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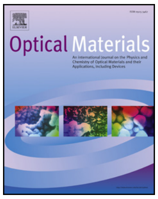

# Ion-beam-induced surface modification of solution-derived indium-doped zinc oxide film for a liquid crystal device with stable and fast switching properties

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ABSTRACT

The characteristics of a solution-derived indium-doped zinc oxide (In:ZnO) film exposed to ion-beam (IB) irradiation as a liquid crystal (LC) alignment layer were investigated. Solution processing was conducted to deposit a thin layer on a substrate and irradiation at various IB irradiation energies was used as an LC alignment method, all of which achieved uniform and homogeneous LC alignment. Atomic force microscopy using three-dimensional imaging and numerical analyses showed that the IB irradiation reduced the surface roughness. Through the X-ray photoelectron spectroscopy, it was revealed that the modification of the chemical composition due to the IB irradiation affected the state of the LC alignment. Increased polarizability of the surface and oxygen vacancies induced strong van der Waals forces between the In:ZnO film surface and the LC molecules, thereby subsequently achieving uniform and homogeneous LC alignment. The electro-optical (EO) characteristics of a twisted-nematic cell made with IB-irradiated In:ZnO film at an IB irradiation energy of 2200 eV, with which outstanding EO performance was observed. Therefore, using the solution-derived In:ZnO film with the IB irradiation as an alignment shows remarkable potential for use in LC device.

## 1. Introduction

Uniform alignment of liquid crystal (LC) molecules is the most important factor for producing high-quality LC devices [1–3], and various methods can be used to achieve this. A typical method is rubbing, which is simple and low cost, and widely used to achieve uniform LC alignment [4–7]. However, the rubbing method has a disadvantage in that it results in the accumulation of defects, debris, and charge owing to the fact that it is a contact alignment method [8]. These disadvantages can cause problems in the manufacturing of high-quality LC displays (LCDs). Hence, non-contact alignment methods such ultra-violet photo-alignment [9,10], plasma treatment [11,12], oblique deposition [13], and ion-beam (IB) irradiation [14–16] are being extensively explored. In particular, IB irradiation is attracting a lot of attention because of its high controllability and reliability. In addition, IB irradiation leads to achieve the surface modification which improves the performance of electronic devices and it is competitive method with the inorganic materials [17].

Indium zinc compound are commonly used as transparent conducting oxide (TCO) materials widely used in solar cells [18], light-emitting diodes [19], and flat panel displays [20]. They are also used in various other applications owing to their high mobility and electrical stability and low deposition temperature [21,22]. Because they have low deposition temperatures, they can be readily deposited in thin-film form through solution-based processing, which is a simple method with several merits such as cost-effectiveness, mole controllability, and good reliability [23]. Furthermore, using indium zinc compounds as an alignment layer in LCDs improves the electro-optical (EO) characteristics.

In this study, we demonstrated the characteristics of the solution-derived indium-doped zinc oxide (In:ZnO) films exposed to IB irradiation. The state of LC alignment using IB-irradiated In:ZnO for

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employment as an LC alignment layer was determine using cross-polarized optical microscopy (POM), while the per-tilt angles were measured using a crystal rotation method. IB irradiation induces the physical and chemical surface modification and this could change the state of the LC alignment on the In:ZnO film. Therefore, atomic force microscopy (AFM), X-ray diffraction (XRD) analysis, and X-ray photoelectron spectroscopy (XPS) were conducted to verify the effect of IB irradiation on the in:ZnO film surface related to LC alignment. Specifically, AFM revealed physical modification of the film surface and XRD showed the crystallinity of the film, while XPS helped determine the chemical composition modification of the surface due to the IB irradiation. Finally, EO characteristics, including response time and threshold voltage, were measured to confirm the applicability of using the In:ZnO film in LC devices.

## 2. Experimental

**Fabrication of In:ZnO film by solution-processing:** A solution of In:ZnO was produced by dissolving 0.01 mol indium(III) nitrate hydrate [$In(NO_3)_3 \cdot xH_2O$] and 0.09 mol zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] in 2-methoxyethanol (2 ME) with acetic acid and mono-ethanolamine used as stabilizers. The In:ZnO solution was stirred at 85 °C at 420 rpm for 2 h and then aged for 1 day. Next, the In:ZnO solution was coated on indium tin oxide (ITO)-coated glass substrate by spin coating for 30 s at 3000 rpm. The spin-coated In:ZnO film was pre-baked on a hot plate for 10 min at 100 °C to remove residual solvent. After being pre-baked, the IZO film was then cured in a furnace for 2 h at 300 °C.

**Ion-beam irradiation on the In:ZnO film surface:** Cured In:ZnO film was placed in the chamber of a DuoPIGatron-type IB system. Ar gas flowed into the chamber at a rate of 1 sccm with $5 \times 10^{-5}$ torr of chamber pressure to generate the Ar plasma and in the IB system. The In:ZnO film was irradiated by accelerated Ar ions at an incident angle of 45° for 2 min using IB irradiation energies of 700, 1200, 1700, and 2200 eV with a current density of 1.0 mA/cm$^2$.

**LC alignment characteristics with the In:ZnO film:** To measure the LC alignment characteristics, anti-parallel cells were fabricated using the In:ZnO film at each IB energy, and LC cells with the non-IB irradiated In;ZnO film were also fabricated to compare the LC alignment state before and after IB irradiation. The empty cells were filled with positive LCs (MJ001929; $n_e = 1.5859$, $n_o = 1.4872$, and $\triangle\varepsilon = 8.2$; Merck) via capillary force, and the state of LC alignment was observed using POM (BXP 51, Olympus) images. The pre-tilt angle of the LC cells with the In:ZnO film were measured using the crystal rotation method (TBA 107, Autronic).

**Surface modification due to the IB irradiation:** Surface modification due to the IB irradiation was observed using several analyses. AFM analysis (Park systems, XE-BIO) was conducted to evaluate the modification of surface topology, while XRD (DMAX-IIIA, Rigaku) analysis was used to check the crystallinity of the In:ZnO film. Chemical surface modification was verified using XPS analysis (K-alpha, Thermo Scientific).

**Electro-optical properties of the LC cells with the In:ZnO film using twisted-nematic mode:** To measure the electro-optical properties of the LC cells, twisted nematic (TN) cells were fabricated with In:ZnO film and filled with positive LCs. The response time and voltage transmittance of the LC cells were measured using an LCD evaluation system (LCMS-200, Sesim).

## 3. Results and discussion

The POM images and pre-tilt angles of the LC cells with the solution-derived In:ZnO film are presented in Fig. 1. Before IB irradiation, the POM images showed strong light scattering over the entire LC cell (Fig. 1(a)), which indicates that the LC molecules were aligned randomly on the In:ZnO film surface before IB irradiation. In the LC system, light passing through the cell and LC molecules on the alignment layer determines the light path, and so the randomly aligned LC molecules induced a random light path. This made the light pass through the entire LC cell randomly and induced locally different transmittance with light scattering. This result indicates that an LC alignment method is required to align LC molecules uniformly for controlling of the light path.

After IB irradiation, all POM images showed black coloration over the entire LC cell (Fig. 1 (b) –(e)) regardless of IB irradiation energy. Uniformly aligned LC molecules controlled the light path and the controlled light passed through the LC cell blocked by analyzer and polarizer ('A' and 'P' in Fig. 1), which caused the black coloration in the POM image. Hence, from the results of the POM images, it was confirmed that uniform LC alignment was achieved after IB irradiation regardless of IB irradiation energy. In addition, this proved that IB irradiation is a useful method to align LC molecules uniformly.

Pre-tilt angle is one of the main LC alignment characteristics and the uniformly aligned LC molecules formed a regular pre-tilt angle with low standard deviation. Thus, measuring the pre-tilt angle gave credence of the results of the POM images, which indicated uniform LC alignment. In this study, the pre-tilt angle was measured several times for each IB energy to improve the accuracy of the measured data. Fig. 1 (f) shows the relationship between the pre-tilt angle and IB irradiation energy. The In:ZnO films corresponding to IB irradiation energies of 700, 1200, 1700, and 2200 eV exhibited pre-tilt angles of 0.06255°, 0.05252°, 0.8362°, and 0.06878°, respectively. Although, the pre-tilt angle was not changed significantly with IB irradiation energy, all of the results showed low standard deviations, which inferred uniform LC alignment. To summarize, we achieved uniform and homogeneous LC alignment using the solution-derived In:ZnO film exposed to IB irradiation.

Normally, IB irradiation changed the characteristics of an irradiated film surface. Because uniform and homogeneous LC alignment was achieved with IB irradiation, it is obvious that the changed surface characteristics affected the state of LC alignment and AFM analysis was conducted as a function of the IB irradiation energy of determine these physical modifications. Fig. 2 (a) – (c) shows the three-dimensional (3D) surface topologies of before IB irradiation and the after IB irradiation at 1200 and 2200 eV. Before IB irradiation, the In;ZnO film had a rough and non-uniform surface (Fig. 2 (a)); the entire surface was bumpy and several agglomerations with irregular height were observed. After IB irradiation, it was evident that the In:ZnO film surface had been physically modified, and at 1200 eV, the overall height of the grains had decreased and the agglomerations had significantly disappeared (Fig. 2 (b)). This indicates that etching by the IB irradiation reduced the height of the grains on the In:ZnO film surface [24]. As the IB irradiation energy increased further, this effect was clearly observed, and at 2200 eV, the overall height of the grains was further reduced and an almost smooth surface was achieved (Fig. 2 (c)). This result implies that IB irradiation induced a smoother In:ZnO film surface than before.

Numerical information of the In:ZnO film surface was collected for specific analysis. Fig. 2 (d) shows the root mean square (Rq) and arithmetic average (Ra) surface roughness values of the In:ZnO film surface as a function of IB irradiation energy. Before IB irradiation of the In:ZnO film, the Rq value was 1.391 nm and that of Ra was 1.046, but after IB irradiation, the Rq value decreased to 1.044, 0.862, 0.719, and 0.570 nm at IB irradiation energies of 700, 1200, 1700, and 2200 eV, respectively. Furthermore, the Ra value decreased to 0.731, 0.617, 0.552, and 0.444 at IB irradiation energies of 700, 1200, 1700, and 2200 eV, respectively. As the IB irradiation energy increased, the values of Rq and Ra indicating roughness gradually decreased. This result numerically shows the smothering effect of the IB irradiation due to etching. In addition, this surface was smoother than a rubbed polyimide surface, which has an Rq value of 3 nm when used industrially [25].

Furthermore, the value of Rz (the average distance between the highest peak and the lowest valley in each collected length) was