Alignment of liquid crystal on a polyimide surface exposed to an Ar ion beam

Jin Seog Gwag, Chul Gyu Jhun, Jae Chang Kim, and Tae-Hoon Yoon[a)]
Department of Electronics Engineering, Research Institute of Computer, Information and Communication, Pusan National University, Busan 609-735, Korea

Gi-Dong Lee
Division of Electronics Engineering, Dong-A University, Busan 604-714, Korea

Seong Jin Cho
Department of Physics, Kyungsung University, Busan 608-736, Korea

(Received 29 December 2003; accepted 18 April 2004)

In this paper properties of nematic liquid crystals aligned on polyimide surfaces exposed to a low-energy Ar ion beam are investigated. We studied how the pretilt angle of a liquid crystal cell is affected by ion-beam conditions, such as the energy of the incident ions, the angle of incidence, and the exposure time. X-ray photoelectron spectroscopy data indicate that ion-beam exposure changes the chemical bonding states of the polyimide surface, which may be one of the main causes of anisotropic liquid crystal alignment. We also found that twisted-nematic cells fabricated by the ion-beam alignment method have the voltage holding time enough for application to thin-film-transistor liquid crystal displays.
[DOI: 10.1063/1.1759391]

I. INTRODUCTION

A liquid crystal layer anisotropic on the surface of both substrates is required for display applications. Generally polyimides are used in liquid crystal displays (LCDs) as the material to align liquid crystals. A number of alternative alignment techniques to induce anisotropy on both surfaces have been reported.[1–5] Although the rubbing method has been widely used in actual production of LCDs because of its high productivity, this technique has many disadvantages. The method leaves debris by the cloth during the rubbing process, which may result in electrostatic discharge that influences electronic circuits just below the surface of the rubbed polyimide. To overcome these problems, a noncontact alignment method is highly desirable for future generations of large, high-resolution LCDs. Since the ion-beam alignment method was reported recently by IBM,[6,7] research on this alignment method has been conducted for wider application of LCDs.[8–10]

To optimize the display performance, it is necessary to control the pretilt angle suitable for each mode of LCDs. One of the potential methods for controlling the pretilt angle is the ion-beam alignment technique. Changes in the ion-beam parameters affect the pretilt angle of a liquid crystal cell. In this paper we report the origin of the pretilt in a liquid crystal cell with polyimide surfaces treated by a low-energy argon ion beam. We examined the change in the pretilt angle of a liquid crystal cell using the polyimide "SE-7492" as the alignment layer under various ion-beam conditions. Optical characteristics of a unit twisted-nematic (TN) cell fabricated by the ion-beam method are compared with the ones fabricated by the rubbing method. To demonstrate the applicability of the ion-beam alignment method to TFT (thin-film-transistor)-LCDs, the charge retention capability of a cell fabricated under various ion-beam conditions was measured.

[a)]Electronic mail: thyoon@pusan.ac.kr

II. EXPERIMENTS

A. Ion-beam treatment

Liquid crystal cells were prepared for experiments in the following manner. Indium-tin-oxide coated on glass substrates was used as the electrodes for each cell. The substrates were spin coated with the polyimide SE-7492, prebaked at 80 °C for 10 min, and cured at 250 °C for 2 h. The polyimide layer was bombarded by a low-energy argon ion beam. Figure 1 shows the schematic drawing of an ion-beam system. A cold hollow cathode (CHC) type was used as the source of ions to yield the ion beam. In order to collimate the ion beam, two perforated grids were used as electro-focusing lenses. The CHC represents a separate cooled chamber supplied with a magnetic system and connected to a discharge chamber through an orifice hole. Argon gas feeding into the ion source is being carried out through the CHC only. A discharge ignition in the cathode takes place at nominal values of discharge voltages and at nominal gas flow rates. A neutralizer filament on the outside of the ion source serves as a source of electrons necessary for the compensation of the ion-beam spatial charge and reduces the repulsive force among ions.

B. Alignment

Effective parameters that influence the surface of polyimide may be the energy, the exposure angle, the exposure time, and the current density. In our experiments, the energy,

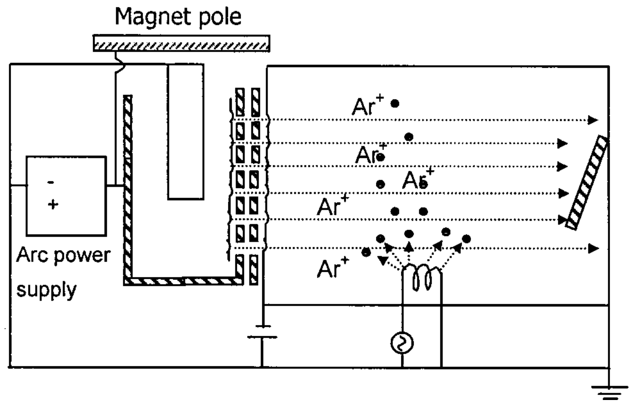

FIG. 1. Schematic drawing of an ion-beam system.

the exposure angle, and the exposure time were varied. After the substrates were bombarded by an atomic beam, antiparallel cells and TN cells were fabricated with a liquid crystal "Merck ZLI-1557." The rubbing direction and the in-plane projection of the ion beam were along the *y* axis, as shown in Fig. 2. Next, the pretilt angles of liquid crystal cells fabricated by the rubbing method and by the ion beam treatment were measured by the crystal rotation method.[11,12]

The ion-beam-treated polyimides orient the liquid crystal director parallel to the *y* axis, while the liquid crystal director was tilted up from the $-y$ axis as shown in Fig. 2. The in-plane direction of the liquid crystals and their pretilt angles on the surfaces of the ion-beam-treated polyimides could be determined by the following origin.

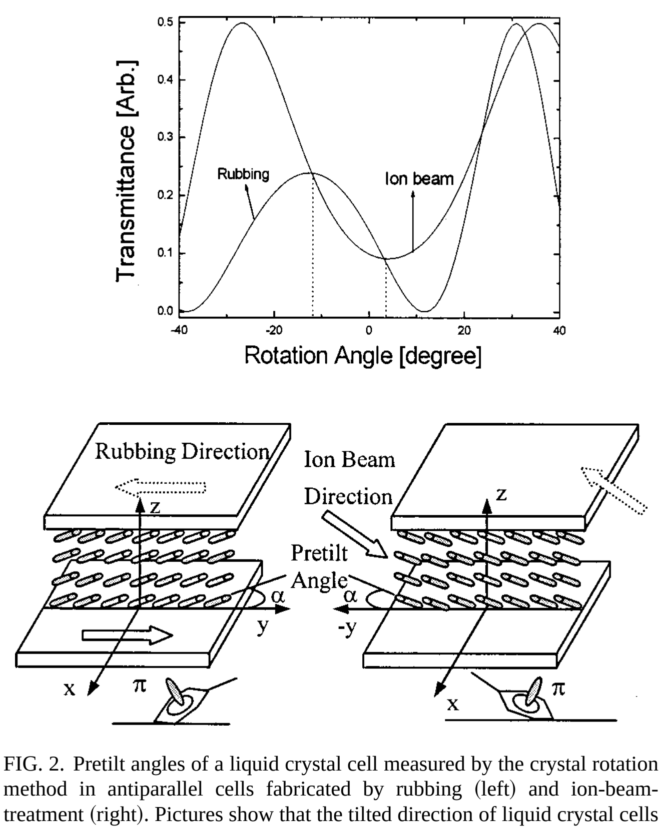

FIG. 2. Pretilt angles of a liquid crystal cell measured by the crystal rotation method in antiparallel cells fabricated by rubbing (left) and ion-beam-treatment (right). Pictures show that the tilted direction of liquid crystal cells is opposite to each other. The pretilt angle is determined by the direction of the π bond in polyimide.

At the rubbed polyimide, the orientational order of liquid crystal is generated from the crystalline order of polymer chains.[13] However, in the ion-beam-treated polyimides, the order may be created by the selective destruction of π bonds of imide rings in the polyimide.[14]

The probability of interaction between the ion beam and π electrons will be high if the ion beam is incident from the normal direction, compared to being parallel to the plane of the *p* orbital. The ion beam will destroy π bonds perpendicular to the incident ion beam, which have larger cross section. Consequently, the pretilt angle of the liquid crystal will be created by the remaining π bonds parallel to the incident ion beam. By varying the conditions of the ion beam, such as the energy of the incident ions, the angle of incidence, and the exposure time, the pretilt angle of the liquid crystal is changed.

III. RESULTS AND DISCUSSION

A. Pretilt angle

With SE-7492 used as the polyimide, Fig. 3(a) shows a plot of the pretilt angle as a function of the angle of incidence of the ion beam with respect to the plane of the substrate, where the ion beam energy, the ion beam exposure time, and the beam current density were 80 eV, 20 s, and 15 $\mu A/cm^2$, respectively. Then a maximum pretilt angle is about 2.7° at the exposure angle of 50°. The pretilt angle decreases with increasing ion-beam energy for samples exposed for 20 s and at an incidence angle of 45°, as shown in Fig. 3(b). The pretilt angle also decreases with increasing the exposure time for samples exposed to an ion beam with the energy of 80 eV and an incidence angle of 45°, as shown in Fig. 3(c). The experiment shows that the control of the pretilt angle is possible, but its value and varied range are low and small. Thus, this ion-beam method can be restrictively applied to liquid crystal modes with a low pretilt angle, such as in-plane switching mode and bistable twisted-nematic mode.

B. *V*–*T* characteristics

Figure 4 shows a plot of transmission of light as a function of voltage for four TN cells, which were fabricated by the ion-beam alignment and by the conventional rubbing alignment. The thickness of the liquid crystal film was 4.2 μm. The incidence angle, the energy, the exposure time, and the current density of the ion beam were 45°, 150 eV (250 eV and 350 eV), 25 s, and 50 $\mu A/cm^2$, respectively. The transmission characteristics are very similar for the two cases. Only a slight difference exists due to the difference in the cell gap and the pretilt angle for the two TN cells. When 5 V was applied to TN cells, their response times were also very similar (20 ms; the rising time of about 6.5 ms and the falling time of about 13.5 ms).

C. X-ray photoelectron spectroscopy

The surface chemical properties of a PI film SE-7492 were studied by x-ray photoelectron spectroscopy (XPS) (An electron spectrometer "Physical Electronics PHI 5700" was used). The core level peaks were analyzed by means of the

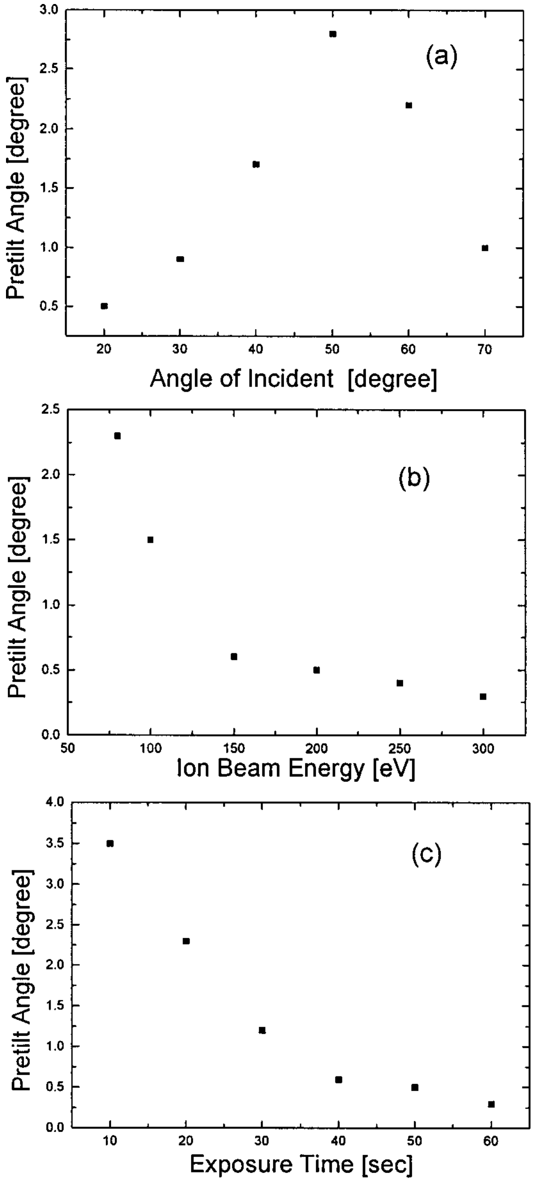

FIG. 3. The pretilt angle as a function of (a) the incident ion-beam angle, (b) the ion-beam energy, (c) the exposure time of the ion beam. SE-7492 was used as the polyimide.

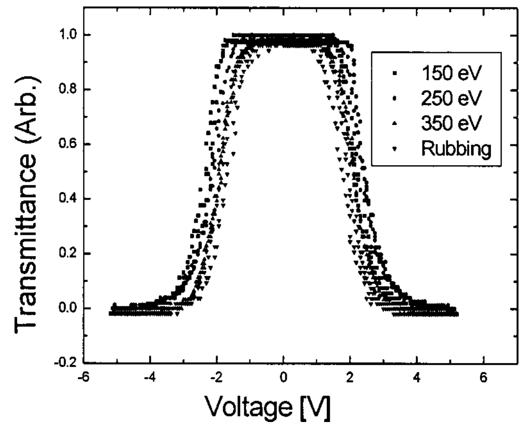

FIG. 4. Comparison of the voltage-transmittance curves of TN cells fabricated by the rubbing method and the ion-beam method. Then, the ion-beam energy: 150, 250, and 350 eV, the incidence angle: 45°, and the exposure time: 25 s.

Gauss-Lorentz-fit algorithm with background subtraction. The C1s level spectrum was recorded using the monoenergetic Al $K\alpha$ radiation with energy of 1486.6 eV. The base pressure in the sample chamber was 2×10^{-10} Torr.

Figure 5 shows XPS detail spectrum of the C1s of the polyimide (SE-7492) surface observed before the atomic beam exposure, and after the exposure (the ion beam energy: 350 eV, the exposure time: 40 s, the current density: 100 μA/cm^2). The peak at 288.5 eV corresponds to carbonyl carbon (C═O) in imide rings. After the atomic beam exposure, the intensity of the peak decreases. This is apparently related to the significant reduction of oxygen in carbonyl groups and nitrogen in imide rings broken by argon atoms. The peak at 284.8 eV appears to correspond to the carbon atoms of the benzene ring. Actually, the peak at 285.7 eV includes three different peaks.[15] The peak at 286.3 eV corresponds to the C–O single bond. Figure 5(b) shows that the intensity of the phenyl carbon peak decreases obviously after the atomic beam exposure, and the intensity of the C–O peak increases relative to the carbon of the phenyl ring. This indicates the destruction of the benzene ring with double bonds. Alignment by an ion beam may be due to the breakdown of π bonds in imide rings, phenyl rings, and carbonyl groups[7,13,14] because disordered systems with π bonding are more readily oriented than those with saturated bonds.[14] The probability of

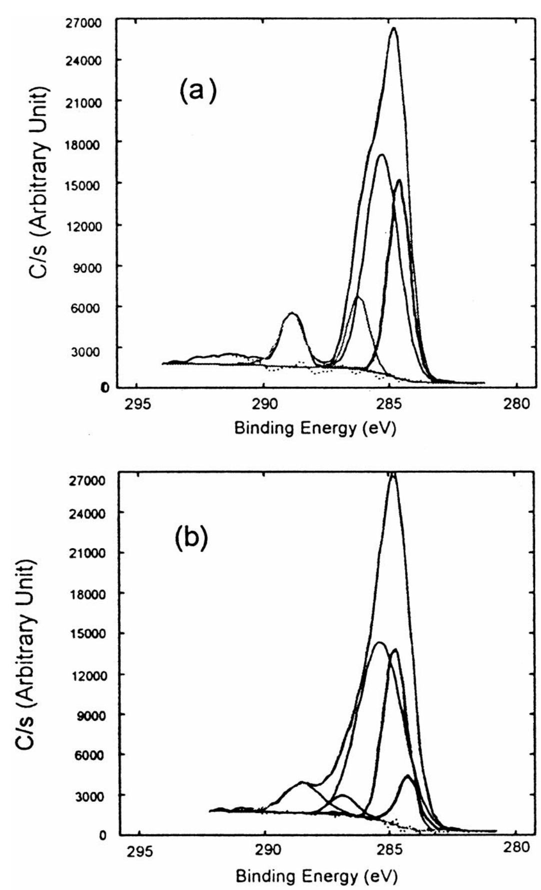

FIG. 5. Curve fitting of XPS data for SE-7492 as polyimide: (a) before the ion-beam exposure, (b) after the ion-beam exposure.

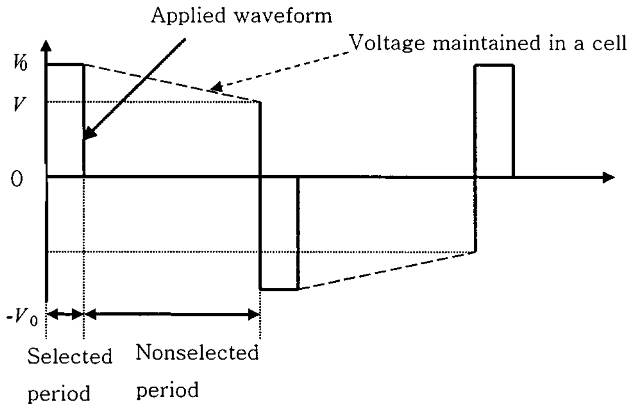

FIG. 6. Schematic drawing of the initial voltage (V_0) applied during selected periods and the final voltage (V) obtained by the relaxation of the liquid crystals during nonselected periods.

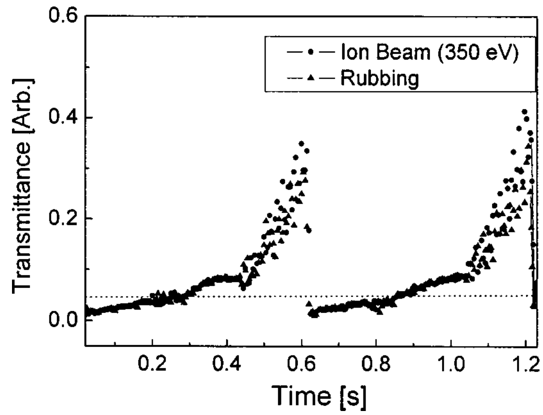

FIG. 7. Charge retention time measurement of TN cells fabricated by the rubbing method and the ion-beam method. The ion-beam energy: 350 eV, the incidence angle: 45°, and the exposure time: 25 s. The dotted line corresponds to the voltage holding of 90%.

interaction between an ion beam and π electrons will have a larger value with the ion beam normal than parallel to the plane of the p orbital.

The broken bonds on the polyimide surface bombarded with Ar ion beams shown in Fig. 5 could induce radicals or ions. When a voltage is applied to a liquid crystal cell, these ionic impurities could result in a charge build up. It will cause the electric field to be different from the intended value, which could affect the voltage holding time that leads to the change in transmission during a frame time.

D. Voltage holding ratio

To check the applicability of the ion-beam alignment method to TFT-LCDs by using an n-channel field-effect-transistor, the voltage holding capability was measured for a cell fabricated under the ion-beam conditions with the beam energy of 350 eV, the incidence angle of 45°, and the exposure time of 25 s.

Figure 6 illustrates the initial voltage (V_0) for selected periods and the final voltage (V) obtained by the relaxation of the liquid crystals during nonselected periods. The voltage, maintained in a cell, must be kept more than 90% of the applied voltage during a frame. To a unit TN cell 5 V was applied fabricated by the ion-beam method for 10 μs, then it remained open for 600 ms. As shown in Fig. 7, the time during which above 90% of applied voltage is kept in the cell was about 200 ms. It is similar to the results for the cell fabricated by the rubbing method, which is enough for application to TFT-LCDs. This result shows that there are few ions or radicals induced by broken bonds on polyimide surfaces bombarded with Ar ion beams.

IV. CONCLUSIONS

SE-7492 polyimide surfaces bombarded by a low-energy Ar ion beam align the liquid crystals parallel to the direction of the ion-beam exposure and create a pretilt angle by controlling ion-beam parameters, such as the energy level of the incident ions, the incidence angle, the exposure time, and the current density. The result of curve fitting with XPS indicates that ion bombardment on polyimide surfaces changes the chemical bonding states of polyimide surfaces, even though its energy is low. The selective destruction of the chemical bonding may be the main cause of anisotropic LC alignment. We also found that a TN cell fabricated by the ion-beam alignment method has a sufficient voltage-holding time for application to TFT-LCDs. This could mean that there are few ions or radicals induced by broken bonds on polyimide surfaces bombarded with Ar ion beams.

ACKNOWLEDGMENT

This work was supported from Information Display R&D Center, one of the 21st Century Frontier R&D Program funded by the Ministry of Science and Technology of Korea.

[1] D. W. Berreman, Phys. Rev. Lett. **28**, 1683 (1972).
[2] J. Ienuing, Appl. Phys. Lett. **21**, 173 (1982).
[3] M. Nakamura and M. Ura, J. Appl. Phys. **52**, 210 (1981).
[4] H. Aoyama, Y. Yamazaki, M. Matsuura, H. Mada, and S. Kobayashi, Mol. Cryst. Liq. Cryst. **72**, 127 (1981).
[5] M. Schadt, K. Suhmitt, V. Kozinkov, and V. Chiqvinov, Jpn. J. Appl. Phys. **31**, 2155 (1992).
[6] P. Chaudhari, Jpn. J. Appl. Phys. **37**, L55 (1998).
[7] P. Chaudhari, Nature (London) **411**, 56 (2001).
[8] J. L. West, L. Su, K. Artyushkova, J. Farrar, J. E. Fulghum, and Y. Reznikov, SID 2002 Digest, **XXXIII**, 1102 (2002).
[9] J. S. Gwag, S. H. Lee, K. H. Park, W. S. Park, K. Y. Han, T.-H. Yoon, and J. C. Kim, *International Meeting on Information Display 2002*, Vol. 409 (2002).
[10] J. S. Gwag, K.-H. Park, D. J. Kang, T.-H. Yoon, and J. C. Kim, Jpn. J. Appl. Phys. **42**, L468 (2003).
[11] T. J. Scheffer and J. Nehring, J. Appl. Phys. **48**, 1783 (1977).
[12] Kwan-Young Han and Tetsuya Miyashita, Jpn. J. Appl. Phys. **32**, L277 (1993).
[13] J. StÖhr and M. G. Samant, J. Electron Spectrosc. Relat. Phenom. **98–99**, 189 (1999).
[14] J. StÖhr *et al.*, Science **292**, 2299 (2001).
[15] A. M. Ektessabi and S. Hakamata, Thin Solid Films **377–378**, 621 (2000).