Homogeneous alignment of liquid crystals on low-temperature solution-derived gallium oxide films via IB irradiation method

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ABSTRACT

In this paper, solution-derived gallium oxide (GaO) films are fabricated for the homogeneous alignment of liquid crystals (LCs) after an ion-beam (IB) irradiation process. GaO thin films are prepared under a variety of temperatures and different IB irradiation intensities, and the physicochemical performances of the fabricated GaO thin films are analysed using a UV-vis spectrometer, an atomic force microscope, and X-ray photoelectron spectroscopy. A higher transmittance of 85.40% from GaO thin film is obtained compared with that of polyimide (PI) film (83.52%), which indicates the feasibility for a GaO thin layer to substitute for a conventional PI layer as an alignment layer. LCs are found to align on the GaO thin film after pre-baking at 100°C and homogeneous and uniform low-IB intensity irradiation. We also determined the electrooptical (EO) characteristics of the twisted nematic (TN) cells fabricated with GaO thin layers and found them to be similar to those of cells fabricated with PI layers. Overall, GaO films achieved via the IB irradiation method are promising LC alignment layers due to the method’s low-temperature solution-derived process.

1. Introduction

Currently, the uniform liquid crystal (LC) alignment technique is essential for fabrication of commercialised high-performance LC displays (LCDs). The conventional rubbing alignment method is widely applied in the LCD industry for its advantages of low cost and mass production. However, the rubbing method has significant disadvantages such as accumulation of electrostatic charge and formation of fine dust due to the contacting technique. Recently, the non-contact aligning of LCs has drawn attention due to its advantages of no debris generation, free from electrostatic discharge, and no streaking, which are extremely serious problems of a commercialised polyimide (PI) alignment layer after rubbing. Strategies to overcome the weaknesses of the rubbing method have included the ultraviolet (UV) photoalignment technique, oblique deposition, nanoimprint lithography, and ion-beam (IB) irradiation. Among these, collimated IB irradiation is a promising non-contact alignment method that uses Ar+ ion-induced plasma to furnish controllability in the manufacture of high-resolution displays in an uninterrupted process. In addition, the IB technique can induce a unidirectional orientation of LC
molecules on both organic and inorganic materials. Due to these merits, the IB technique has been intensively investigated with optically transparent insulating inorganic materials, such as diamond-like carbon, [19,23] SnO\textsubscript{2},[21] SiO\textsubscript{x},[24] SiN\textsubscript{x},[25] and Ta\textsubscript{2}O\textsubscript{5},[26] as well as a variety of organic PI materials.[27] Conventional deposition methods to prepare inorganic thin films, such as sputtering, spraying and chemical vapour deposition (CVD), require high power and extreme vacuum environments. Compared with conventional techniques, the solution-derived method has desirable characteristics of saving energy,[28,29] coating large surfaces, applicability to complex forms and simple operation.[30] Gallium oxide (GaO) is a kind of transparent conductive oxide that demonstrates catalytic properties and has been used for lasers, phosphors, luminescent materials and insulating barriers in tight junctions. GaO has five modifications, \(\alpha, \beta, \delta, \gamma,\) and \(\varepsilon\), among which \(\beta\)-Ga\textsubscript{2}O\textsubscript{3} is the most stable. Generally, GaO is fabricated using a high-temperature annealing method. In this study, a solution-derived GaO alignment layer with adjustment of the annealing temperature and individual IB irradiation intensities is proposed. The peak shifts and bonding energy transitions of the IB-irradiated GaO films indicated the formation of a GaO thin layer, and the morphology of the obtained GaO thin layers was characterised using atomic force microscope (AFM). Furthermore, the alignment performance of LCs on IB-irradiated GaO thin layers was evaluated, and the electro-optical (EO) properties of a GaO thin layer-based alignment layer cell were compared with those of a conventional rubbed PI layer-based alignment layer cell in twist nematic (TN) mode.

2. Experiment

First, a 0.5 mol L\(^{-1}\) GaO solution was prepared by mixing Gallium (III) nitrate hydrate 99.9\% (Ga(N\textsubscript{3}O\textsubscript{3})\textsubscript{3} H\textsubscript{2}O) in 10 mL 2-methoxyethanol (2ME). Several drops of monoethanolamine (MEA) and acetic acid (AA) were added drop-wise to this mixture in order to achieve a stable and homogeneous GaO solution. The molar ratio of MEA and AA was maintained at 1:1. Then, the solution was stirred at 70°C for 2 h using a hotplate magnetic stirrer and was aged at room temperature for at least 1 day. ITO-glass substrates (Samsung Corning 1737: standard 32 \(\times\) 22 \(\times\) 1.1 mm\(^2\), sheet resistance 10 \(\Omega/cm\)) were ultrasonically cleaned with acetone, methanol and deionised water for 10 min each and then dried with \(\text{N}_2\) gas. The GaO solution was spin-coated onto the clean ITO-glass at 3000 rpm for 1 min. The GaO-coated substrates were then preheated at 100°C for 10 min to remove any residual solvent. The resulting thin films were annealed at 100°C, 200°C, 300°C, 400°C or 500°C in a furnace for 1 h. The GaO films were exposed to Ar\textsuperscript{+} IB plasma (\(10^4\)–\(10^5\) ions/cm\(^2\)) at an IB current of 1.6–4.9 mA cm\(^{-2}\) at an energy of 600, 1200, 1800 or 2400 eV for 3 min at an incident angle of 45° using a DuopIGatron-type IB system.[27] The empty cells were fabricated with a pair of the substrates mounted anti-parallel or perpendicular to each other with cell gaps of 60 and 5 \(\mu\)m, respectively. The dielectric nematic LC (\(n_e = 1.5702, n_n = 1.4756,\) and \(\Delta n = 0.7;\) Merck, Darmstadt, Germany) was injected into empty cells in the isotropic state by capillary force. The optical images of the anti-parallel LC cells were obtained using a polarised optical microscope (BXP 51; Olympus, Tokyo, Japan). The pre-tilt angle of the LC cells was measured using the crystal rotation method at room temperature (TBA 107, Auotronic, Karlsruhe, Germany). The transmittance of the GaO films was determined using a UV/VIS spectrophotometer (V-650, JASCO Corporation, Tokyo, Japan). Physicochemical transitions of the GaO films before and after IB irradiation were characterised using an AFM (XE-Bio, Park Systems, Santa Clara, CA, USA) and X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific, West Palm Beach, FL, USA). Finally, the EO characteristics of the TN-cell were evaluated using an LCD evaluation system (LCMS-200, Sesim Photonics Technology, Uiwang, Korea).

3. Results and discussion

Transparency is one of the most crucial factors for the application of inorganic films in LCD devices. Therefore, the transmittance of GaO films deposited on ITO-coated glass substrate was evaluated at room temperature using a UV/VIS spectrophotometer. As shown in Figure 1, in the visible light region (420–780 nm), the average transmittance of the GaO films annealed at 100°C, 200°C, 300°C, 400°C or 500°C was 85.40%, 84.31%, 81.97%, 82.81% and 82.66%, respectively, which is similar to the values for as-prepared ITO-glass and PI-coated ITO glass with transmittances of 83.23% and 83.52%, respectively. Therefore, GaO films have the potential to be applied as the key transparent component in high-transparency devices.[31,32] After 1800 eV IB irradiation, the LC alignment performance on the IB-irradiated GaO thin layer was evaluated using POM. Photomicrographs of anti-parallel cells composed of GaO films produced at various annealing temperatures are shown in Figure 2. For annealing temperatures above 200°C, random
alignment was observed. However, uniform and homogeneous LC alignment was observed for annealing temperature of 100°C. Consequently, we conducted a study of the GaO layers annealed at 100°C and irradiated with IB of various intensities.

Figure 3(a) presents photomicrographs of the LCs in the anti-parallel cells prepared with GaO layers annealed at 100°C and irradiated with IB of various intensities with an incident angle of 45° for 3 minutes. While random LC alignment was observed on the non-IB-irradiated GaO film as shown in Figure S1, uniformly aligned LCs were observed on the surfaces of the IB-irradiated GaO films regardless of the intensity of IB energy. Partially distinguishable line defects were observed in the POM images; however, these defects were invisible to the naked eye. Even though the IB irradiation of low intensity, the increased anisotropy of the GaO films by IB irradiation induced uniform LC alignment. At an annealing temperature of 100°C, residual solvent remained in the solution-derived GaO films; however, the residual solvent did not affect the IB irradiation-induced alignment of the LCs. This result indicates that IB irradiation is a powerful technique for achieving uniform LC alignment. Every level of irradiation energy was sufficient to align LCs, and the photographic images appeared to be uniform, confirming that the LC molecules on the GaO surface were aligned parallel to the IB exposure direction. The average pre-tilt angle of the GaO films irradiated with IB at 600, 1200, 1800 or 2400 eV was measured as 0.0726°, 0.0775°, 0.1509° and 0.0153°, respectively, as shown in Figure 3(b).

Physicochemical analyses were used to determine the mechanism of alignment of the LC molecules, including XPS and AFM, because the alignment of the LCs depends on both the chemical nature and the topography of the surface. The XPS spectra of C1s, O1s and Ga2p peaks obtained from the surfaces of the films produced by annealing at 100°C before and after IB irradiation are presented in Figure 4. Following the transformation of the solution-derived GaO films as a function of the intensity of IB energy, the change in C1s peak was monitored. The binding energy of the C1s signal is referenced at 284.6 eV. The C1s signal indicates the hydrocarbons adsorbed.
on the film surface due to air exposure during transfer from the growth chamber to the XPS instrument.[33] Thus, as the intensity of IB energy increases, the C1s peak intensity decreases correspondingly.

When the IB irradiation intensity was increased to 1800 eV, the peak of O1s branched into two peaks located at 531.0 and 532.4 eV. This result indicates that the binding energy value of the top peak gradually increased as the Ga–O bond increased. The peak is located at about 20.2 eV, indicating the mixed-oxide state of Ga with GaIII (3d) and Ga° (3d) photoelectron lines. A significant increase in the intensity of this peak was observed, revealing that, with IB irradiation, the oxidation of Ga increased and induced a redistribution of electrons around the constituent atoms of the GaO crystal.[34] In addition, the binding energy of Ga3d increased after IB irradiation, which indicates that, as the Ga2p–O and Ga3d–O bonds on the GaO films are increased by IB irradiation, the atomic ratio of oxygen in the IB-irradiated GaO films is slightly increased. The uniform LC alignment on the IB-irradiated GaO films was attributed to van der Waals interactions between the LC molecules and the GaO films due to these anisotropic characteristics. The van der Waals interactions between the LC molecules and the Ga2p and Ga3d increased to core levels that were sufficient for maintaining a strong balance in the LC molecule interactions, thereby leading to a homogeneous alignment of LC molecules. Differences in chemical bonding of GaO films formed at low temperature are due to IB irradiation effects,[33] through which a reconstructed stable chemical structure was formed.

The morphology analysis of the GaO thin layers using AFM before and after IB irradiation is presented in Figure 5. IB irradiation did not strongly affect the roughness of the GaO film, and crystalline amorphous film surface was not formed when the annealing temperature was less than 500°C.[33] The root mean square (RMS) roughness values of the non-IB-irradiated and the IB-irradiated GaO films annealed at 100°C were 0.719 and 0.658 nm, respectively. These results suggest that the LC alignment was less affected by the morphologies of the IB-irradiated films.

The EO characteristics were determined to be appropriate for pragmatic LCD applications, and the voltage–transmittance (V–T) and response time (R–T) curves are shown in Figure 6. The EO properties of the rubbed PI alignment cell under the same conditions were compared with those of GaO film cells IB-irradiated at various intensities. As shown in Figure 6(a), the threshold voltages of the TN cells fabricated with 600, 1200, 1800 or 2400 eV IB-irradiated GaO films and a rubbed PI layer were 1.578, 1.661, 2.124, 1.580 and 2.010 V,[36] respectively. The

Figure 3. (a) Photomicrographs of anti-parallel cells with IB-irradiated GaO films at an incident angle of 45°, an incident energy of 1800 eV, and an irradiation time of 3 min as a function of IB-irradiation energy densities. 'A' indicates analyser, and 'P' indicates polariser. (b) The pre-tilt angle of LC molecules on IB-irradiated GaO films as a function of IB-irradiation energy density.
cell based on the 600 eV IB-irradiated GaO thin layer showed higher performance than the cell based on the rubbed PI layer. The superior response performance of the cell based on the 600 eV IB-irradiated GaO thin layer was achieved with an RT of 3.185 ms and an FT of 5.882 ms, which is much shorter than the cells based on the 1200 eV IB-irradiated GaO layer (RT of 3.350 ms and FT of 6.218 ms), the

**Figure 4.** XPS spectra of the (a) C1s peaks non-IB-irradiated, 600 eV and 1800 eV. (b) O1s peaks non-IB-irradiated, 600 and 1800 eV. (c) Ga2p1/3 peaks non-IB-irradiated, 600 and 1800 eV.

**Figure 5.** AFM 3D images of (a) non-IB-irradiated and (b) IB-irradiated GaO films annealed at $T = 100^\circ$C.
1800 eV IB-irradiated GaO layer (RT of 3.274 ms and FT of 6.906 ms), and the 2400 eV IB-irradiated GaO layer (RT of 6.358 ms and FT of 8.627 ms). The rubbed PI layer-based cell had an RT of 2.433 ms, an FT of 10.948 and a total response time of 13.381 ms, which is much longer than that for the cell based on the 600 eV IB-irradiated GaO thin layer (9.067 ms). The super-fast response of the LCs on the IB-irradiated GaO thin layer might be due to its high dielectric constants: the GaO thin layer has dielectric constants in the range of 9.9–10.2, while the PI has much smaller dielectric constants in the range of 2.7–3.4.[37,38] Therefore, GaO films show the potential to be used for advanced LC applications, especially for fast-response LCDs.

4. Conclusions

In summary, we investigated a super alignment layer candidate based on a low-temperature-annealed GaO thin layer for commercial LCDs fabrication via an IB-irradiation process. A GaO thin layer annealed at 100°C and 600 eV IB-irradiated showed homogeneous alignment of LCs. The change in average transmittance of the GaO films as a function of annealing temperature was negligible. XPS analysis of the GaO films indicated that IB irradiation changed the chemistry structure of the thin layer with changing intensities of the Ga2p, Ga3d, and O1s peaks. LC alignment on the GaO surfaces was due to the formation of Ga–O bonds and the modification of GaO surfaces by the increase in Ga–O bonds as a result of IB irradiation. In addition, the threshold voltages of the TN cells with varied intensity of IB-irradiated GaO films were compared with those of the rubbed PI layers, showing superior EO characteristics for the GaO film-based cell, which is faster than the rubbed PI-based cell. Particularly, the orientation of GaO films at low temperature is suitable for advanced LCD applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

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