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# Molecular Crystals and Liquid Crystals

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## Ion Beam Alignment of Liquid Crystal on Amorphous SiO<sub>x</sub> Film

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Liquid crystal alignment on a-SiO $_x$  film surfaces through the ion beam exposure is studied. The pre-tilt angle of liquid crystals on a-SiO $_x$  film surfaces can be controlled from about  $8^{\circ}$  to about  $89^{\circ}$  by changing the ion beam incident angle from  $25^{\circ}$  to  $80^{\circ}$ . Vertical alignment of liquid crystal can be ascribed to high contact angles on ion-beam exposed inorganic film surfaces.

Keywords: a-SiOx; ion beam; liquid crystal; vertical alignment

#### 1. INTRODUCTION

The rubbing process for liquid crystal alignment [1] has many problems, such as the lack of controllability, the need to wash rubbed surfaces to remove debris, and the difficulty in achieving multidomain structure. Various alignment techniques have been proposed as potential replacements of the rubbing method, such as the oblique evaporation [2], the photo-alignment method, and ion beam alignment

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method [3]. Recently, a non-contact alignment method using an inorganic film was also proposed as potential replacements of the rubbing method. As for the control of the pre-tilt angle using inorganic SiO, the pre-tilt angle is ranging from  $0^{\circ}$  to  $15^{\circ}$  for the double deposition of SiO (evaporation angle  $60^{\circ}$ ,  $85^{\circ}$ ) [4,5], from  $15^{\circ}$  to  $40^{\circ}$  for the oblique evaporation of SiO (evaporation angle  $85^{\circ}$ ) [2], from  $60^{\circ}$  to  $90^{\circ}$  for the combination of oblique evaporation and homeotropic surface treatment [6], and from  $0^{\circ}$  to  $60^{\circ}$  for the rotational oblique evaporation of SiO [7]. By changing dielectric anisotropy of liquid crystal, its alignment can be controlled to obtain the desired pre-tilt angle on SiO<sub>x</sub> film surfaces [8,9].

In ion beam approach, non-contact processes using deposited inorganic materials with the Ar<sup>+</sup> ion beam exposure have been applied to align liquid crystal [10–12]. Chaudhari *et al.* reported the electro-optical switching behavior of an ion beam aligned twisted nematic (TN) cell and an in-plane switching (IPS) cell with ion beam exposure on the diamond like carbon (DLC) film surfaces [10]. However, it does not cover full pre-tilt angle range. The pre-tilt values of ion beam alignment were ranging from approximately zero to 10°. For homeotropic alignment, many attempts have been made to find a simplified and reliable method for tilted alignment, but none of them provided consistent alignment results with a large enough process windows for practical applications.

In this article, we have shown that the pre-tilt angle of liquid crystals on  $a\text{-}SiO_x$  film surface can be controlled to an arbitrary incident angle by using ion beam. We also investigated the dependence on the incident angle of the pre-tilt angle in vertically aligned liquid crystal cells via the contact angle measurement, the anchoring energy, and the thermal stability test at different deposition temperatures.

#### 2. EXPERIMENTS

We deposited a-SiO<sub>x</sub> film on indium-tin-oxide (ITO)-coated glass substrates by using an r. f. magnetron sputtering system. High purity argon and oxygen gas mixture (purity: 99.99%) were used as the reaction gas in the chamber. All substrate samples were placed at a distance of 8 cm from the target. Deposited layer thickness was normally in the range of 50 to 100 nm. The deposition temperature was ranging from 30°C to 400°C. In our experiment we varied the thickness of deposited films up to 50 nm at the deposition temperature of 150°C. Pre-tilt angle measurement of liquid crystals aligned on ion-exposed a-SiO<sub>x</sub> film surfaces was carried out as a function of the incident angle (ion beam energy:  $70 \, \text{eV}$ , exposure time: 1 s and ion beam flux density:

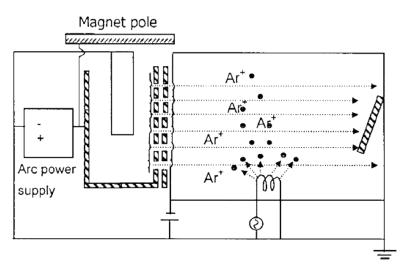


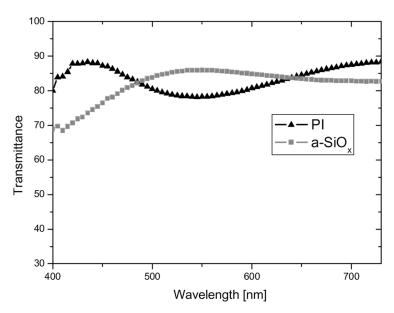
FIGURE 1 Schematic diagram of an ion beam system.

 $3.12\times10^{13}\,Ar^+/s.cm^2).$  Both the crystal rotation method and the magnetic null method were used to determine pre-tilt angles. Liquid crystal cells with cell gap of  $3.8\,\mu m$  were fabricated with a negative liquid crystal 'Merck MLC-6608'.

Figure 1 shows the schematic drawing of ion beam system. A cold hollow cathode (CHC) type was used as the source of Ar<sup>+</sup> ions to yield the ion beam. Optical transmittance measurements were carried out with a UV/VIS/NIR spectrometer. The wetting properties of surfaces were determined by the static contact angle method. The contact angles were measured by increasing and then decreasing the volume of a drop of liquid (distilled water) deposited on the sample surface. Recorded images are digitized and analyzed with a software routine that evaluates the tangent at the point of contact between the drop and the surface (i.e. the contact angle). The polar anchoring energy was determined by the voltage-capacitance method. In order to test the thermal stability of the device, the thermal tolerance of the vertical aligned LC cell was studied.

#### 3. RESULTS AND DISCUSSION

The transmission of the white light through a-SiO<sub>x</sub> film/ITO/glass and a polyimide layer/ITO/glass are shown in Figure 2. The thickness of a-SiO<sub>x</sub> film deposited at  $150^{\circ}$ C was about 50 nm and that of the polyimide was about 50 nm. A-SiO<sub>x</sub> film deposited by introducing pure



**FIGURE 2** Transmittance of polyimide and  $a\text{-}SiO_x$  films deposited on an indium-tin-oxide coated glass substrates as a function of the wavelength.

argon gas only into the chamber showed the transmittance about 13% lower than a polyimide. As an alternative method, argon  $(30\,\mathrm{sccm})$  and oxygen  $(20\,\mathrm{sccm})$  was used initially until thickness is about  $40\,\mathrm{nm}$ . Then, argon gas mixed gases was flowed into the chamber. The polyimide layer has higher transmittance at short wavelengths lower than  $480\,\mathrm{nm}$  or at long wavelengths higher than  $630\,\mathrm{nm}$ , whereas a-SiO<sub>x</sub> film has higher transmittance in the wavelength ranges between  $480\,\mathrm{nm}$  and  $630\,\mathrm{nm}$ . The average transmittances of polyimide and a-SiO<sub>x</sub> were 83.7% and 81.3% in the visible wavelength, respectively.

To investigate the device quality of a vertically-aligned cell, the light leakage of a LC cell ion-beam-aligned on a-SiO<sub>x</sub> films is compared to a rubbing-aligned cell. Liquid crystal cells with the pre-tilt angle of  $89^{\circ}$  and the cell-gap of  $3.8\,\mu m$  were fabricated by using 30 nm-thick films. The relative light leakage can be defined as the ratio of the transmittance of LC cells between crossed polarizers to the transmittance of the crossed polarizers themselves. The relative light leakage of an ion beam aligned cell with the pre-tilt angle of  $89^{\circ}$  deposited at temperatures ranging from  $30^{\circ}$  to  $300^{\circ}$  was between 4.4 and 12, when the ion beam energy, the incident angle, the exposure time, and the ion beam flux density are  $70\,eV,\,80^{\circ},\,1\,sec.,\,$  and  $3.12\times10^{13}\,Ar^{+}/s.cm^{2},\,$ 

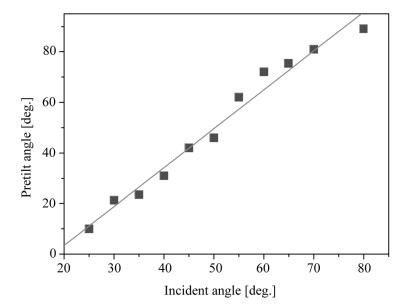
respectively. The relative light leakage of a rubbing aligned cell was between 6.8 and 10. The light leakage of an ion beam aligned cell is similar to a rubbing aligned cell.

Figure 3 shows the measured pre-tilt angles of liquid crystal cells aligned by using the ion beam exposure on a-SiO<sub>x</sub> film surface, as a function of the incident angle (ion beam energy:  $70\,\mathrm{eV}$ , exposure time:  $1\,\mathrm{s}$  and ion beam flux density:  $3.12\times10^{13}\,\mathrm{Ar}^+/\mathrm{s.cm}^2$ ). Pre-tilt angles of fabricated liquid crystal cells were measured by the crystal rotation method and the magnetic null method. We fabricated vertically aligned cells by using the ion beam exposure on a-SiO<sub>x</sub>. We found that pre-tilt angles can be controlled ranging from about  $8^\circ$  to about  $89^\circ$  by changing the ion beam incident angle from  $25^\circ$  to  $80^\circ$ . The relation between the pre-tilt angle and the ion-beam incident angle was as follows:

$$\theta = 1.54\alpha - 26.8\tag{1}$$

where,  $\theta$  is the pre-tilt angle along the incident direction, and  $\alpha$  is the ion-beam incident angle. The pre-tilt angle can be modified with the control of the exposure time, the ion flux density, and the ion beam energy.

M. Ohgawara *et al.* reported that liquid crystal molecules can be aligned on the surfaces of SiO<sub>2</sub> thin films homogeneously [13].

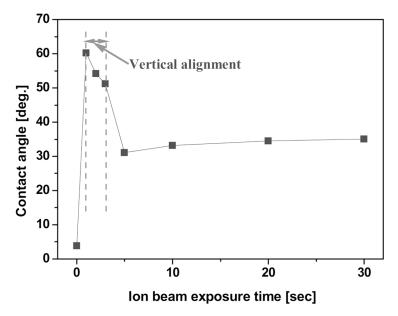


**FIGURE 3** Pretilt angle of ion-beam-aligned liquid crystal cells as a function of the incident angle.

However, we found that a-SiO $_x$  film deposited at a temperature between 30°C and 300°C can align liquid crystal molecules, while those deposited at a temperature higher than 300°C do not align them [14]. We also found that a-SiO $_x$  film surface exposed (ion beam energy: 70 eV, incident angle: 80° and the ion beam flux density:  $3.12 \times 10^{13} \, \text{Ar}^+/\text{s.cm}^2$ ) shorter than 3 s results in the vertical alignment, while those exposed longer than 4 s results in the homogeneous alignment.

To observe the effect of the ion beam exposure on a-SiO<sub>x</sub> film surface, we measured contact angles. Figure 4 shows contact angle data of a-SiO<sub>x</sub> film surfaces as a function of the exposure time. The ion beam energy, incident angle, and ion beam flux density were fixed to  $70\,\mathrm{eV},\,80^\circ$  and  $3.12\times10^{13}\,\mathrm{Ar^+/s.cm^2}$  respectively. The contact angle was dramatically changed when the exposure time was about  $1\!\sim\!3\,\mathrm{s}.$  At these values of the exposure time, liquid crystal cells showed vertical alignment and the contact angle had a high value. However, when the exposure time was longer than  $4\,\mathrm{s}$ , liquid crystals can be aligned homogeneously and the contact angle was lower than that of the vertical alignment.

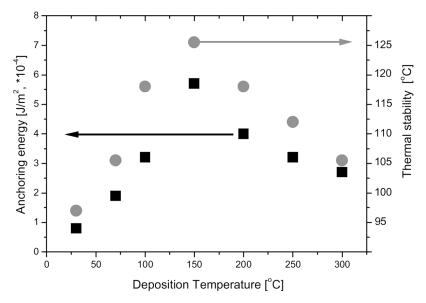
To better understand the mechanism of the liquid crystal alignment on inorganic films by ion beam exposure, we measured AFM (atomic



**FIGURE 4** Contact angle data of ion-beam-aligned liquid crystal cells as a function of ion beam exposure time.

force microscope) and XPS (x-ray photoemission spectroscopy) of a-SiO<sub>x</sub> film surfaces irradiated by ion beam as a function of the ion beam exposure time. We found from AFM data that the surface roughness of a-SiO<sub>x</sub> remained nearly constant, irrespective of the ion beam exposure time. No connection might be found between vertical alignment and the roughness of inorganic surface. However, we found from XPS data that the absorption curve observed at inorganic surface for the vertical alignment was shifted toward lower energies, while that for the homogeneous alignment was shifted toward higher energies [11]. The shape of curves was kept nearly the same when the exposure time is shorter than 20 s. Therefore, we can conclude that the lowenergy ion beam exposure does affect the surface charge of the a-SiO<sub>x</sub> film. Based on XPS data and the contact angle data, we suggest that ion beam does not "etch" but generate "surface charge" on a-SiO $_{x}$  film surface when the exposure time was shorter than 3 s. Therefore, vertical alignment by low-energy ion beam with the exposure time shorter than 3s results in the "surface charge" on a-SiO<sub>x</sub> film surface.

The anchoring energy is an important parameter for a liquid crystal cell because it affects not only the liquid crystal alignment but also the electro-optic properties such as the threshold voltage and the response time. Figure 5 shows the polar anchoring energy and thermal stability



**FIGURE 5** Measured polar anchoring energy of ion-beam-aligned liquid crystal cells as a function of the deposition temperature.

of ion beam irradiated a-SiO $_{\rm x}$ . The data shows a peak at the deposition temperature of 150°C when the incident angle of ion beam is about 80°. The long-term stability of ion-beam alignment was also studied by monitoring thermal tolerance of vertically aligned liquid crystal cells subjected to accelerated aging experiment. The vertical alignment in liquid crystal cells deposited at the temperature of 150°C was preserved without deterioration for 24 hours up to 120°C. The behavior of the polar anchoring energy measured by voltage-capacitance method was changed at the critical temperature of 150°C. The maximum value of polar anchoring energy could be found at the deposition temperature of 150°C. There is strong connection between thermal stability and polar anchoring energy due to the similar inclination with the changes in the deposition temperature.

#### 4. CONCLUSION

In conclusion, we have demonstrated the alignment of liquid crystal molecules by the ion beam exposure on  $a\text{-}SiO_x$  film surfaces as a non-contact alignment process. We found that the pre-tilt angle of liquid crystal cells can be controlled over wide ranges  $(8^\circ {\sim} 89^\circ)$  by changing the ion-beam incident angle  $(25^\circ {\sim} 80^\circ)$  on a-SiO\_x film surfaces. We found from the AFM experiment that not the surface roughness but surface charges play the key role in achieving the vertical alignment.

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