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Liquid Crystals

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Liquid crystal alignment on a ZrO₂ thin film as a function of ion beam incident angle

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Nematic liquid crystal alignment capabilities and electro-optical performance characteristics have first been embodied in a ZrO_2 layer using ion-beam irradiation. The study demonstrates that liquid crystal layers can be aligned homogeneously as a function of the incident angle of the ion beam device, which causes a uniform dense plasma. X-ray photoelectron spectroscopy indicated that full oxidation of the ZrO_2 thin-film surfaces was produced by ion irradiation, shifting the Zr 3d spectra to lower binding energies. In addition, the electro-optical performance characteristics of twisted nematic cells on a ZrO_2 thin-film layer after ion beam irradiation showed similar characteristics to those of a rubbed polyimide cell.

Keywords: zirconium oxide; ion beam irradiation; liquid crystal alignment; XPS analysis

1. Introduction

In recent years liquid crystal displays (LCDs) have become an important feature of the rapidly evolving field of information display devices. LCDs are widely employed in notebook computers, personal computer monitors, television screens and similar devices. Alignment of the liquid crystal (LC) without disclination lines is very important in LCDs. Alignment of a nematic liquid crystal (NLC) using the rubbing process produces a number of problems, including electrostatic discharge, formation of debris, and difficulty in achieving a multi-domain structure [1-5]. Non-contact alignment methods are therefore highly desirable. A number of alternative alignment techniques have been developed, including ultraviolet exposure [6], oblique deposition [7, 8] and nanoimprint lithography [9], and these have attracted attention both in industry and in research organisations [10, 11]. As an alternative to these, ion beam irradiation is a preferred option since it is easy to change the alignment properties by controlling the ion beam (IB) irradiation time, incident angle and energy, and since it is a non-contact method it is free from dust generation and contamination [12, 13]. In addition, the use of thin inorganic films as an LC alignment layer is a promising new concept in LCD process technology. A great variety of optically transparent and insulating films have been developed, including diamond-like carbon, with or without nitrogen doping, SiOx, SiNx and Ta₂O₅ [14, 15].

Among many other potential inorganic materials, in the present study we have selected for study the electron-beam evaporation layer-controlled deposition of thin ZrO_2 films in the alignment of LC layers, on account of its high dielectric constant, relatively low leakage current, and large band gap [16, 17]. In the study, we have considered the orientational characteristics of LCs on surface-modulated ZrO_2 caused by IB irradiation, and also the spectra of the ZrO_2 in relation to the irradiation energy of the IB. These have been analysed by X-ray photo-electron spectroscopy (XPS) in order to determine the mechanism of the LC alignment. Moreover, the electro-optical (EO) characteristics exhibited were compared with those of rubbed polyimide (PI).

2. Experimental

The ZrO_2 thin-film layers were deposited on indium tin oxide (ITO)-coated Corning 1737 glass substrates by electron-beam evaporation, at an average deposition rate of 2 Å s⁻¹ at room temperature. A stepper motor that rotated the substrate during film deposition was used to drive the substrate holder. Before deposition, the ITO-coated glass was cleaned using a supersonic wave in a trichloroethyl-acetone/methanol/deionised water solution for 10 min and then dried under nitrogen. The 10 Å ZrO_2 thin films, measured using a surface profiler alpha step and a field emission-scanning electron microscope, were exposed to IB radiation using a DuoPIGatron Type IB system at incident angles ranging from 15° to 75° at increments of 15° for 1 min, and at an exposure energy of 1.8 keV. The IB chamber was initially evacuated to a base pressure of about 10⁻⁶ Torr, and the working pressure was maintained at 10^{-4} Torr with an argon (Ar) gas

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flow of 1.4 cm³ min⁻¹ (SCCM). The dosages of Ar⁺ IB plasma were 10^{14} – 10^{15} ions cm⁻² energy. The ITOcoated glass substrates with the ZrO₂ layers on the ITO surface were assembled in an antiparallel configuration with a cell gap of 60 µm, in order to measure the tilt angles using the crystal rotation method (107 tilt–bias angle evaluation device; Autronic). The LCDs were assembled with a cell gap of 5 µm in order to examine the EO characteristics. Commercial negative LCs ($T_c = 75^{\circ}$ C, $\Delta \varepsilon = 8.2$; MJ001929, Merck Corp.) were used for fabricating the LCDs.

3. Results and discussion

Figure 1 shows images of twisted nematic cells between crossed polarisers, with and without IB irradiation. Without IB irradiation, non-uniform alignment and disclination lines can be observed. On the other hand, with the IB irradiation as a function of the incident angle, we can achieve uniformity between crossed polarisers for LC alignment at an IB intensity of 1800 eV and an incident time of 1min.

The pretilt angle of the LC molecules on the ZrO_2 is shown in Figure 2 as a function of incident angle under similar experimental conditions. The resultant contour was built up at a low range of angles between 0.6° and 0.9° , and demonstrated the possibility of a controllable pretilt angle, including adaptability to LC modes at a low pretilt angle, such as an in-plane switching mode.

To explain the mechanism governing LC orientation on IB-irradiated surfaces, XPS spectra for Zr 3d and the O 1s peak were determined at the surfaces. The binding energies with reference to the neutral



Figure 2. Pretilt angles on the IB-irradiated ZrO_2 as a function of the incident angle of IB at an IB energy of 1800 eV and exposure time of 1 min.

adventitious C 1s peak, defined at 285.0 eV, are shown in Figure 3 [18]. As seen in Figure 3(a), the Zr 3d peaks before IB irradiation were centred around 182.5 and 184.8 eV. IB irradiation of 1800 eV shifted the Zr 3d peaks to lower energy levels, namely 181.3 eV and 183.8 eV.

The binding energy of the oxygen deficiency was higher than that for the fully oxidized oxide (Zr^{4+}). This result indicated that the ZrO_2 had been converted to $ZrO_{x<2}$ by the IB irradiation [19].

As seen in Figure 3(b), the XPS spectra for the O 1s peaks resolved into two components, and the full width at half maximum value of the O 1s bonds was 1.5 eV. The low binding energy component at 529.5 \pm 0.5 eV corresponds to an O–Zr peak and



Figure 1. Photomicrographs of twisted nematic LCD cells on ZrO_2 surfaces, (a) before IB irradiation, and irradiated with incident IB angle at (b) 15°, (c) 30°, (d) 45°, (e) 60° and (f) 75°. Note: A: analyser, P: polariser. (colour version online.)



Figure 3. XPS spectra for peaks (a) Zr 3d and (b) O 1s, before and after IB irradiation of ZrO_2 at 1800 eV energy and 45° incident angle (colour version online).

the high binding energy peak located at 534.5 \pm 0.5 eV is due to surface contamination, for example due to OH⁻ [18]. Regarding the O–Zr peak, the lowest amplitude was optimised after IB irradiation. As a result of the XPS analysis, it was thought that the activated amorphous network of high polarisability could be attributed to stronger π - π interaction with the LC molecules. Thus the amorphous network near the IB-irradiated surfaces demonstrated preferential orientation due to breaking of bonds according to the direction of the IB.

Figure 4 shows the EO characteristics of TN cells produced by IB irradiation of ZrO_2 thin films. The ion energy intensity, incident angle and exposure time were 1800 eV, 45° and 60 s, respectively. The transmission characteristics were fairly similar for the two alignment methods when applying 5V to each cell. The threshold voltage of the IB-irradiated ZrO_2 was 1.78 V, whereas that for rubbed PI was 1.55 V. Figure 5 shows the response time characteristics. The ZrO_2 exhibited superior performance in this respect also, with a rise time of 7.6 ms and a fall time of 7.8 ms, whereas the PI gave a rise time of 11.8 ms and a fall time of 12.5 ms. The ZrO_2 film layer described therefore offers considerable potential for use in fast-response applications.

4. Conclusions

In this study, the ZrO_2 irradiated by IB was first introduced as a LC alignment layer without disclination lines. We were able to obtain a favourable pretilt angle by modifying the incident angle, the IB energy and the exposure time. We have confirmed that the alignment of LCs on ZrO_2 thin-film layers is dependent on the binding energy of the deposited layers. The IB irradiation energies change the molecular orientation of LCs by preferentially breaking bonds relative to the



Figure 4. Transmission of light as a function of voltage for TN cells, comparing rubbed polyimide and IB-irradiated ZrO_2 (colour version online).



Figure 5. Response time as a function of voltage for TN cells, comparing rubbed polyimide and IB-irradiated ZrO_2 (colour version online).

incident IB direction. It is therefore considered that ZrO_2 surfaces in which orientational order has been induced by directional irradiation using IB can be used for LC alignment. We have found that the voltage–transmittance (*V*–*T*) curve of an ion beam-aligned cell is similar to that for a rubbed PI cell.

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