RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Ion-beam-irradiated solution-derived tin oxide films for liquid crystal orientation

Hong-Gyu Park, Hae-Chang Jeong, Tae-Kyu Park, and Dae-Shik Seo[a,*]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

We present the alignment characteristics of liquid crystal (LC) molecules on solution-derived tin(IV) oxide (SnO_2) films. Solution processing was used in place of the sputtering method to deposit SnO_2 films as LC alignment layers. The LC molecules on the SnO_2 surfaces could be homogeneously and uniformly aligned by ion-beam (IB) irradiation. X-ray photoelectron spectroscopy (XPS) analysis indicated surface reformation of the SnO_2 films resulting from annealing and that IB irradiation affects the uniform LC orientation. Fast response times of twisted nematic cells constructed with IB-irradiated SnO_2 films were observed, which indicates that the proposed IB-irradiated solution-derived SnO_2 films have considerable potential for use in the production of advanced LC displays.

Introduction

The use of inorganic thin films as liquid crystal (LC) alignment layers is a promising concept in LC-based applications. The alignment of LCs on inorganic thin films using ion-beam (IB) irradiation as an alternative to the conventional rubbing method has been investigated by several groups[1-8]. Alternative methods, such as ultraviolet (UV) exposure[9-11], plasma treatment[12], nanoimprint lithography[13,14], traditional oblique evaporation[15,16], and IB irradiation[1-8,17,18], have been investigated because the mechanical rubbing method has serious problems resulting from the rubbing contact, including the accumulation of electrostatic charge and the generation of fine dust. Among these other candidate approaches, the IB irradiation method has attracted the greatest interest because it provides controllability, is reliable, involves a non-stop process, and can be used to create high-resolution displays with inorganic materials. IB irradiation has been intensively investigated with optically transparent insulating inorganic materials, such as diamond-like carbon[1,2], SiC[3], SiO_x[4], SiN_x[5], Ta_2O_5[6], SnO_2[7], and Al_2O_3[8], as well as with a variety of organic polyimide (PI) materials.

Many techniques may be used to deposit inorganic thin films, such as sputtering, spraying and chemical vapor deposition. Compared with these techniques, solution processing has some valuable characteristics: it allows the coating of large surfaces, it can be applied to complex shapes, and it is simpler than other techniques[19]. Moreover, the possibility of obtaining coatings with various dopants at different concentrations is an interesting feature of this solution method. SnO_2, which is considered to be one of the most promising inorganic materials as an LC alignment layer because of its high permittivity and high transparency[7], has already been well prepared and has shown excellent characteristics when fabricated through the solution process.

In this study, we demonstrate the use of a solution-derived SnO_2 film treated by IB irradiation as an LC alignment layer. We achieved homogeneous LC alignment on the solution-derived SnO_2 films by adjusting the annealing temperature. To elucidate the LC alignment mechanism, we conducted physicochemical analyses using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). In addition, we measured the properties of the alignment film and the electro-optical (EO) properties of twisted nematic (TN) LCDs using various techniques.

Experiment

Prior to the deposition process, indium-tin-oxide (ITO) glass substrates were cleaned using several steps. The substrates were ultrasonically cleaned with acetone, methanol, and deionized water for 10 min each and then dried with N_2 gas. A SnO_2 solution (0.1 M) was prepared by adding tin(II) chloride ($SnCl_2$) to a solvent of 2-methoxyethanol (2ME) with acetic acid and mono-ethanolamine (MEA) as stabilizers to obtain a homogeneous solution. Then, the solution was stirred for 2 h at 75 °C and aged for at least for 1 day. The SnO_2 solution was uniformly spin-coated onto the cleaned ITO-glass substrates for 1 min at 3000 rpm at room temperature. The SnO_2-coated substrates were then preheated at 100 °C for 10 min to remove any residual solvent. The resulting thin films were annealed for 1 h in a furnace at 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C.

The SnO_2 films were exposed to Ar^+ IB plasma at an energy of 1800 eV for 2 min at an incident angle of 45° using a DuoPIGatron-type IB system. The dosages of Ar^+ IB plasma were 10^{14}-10^{15} ions/cm^2. The current density in a beam of positively charged particles measured using a Faraday cup system was 3.7 mA/cm^2. The plasma ion density measured using double Langmuir probe tips was approximately 10^{11} cm^{-3}. To investigate the LC alignment properties, the SnO_2-coated substrates were

assembled in an antiparallel configuration with a cell gap of 60 μm. The TN cells were assembled with a cell gap of 5 μm to determine the EO properties of the TN cells. A nematic LC (MJ001929, n_e = 1.5859, n_o = 1.4872, and Δε = 8.2; Merck) was injected into the cells. Images of the LC alignment states were obtained using a polarized optical microscope (POM, Olympus BXP51). The pretilt angle of the LC cells was measured using the crystal rotation method (TBA 107 tilt-bias angle evaluation device, Autronic). The morphologies of the solution-derived SnO_2 films before and after IB irradiation were observed using AFM (Park Systems, XE-BIO). XPS (ES-CALAB 220i-XL, VG Scientific) was employed to investigate the molecular binding energy states on the IB-irradiated SnO_2 films. Finally, the EO characteristics of the TN cells with IB-irradiated SnO_2 films were measured using an LCD evaluation system.

Results and discussions

The LC alignment property and pretilt angle of the IB-irradiated SnO_2 films deposited by solution processing were measured to determine the potential of these films for practical applications. Figure 1 presents POM images of antiparallel cells of IB-irradiated SnO_2 films annealed at various temperatures. As shown in Fig. 1, uniformly aligned LCs were observed on the surfaces of the IB-irradiated SnO_2 films regardless of the annealing temperature. Partially distinguishable line defects were observed in the POM images; however, these defects were invisible to the naked eye. The increased anisotropy of the SnO_2 films due to the IB irradiation on the SnO_2 surfaces induced uniform LC alignment. At an annealing temperature of 300 °C, residual solvent remained in the solution-derived SnO_2 films; however, the residual solvent did not affect the IB irradiation-induced alignment of the LCs. This result indicates that IB irradiation is a powerful technique for achieving uniform LC alignment.

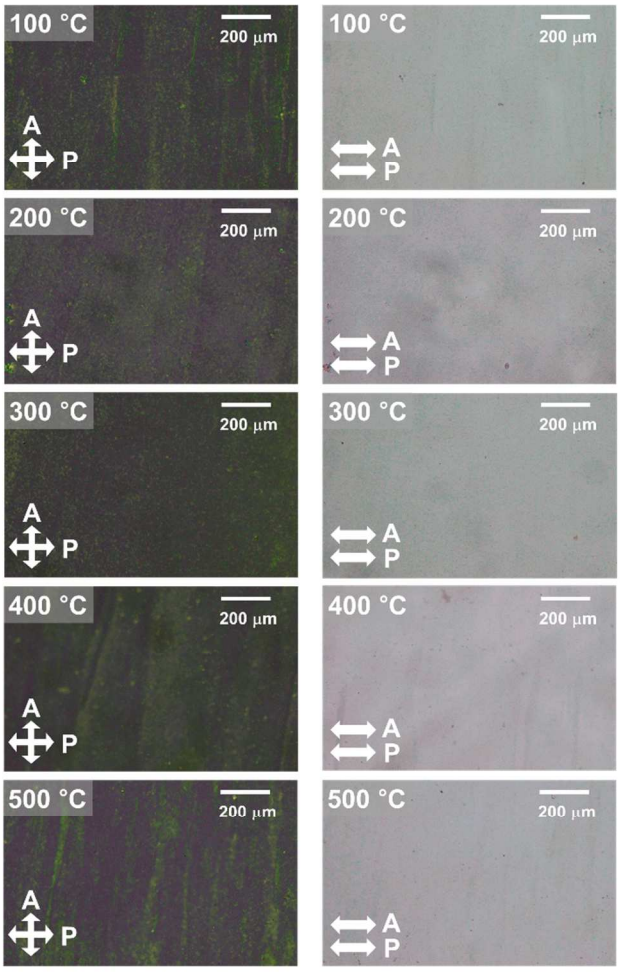

Fig. 1 Photomicrographs of anti-parallel cells with IB-irradiated SnO_2 films at an incident angle of 45°, an incident energy of 1800 eV, and an irradiation time of 2 min as a function of the annealing temperature. "A" indicates analyzer, and "P" indicates polarizer.

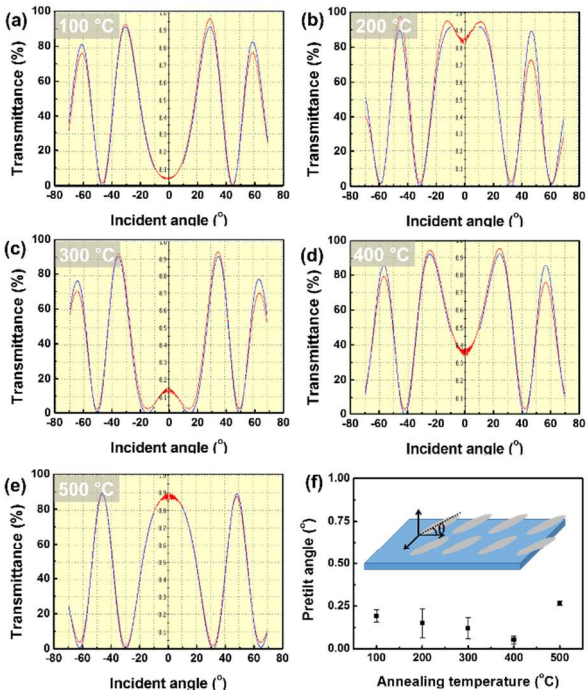

Fig. 2 (a-e) Transmittance versus incident angle of the LCs on IB-irradiated SnO_2 films fabricated at various annealing temperatures, and (f) the measured pretilt angle.

An LC orientation with a regular pretilt angle is important for LC applications[6]. The measurement of the pretilt angle not only showed the tilt angle of the LC molecules against the SnO_2 surface but also indicated that a uniform LC orientation was achieved. The measured TBA 107 transmittance curves of each antiparallel LC cell with IB-irradiated SnO_2 films are shown in Figs. 2(a)-(e). The transmittance of each antiparallel 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 (blue line) and simulated (red line) curves are identical, then the LC alignment is uniform and it is possible to accurately estimate the pretilt angle of the LCs. The graphs of the measured pretilt angles indicated that the pretilt angles of the SnO_2 films can be determined with high reliability and that uniform LC alignment was achieved. The pretilt angles of the LC molecules on the IB-irradiated SnO_2 films ranged from 0.05° to 0.26°, indicating that the pretilt angles of the LC molecules were relatively constant with respect to the annealing temperature.

To determine the mechanism for the orientation of LC molecules, we used physicochemical analyses, including AFM and XPS,

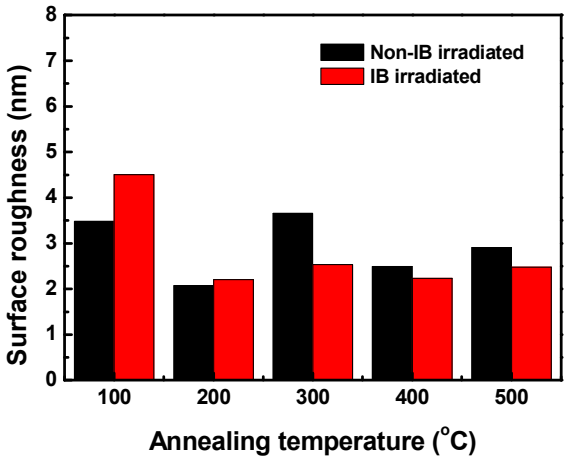

Fig. 3 RMS roughness determined using AFM of the solution-derived SnO_2 surfaces before and after IB irradiation at an incident angle of 45°, an incident energy of 1800 eV, and an irradiation time of 2 min.

because it is well known that the alignment of LCs depends on both the chemical nature of the surface and on the surface topography. First, the morphology of the SnO_2 films deposited by solution processing was observed using AFM. The bar graphs of the root-mean-square (RMS) values shown in Fig. 3, which were obtained from the AFM data before and after IB irradiation for 2 min, indicate that the IB irradiation does not strongly affect the roughness of the SnO_2 films, even those fabricated with low annealing temperatures. This result also suggests that the LC orientation was not greatly affected by the morphologies of the IB-irradiated films.

The C1s, Sn3d, and O1s peaks in XPS spectra obtained from the surfaces of films produced using various annealing temperatures

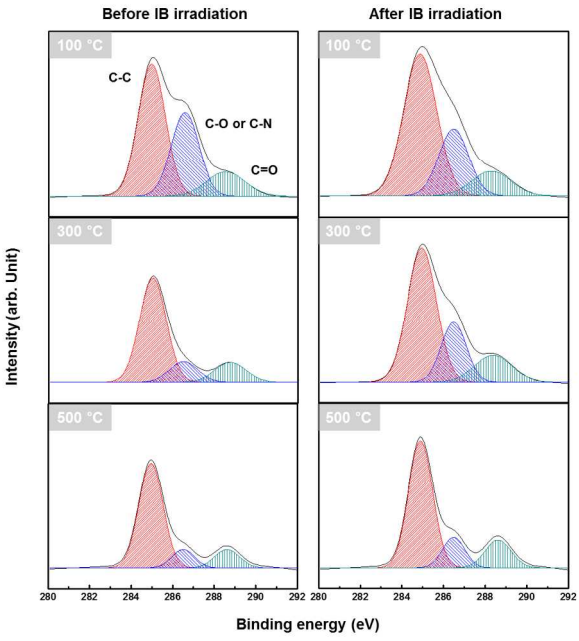

Fig. 4 XPS C1s core-level spectra of as-deposited and IB-irradiated SnO_2 films annealed at temperatures of 100 °C, 300 °C, and 500 °C.

before and after IB irradiation were analyzed. All of the binding energies were referenced to the C1s signal at 284.6 eV. To follow the transformation of the solution-derived SnO_2 films as a function of the annealing temperature, the change in the C1s spectra was monitored. Organic compounds were present in the prepared 0.1 M SnO_2 solution. These compounds were vaporized during the annealing process to form the SnO_2 films; however, these compounds remained in the films when the annealing temperature was less than 300 °C due to their high boiling points[20]. As shown in Fig. 4, the intensity of the peak at 286.5 eV corresponding to C-O in the solvent decreased as the annealing temperature increased. These results indicate that the SnO_2 films were not fully formed at annealing temperatures below 300 °C due to the presence of residual solvents. At annealing temperatures greater than 300 °C, the SnO_2 films were fully oxidized. In addition, the C1s spectra of the IB-irradiated SnO_2 films indicated that IB irradiation induces a chemical transformation in the solution-derived SnO_2 films.

Figure 5(a) presents the $Sn3d_{5/2}$ and $Sn3d_{3/2}$ XPS spectra of the solution-derived SnO_2 surfaces before and after IB irradiation. The binding energy of the $Sn3d_{5/2}$ component for the as-deposited SnO_2 film shifted from 487.3 eV to 486.7 eV compared to that of the SnO_2 films annealed at 500 °C, and this shift was attributed to thermal oxidation[21]. The upper binding energy of $Sn3d_{5/2}$ at annealing temperatures of less than 300 °C was due to the coexistence of various Sn-O and Sn-Cl bonds in the $SnCl_2$-SnO_2 composite films because less oxidation occurred at these annealing temperatures. However, IB bombardment on the SnO_2 surfaces strongly induced a surface transformation, irrespective of the initial state of the SnO_2 film. The surfaces were reformed within nanoscale depths due to IB irradiation. The accelerated Ar^+ ions of the IB system might have destroyed the bonding structure of the SnO_2 surfaces and induced surface reformation to preserve the anisotropic characteristics. The uniform LC alignment on the IB-irradiated SnO_2 films was attributed to van der Waals interactions between the LC molecules and the SnO_2 films due to these anisotropic characteristics. The van der Waals interactions between the LC molecules and the SnO_2 film increased to a level that was sufficient for maintaining a good balance in the LC molecule interactions, thereby leading to a homogeneous alignment of LC molecules. The chemical reformation was also observed in the O1s peak, as shown in Fig. 5(b). The SnO_2 films were gradually oxidized as the annealing temperature increased and were reformed irrespective of the initial state of the SnO_2 film. After IB irradiation, the SnO_2 films had similar chemical compositions, regardless of the annealing temperature. Figure 5(c) shows the changes in the atomic percentages of tin and oxygen before and after IB irradiation at various annealing temperatures. The atomic ratio of tin and oxygen in the SnO_2 films increased proportionally to the formation of SnO_2 films at annealing temperatures up to 300 °C. Then the ratios were saturated at annealing temperatures greater than 300 °C because the SnO_2 films were fully oxidized. After IB irradiation, the atomic ratio of tin and oxygen in the IB-irradiated SnO_2 films slightly decreased. This result indicates that the Sn-O bonds in the SnO_2 surface were broken by IB irradiation.

The EO characteristics were confirmed to be appropriate for pragmatic LCD applications. Figure 6 shows the EO

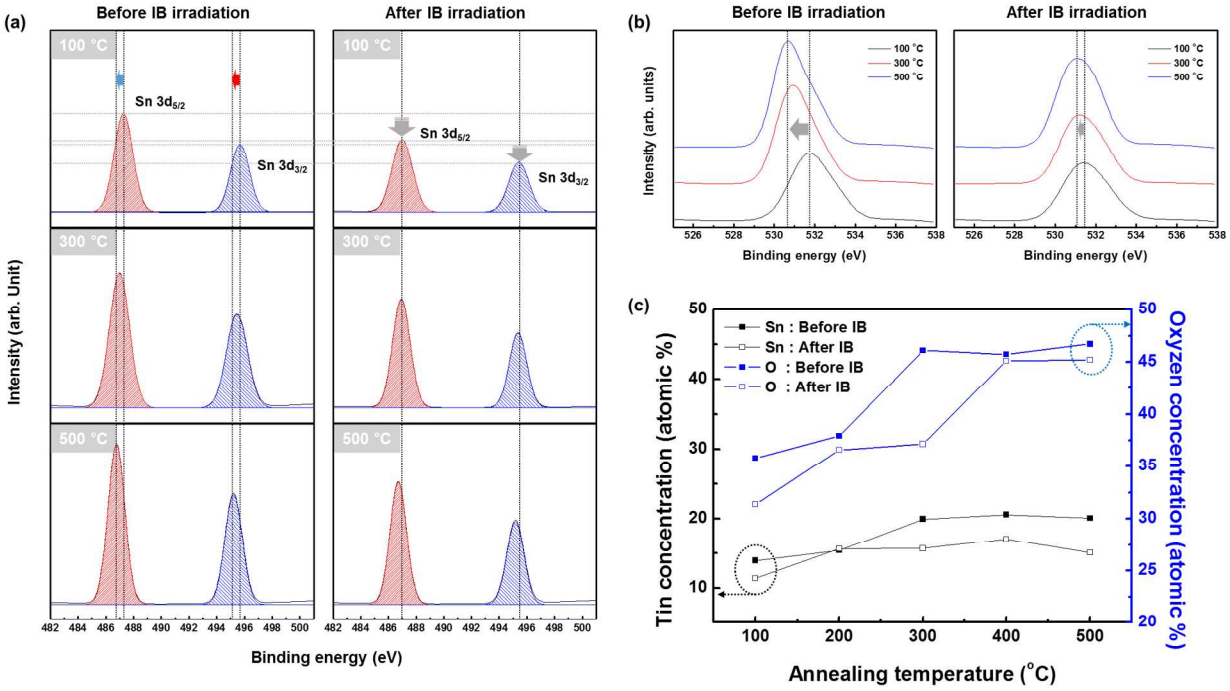

Fig. 5 XPS (a) Sn3d and (b) O1s core-level spectra of as-deposited and IB-irradiated SnO_2 films annealed at temperatures of 100 °C, 300 °C, and 500 °C. (c) The atomic percentages of tin and oxygen atoms for the XPS survey of the solution-derived SnO_2 film as a function of the annealing temperature before and after IB irradiation.

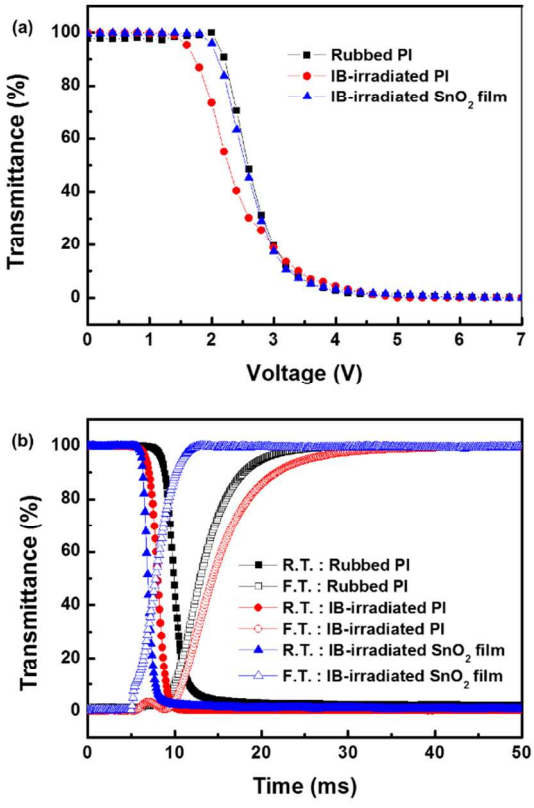

Fig. 6 (a) V-T curves and (b) response times of the TN cells with SnO_2 films and PI layers via IB irradiation and rubbing.

characteristics of a TN cell with IB-irradiated SnO_2 films that were annealed at 400 °C. The IB irradiation intensity, exposure time, and incident angle were 1800 eV, 2 min, and 45°, respectively. In addition, TN cells with layers of rubbed and IB-irradiated PI under the same conditions were used for comparison. The voltage-transmittance (V-T) characteristics of the TN cells are shown in Fig. 6(a). The threshold voltage at a transmittance of 90% for the TN cells with IB-irradiated SnO_2 films and those of the rubbed and IB-irradiated PIs were 2.1 V, 2.3 V and 1.7 V, respectively. In addition, contrast ratios of all the TN cells were approximately 190:1. From the results, the TN cells with IB-irradiated SnO_2 films were comparable to conventional TN cells with rubbed PI layers. Figure 6(b) shows the response times of the TN cells. Superior performance was obtained from the IB-irradiated SnO_2 film, as indicated by a rise time (R.T.) of 1.4 ms and a fall time (F.T.) of 4.7 ms, whereas the rubbed and IB-irradiated PI layers had R.T. of 2.6 ms and 2.0 ms and F.T. of 7.9 ms and 10.9 ms, respectively. The performance of the TN cells with IB-irradiated solution-derived SnO_2 films was similar to that of TN cells with IB-irradiated SnO_2 films deposited by sputtering. In addition, the reduced response time of the LC has potential for advanced LC applications, which are needed in industrial fields.

Conclusions

In this study, we investigated the characteristics of solution-derived SnO_2 films treated with IB irradiation for use as LC alignment layers. Uniform LC alignment was achieved on solution-derived SnO_2 films by IB irradiation regardless of the annealing temperature. As the annealing temperature increased, the SnO_2 films oxidized. However, the LC orientation on the SnO_2 surfaces was due to surface reformation induced by the breaking of Sn-O bonds as a result of IB irradiation. In addition,

superior EO characteristics of TN cells with IB-irradiated SnO_2 films were observed compared with those of cells fabricated with conventional rubbed PI layers. The threshold voltages of the TN cells were similar; however, the response time of the TN cells with IB-irradiated SnO_2 films was greatly enhanced compared with those of the TN cells with rubbed and IB-irradiated PI layers. These results indicate that IB-irradiated solution-derived SnO_2 films are promising candidates for advanced LCD applications.

Notes and references

Department of Electrical and Electronic Engineering, Yonsei University,50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Korea.. Fax: +82-2-2123-3147; Tel: +82-2-2123-4617; E-mail: dsseo@yonsei.ac.kr

1. 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. St¨ohr, Y. Nakagawa, Y. Katoh, Y. Saitoh, K. Sakai, H. Satoh, S. Odahara, H. Nakano, J. Nakagaki and Y. Shiota, *Nature*, 2001, **411**, 56.
2. 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*, 2001, **292**, 2299.
3. P. K. Son, J. H. Park, J. C. Kim, T.-H. Yoon, S. J. Rho, B. K. Jeon, S. T. Shin, J. S. Kim and S. K. Lim, *Appl. Phys. Lett.*, 2007, **91**, 103513.
4. P. K. Son and S.-W. Choi, *Surf. Interface Anal.*, 2012, **44**, 763.
5. B.-Y. Kim, W.-K. Lee, Y.-H. Kim, H.-G. Park, T.-K. Park and D.-S. Seo, *Liq. Cryst.*, 2011, **38**, 349.
6. J. Y. Kim, B. Y. Oh, B. Y. Kim, Y. H. Kim, J. W. Han, J. M. Han and D.-S. Seo, *Appl. Phys. Lett.*, 2008, **92**, 043505.
7. Y.-G. Kang, H.-J. Kim, H.-G. Park, B.-Y. Kim and D.-S. Seo, *J. Mater. Chem.*, 2012, **22**, 15969.
8. H.-G. Park, Y.-H. Kim, B.-Y. Oh, W.-K. Lee, B.-Y. Kim, D.-S. Seo, J.-Y. Hwang, *Appl. Phys. Lett.*, 2008, **93**, 233507.
9. P. J. Shannon, W. M. Gibbons and S. T. Sun, *Nature*, 1994, **368**, 532.
10. K. Ichimura, *Chem. Rev.*, 2000, **100**, 1847.
11. M. Schadt, H. Seiberle, A. Schuster, *Nature*, 1996, **381**, 212.
12. C.-Y. Lee, Y.-L. Liu, K. Y. Wu, M.-Y. Chen, and J.-C. Hwang, *Jpn. J. Appl. Phys.*, 2008, **47**, 226.
13. H.-G. Park, J.-J. Lee, K.-Y. Dong, B.-Y. Oh, Y.-H. Kim, H.-Y. Jeong, B.-K. Ju, D.-S. Seo, *Soft Matter*, 2011, **7**, 5610.
14. C. H. Chiu, H. L. Kuo, P. C. Chen, C. H. Wen, Y. C. Liu and H. M. P. Chen, *Appl. Phys. Lett.*, 2006, **88**, 073509.
15. J. L. Janning, *Appl. Phys. Lett.*, 1972, **21**, 173.
16. M. Lu, *Jpn. J. Appl. Phys.*, 2004, **43**, 8156.
17. 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.*, 2008, **104**, 064502.
18. H.-G. Park, B.-Y. Oh, Y.-H. Kim, B.-Y. Kim, J.-M. Han, J.-Y. Hwang, and D.-S. Seo, *Electrochem. Solid-State Lett.,* 2009, **12**, J37.
19. S. Jeong, Y.-G. Ha, J. Moon, A. Facchetti, and T. J. Marks, *Adv. Mater.*, 2010, **22**, 1346.
20. H.-G. Park, H.-C. Jeong, J.-J. Han, S. Y. Kim, J.-H. Kim, D.-H. Kim, and D.-S. Seo, *J. Mater. Chem. C*, 2014, **2**, 3960.
21. J. Szuber, G. Czempik, R. Larciprete, D. Koziej and B. Adamowicz, *Thin Solid Films*, 2001, **391**, 198.