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Solution-Derived Hafnium Lanthanum Oxide Films Prepared Using Ion-Beam Irradiation and Their Applications as Alignment Layers for Twisted-Nematic Liquid Crystal Displays

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We present the alignment characteristics of LC (liquid crystal) molecules on solution-derived HLO (hafnium lanthanum oxide) films fabricated using IB (ion-beam) irradiation. We then demonstrated that LC molecules can be homogeneously and uniformly aligned on the HLO film irradiated at an IB incident energy of 1.2 keV. Physicochemical analysis methods such as atomic force microscopy and X-ray photoelectron spectroscopy were used to verify the LC alignment mechanism on the IB-irradiated HLO film. In addition, the electro-optical performance of a TN (twisted-nematic) cell fabricated using the IB-irradiated HLO film exhibited characteristics superior to those of the conventional TN cell fabricated using a rubbed polyimide layer.

Keywords: Liquid crystal alignment layer, Solution process, Hafnium lanthanum oxide, Ion-beam irradiation, Electro-optical properties

1. INTRODUCTION

The alignment of LCs (liquid crystals) is a key technology in the development of LCDs (liquid crystal displays). Understanding how the unidirectional anisotropy of LC molecules is induced on a surface of LC alignment layers is important for achieving uniform LC alignments in LCDs because the initial orientations of LC molecules depend mainly on the reorientation of the average molecular direction within the bulk of an LC layer [1-3]. Because of its simplicity and cost effectiveness, the rubbing method is most commonly used to induce anisotropy in the LC alignment layer [4]. However, mechanical contact with a roller can introduce a number of drawbacks such as electrostatic charge accumulation, broken debris, and film damage [3,5-7].

Recently, alternative methods of LC alignment based on non-contact processes have been intensively studied to overcome these disadvantages. These alternative methods include the photoalignment technique, nanoimprint lithography, oblique vapor deposition, and IB (ion-beam) irradiation [3,8-18]. While good experimental results have been obtained from these alternative techniques, more reliable and effective studies of LC alignment are still sought for improving the performance of LCs in LCD applications.

Collimated IB alignment is applicable for both inorganic and organic materials. In particular, irradiation with high-energy Ar^+ ions of a few hundred electron volts or more can be used to align LC molecules on the surface of inorganic thin films such as SiOx, ZnO, Al_2O_3, Ta_2O_5, YZO, and HfYGaO films [14-18]. Although a substantial amount of research on the alignment layers has been carried out, considerably more research is needed to improve LC alignment characteristics and LCD performance.

In this study, we adopted HLO (hafnium lanthanum oxide) film instead of the conventional PI (polyimide) layer as an LC alignment layer to improve LC device performance. To align LC

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molecules on the HLO film, we used the IB alignment method. We also used a solution process to deposit the HLO film because solution processing is simpler, has a high throughput, allows for easier compositional modification, and is less expensive than vacuum deposition methods [19]. The LC alignment on the HLO film irradiated at an IB incident energy of 1.2 keV was evaluated and the EO (electro-optical) characteristics of the TN (twisted-nematic) cell were measured to assess the suitability of the films for LCD applications. Additionally, XPS (X-ray photoelectron spectroscopy) analysis was conducted to clarify the mechanism of LC alignment on the IB-irradiated HLO film.

2. EXPERIMENTS

A 0.1 M solution of HLO precursors, used as the solvent, was prepared from hafnium (IV) chloride ($HfCl_4$), lanthanum nitrate hydrate [$La(NO_3)_3 \cdot xH_2O$], and 2-methoxyethanol. A few drops of acetic acid and mono-ethanolamine were then added in an equivalent molar ratio as a stabilizer to enhance the solubility of the metal precursor, resulting in a homogeneous solution. The final HLO solution was stirred at 75℃ at 600 rpm for 2 hr and aged for 1 day to completely dissolve the metal compounds. ITO (indium tin oxide)-coated glass substrates (Samsung Corning 1737) with dimensions of 32×22×1.1 mm^3 and a sheet resistance of 10 Ω/sq. were ultrasonically cleaned in acetone and methanol. The substrates were then rinsed with deionized water. The HLO solution was dropped onto the ITO glass substrates, rotating at 3,000 rpm over a period of 1 min. After deposition by spin coating, the films were prebaked at 100℃ for 10 min on a hotplate and then annealed in a furnace for 1 hr at 300℃. The final HLO films were exposed to Ar^+ IB plasma (~10^4 ions/cm^2) with an IB incident energy of 1.2 keV for 2 min at an incident angle of 45° using a DuoPIGatron-type IB system.

Antiparallel cells and TN cells were fabricated with cell gaps of 60 μm and 5 μm for the measurement of the alignment characteristics and EO characteristics, respectively. The empty cells were then filled with positive nematic LCs (MJ001929; n_e = 1.5859, n_o = 1.4872, and Δε = 8.2; Merck) at room temperature by capillary force. The LC alignment condition was observed using a cross-polarized photomicroscope (BXP51, Olympus), and the pretilt angle of the LC molecules was measured using the crystal rotation method (TBA 107, Autronic). The UV transmittance of the HLO films was measured by UV-visible-near-infrared (UV-VIS-NIR) spectrophotometry (UV-3101PC, Shimadzu). The nanostructure of the HLO films was observed by tapping-mode AFM (atomic force microscopy) (XE-BIO, Park Systems). The chemical bonding states of the HLO films were analyzed using XPS (ESCALAB 220i-XL, VG Scientific). The EO characteristics of the TN cell were measured using an LCD evaluation system (LCMS-200, Sesim Photonics Technology).

3. RESULTS AND DISCUSSION

We first investigated the alignment characteristics of the LC molecules on the surface of the HLO films. Figure 1 shows photomicrographs of the antiparallel cells and the pretilt angle of the LC molecules on the IB-irradiated HLO film. Figure 1(a) shows the random orientation of the LC molecules on the surface of the non-irradiated HLO film for comparison when the sample was at 0° relative to the polarizer. On the other hand, the cell based on the HLO film irradiated at an IB incident energy of 1.2 keV exhibited a dark state (Fig. 1(b)), resulting from the uniformly oriented LC molecules by IB irradiation. This result was verified by the curves from the TBA 107 measurements of the pretilt angle of the

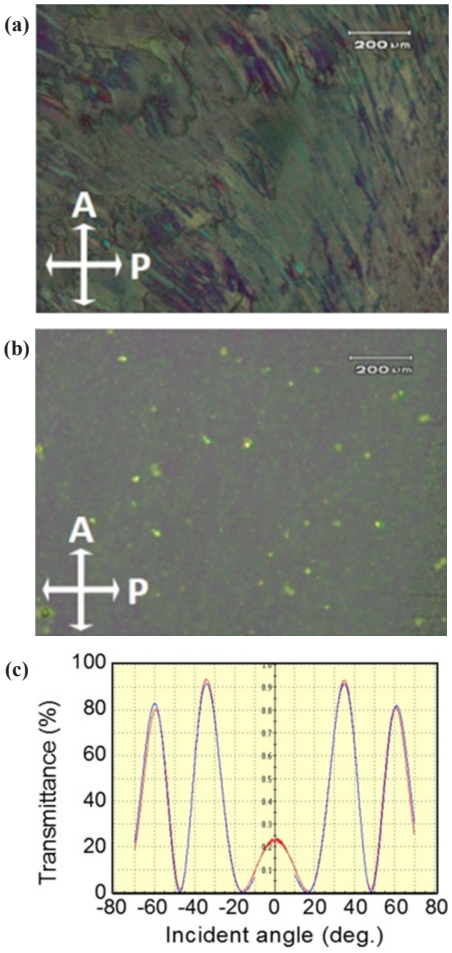

Fig. 1. Photomicrographs of LC alignment states of LC cells with (a) non-irradiated and (b) IB-irradiated HLO films. "A" denotes "analyzer" and "P" denotes "polarizer." (c) Transmittance versus incident angle curves (red line: experimental data; blue line: simulation data) for measurements of the pretilt angle of LC cell with the IB-irradiated HLO film.

LC molecules on the IB-irradiated HLO film. The transmittance of the LC cell was measured with a latitudinal rotation of ±70°, and the oscillation of the transmittance was measured from the LC cell rotation. If the measured (red line) curves are identical to the simulated (blue line) curves, the LC alignment is uniform and the pretilt angle of the LC molecules can be accurately calculated. The graphs of the measured pretilt angle indicated that the pretilt angle of the HLO film could be determined with high reliability and that uniform LC alignment was achieved as shown in Fig. 1(c). The pretilt angle of the LC molecules on the IB-irradiated HLO film was found to be 0.31°.

We used physicochemical analysis methods such as AFM and XPS to investigate the surface topography of the IB-irradiated HLO film, since the surface of the film can be affected by IB irradiation. The AFM images of non-irradiated and IB-irradiated HLO films are shown in Fig. 2. The measured area roughness of non-irradiated and IB-irradiated HLO films was 14.9 nm and 6.3 nm, respectively. These results indicate that the IB irradiation affects the surface morphologies of the HLO film and that the roughness of the film can be reduced.

Furthermore, the XPS analysis was used to elucidate the effects of the incident energy of the IB on the behavior of the uniform LC alignment. All binding energies were corrected with

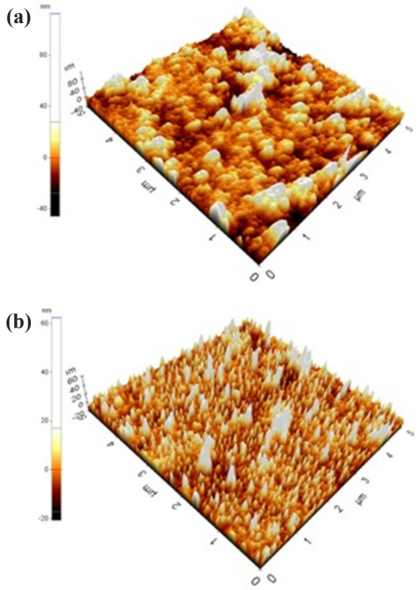

Fig. 2. AFM images of solution-derived HLO films (a) non-irradiated and (b) irradiated at IB incident energy of 1.2 keV.

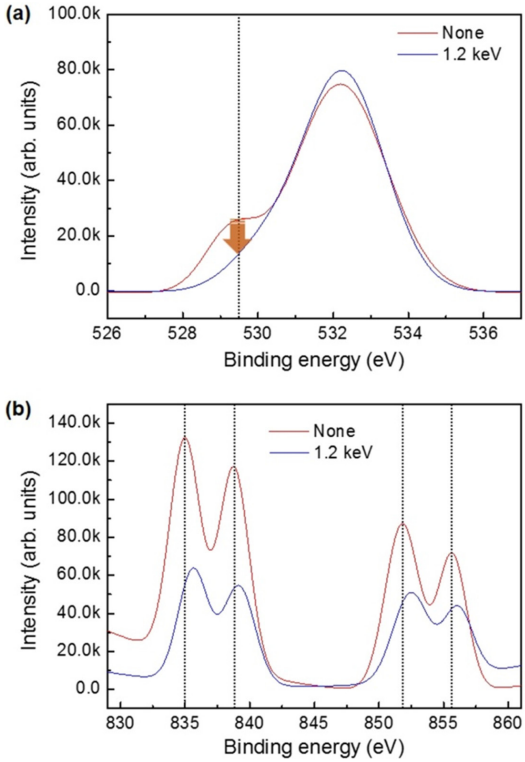

Fig. 3. XPS spectra for (a) O 1s and (b) La 3d peaks of non-irradiated and IB-irradiated HLO films at 1.2 keV.

reference to the C 1s line at 285.0 eV. The XPS spectra for the O 1s and La 3d peaks from non-irradiated and IB-irradiated HLO films are shown in Fig. 3. Figure 3(a) shows the XPS spectra of the O 1s peaks. The IB irradiation resulted in a considerable decrease in intensity of the subpeak of the O 1s peak at 529.5 eV and an increase in intensity of the O 1s core level at 532.2 eV. These results indicate that the IB irradiation induced La-O bond breaking and imply that the IB irradiation contributed to the creation of

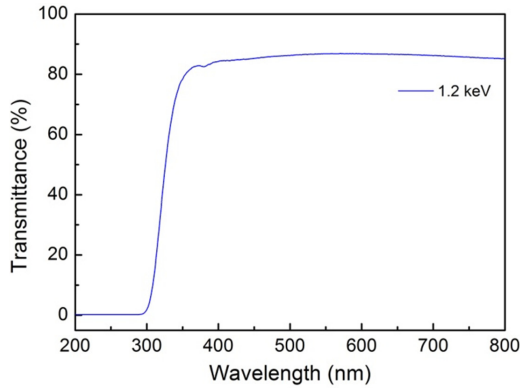

Fig. 4. Optical transmittance spectrum of the HLO film irradiated at IB incident energy of 1.2 keV.

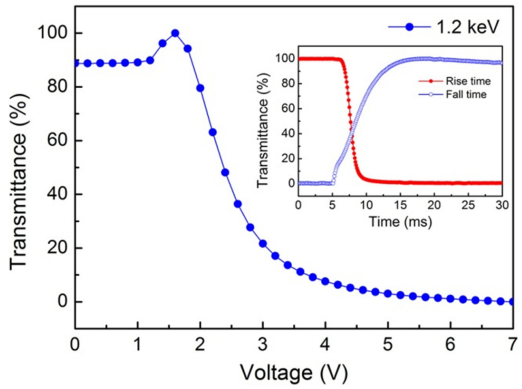

Fig. 5. V-T characteristic of TN cell based on the HLO film irradiated at IB incident energy of 1.2 keV. The inset shows the RT characteristic.

anisotropy to align the LC molecules on the HLO film. The XPS spectra for the La 3d peaks shown in Fig. 3(b) support this interpretation. After IB irradiation, a decrease in intensity and peak shifting toward a higher binding energy of the La 3d peak was observed [20,21]. The IB incident energy also affects the breaking of La-O bonds. The accelerated Ar^+ ions of the IB system destroyed the bonding structure of the HLO film, especially the La-O bonding, and induced surface re-formation to preserve the anisotropy to uniformly align the LC molecules on the HLO film.

The optical transparency of the IB-irradiated HLO film was investigated via UV-Vis transmittance, as shown in Fig. 4. The optical transmittance is an important parameter in evaluating the optical performance of LC alignment films. A high transparency of the LC alignment films in the visible region is required in applications involving optoelectronic devices. The transmittance of the film exceeded 86.2% in the visible region ranging from 420 nm to 780 nm, of which the value was almost the same as that of the non-irradiated HLO film and was much higher than that of the rubbed PI (polyimide) (83.5%) [3].

The EO characteristics of the TN cell fabricated using the IB-irradiated HLO film were investigated. Figure 5 shows a plot of the V-T characteristic of the TN cell on the IB-irradiated HLO film. Although optical bounce due to the backflow bounce effect was observed, the TN cell functioned well with a low operating voltage. The RT characteristic of the HLO film is shown in the inset to Fig. 5. The IB-irradiated HLO film irradiated at an IB incident energy of 1.2 keV exhibited a rise time of 1.92 ms and a fall time of 7.17 ms. These results are superior to those for the conventional PI-based TN cell (rise time of 1.4 ms and fall time of 12.3 ms) [2],

indicating that the IB-irradiated HLO film developed in this work can potentially be used in LCD applications.

4. CONCLUSIONS

In this study, solution-derived HLO films for an LC alignment layer were re-formed by Ar^+ IB as a replacement for the rubbing method. Uniform LC alignment with a pretilt angle was achieved on the IB-irradiated HLO films and the surface morphologies of the film were changed. Through XPS analysis of the HLO films, we observed that the La-O bond breaking increased, resulting in increased polarity of the surfaces after IB irradiation, which is considered interactive between the LC molecules and HLO film. The TN cell fabricated using the IB-irradiated HLO film exhibited competitive EO performances compared to those of a conventional PI layer, indicating that the HLO film developed in this work is a strong candidate for a novel LC alignment layer.

REFERENCES

[1] H. Wang, T. X. Wu, X. Zyu, and S. T. Wu, *J. Appl. Phys.*, **95**, 5502 (2004). [DOI: http://dx.doi.org/10.1063/1.1707210]
[2] B. Y. Oh, K. M. Lee, B. Y. Kim, Y. H. Kim, J. W. Han, J. M. Han, S. K. Lee, and D. S. Seo, *J. Appl. Phys.*, **104**, 064502 (2008). [DOI: http://dx.doi.org/10.1063/1.2978364]
[3] B. Y. Oh, *Trans. Electr. Electron. Mater.*, **17**, 109 (2016). [DOI: http://dx.doi.org/10.4313/TEEM.2016.17.2.109]
[4] Y. J. Kim, Z. Zhuang, and J. S. Patel, *Appl. Phys. Lett.*, **77**, 513 (2000). [DOI: http://dx.doi.org/10.1063/1.127028]
[5] J. M. Han and H. S. Hwang, *Trans. Electr. Electron. Mater.*, **11**, 285 (2010). [DOI: http://dx.doi.org/10.4313/TEEM.2010.11.6.285]
[6] P. Chaudhari, J. Lacey, J. Doyle, E. Galligan, S.C.A. Lien, A. Callegary, G. Hougham, N. D. Lang, P. S. Andry, R. John, K. H. Yang, M. Lu, C. Cai, J. Speidell, S. Purushothaman, J. Ritsko, M. Samant, J. Stöhr, Y. Nakagawa, Y. Katoh, Y. Saitoh, K. Sakai, H. Satoh, S. Odahara, H. Nakano, J. Nakagaki, and Y. Shiota, *Nature*, **411**, 56 (2001). [DOI: http://dx.doi.org/10.1038/35075021]
[7] J. Stöhr, M. G. Samant, J. Lüning, A. C. Callegari, P. Chaudhari, J. P. Doyle, J. A. Lacey, S. A. Lien, S. Purushothaman, and J. L. Speidell, *Science*, **292**, 2299 (2001). [DOI: http://dx.doi.org/10.1126/science.1059866]
[8] M. Schadt, H. Seiberle, and A. Schuster, *Nature*, **381**, 212 (1996). [DOI: http://dx.doi.org/10.1038/381212a0]
[9] K. Usami, K. Sakamoto, and S. Ushioda, *J. Appl. Phys.*, **93**, 9523 (2003). [DOI: http://dx.doi.org/10.1063/1.1572548]
[10] O. Yaroshchuk and Y. Reznikov, *J. Mater Chem.*, **22**, 286 (2012). [DOI: http://dx.doi.org/10.1039/C1JM13485J]
[11] R. Lin and J. A. Rogers, *Nano Lett.*, **7**, 1613 (2007). [DOI: http://dx.doi.org/10.1021/nl070559y]
[12] H. G. Park, J. J. Lee, K. Y. Dong, B. Y. Oh, Y. H. Kim, H. Y. Jeong, B. K. Ju, and D. S. Seo, *Soft Matter*, **7**, 5610 (2011). [DOI: http://dx.doi.org/10.1039/C1SM05083D]
[13] J. L. Janning, *Appl. Phys. Lett.*, **21**, 173 (1972). [DOI: http://dx.doi.org/10.1063/1.1654331]
[14] J. J. Lee, J. J. Han, H. G. Park, D. H. Kim, S. U. Byun, and D. S. Seo, *Opt. Mater.*, **35**, 2658 (2013). [DOI: http://dx.doi.org/10.1016/j.optmat.2013.08.005]
[15] H. G. Park, Y. H. Kim, B. Y. Oh, W. K. Lee, B. Y. Kim, D. S. Seo, and J. Y. Hwang, *Appl. Phys. Lett.*, **93**, 233507 (2008). [DOI: http://dx.doi.org/10.1063/1.3046728]
[16] J. H. Lim, B. Y. Oh, W. K. Lee, K. M. Lee, H. J. Na, B. Y. Kim, D. S. Seo, J. M. Han, and J. Y. Hwang, *Appl. Phys. Lett.*, **95**, 123503 (2009). [DOI: http://dx.doi.org/10.1063/1.3232239]
[17] J. W. Lee, H. G. Park, H. C. Jeong, S. B. Jang, T. K. Park, and D. S. Seo, *Opt. Express*, **22**, 31396 (2014). [DOI: http://dx.doi.org/10.1364/OE.22.031396]
[18] Y. G. Lee, H. G. Park, H. C. Jeong, J. H. Lee, G. S. Heo, and D. S. Seo, *Opt. Express*, **23**, 17290 (2015). [DOI: http://dx.doi.org/10.1364/OE.23.017290]
[19] S. Jeong, Y. G. Ha, J. Moon, A. Facchetti, and T. J. Marks, *Adv. Mater.*, **22**, 1346 (2010). [DOI: http://dx.doi.org/10.1002/adma.200902450]
[20] W. J. Zhu, T. Tamagawa, M. Gibson, T. Furukawa, and T. P. Ma, *IEEE Electron Device Lett.*, **23**, 649 (2002). [DOI: http://dx.doi.org/10.1109/LED.2002.805000]
[21] H. Y. Yu, M. F. Li, B. J. Cho, C. C. Yeo, M. S. Joo, D. L. Kwong, J. S. Pan, C. H. Ang, J. Z. Zheng, and S. Ramanathan, *Appl. Phys. Lett.*, **81**, 376 (2002). [DOI: http://dx.doi.org/10.1063/1.1492024]