignment layer, but this is difficult due to the high viscosity. Dichloromethane was used as a solvent which is not affected to chemical structure. When dichloromethane was mixed with PDMS at 100 wt.%, the membrane thickness was 120 nm.

The TN LCDs and VA LCDs were prepared with a cell gap of 5 μm to examine the EO characteristics. The positive and negative

LCs were then injected into the LCDs. Fig. 5 depicts the EO characteristics of TN-LCD cells with homogeneous LC, produced by IB irradiation of PDMS layers at 800 eV for 1 min; the performance of rubbed PI was used for comparison. Generally, organic materials have a lower dielectric constant. The Si-CH₃ group in the film has a lower dielectric constant due to the organic group [14]. However, as shown in the PDMS chemical structure, the Si-CH₃ bonds were broken and the CH₃ was replaced by oxygen. We assume that the capacitance of IB-irradiated PDMS membranes was improved by decreasing the portion of CH₃ in the monomer unit. The V-T characteristics of IB-irradiated PDMS are depicted in Fig. 5(a). The threshold voltage of the TN-LCD cells using a PDMS layer was measured at 4.093 V, whereas the PI showed 5.036 V. Despite a lower dielectric constant than that of PI, PDMS holds potential for operating at lower external voltages, with lower power consumption. As illustrated in Fig. 5(b), the PDMS thin film showed good performance in response time, with a rise time of 5.153 ms and decay time of 11.929 ms, whereas the rubbed PI had a rise time of 1.8 ms and decay time of 7.0 ms.

The PDMS layer IB-irradiated at 2400 eV for 1 min exhibited homeotropic alignment. Compared with the rubbed PI, the results were similar. The rubbed PI and PDMS films had a low threshold voltage; IB-irradiated PDMS had a lower threshold voltage (2.673 V) than that of PI (3.1 V).

4. Conclusions

In conclusion, our results demonstrate the high potential of PDMS as an alternative alignment layer and treatment. We found experimentally that IB irradiation on PDMS layers could be used to fit the different types of LCs, with control of the degree of chemical reformation by varying the IB energy. The mechanism of alignment for both cases would be depends on the dielectric anisotropy of the alignment layer in which Si-C bonds are replaced by Si-O. The use of IB-irradiated PDMS alignment layers has the advantage of a non-contact alignment process without a high temperature process, and can allow for control of the pretilt angle.

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