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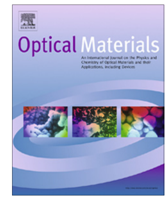

Superior switching behavior of liquid crystals on surface-modified compound oxide films

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ABSTRACT

We demonstrate high-performance liquid crystal (LC) devices using alignment layers formed of solution-processed HfYO films that were subjected to ion-beam (IB) irradiation. IB irradiation entails the increment of the surface roughness and chemical modification of the surface. Our X-ray photoelectron spectroscopy (XPS) analysis revealed that IB irradiation also breaks oxygen bonds, and thereby creates oxygen vacancies with lattice displacement of the metal atoms. This variation stabilizes the homogeneous LC alignment. The LC cells formed using the IB-irradiated HfYO films with an intensity of 2200 eV yielded a rapid response time of 6.579 ms. Therefore, our fast switching application based on IB-irradiated HfYO films has great potential for application of display devices.

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1. Introduction

Achieving a uniform alignment of liquid crystal (LC) molecules is important for high-quality display devices. Conventional rubbing processes have been used in industrial applications to align LC molecules uniformly on polyimide (PI) as an alignment layer. However, mechanical contact with a roller can result in debris generation, local defects, and the accumulation of electric charge, which degrades the performance of LC devices [1–3]. Various non-contact methods have been developed to overcome these disadvantages of the rubbing process, including photo-alignment [1], plasma treatment [4], and ion-beam (IB) irradiation [2,3,5–9]. In particular, IB irradiation has attracted much attention because it provides favorable controllability and reliability, and can be used to create high-performance and high-quality LC devices using inorganic materials with a large dielectric constant (i.e., high-*k* materials).

High-*k* inorganic materials are suitable for applications as alignment layers because they reduce the power consumption due to charge transfer into and out of trap states on the surface [5,7–9]. However, either sputtering or chemical vapor deposition is required to fabricate high-*k* inorganic material films, both of which require expensive equipment. Recently, cost-effective solution processes have been investigated for depositing inorganic materials to form thin-film transistors [10]. Solutions processes involve low fabrication costs, but can still fabricate compound oxide films with good stability and performance. For example, yttrium oxide (Y_2O_3) and hafnium oxide (HfO_2) are high-*k* materials with large band gaps (6.0 eV and 5.7 eV, respectively), and techniques to integrate with these materials have already been established for applications in microelectronics; highly stable structures with high-*k* can be formed of Y_2O_3 or HfO_2 [11–16].

Here, we report superior electro-optical (EO) performance of IB-irradiated HfYO films with homogeneous alignment of LCs. The IB intensity was controlled to achieve high performance. Atomic force microscopy (AFM) and X-ray diffraction (XRD) were used to investigate the physical properties of the HfYO films before and after IB irradiation. X-ray photoelectron spectroscopy (XPS) was used to investigate the alignment mechanism of the LCs. The results of polarized optical microscopy (POM) and pretilt angle measurements demonstrated uniform and homogeneous alignment. Superior EO performance of LC cells based on IB-irradiated HfYO films was observed in terms of the response time, voltage–transmittance curves, and anchoring energy. Optical transmittance ranged from 250 to 800 nm at room temperature, which is significant for display devices.

2. Experimental details

A 0.2-M solution of hafnium yttrium oxide (HfYO) was prepared using yttrium nitrate hexahydrate [$Y(NO_3)_3{\cdot}6H_2O$] (manufactured

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by Sigma Aldrich Co.) and hafnium chloride [$HfCl_4$] (Sigma Aldrich Co.) in a solvent of 2-methoxyethanol, with acetic acid and monoethanolamine as stabilizers to provide a homogeneous solution. The solution was stirred for 5 h at 75 °C and aged at least 1 day. Indium-tin-oxide (ITO)-coated glass (Samsung Corning 1737: standard $32 \times 22 \times 1.1$ mm^3) substrates were used, and the HfYO solution was spin-coated to form an alignment layer. The samples were then annealed for 2 h on a hot plate at 300 °C. After the deposition of HfYO films, the resulting films were approximately 50 nm. The surface of each sample was irradiated using an ion beam with intensities of 1200 eV, 1700 eV, and 2200 eV. The current density was 1 mA/cm^2, the angle of incidence of the ion beam was 45°, and the time was 2 min. Anti-parallel cells with a 60-μm gap were formed, as well as twisted-nematic cells with a 5-μm gap. LC cells were filled with positive nematic LCs (MJ001929 from Merck, $T_C = 72$ °C, $\Delta\varepsilon = 8.2$, $\Delta n = 0.077$). The LC was injected into the empty LC cells in the isotropic state using capillary force. A polarizing optical microscope (Olympus) was used to observe the alignment state. Pretilt angles of the cells were measured using the crystal rotation method (TBA 107, Autronic). The EO properties of the TN-cell, including the response time and transmittance, were measured using an LCD evaluation system (LCMS-200, Sesim photonics technology). The surface roughness of the HfYO films was measured using AFM. The structural properties of the HfYO films were characterized using XRD (DMAX-IIIA, Rigaku). The chemical bonding states of the HfYO films were investigated using XPS (Thermo U.K.) using a monochromatic Al X-ray source (Al Kα line: 1486.6 eV) and a 12-kV, 3-mA power source. The elemental composition was calibrated via comparison with C 1s (284.8 eV). Capacitance–voltage (C–V) measurements (LCR meter, Agilent 4284A) were carried out to obtain the anchoring energy of the TN cells at room temperature. The optical transmittance was measured in the range 250–800 nm at room temperature using an ultraviolet–visible (UV–vis) near-infrared scanning spectrophotometer (UV-3101PC, Shimadzu).

3. Results and discussions

Fig. 1 shows LC alignment characteristics on the IB-irradiated HfYO films as alignment layers deposited via solution processing. Fig. 1a shows POM images of LC cells fabricated using IB-irradiated HfYO films, as well as those of LC cells fabricated using non-IB irradiated HfYO films. The LC cells with the non-irradiated alignment layer did not exhibit uniform homogeneous alignment, and had oily streaks in the filling direction. In contrast, the LC cells formed using the IB-irradiated HfYO films exhibited good alignment irrespective of IB intensity. The LC molecules were injected along the IB irradiation and the samples were positioned parallel to one axis of the polarizers. The maximum transmittance occurred when the samples were rotated by 45° relative to the polarization direction (see the right inset of Fig. 1a), which is indicative of uniform and homogeneous alignment. Fig. 1b shows rotational transmittance curves, from which the pretilt angles of the LC were computed via a comparison between simulated and measured data. Valid data were obtained when the LC molecules were well aligned along the preferred direction. The measured rotational transmittance curves of samples with non-irradiated films differed significantly from the simulated curves, indicating that the LC molecules were not aligned along the preferred direction. The measured data for IB-irradiated films were in good agreement with the calculations, regardless of the IB intensity, indicating that good alignment was achieved over the entire area. Fig. 1c shows the calculated pretilt angles extracted from rotational transmittance measurements. Ten samples were measured, and the pretilt angles were less than 0.5° for all samples, regardless of the IB intensity. This is indicative of homogeneous alignment, and is consistent with the results of the POM analysis. Schematic of the IB irradiation process for HfYO films was shown in Fig. 1d.

Fig. 2 shows XRD spectra of the films before and after IB irradiation. No distinguishable diffraction peaks were observed either before or after irradiation, indicating an amorphous state of the HfYO films. Oxide films prepared via solution processes are typically amorphous, provided that the annealing temperature is below 500 °C [17], and our oxide films were annealed at 300 °C. Moreover, the IB irradiation did not appear to affect the crystallinity of the films.

Fig. 3 shows AFM surface profiles of the HfYO films before and after IB irradiation. IB irradiation typically results in some changes in surface roughness, regardless of the gas used [18,19]. A small increase in surface roughness was observed due to the IB irradiation, as shown in Fig. 3. The HfYO films were relatively smooth prior to IB irradiation, with a root-mean-squared surface roughness of $R_a = 2.95$ nm, whereas following IB irradiation $R_a = 9.8$ nm. Surface roughness is an important factor for LC alignment. With conventional LC cells, the alignment process via rubbing typically results in $2 < R_a < 5$ nm [20,21]; however, with the modified surface obtained via IB irradiation $R_a > 5$ nm, which may adversely affect the uniform alignment of the LC molecules. Therefore, to investigate the mechanism for the homogeneous alignment of LCs observed here, chemical modifications to the surface of HfYO films should be considered.

Fig. 4 shows XPS spectra of the Hf 4f, Y 3d, and O 1s core levels of the IB-irradiated and non-irradiated HfYO films. These peaks were referenced to the neutral adventitious C 1s peak at 284.8 eV. With the HfO_2 films, the Hf 4f peak was observed as a spin–orbit split doublet, with oxidized Hf $4f_{7/2}$ and Hf $4f_{5/2}$ peaks at 16.2 eV and 18.0 eV, respectively [22]. The Hf 4f core levels were located at 16.4 eV and 18.1 eV, and no shift was observed following IB irradiation. The shift compared with the conventional oxidized Hf peaks may be related to differing bonding states between the incorporated components. However, IB irradiation did not appear to significantly affect the bonds related to Hf atoms.

The oxidized Y 3d doublets of Y_2O_3, $3d_{5/2}$ and $3d_{3/2}$, occur at 156.8 eV and 158.8 eV, respectively [23]. However, the Y 3d doublet peaks were measured at 157.7 eV and 159.6 eV for the solution-processed films, which represents a shift to higher binding energies compared with Y_2O_3. This higher binding energy is indicative of the presence of hydroxyl groups and/or oxygen trap [23]. Moreover, as with the Hf 4f core levels, the bonding states differed between the incorporated components, which induces a higher binding energy in the Y 3d spectra, and indicates that the solution process had a stronger influence on Y during the film formation than on Hf. Subsequently, a slight negative shift of the Y 3d peaks was observed following IB irradiation, which indicates that the IB irradiation resulted in lattice displacement of the films and surface damage.

Following IB irradiation, the largest variation was observed in the O 1s sub-peak. The O 1s peak can be deconvolved into three sub-peaks at 530 eV, 532 eV, and 533.5 eV, which correspond to oxide–lattice bonds with metal ions (O_{1st}), oxide–lattice bonds with oxygen vacancies (O_{2nd}), and the presence of surface hydroxyl groups (O_{3rd}), respectively. Some hydroxyl groups were present on the surface of the oxide films prior to IB irradiation, which may have resulted from residual solvent from the sol–gel process. Following IB irradiation, no peaks corresponding to surface hydroxyl groups were observed, indicating that the residual solvent was removed. The high fraction of the O_{2nd} peak (64%) observed prior to IB irradiation was consistent with oxide films prepared via solution processes. The IB-irradiated HfYO films exhibited a higher fraction of the O_{2nd} peak (89%) than the non-irradiated HfYO film (see Table 1). IB irradiation breaks oxygen bonds and increases

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