

# Modification of Thin Polyimide Film Surface by Atmospheric Pressure Dielectric Barrier Discharge for Liquid Crystal Alignment

Alibi Baitukha, Shinsuke Mori, Masaaki Suzuki

Department of Chemical Engineering, Tokyo Institute of Technology, Japan

## Abstract

Present research work is devoted to clarify the alignment mechanism of Liquid Crystal (LC) molecules on the Atmospheric Pressure Plasma Jet (APPJ) treated Polyimide films. On glass substrates thin Polyimide films were spin-coated. To impart alignment properties these substrates are exposed under the APPJ Scanning System. FTIR spectroscopy is used to describe structural change on the surface of Polyimide film. Polarizing Optical Microscope is used to describe the optical properties and overall performance of the composed LC cells.

**Keywords:** Atmospheric Pressure Plasma Jet, Liquid Crystal Alignment, Polyimide Thin Film Treatment

## 1. Introduction

The alignment layer is a thin layer between the substrate and the LC molecule volume. This alignment layer orients LC molecules on its surface in a particular direction. Mechanical rubbing of a Polyimide surface is the conventionally used method to create an alignment layer. As a contact method of treatment it introduces debris and can cause defects which can be detected only after LCD will be manufactured. To overcome these disadvantages several alternative non-contact methods like Ultraviolet Photoalignment [1-3], Kaufman Ion Beam alignment [4,5], Atmospheric Pressure Plasma Jet treatment [6-8] and others were developed. Among those techniques we paid special attention to the Atmospheric Pressure Plasma Jet (APPJ) Scanning System, as its simple construction and operation at favorable ambient air conditions represents one of the easy and possible replacements for the conventional method.

## 2. Experimental Procedure

Glass substrates ( $2 \times 2 \text{ cm}^2$  and 1 mm thick) were coated with PI film using spin-coating method. SE7492 Polyimide film (supplied by Nissan Chemical Industries) was deposited at 2000 rpm for 30 sec and then baked at 220 °C for 30 min with 200 nm thick uniform film over the all substrate.

The next step is to impart LC alignment properties to the deposited PI film by modifying this film. Glass substrates with deposited film were treated by the APPJ Scanning System. The schematic of the processing system is shown in fig.1. APPJ is composed of a coaxial tube in which a 20 kHz

generator drives one power electrode and the second electrode is grounded. Argon gas is used as a working gas and is fed into annular space inside of the coaxial tube. The ambient atmosphere is air. The input power was equal to 15 W and Ar is flown at the rate of 2 slm.

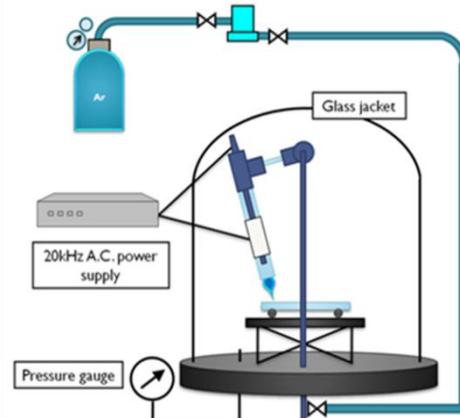


Figure 1. Atmospheric Pressure Plasma Jet (APPJ) scanning system

The stage on which substrate is mounted could be moved on both X and Y-axis by two installed motorized stages (SGSP20-35 controlled by a SHOT-602 Two-Axis Stage Controller). LabVIEW 8.2 is used to compose the controlling program, thus making possible scanning of the substrate and providing directional treatment over the all substrate. The scanning speed in X direction is 2 mm/s and steps in Y direction between each scanning cycle is 0.5 mm.

After treatment glass substrates with deposited PI film are used to fabricate LC cells in order to evaluate the system's overall performance. The gap between two substrates is 10 micron and is filled with "5CB" (4-pentyl-4'-cyanobiphenyl) LC molecules. The melting point and refractive index are equal to 34 °C and 1.532 for 5CB LC molecules respectively.

Yashima TBR-1 Optical Microscope with installed cross-linked polarizer filters is used to analyze alignment uniformity of the completed LC cell. Si wafers are used as substrates for FTIR analysis of treated and as-deposited PI films.

### 3. Results and Discussion

The alignment mechanism of LC molecules to the alignment layer is still under intense discussion [9, 10]. At this moment we know that the conventional method of fabricating an alignment layer creates grooves by mechanical rubbing on the surface of the polyimide film and it could be responsible for the alignment of LC molecules. Also another type of alignment mechanism considers the profile of carbon rings distribution on the surface of treated Polyimide film. For the alternative non-contact methods, it was shown that aromatic rings in the alignment layer material are destroyed by energetic ion particles during low pressure treatment or by directional UV light treatment [11]. Aromatic rings perpendicular to the incident ion beam or UV light have a higher probability to be destroyed by delivered energy and thus directional treatment can generate specific distribution of carbon rings. That sort of change creates anisotropic distribution of the planar angle of carbon rings on the surface and generates a beneficial condition for the process of aligning LC molecules. By dipole dipole interactions with carbon rings LC molecules fixes its spatial orientation throughout the entire treated substrate surface. In the case of APPJ treatment the alignment mechanism is not clear. As it operates at atmospheric pressure it is not likely to achieve directional treatment by energetic particles and destroy carbon rings to achieve specific distribution for the alignment of LC molecules. In our present research work we tried to investigate and try to clarify principles behind interaction of LC molecules with the APPJ treated Polyimide film.

LC cells were constructed from substrates with as-deposited and treated Polyimide films. In the last case treatment direction of each substrate is anti-parallel to each other. To examine qualitatively the performance of the LC cells Polarizing Optical Microscope (POM) was used. In fig.2 three different LC cells images are illustrated in different phases.

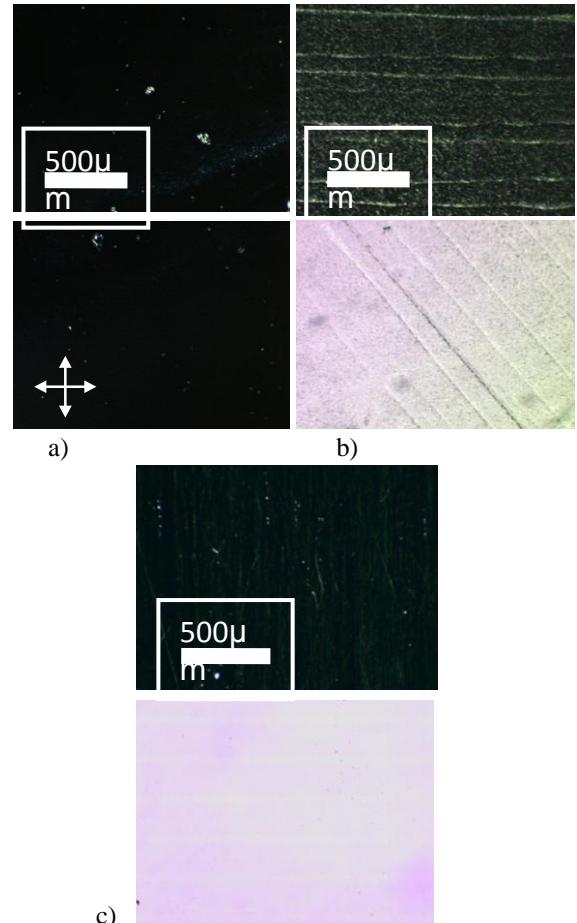


Figure 2. Polarizing Optical Microscope (POM) images of LC cells made of: a) as-deposited polyimide film generates homeotropic alignment (white cross arrows indicate orientation of Polarizer and analyzer in the POM); b) APPJ treated polyimide film substrates; c) mechanically rubbed polyimide film. Lower images are with the rotation of LC cell for 45°

Untreated surface of as-deposited Polyimide film orients molecules in homeotropic orientation (LC molecules perpendicular to the surface of the film fig.2, a). With the rotation of LC cell for 45° it remains black. However, with APPJ treated Polyimide film surfaces LC molecules are aligned in a particular direction (fig.2, b) and we can obtain cells with modified optical properties over the all substrate. And the LC cell clearly shows anisotropic nature when it is rotated for 45°, changing transparency from black to bright as well as a cell prepared by conventional mechanical rubbing technique (fig.2, c). In the case of APPJ treated Polyimide film on the images from POM parallel lines both in dark and bright states are noticeable. These defects occur during the injection of LC molecules process into the LC cell. Heat treatment does not lead to the disappearance of such defects. Observation through the POM allows us to describe

fabricated cells qualitatively, where the most important uniformity properties of LC molecule alignment could be evaluated. The optical properties are cardinally different from untreated as-deposited Polyimide film substrates and show good LC molecules alignment.

APPJ treatment activates the surface by generating active species and dangling bonds on the surface, also increasing surface energy and making the surface more hydrophilic. Water droplet contact angle measurements were carried out before and after treatment with APPJ treatment and presented in figure 3. As the contact angle decreases the surface energy of treated Polyimide film increases. At the same time LC molecules tilt angle to the surface changes from 90° (homeotropic) to 3° (planar).

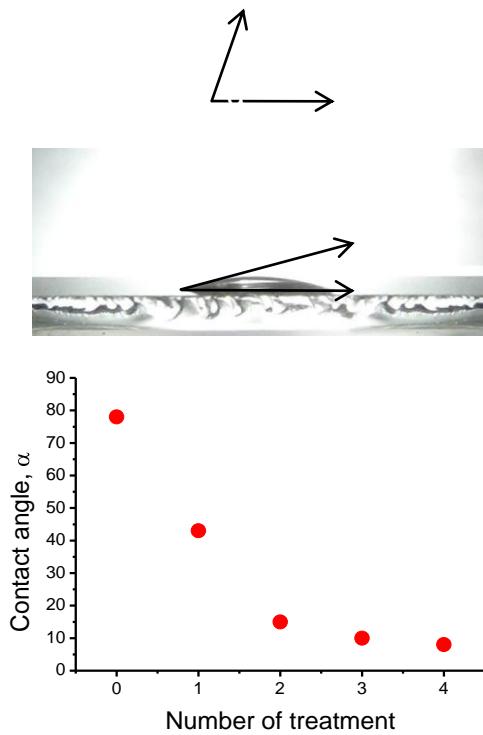
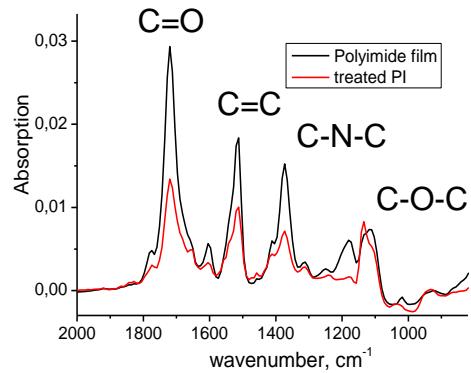
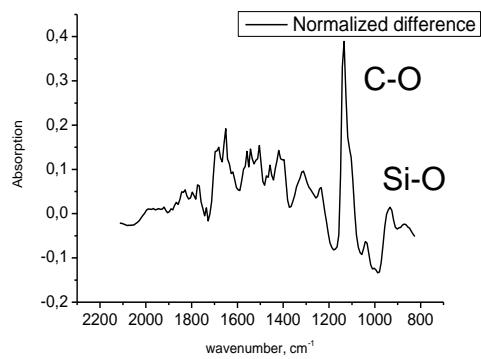


Figure 3. Water drop Angle Measurements

To investigate structural changes FTIR spectra were taken from untreated and treated PI films on Si substrates (Figure 4), as Si substrates are transparent to the IR range in comparison to the glass substrates. Treatment by APPJ system etches the surface of the film (was confirmed from SEM observation). Therefore all peaks on FTIR spectra decrease and make structural changes difficult to see. To highlight changes in the film after treatment we normalized (in corresponding with C = O bond absorption peak) both



a)



b)

Figure 4. a) FTIR spectra of as-deposited and treated by APPJ system Polyimide b) Difference of normalized FTIR spectra of as-deposited and treated by APPJ system Polyimide film

as-deposited and treated films spectra and analyze difference (Fig.4, b).

It is clear that the C-O bond is the most influenced part in PI film. Increase of C-O bonds could be explained by passivation of the dangling bonds on the surface with the oxygen from the environment during its exposure to the ambient air. Increase of C-O bonds on the surface is also confirmed by XPS measurements in the work of Wu et al [12, 13], where substrates were treated by low pressure plasma treatment systems. Both low and high pressure systems generate C-O elements on the surface to enhance alignment properties. Change of C-O bond and carbon ring profile on the surface are considered to be anchoring elements and the clue for the alignment mechanism of LC molecules to the surface.

#### 4. Conclusion

Experimental study has been carried out to demonstrate that the alignment of LC molecules could be achieved by the treatment of Atmospheric Pressure Plasma Jet Scanning System on Polyimide

film surfaces. FTIR spectra show that the structural changes after treatment mainly corresponded to the increase of C-O bonds on the surface and considered to be a clue to the alignment mechanism. To fully understand alignment mechanism further research is required. Particular interest also represents further research of alignment patterns of 5CB LC molecules on the treated polyimide films. Comparable results to the conventionally manufactured LC cell make this technology applicable for the processes of producing LCD.

## 5. References

- [1] D. Dantsker, J. Kumar, S.K. Tripathy, *J. Appl. Phys.* 89 (2001).
- [2] X. Lu, Q. Lu, Z. Zhu, J. Yin, Z. Wang, *Chem. Phys. Lett.* 377, (2003)
- [3] D. Seo, H. Kim, H. Jeon, *Liq. Cryst.*, 28 (2001)
- [4] P. Chaudhari, J. Lacey, S. Lien, J. Speidell, *Jpn. J. Appl. Phys.*, 37 (1998).
- [5] P. Chaudhari, J. Lacey, J. Doyle, E. Galiggan, S. Lien, A. Callegari, C. Cai, J. Speidell, J. Ritsko, M. Samant, J. Stohr, Y. Nakagawa, Y. Katoh, Y. Saitoh, K. Sakai, H. Satoh, S. Odahara, H. Nakano, J. Nakagaki, Y. Shiota, *Nature*, 411 (2001)
- [6] H. Wei, C. Kou, K. Wu, J. Hwang, *Diam. Relat. Mater.*, 17 (2008)
- [7] E. Jang, H. Song, S. Lee, *Jpn. J. Appl. Phys.*, 45 (2006)
- [8] A. Baitukha, S. Mori, M. Suzuki, *Thin Solid Films*, 523 (2012).
- [9] K. Wu, C. Chen, C. Yeh, J. Hwang, P. Liu, H. Wei, C. Kou, C. Lee, *J. Appl. Phys.*, 98 (2005).
- [10] K. Wu, W. Chen, C. Wang, J. Hwang, C. Lee, Y. Liu, H. Huang, H. Wei, C. Koub, *J. of The Elec Soc*, 155 (2008).
- [11] Ref: J. Stohr, M. G. Samant, J. Luning, A. C. Callegari, P. Chaudhari, *Liquid Crystal Alignment on Carbonaceous Surfaces with Orientational Order*, *SCIENCE* 2001
- [12] K. Wu, C. Chen, C. Yeh, J. Hwang, P. Liu, C. Lee, C. Chen, H. Wei, C. Kou, C. Lee, *J. Appl. Phys.*, 98 (2005)
- [13] C. Lee, Y. Liu, K. Wu, M. Chen, J. Hwang, *Jpn. J. Appl. Phys.*, 48 (2008)