Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Controllable Alignment Modes of Nematic Liquid Crystals on Argon Ion Beam Bombarded Polyimide Films

Hsin-Ying Wu [a], Chih-Chieh Wang [a], Ru-Pin Pan [a], Tsung-Ta Tang [b], Shao-Ju Chang [c] & Jenn-Chang Hwang [c]

[a] Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

[b] Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

[c] Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.

Version of record first published: 22 Sep 2010

Mol. Cryst. Liq. Cryst., Vol. 475, pp. 45–55, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701681612

Controllable Alignment Modes of Nematic Liquid Crystals on Argon Ion Beam Bombarded Polyimide Films

Hsin-Ying Wu
Chih-Chieh Wang
Ru-Pin Pan
Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

Tsung-Ta Tang
Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

Shao-Ju Chang
Jenn-Chang Hwang
Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.

We investigate the alignment properties of nematic liquid crystal on polyimide films bombarded by Ar ion beams with a small diode sputter type ion-beam source. The alignments of nematic liquid crystal 4′-n-pentyl-4-cyanobiphenyl (5CB) on treated polyimide surface are characterized by using polarizing optical microscope and conoscope. The polyimide surfaces are also studied by using atomic force microscope and x-ray photoemission spectroscopy. We have demonstrated that the polyimide surface treated by Ar ion beams can give both homogeneous and homeotropic alignments with the same ion beam apparatus but varying the energy of ion beam and the bombarding time.

Keywords: ion beam; nematic liquid crystals; polyimide films; pretilt angle; surface alignments

This work is supported in part by MOE-ATU Program and the National Science Council of R.O.C. under Grants No. NSC 91-2112-M-009-024, NSC 93-2215-E-009-065, and PPAEU-II.

Address correspondence to Ru-Pin Pan, Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan. E-mail: rpchao@mail.nctu.edu.tw

1. INTRODUCTION

Surface alignments of liquid crystals (LCs) are essential in liquid crystal displays (LCDs) and other LC devices. It determines the boundary condition for the molecular orientation at the surface. Currently, the most common alignment method used in LCDs industries is the rubbing method, which employs a velvet rubbing process on polyimide (PI) coated on substrates. In spite of its high popularity and success, this method has some drawbacks such as leaving debris and electrostatic charges on the rubbed surfaces. It becomes increasingly difficult to maintain uniformity as the substrate size of LCD gets larger rapidly in industry. In order to enhance the qualities of LC products, non-contact alignment methods are highly desirable. One of the alternative alignment methods, ion beam alignment, had been reported by an IBM group [1–4]. They have successfully realized this non-contact alignment technology by integrating both a low energy ion beam and diamond-like carbon (DLC) thin films into LCD manufacturing processes. The mechanism of this alignment method was contributed to the anisotropical change of bindings between carbon atoms caused by ion beam bombardment [4]. Although the ion-beam bombarded DLC film has shown excellent electro-optical performances in some aspects for the twisted nematic liquid crystal display, which employs homogeneous alignments [5], and the homeotropic alignment can be obtained by using fluorinated DLC thin film as the alignment layer [6]. The properties of ion-beam bombarded PI films are also worth studying. Especially, the coating processes have already been built in the existing manufacturing lines.

In this work, we study the alignment properties of nematic liquid crystal on the PI films treated by Ar ion beams with various energy and bombarding time by using a commercial diode sputter as the ion-beam source. This method is very convenient and inexpensive for small samples. We found that there exist two alignment modes, homeotropic and homogeneous alignments, which can be controlled by varying the energy of ion beams and the bombarding time. We have studied the surface morphology change of the PI films by using atomic force microscope (AFM) and the chemical change by using the surface-sensitive x-ray photoemission spectroscopy (XPS). The alignment mechanism is discussed by comparing the alignment properties with AFM and XPS results.

2. EXPERIMENTS

In this research, an ion coater (model IB-2 from EIKO Engineering Co., Ltd.) has been used for ion-beam treatment on PI surface.

Its operational principles are the same as those of a diode sputter. The ion beam coater can be used either as a coating or etching device, depending on the polarity of the voltage. The etching mode is selected in this work. Figure 1(a) shows the spatial distribution of glow discharge in our ion coater under the etching mode. The spacing between the electrodes is 30 mm. The diameters of upper and lower electrodes are 50 mm and 52 mm, respectively. The cathode dark space has the most energetic ions and provides the main region for ion-beam treatment. Therefore, the size of substrates has to be controlled such that they are totally immersed in this region as shown in Figure 1(b). The arrows indicate the direction of incident ion beam. In our system, the incidence angle θ_{ion}, bombarding time τ, current density and the energy of ions E_{ion} are all controllable. The energy of ions can be varied by changing the dc voltage between electrodes. Before each ion-beam process, the chamber is pumped down to a base pressure of 30 m Torr and then argon gas is fed into the chamber to a target pressure. To keep the current density unchanged, 255 $\mu A/cm^2$ in this work, the total pressure of the chamber has to be adjusted between 50 and 180 m Torr when the applied dc voltage is changed. The incidence angle θ_{ion} is also fixed at 60° throughout this work.

The indium-tin-oxide coated glasses with size of 20 mm × 10 mm are used as the substrates. The substrates are spin coated with the polyimide SE-130B (Nissan Chemical Industries, Ltd.), which is commonly used as an alignment agent in super twisted nematic LCD. The spin rate is 2000 rpm for the first 15 seconds and 4000 rpm for the 25 seconds afterward. The substrates are then pre-baked at 70°C for 15 minutes and cured at 180°C for another one hour. This thermal treatment process is chosen according to the company's instruction

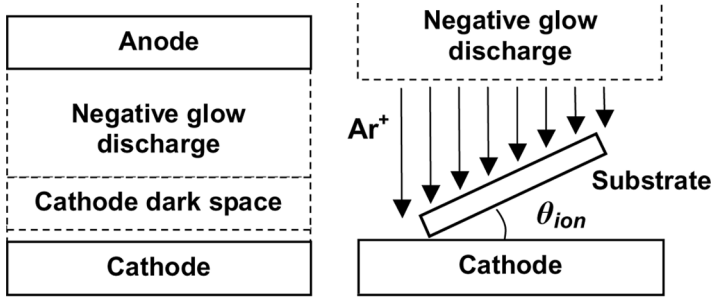

FIGURE 1 Sketch of Ar ion-beam bombardment: (a) The space distribution of glow discharge in a diode sputter, and (b) the arrangement of glass substrates in the sputter.

for achieving a pretilt angle of 3° with rubbing method. Two substrates are bombarded in ion beam chamber simultaneously and then combined with a 23 μm Mylar spacer in between with anti-parallel alignment direction to form an empty cell. The nematic liquid crystal (NLC) 4′-n-pentyl-4-cyanobiphenyl (5CB, Merck) with a nematic range between 24.0°C and 35.3°C is filled into the empty cell for alignment characterization.

The alignment modes are checked with conoscope and polarizing optical microscope (POM). The pretilt angle of 5CB molecules near the surface is measured by using the "crystal rotation method" [7], and the azimuthal anchoring strength E_a is determined by using the twisted cell method [8]. In addition, the surface morphologies of ion-beam treated PI films are characterized by using a DINS3a atomic force microscope with tapping mode. To study the possible reactions caused by ion-beam bombardment, the compositions of chemical bonds of the polyimide film after ion-beam treatment at various conditions are also analyzed by using x-ray photoemission spectroscopy (XPS, PHI-1600).

3. RESULTS AND DISCUSSION

We have observed both of the homeotropic and homogeneous alignments with the ion bombarded films. Figure 2 shows the POM photographs of 5CB cells with crossed polarizer. The substrates treated by Ar ion beam with various energies exhibit good alignment qualities. In Figure 2(a), the homogeneous alignment of 5CB is obtained by using substrates bombarded with the following ion beam parameters: the dc voltage of 560 V and bombarding time of 40 min. The easy axis of 5CB lies in the incidence plane of ion beam and tilts toward the direction of incident ion beam. These alignment properties agree with the results reported by an IBM group [1]. In Figure 2(b), we show the homeotropic alignment obtained with another set of ion beam parameters: the dc voltage of 1120 V and bombarding time of 7 min. The conoscopic pattern shown in the inset further indicates that the cell is homeotropically aligned.

The measured pretilt angles for two dc voltage are shown in Figure 3 with respect to the bombarding time. In the case of homogeneous alignment ($E_{ion} = 560$ V), the pretilt angle approaches to a maximum value about 6.43° and then decreases with the increasing bombarding time. However, the pretilt angle of homeotropic cell ($E_{ion} = 1120$ V) remains constant with the increasing bombarding time. The pretilt angle can achieve as high as 89.98° at bombarding time of 7 min.

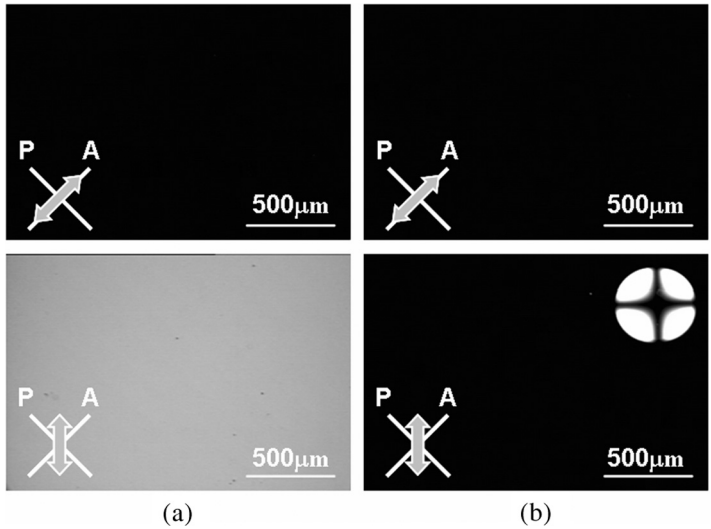

FIGURE 2 The POM photographs of NLC cells treated by different ion beam parameters: (a) homogeneous alignment, and (b) homeotropic alignment. (Inset: conoscopic pattern).

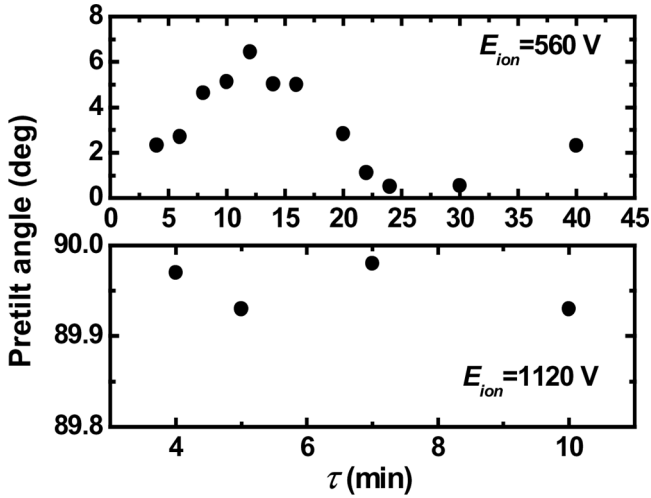

FIGURE 3 The pretilt angle vs. the ion beam bombarding time for two different ion energy $E_{ion} = 560\,\text{V}$ (top) and 1120 V (bottom).

With substrates treated with $E_{ion} = 560\,\text{V}$, the measured azimuthal anchoring strength E_a as a function of bombarding time from 15 min to 30 min is plotted in Figure 4. The cells with bombarding time less than 15 min have lower alignment qualities. We can see that the azimuthal anchoring strength is maximized at bombarding time of 24 min. While the bombarding time is over 24 min, the E_a decreases abruptly with time. This is possibly due to that the PI film is etched away as it is common in the ion beam system running in the etching mode.

To investigate the possible alignment mechanism for liquid crystals on treated PI films, the surface topology are surveyed using AFM. The surface roughness clearly increases with bombarding time as shown in Figure 5. The mean roughness of Figures 5(a)–(d) is 0.2 nm, 1.7 nm, 1.8 nm, and 4.8 nm, respectively. All of the treated substrates shown in Figure 5 give homogeneous alignments.

Figure 6 also shows the AFM images of the PI surfaces but bombarded by various ion energies. The mean roughness for ion energy, 560 V, 840 V, and 1120 V is 1.2 nm, 1.4 nm, and 0.3 nm respectively. The roughness of PI surface bombarded by high energy ion (dc voltage 1120 V) is much smaller. It is expected because the higher energy ions have better etching ability and reduces the roughness more. There is not a straightforward relation between the alignment modes and surface topologies induced by ion beam bombardment with different ion energy.

Although the generation of micro-scaled directional grooves is one of the major alignment mechanisms for traditional rubbing method, the

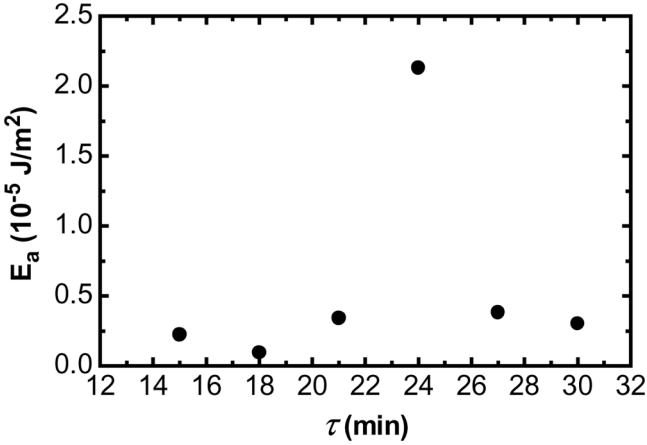

FIGURE 4 The azimuthal anchoring strength E_a as a function of the bombarding time τ with $E_{ion} = 560\,\text{V}$.

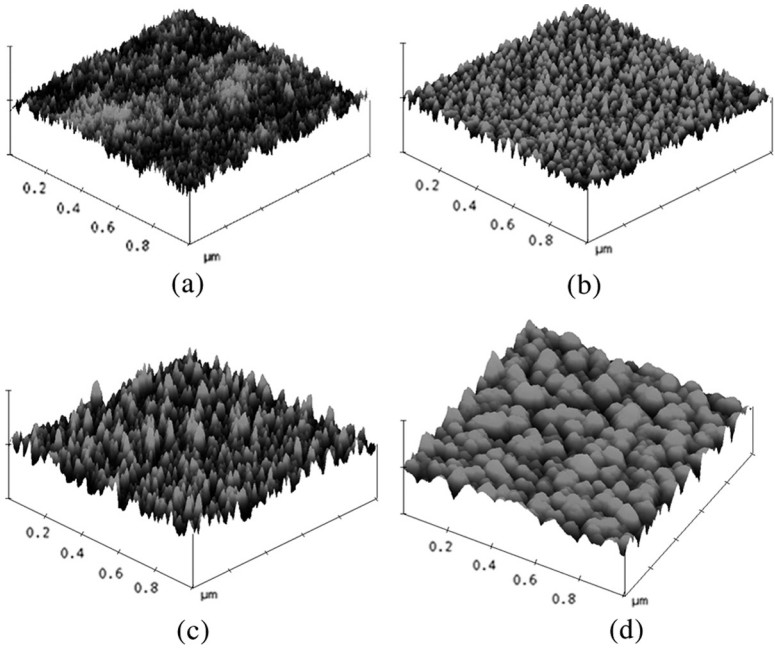

FIGURE 5 AFM images of the PI films treated for different bombarding time: (a) As-deposited, (b) 6 min, (c) 14 min, and (d) 30 min with ion energy E_{ion} of 560 V. The films here give homogeneous alignments.

groove structures are not found on the ion-beam treated surfaces. The more possible mechanism for aligning liquid crystals is the intermolecular interactions.

To investigate the changes of chemical bonds on ion beam treated PI films with different ion energy, the XPS is used. Because the liquid crystal molecules interact directly with the carbon bonds, the type of carbon bonds are important and can be extracted from XPS core-level spectra C_{1s} as shown in Figure 7. The binding energies of several carbon bonds (C–C/C–H at 284.7 eV, C–N at 285.68 eV, C–O–C at 286.29 eV, and N–C=O at 288.61 eV) [9] are investigated in this study. As an example of the peak fitting procedure, the results of the line separation for the C_{1s} signal from as-deposited PI films are plotted below the raw signal. The carbon bonds except the N–C=O are all decreased after ion beam bombardment. It indicates the etching effect that the ion beams with higher energy destroy significantly the main structures of PI films including the C–N, C–O–C bonds, and the aromatic rings. Since the bond-breaking process is dominant in ion beam

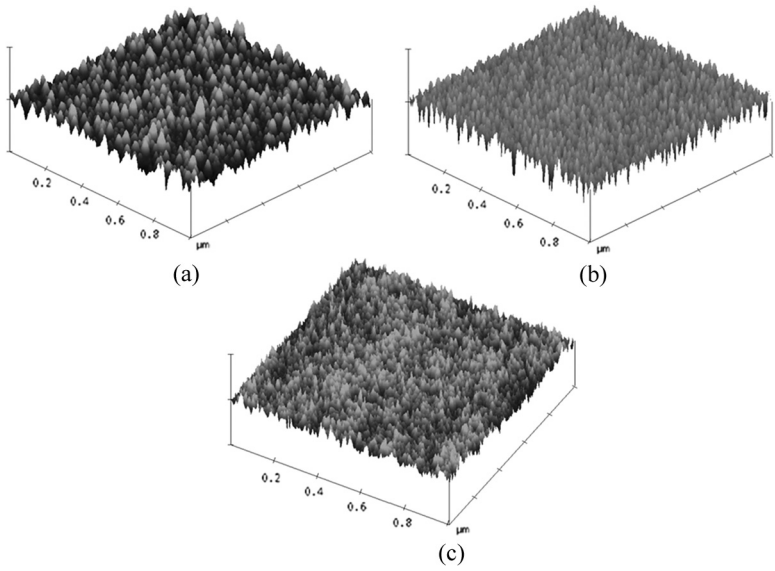

FIGURE 6 AFM images of the PI films treated by different ion energies: (a) 560 V, (b) 840 V, and (c) 1120 V with bombarding time τ of 5 min.

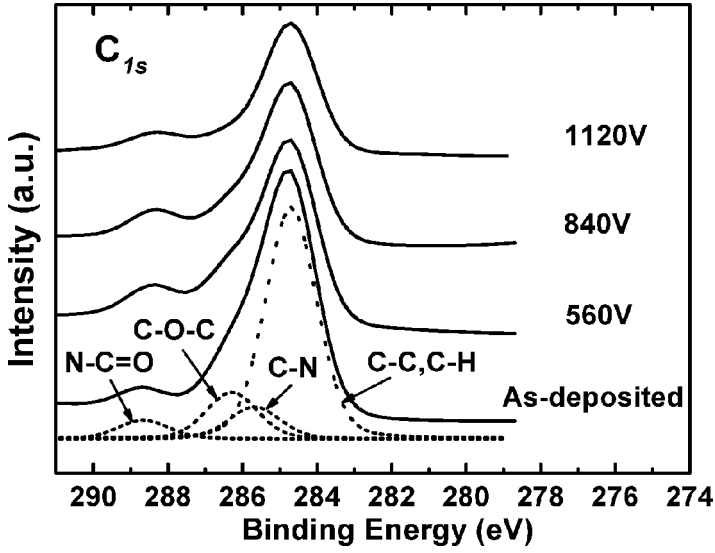

FIGURE 7 C_{1s} spectra for the as-deposited and ion beam treated PI films with various ion energies.

treatments, many dangling bonds will be created. Once the treated surface are exposed to the air, the re-oxidization will occur to form new N−C=O bonds. Figure 8 shows the relative compositions of carbon bonds on PI films treated with different ion energy E_{ion}. The compositions of C−N and C−O−C bonds decrease slightly with the ion energy. These results indicate that the backbones of PI are divided into shorter segments and more dangling bonds are available to grab more oxygen.

The bond-breaking effects of PI films to the LC alignment induced by ion beams here are similar to that induced by polarized ultraviolet (UV) light irradiation [10,11]. They are both attributed to the intermolecular interactions between the liquid crystals and the unbroken polyimide chains. To confirm that the alignment in this work is indeed induced by ion beam rather than the UV irradiation in the ion beam chamber, we have formed a cell with substrates partially covered by a fused silica plate while performing the ion-beam treatment. At the covered area the UV light can transmit through the silica plate while the ion beam is blocked. The pictures of this cell between crossed-polarizers are shown in Figure 9, only the uncovered area (right hand side) shows good alignment. Since no alignment effect appears in the untreated area (left hand side), we can conclude that the alignment effects are not caused by the UV light from plasma discharge.

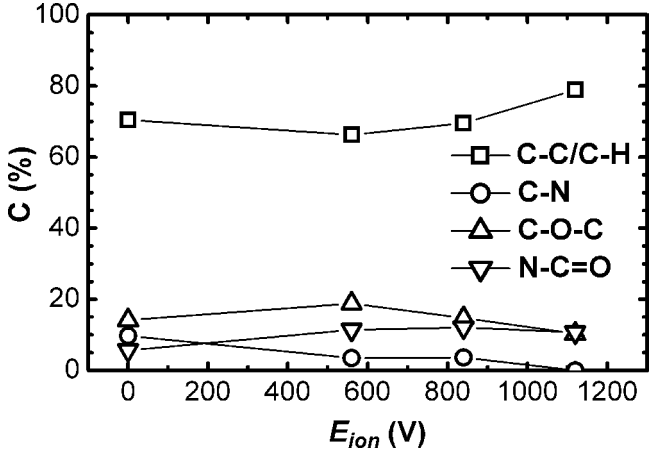

FIGURE 8 The compositions of chemical bonds C of as-deposited and ion-beam treated PI films as a function of the ion energy E_{ion} with bombarding time of 5 min.

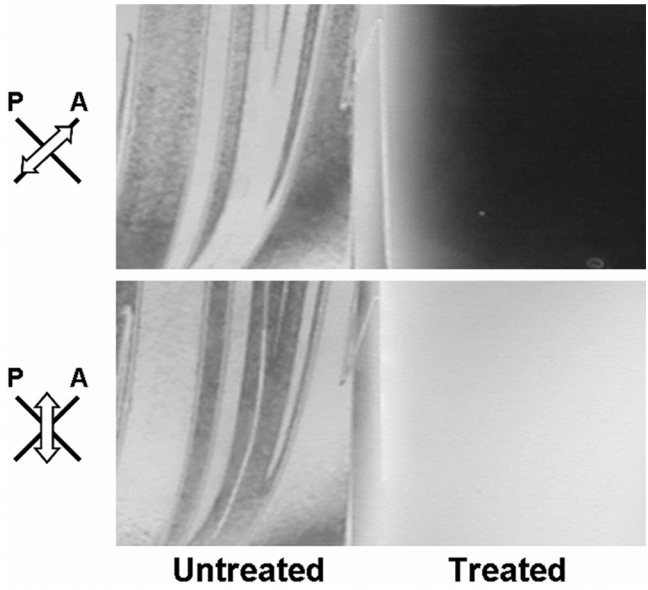

FIGURE 9 Photographs of an ion beam treated NLC cell placed between crossed-polarizers. The left side of the substrates was covered with fused silica plate while being ion-beam treated. The ion beam energy and bombarding time are 560 V and 20 min, respectively.

However, the mechanism of homeotropic alignments induced by Ar ion beam bombardment with higher energy is still unclear. More studies on this subject are still being carried on.

A different kind of PI, HTX-6700 (Hitachi Chemical Co., Ltd.), has also been used as alignment layer with the same ion beam procedure. We can also obtain these two alignment modes selectively by controlling the bombarding time at a specific energy of ion beams.

4. CONCLUSION

We have demonstrated that both homeotropic and homogeneous alignments can be obtained with the same ion beam apparatus and polyimide by varying the ion beam energy or the bombarding time. This apparatus can be very small and inexpensive. It is also very convenient particularly for small size samples. Both of the homeotropic and homogeneous cells have uniform and high contrast under the crossed polarizer. AFM images of polyimide surfaces treated by ion beams show no microgroove structure but only with roughness

changing with bombarding time and ion-beam energy. The ion-bombarding-time-dependent azimuthal anchoring strength and pretilt angle measurements suggest that the etching effect of the ion beams place an important role for the alignment properties. The XPS results show that the main structures including the C−N, C−O−C bonds, and the aromatic rings of polyimide films are significantly destroyed in high energy ion beam bombardments and the N−C=O bonds formation is considered as the neutralization of dangling bonds when exposed to the air. The possibility of UV light induced alignment effect has been excluded in our ion beam treatment process.

REFERENCES

[1] Chaudhari, P., Lacey, J., Lien, S.-C. A., & Speidell, J. L. (1998). *Jpn. J. Appl. Phys. 37*, L55.
[2] Chaudhari, P. et al., (2001). *Nature*, (London) *411*, 56.
[3] Doyle, J. P., Chaudhari, P., Lacey, J. L., Galligan, E. A., Lien, S. C. et al., (2003). *Nuclear Instruments and Methods in Physics Research B*, *206*, 467.
[4] Stöhr, J., Samant, M. G., Lüning, J., Callegari, A. C., Chaudhari, P., Doyle, J. P., Lacey, J. A., Lien, S. A., Purushothaman, S., & Speidell, J. L. (2001). *Science*, *292*, 2299.
[5] Hwang, J. Y., Jo, Y. M., Rho, S. J., Baik, H. K., & Seo, D. S. (2002). *Jpn. J. Appl. Phys.*, *41*, L992.
[6] Ahn, H. J. et al., (2005). *Jpn. J. Appl. Phys.*, *44*, 4092.
[7] Scheffer T. J. & Nehring, J. (1977). *J. Appl. Phys.*, *48*(5), 1783.
[8] Saitoh, Y. & Lien, A. (2000). *Jpn. J. Appl. Phys.*, *39*, 1743.
[9] Wolany, D., Fladung, T., Duda, L., Lee, J. W., Gantenfort, T., Wiedmann, L., & Benninghoven, A. (1999). *Surf. Interface Anal.*, *27*, 609.
[10] Lu, J., Deshpande, S. V., Gulari, E., Kanicki, J., & Warren, W. L. (1996). *J. Appl. Phys.*, *80*(9), 5028.
[11] Oh-e, M., Kim, D., & Shen, Y. R., (2001). *J. Chem. Phys.*, *115*, 5582.