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We studied homogeneous liquid crystal (LC) alignment properties on ion-beam (IB) irradiated TiO_2 films deposited by the electron beam evaporation method. Stable homogeneous LC alignment on a TiO_2 surface resulted from IB irradiation energy over 1800 eV. X-ray photoelectron spectroscopy analyses showed that Ti^{4+} $2p_{3/2}$ and Ti^{4+} $2p_{1/2}$ peaks were increased with increasing IB energy. Assuming that the increased peaks produced anisotropy dipole fields in the direction of the IB exposure process, we confirmed that the increasing IB energy induced strengthened the surface energy for entirely clear and stable LC molecule orientation. The voltage-transmittance characteristics of the twisted-nematic cell on the TiO_2 surface indicate that the TiO_2 film has potential for use as the LC alignment layer.

Keywords: TiO_2; ion-beam; liquid crystal alignment; anisotropy dipole field

1. Introduction

Interactions between liquid crystal (LC) molecules and solid-substrate surfaces have significant meaning in both fundamental research and liquid-crystal display (LCD) applications [1, 2]. LC alignments on indium-tin oxide (ITO)-coated glass substrates can be achieved on different material surfaces using various methods, such as the rubbing process [3], oblique SiO film deposition [4], ultraviolet (UV) exposure [5] and ion-beam (IB) bombardment [6, 7]. In particular, the IB irradiation method on inorganic or organic LC alignment layers has been investigated intensively, as it provides controllability in a non-stop process for producing high-resolution displays [6–9]. Many optically transparent and insulating films, such as nitrogen-doped diamond-like carbon (NDLC) [10], SiC [8] and SiO_x [9], have been investigated as potential candidates for inorganic alignment materials. However, the study of LC orientation on a new inorganic material having superior capacity is required to produce high-performance displays, because inorganic materials with high dielectric constants can reduce LC driving voltage to decrease effective power consumption for LCD operation [11–13].

Among the many other potential high-*k* oxides, TiO_2 shows outstanding chemical stability, a high refractive index, great UV absorptivity and photochemical activity [14–16]. Above all, TiO_2 has a permittivity value of over 80 [17], which can be ideally applied as a high-*k* alignment layer in LCDs.

In this paper, we report homogeneous LC alignment characteristics on IB-irradiated TiO_2 surfaces deposited by the electron beam evaporation method. Increasing IB energy resulted in favourable pretilt angles on fabricated LC cells (60 μm gap) with clear and uniform photomicroscopes. We also observed thermal stability for LC cells using a photomicroscope. To investigate the reason why LCs could be clearly aligned, we used an atomic force microscope (AFM) to measure the contact angle on IB-irradiated TiO_2 surfaces. We also researched X-ray photoelectron spectroscopy (XPS) spectra with different IB exposure energies to examine the phenomenon of anisotropic dipole–dipole interactions on IB-irradiated TiO_2 surfaces. Finally, the voltage–transmittance (*V–T*) characteristic of twisted-nematic (TN) cells (5 μm gap) on the TiO_2 surface was explored.

2. Experiment

TiO_2 layers of 1000 Å thickness were deposited on ITO-coated glass (Samsung Corning 1737) by electron beam evaporation at the vacuum condition of 10^{-6} Torr. The TiO_2 surfaces were irradiated by a DuoPIGatron-type IB system causing a dense and uniform Ar^+ plasma environment. The used IB exposure energies were 0, 600, 1200, 1800 and 2400 eV with a fixed exposure angle of 45° and time of 1 minute. Anti-parallel figure LC cells were prepared to measure

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pretilt angles, polarised photomicroscope (MX50-CF; Olympus) images and thermal stability. To measure thermal stability, we observed photomicroscope images of the LC cells annealed for 10 minutes from 60°C to 240°C per 30°C. X-ray diffraction (XRD) measurements were performed using 1.5 kW Cu-radiation (λ = 1.5406 Å) (Rigaku). A crystal rotation method (TBA 107 tilt-bias angle evaluation device; Autoronic) was used to measure pretilt angles and compare the measured transmittance graph to the simulated graph produced by the given LC information. We used an AFM (AutoProbe CP Research sys.) to measure the effect of IB irradiation on TiO_2 surface roughness. XPS (ESCA LAB 220-XL, VG Scientific, USA) analyses were utilised to investigate the chemical mechanism of a TiO_2 surface with IB irradiation used for LC alignment. Finally, contact angles for the surfaces were measured using a Rame-Hart telescopic goniometer and a contact analyser with a Gilmont syringe and a 25 gauge flat-tipped needle (Phoenix 450, Surface Electro Optics, Seoul, Republic of Korea). Distilled water was used as the probe fluid. The *V–T* characteristic of the TN cell was obtained with a LCD evaluation system (LCMS-200, Sesim Photonics Technology).

3. Results and discussion

Figure 1 shows polarised photomicroscope images of LC alignment states on TiO_2 thin film surfaces deposited by electron beam evaporation on ITO-coated glass substrates. We confirmed that 600 and 1200 eV of IB irradiation did not induce clear and uniform LC alignment. However, Figures 1(c) and 1(d) showed uniformly aligned LC molecular states on the TiO_2 thin film surface with any partial defect.

As shown in Figure 2, the experimental (red line) and simulated (blue line) (colour refers to the online version) transmittance graphs of LC cells on TiO_2 surfaces with a latitudinal rotation angle from –70° to 70° were measured and the oscillation of the transmittance was observed through the variation of the birefringence of the LC cell rotation. The pretilt angle of aligned LCs was produced in the direction of the IB irradiation process. As confirmation that the experimental transmittance graph identically approached the graph simulated from the rotation method system, we assumed that relatively high IB exposure energy produced an anisotropic dipole field on the entire TiO_2 surfaces. Eventually, the strengthened uniform dipole field would induce clear and uniform LC alignment properties as shown in Figures 1(c) and (d), although it could ascertain that 1800 eV was a transition point to align homogeneous LCs clearly on TiO_2 surfaces.

To analyse the LC alignment mechanism, we observed a non-IB irradiated cell (0 eV), an IB-irradiated but poorly aligned LC cell (600 eV) and an

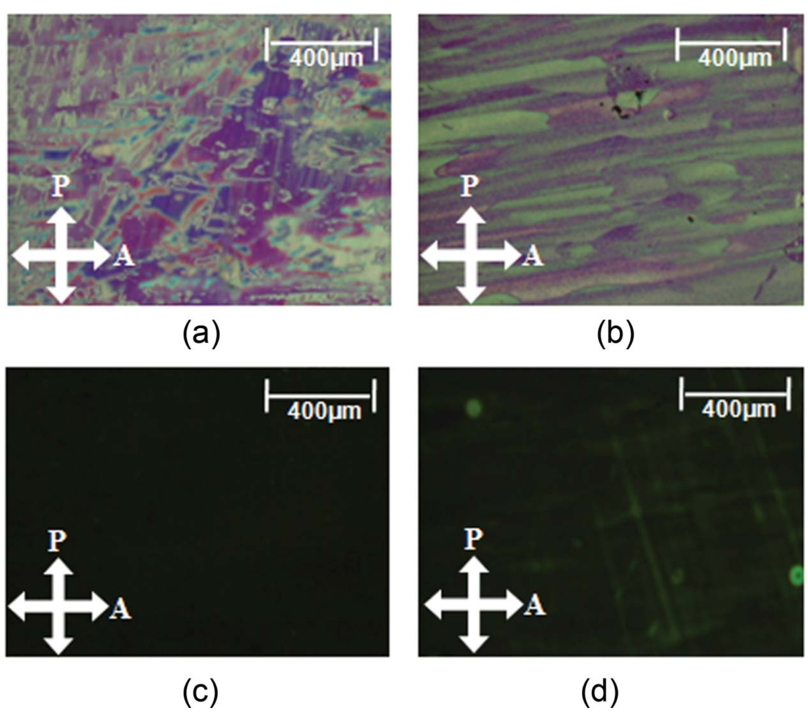

Figure 1. Photomicroscope images of LCs on IB-irradiated TiO_2 film surfaces (in crossed Nichols). (a) 600 eV, (b) 1200 eV, (c) 1800 eV and (d) 2400 eV.

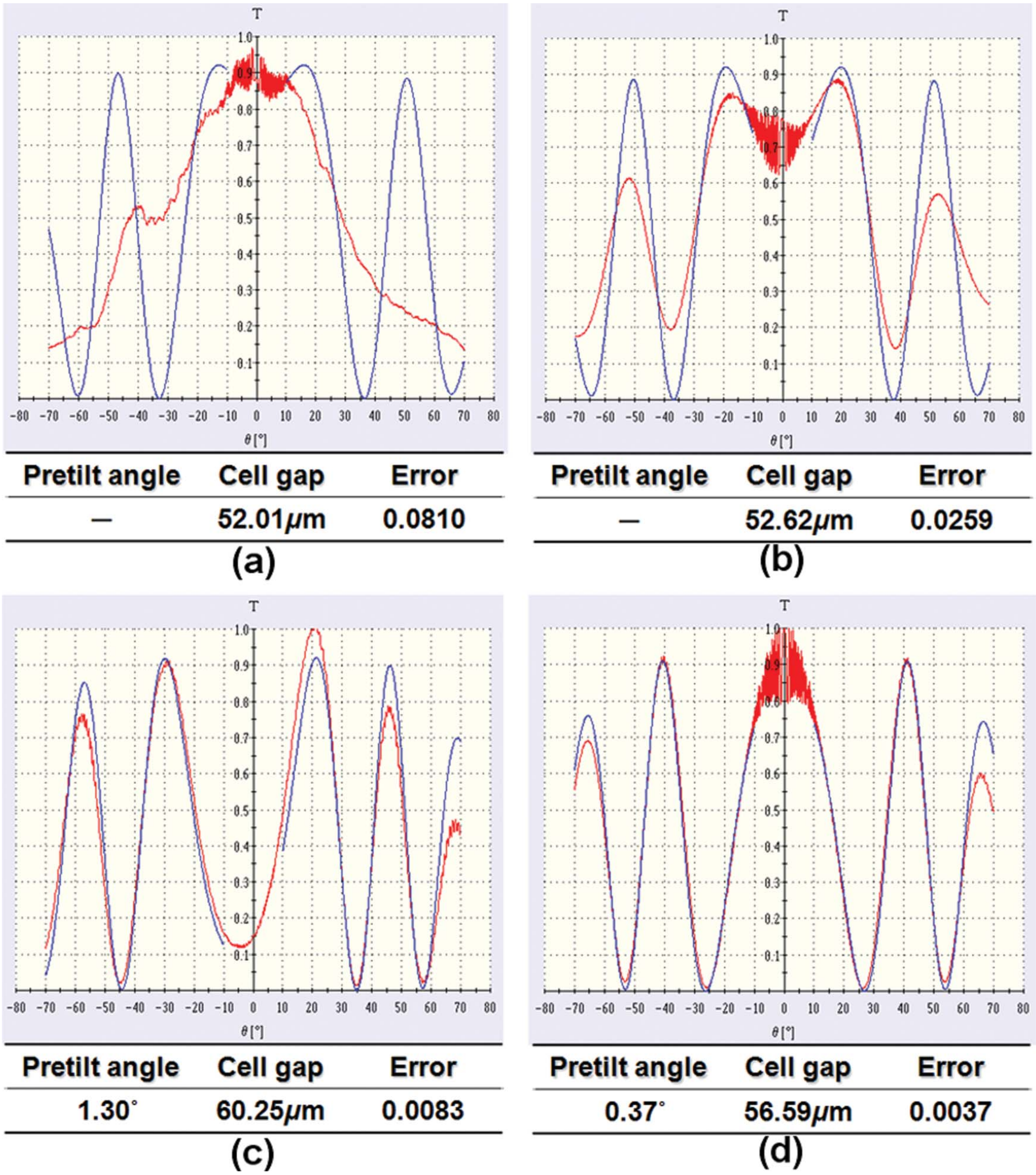

Figure 2. Pretilt angles of LC cells on IB-irradiated TiO_2 surfaces measured by a crystal rotation method using the transmittance measurement with latitudinal rotation. The red and blue graphs indicate experimental measured and simulated graphs, respectively. Colour refers to the online version.

IB-irradiated well-aligned LC cell (1800 eV) through AFM measurements. Figure 3 shows the measured AFM images of TiO_2 thin film surfaces with IB exposure energies of 0, 600 and 1800 eV under the other same conditions with IB exposure angle of 45° and time of 1 minute. As shown in these images, there were no topological differences. This indicates that the mechanism of LC alignment on TiO_2 thin films via IB exposure could not be explained by the physical impacts such as the groove effect. Moreover, the XRD pattern in Figure 3(d) means that the deposited TiO_2 structures have an amorphous phase.

Figure 4 shows XPS analyses of IB-irradiated TiO_2 surfaces using 0, 600 and 1800 eV IB exposure energy. A sub peak of Ti^{4+} 2p was displayed based on our previous work (Ti^{4+} $2p_{3/2} = 458.75$ eV, Ti^{4+} $2p_{1/2} =$ 464.4 eV) [18]. The film surfaces irradiated by IB exposure process at energies of less than 600 eV had little peak change for Ti $2p_{3/2}$ and Ti $2p_{1/2}$. That is, the weak intensity of the IB irradiation did not really alter

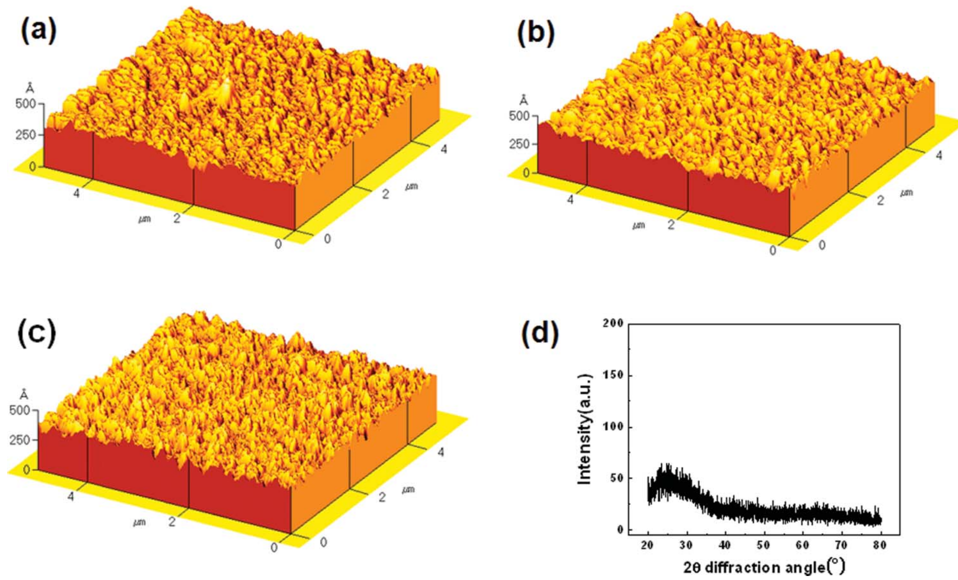

Figure 3. AFM images on TiO_2 film surfaces with IB energy of (a) 0 eV, (b) 600 eV and (c) 1800 eV. (d) XRD pattern on the deposited TiO_2 film.

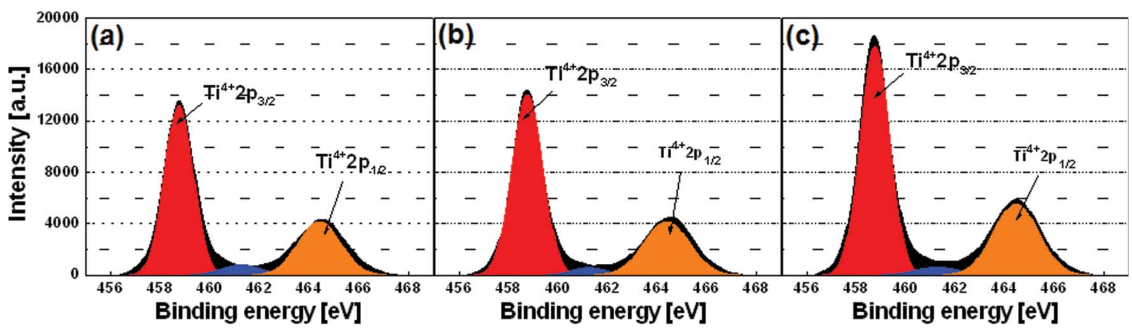

Figure 4. XPS analyses of TiO_2 films. (a) 0 eV, (b) 600 eV and (c) 1800 eV.

the chemical structure of the TiO_2 film surface. However, on increasing the IB energy to 1800 eV, the peak intensities of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ were considerably increased. This means that IB irradiation intensities over 1800 eV could change the states of TiO_2 surface bonds. Consequently, we deduced that the LC alignment on the TiO_2 surface via IB irradiation depends strongly on the increased Ti $2p_{3/2}$ and Ti $2p_{1/2}$ orbital. Moreover, the increased orbital would produce anisotropic dipole–dipole interactions between LC molecules and IB-irradiated TiO_2 surfaces.

Figure 5 shows contact angle images of TiO_2 thin film surfaces. The cells with 0, 600 and 1800 eV IB intensities were measured. If anisotropic dipole–dipole interactions were produced on TiO_2 surfaces using high IB exposure energy, we assumed that the surface energy on the surfaces could be strengthened by increasing the energy. As shown in Figure 5, the

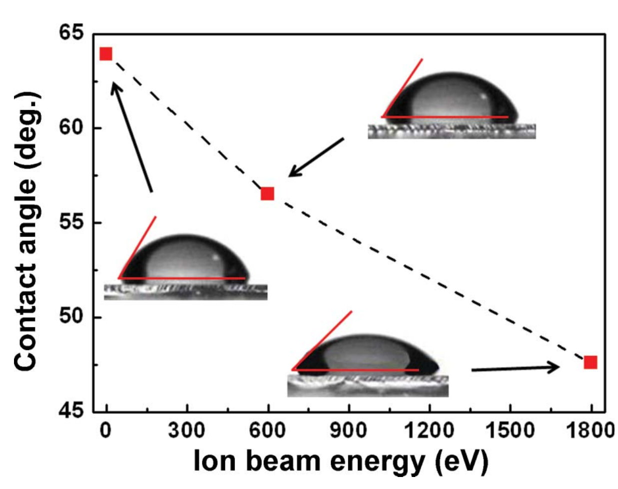

Figure 5. Graph of the measured contact angles on IB-irradiated TiO_2 surfaces with IB energy of 0, 600 and 1800 eV. The insets show contact angle images on the TiO_2 film surfaces.

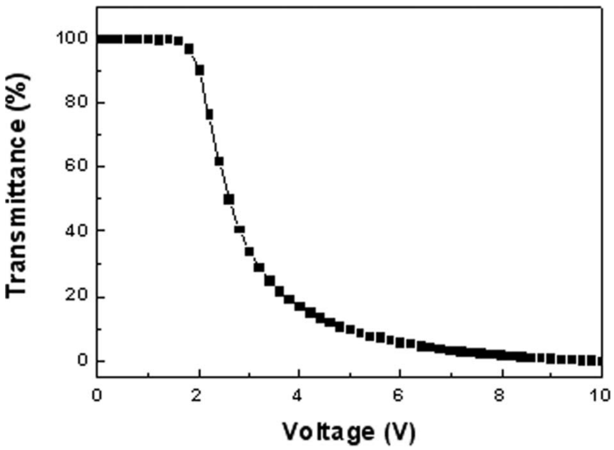

Figure 6. *V–T* characteristic for a TN cell on TiO_2 film with IB irradiation at an incident energy of 1800 eV.

measured contact angle was decreased with increasing IB energy and the smallest value of 47.6° was observed at the IB energy of 1800 eV. In addition, the surface energy of 35 mN m^{-1} did not change when the cell was exposed to an IB intensity of 600 eV, but the value increased to 42 mN m^{-1} when the cells were exposed to IB energy of 1800 eV. From these results, we concluded that the increment of IB energy traced out the increase of polar surface energy [19]. This means that there is a transition point of IB energy in producing proper surface energy that causes uniform and clear homogeneous LC molecular orientation. Therefore, it was revealed that increased polar surface energy sufficient to induce dipole–dipole interactions between LC molecules and the TiO_2 surface is essential for LC orientation [20].

Figure 6 shows the transmittance curves via applied voltage to the TN cell on the TiO_2 film with IB irradiation at an incident energy of 1800 eV. The measured transmittance curves are clear and did not have any different optical bounce, such as the backflow effect. The threshold voltage of TN cells was 2.0 V, which is comparable to the value of a conventional polyimide (PI)-based TN cell [11]. This means that TiO_2 film is sufficient to replace the alignment layer.

To estimate LC anchoring energy, we observed the thermal stability for a LC cell. After the LC cell was annealed by specific heat and cooled gradually, the LC alignment effect was observed by photomicroscope. As shown in Figure 7, LC alignment was good when the annealing temperature was from room temperature (RT) up to 180°C. However, destruction of LC alignment started at 210°C, and LC alignment was entirely destroyed at 240°C. From these results, we can see that LC cells fabricated by TiO_2 film have good thermal stability. This means that the anchoring energy at the interface between the LC cell and the TiO_2 film was similar to that of a PI-based LC cell [21, 22]. The anchoring energy produced on IB-irradiated TiO_2 surfaces could be 1.0–2.0 × 10^{-3} Jm^{-2}.

4. Conclusions

In this study, we investigated the effects of homogeneous LC alignment on IB-irradiated TiO_2 surfaces using a DuoPIGatron-type IB exposure system. As IB exposure energies were increased, we observed that homogeneous LC molecule orientation achieved clear and uniform alignment properties on the TiO_2 surfaces. Through XPS analyses, we confirmed that the IB irradiation changed the surface bonds of the TiO_2 films and increased the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ orbital, which would produce an anisotropic dipole field on the TiO_2 surfaces. In addition, it was also confirmed that the increased surface energy on the IB-irradiated TiO_2 surfaces resulted in homogeneous LC alignment uniformly. Finally, a good *V–T* characteristic of the TN cell was achieved, and TiO_2 films have potential as LC alignment layers comparable to PI.

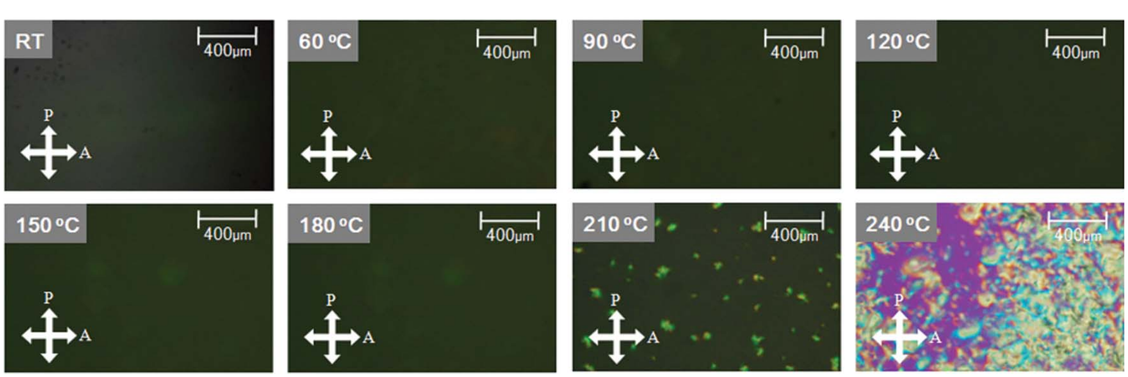

Figure 7. Photomicroscope images of aligned LC on IB-irradiated TiO_2 surface at various annealing temperature (in crossed Nichols).

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