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Ion beam-induced topographical and chemical modification on the poly(styrene-co-allyl alcohol) and its effect on the molecular interaction between the modified surface and liquid crystals

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ABSTRACT

We demonstrated uniform liquid crystal (LC) alignment on ion beam (IB)-irradiated poly(styrene-co-allyl alcohol) by modifying the chemical bonding on the surface. An IB-irradiated copolymer was used for the alignment layer. We used physico-chemical analysis to determine the IB-irradiated surface modification and LC alignment mechanism on the surface. During IB treatment on poly(styrene-co-allyl alcohol), IB irradiation induces breaking of chemical bonds on the surface to give rise to new bonds with oxygen atoms. This causes a strong Van der Waals interaction between LCs and the modified surface, thereby resulting in uniform LC alignment. The results of contact angle (CA) studies of the copolymer support the chemical bonding changes that were investigated by XPS. We achieved uniform homogeneous LC alignment and obtained stable electro-optical performance by controlling the IB energy. Therefore, the LC cells with IB-irradiated poly(styrene-co-allyl alcohol) exhibited a good potential for alternative alignment of layers in LC applications.

1. Introduction

Surface modification is one of the most important academic fields in materials engineering, irrespective of the polymer or inorganic materials. Among the surface modification methods, plasma treatment including ion beam (IB) irradiation has a distinct ability to initiate ions to react with the surface without a catalyst or heat [1–6]. For several decades, much of the research on surface modification via plasma treatment has been performed to improve their adhesion or wettability to improve layer interactions in new multi-layered electronics [7–11]. This is important because when tuning the surface functionality, the interactions between adjacent layers can be improved, thereby yielding better performance in their applications. Recently, plasma treatment of the surface has been studied to satisfy the need for enhancing the performance of their applications, despite their excellent intrinsic characteristics. Recently, the application areas have been widened to include applications such as controllable nano/micro patterning [11–13], tissue engineering [14], and liquid crystal (LC) alignment [15].

LC alignment is one of the important core technologies in LC applications. A rubbing treatment of the surface has been conventionally used to align LCs uni-directionally. However, since the method leads to a local defect, generation of debris, and electro-charge accumulation, an alternative alignment method is necessary for advanced LC applications [16,17]. To obtain stable LC alignment, interaction between LCs and the surface is most important. The IB method, a type of plasma treatment, allows for reactive ions to penetrate through the surface to change the surface properties [13,17,18]. The modified surface characteristics of the materials could then be expected to satisfy the interactions between LCs and the surface. Moreover, it has been demonstrated that the wettability of materials can be controlled by tuning the functionality of

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the surface via the IB method [19]. Since hydrophilic films exhibited a stable homogeneous alignment state at the LC alignment, the control of wettability via IB irradiation is expected to allow the LCs to stably align on the modified surface [20].

In our group, various kinds of organic and inorganic materials have been examined for use in LC alignment films using IB irradiation method. When the PDMS was exposed by IB irradiation, a wrinkle structure was formed on the surface. We construct the wrinkled wall by local IB irradiation, which used as a director aligning LC molecules [21]. Metal oxide materials of GaO [22], ZnO [23], SnO [24], and LaO [25], which are characterized by high dielectric constant, exhibited excellent electro-optical performances including fast response time and reduced threshold voltage. Recently, doping those materials with Hafnium, Zinc and Yttrium atom, has been examined. HfO doped with Yttrium oxide exhibited fast response characteristics which is results from the addition of Yttrium atoms increasing the dielectric constant of the materials [26]. HfSnO exhibited hysteresis free characteristics because strong IB irradiation reformed the surface inducing the release of residual charges effectively upon switching of the LC molecules [27]. Although metal oxide exhibited various and excellent electro-optical performances, it need high annealing temperature because solvent remained under low annealing temperature. In contrast, polymer could be deposited at low annealing temperature due to their low melting point. Previously, poly(vinylidene fluoride-trifluoroethylene) has been researched as an LC alignment layer, which could be deposited at 135 °C which is lower than those of conventionally used polyimide which annealed above 180 °C [28]. Although a substantial amount of research has been conducted alignment layers, much more research is needed to improve the LC alignment characteristics and LCD performance.

In this study, we demonstrated uniform LC alignment on IB-irradiated poly(styrene-co-allyl alcohol) by modifying the chemical bonding on the surface, where poly(styrene-co-allyl alcohol) was used as an alignment layer. The copolymer is composed of two kinds of polymers, styrene and allyl alcohol; hence, it has hydrophobic properties from the phenyl ring of styrene and hydrophilic properties from the hydroxyl groups of allyl alcohol. The material has been used as a template for an organic/inorganic composites due to the surfactant characteristics [29]. In addition, poly(styrene-co-allyl alcohol) has low glass transition temperature of 62 °C, which indicates that the material could be deposited at low annealing temperature. IB irradiation was used for the alignment method. It has been demonstrated that IB irradiation modifies the surface chemically and topographically. The ability to control the functionality is desirable for interactions between adjacent materials, such as those between LC molecules and the surface; hence, IB irradiation could be a desirable method for LC alignment. We used physico-chemical analysis to determine the surface modification resulting from IB irradiation and the LC alignment mechanism on the modified surface. Using a IB-irradiated poly(styrene-co-allyl alcohol) as an alignment layer, we achieved uniform homogeneous LC alignment and stable electro-optical performance by controlling the IB energy.

2. Experimental

2.1. Preparation of poly(styrene-co-allyl alcohol) via solution process

Poly(styrene-co-allyl alcohol) was purchased from Sigma-Aldrich. The number average molecular weight (Mn) ~1,200, the weight average molecular weight (Mw) ~2,200, and polydispersity index was ~1.83 which is used as a measure of the breadth of the molecular weight distribution. polydispersity index is defined by weight average molecular weight (Mw) divided by the number average molecular weight (Mn). The composition ratio of styrene unit and allyl alcohol unit were 60 mol% and 40 mol%. 10 w% of poly(styrene-co-allyl alcohol) was dissolved in 2-methoxyethanol (2ME) with acetic acid and mono-ethanolamine (MEA) to increase the stability of the solution. The solution was stirred for 2 h at 75 °C and aged for 1 day. The prepared solution was spin-coated onto ITO glass at a spin rate of 3000 rpm for 30 s. The coated substrate was annealed at 100 °C for 1 h on a hot plate.

2.2. Surface modification of poly(styrene-co-allyl alcohol) via ion beam irradiation

A Duo PI Gatron IB system was used for IB irradiation. The poly(styrene-co-allyl alcohol) film on the substrate was exposed to Ar^+ IB plasma at different IB energies of 600, 1200, 1800, and 2400 eV with a current density of 1.1 mA cm^{-2} for 2 min at incidence angle of 45°.

2.3. Topographical and chemical modification analysis

Atomic force microscopy (AFM; Park Systems, XE-BIO) and X-ray photoelectron spectroscopy ((ES-CALAB 220i-XL, VG Scientific) were used for measuring the physico-chemical properties of the surface of the poly(styrene-co-allyl alcohol) films. Contact angle (CA) measurements of the poly(styrene-co-allyl alcohol) films were conducted using a Phoenix 300 surface angle analyzer (SEO) and were further analyzed using IMAGE PRO 300 software.

2.4. Evaluation of liquid crystal alignment state and electro-optical performance in TN mode

The LC cells were fabricated based on the IB-treated poly(styrene-co-allyl alcohol). To evaluate the alignment state, the oscillation of the transmittance was measured by rotating the LC cell via TBA 107 (Autronic) which could calculate pretilt angle of the LC cell from the oscillation of the transmittance, and polarized microscopy (POM) images were observed via BXP 51 (Olympus). The LC cells for alignment state evaluation were fabricated in an anti-parallel configuration with a cell gap of 60 μm and filled with a positive LC (MJ001929, $n_e = 1.5859$, $n_o = 1.4872$, and $\Delta\varepsilon = 8.2$; Merck). The electro-optical properties including transmittance vs response time and transmittance vs applied voltage was measured via LCD evaluation system (LCD-700; Otsuka Electronics) using twisted nematic (TN) mode cells with a 4.25 μm cell gap.

3. Results & discussion

Fig. 1 shows POM images and the pretilt angle of the LC cells made by IB-irradiated poly(styrene-co-allyl alcohol) (referred to as copolymer herein) as an alignment layer, both of which can evaluate LC alignment properties. Before IB irradiation, the POM images exhibited locally different transmittances (Fig. 1(a)). This indicates that the LC molecules were not uni-directionally anchored on the copolymer, and a poorly aligned LC cell was obtained on this copolymer. The IB-irradiated LC cells exhibited a homogeneous alignment state regardless of the IB irradiation energy. This result is also confirmed from the pretilt angle calculation. A pretilt angle on the LC cells with a non-treated copolymer was not obtained, but the pretilt angle of IB-irradiated LC cells is displayed in Fig. 1(f). The average pretilt angles of LC cells calculated by the crystal rotation method were 0.67° (at 600 eV), 0.35° (at 1200 eV), 0.27° (at 1800 eV), and 0.32° (at 2400 eV). These pretilt angles show little difference between these conditions. The deviations in the pretilt angles were 0.22, 0.19, 0.11, and 0.04 with energies of 600, 1200,