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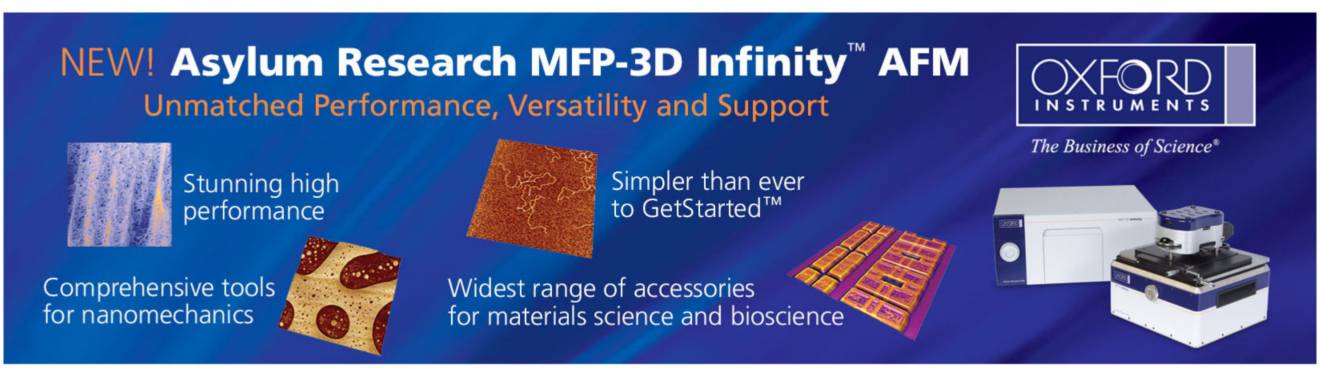

Liquid crystal surface alignments by using ion beam sputtered magnetic thin films

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A method for liquid crystal surface alignment by using a one-step, ion beam bombardment of the glass substrates is demonstrated. Precoating by polyimide is not necessary. The authors show that the homeotropic alignment is achieved due to orientation of the diamagnetic nematogenic molecules by the magnetic field from the γ-Fe_2O_3 ferrimagnetic thin films created on the substrates by ion beam bombardment. The film exhibits a high Curie temperature well above 300 K and a compensation temperature which is the typical feature of ferrimagnetism. This is a simple, noncontact, and reliable alignment method for liquid crystal devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2770763]

It is well known that the liquid crystal (LC) molecules can be reorientated by electric and magnetic fields due to their anisotropic electrical permittivity and magnetic susceptibility.[1] In the past decades, the electro-optical effect of nematic liquid crystals (NLCs) has been widely used in liquid crystal displays (LCDs). On the other hand, surface alignments of liquid crystals are essential in fabrication of 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 LCD industries is the rubbing method, which employs a velvet rubbing process on polyimide (PI) coated on substrates. In spite of its success, this method has some drawbacks such as leaving debris and electrostatic charges on the rubbed surfaces.[2] Besides, 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, noncontact alignment methods are highly desirable. One of the alternative alignment methods, ion beam (IB) alignment, had been reported by the IBM group.[3–5] They have realized this noncontact alignment technology by integrating low energy ion beam equipments and diamondlike carbon (DLC) thin films into LCD manufacturing processes. The mechanism of this alignment method was attributed to the anisotropical change of bindings between carbon atoms caused by ion beam bombardment.[5] Over the past few years, several studies devoted to ion beam bombarded DLC and PI films have also been reported.[6–8] One of the most remarkable results is that the homeotropic alignments can be obtained by using fluorinated DLC thin films as the alignment layer and the pretilt angle can also be controlled by choosing different ion beam parameters or the concentration of fluorine doped in DLC films.[8] In addition, both homogeneous and homeotropic alignments can be obtained with the same kind of organic alignment layers bombarded by ion beams with different energies.[6,7] This remarkable ability of controlling the alignment modes makes the ion-beam alignment method potentially useful in LC-based applications, especially in LCDs industry.

Recently, we have reported that both homogeneous and homeotropic alignments can be induced by argon ion beam bombardments with low and high energies, respectively, on the same kind of polyimide film (SE-130B, from Nissan Chemical Industries, Ltd.).[9] However, the alignment mechanisms were still to be clarified.

In this letter, we unambiguously demonstrate that even the glass substrates without PI films, bombarded with high energy ion beam (HEIB), can achieve homeotropic alignment of the LCs. This is a reliable alignment method for LC devices. We will show that the homeotropic alignments are due to the field from the magnetic thin films created on substrates by ion beam bombardment, based on the systematic analyses on x-ray photoemission spectroscopy (XPS), ultraviolet-visible spectroscopy (UV/Vis), and superconducting quantum interference device (SQUID) data.

We employ a direct-current (dc) diode-type ion beam sputter[10] (model IB-2 from EIKO Engineering Co., Ltd.) for ion beam treatments. The sputter can be used either as a coating or etching device, depending on the polarity of the voltage. When the etching mode is selected, the bottom electrode, on which the sample substrates are set, acts as the cathode. The substrates are etched by ion beams from induced glow discharge near the top electrode. For the coating mode, the bottom electrode is chosen as the anode, the sample substrates are then uniformly coated with the target material mounted on the top. Stainless steel electrode is used for the top electrode. With an attached sample holder, the incidence angle, bombarding time, current density, and the energy of ions are all controllable parameters in our system. The energy of ions is varied by changing the dc voltage between electrodes. Before each ion beam process, the chamber is pumped down to a base pressure of 30 mTorr and then argon gas is fed into the chamber to a target pressure of 55 mTorr.

The indium tin oxide (ITO) coated glasses with area of $20 \times 10\ mm^2$ are used as the substrates. The thickness of ITO layer measured by using ellipsometry is 167 nm. After cleaning, the substrates are directly treated by ion beams (etching mode) without any PI coating. The ion energy, current density, incidence angle, and bombarding time for ion beam treatment are 1120 V, 255 $\mu A/cm^2$, 60°, and 5 min, respectively. We should use the notation (ion energy, current density, incidence angle, and bombarding time) for parameters of ion beam treatment in the following text. Then two substrates are combined together with a 23 μm Mylar spacer in between to form an empty cell with an antiparallel arrange-

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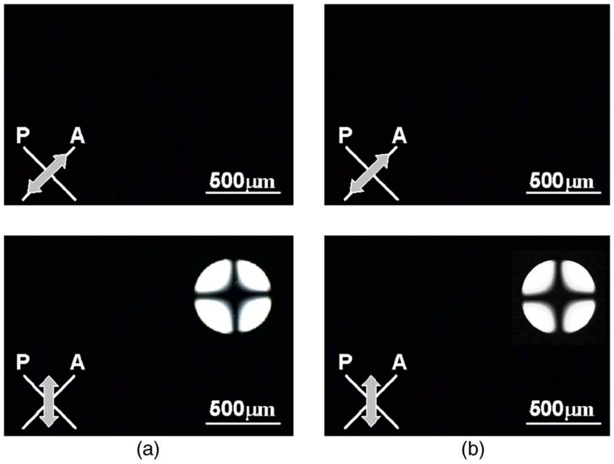

FIG. 1. (Color online) Polarizing optical microscope photographs of NLC cells treated by HEIB: (a) with PI film coating and (b) without PI film coating (inset: conoscopic pattern, A: analyzer, and P: polarizer).

ment. The liquid crystal 4′-*n*-pentyl-4-cyanobiphenyl (5CB) (Merck) with a nematic range between 24.0 and 35.3 °C is then filled into the empty cell for alignment characterization.

Figure 1 shows the optical micrographs of 5CB cells between crossed polarizers. The 5CB cell with substrates coated with ion beam treated PI films shows good homeotropic alignments because the good dark state is observed while rotating the cell, as shown in Fig. 1(a).[9] Remarkably, the cell employing two substrates without PI films also shows the homeotropic alignment [see Fig. 1(b)]. The conoscopic patterns shown in the insets further indicate achievement of the homeotropic alignment.

To find out the possible mechanisms for alignment, we have carried out XPS (PHI-1600 from Physical Electronics, Inc.) analyses on the substrate surface. Three kinds of samples, (i) as-deposited PI film, (ii) HEIB-etched PI film, and (iii) HEIB-etched ITO film (without PI), are scanned in survey mode with a step size of 1 eV and analyzer pass energy of 117.4 eV. The data are shown in Fig. 2. A significant amount of Fe element is found in the compositions of samples (ii) and (iii) but not in sample (i). The Fe 2*p* and Fe 3*p* core-level signals are located in the ranges of 705–735 and 53–60 eV, respectively.[11] The signals between 530 and 700 eV are confirmed to be the Auger signals of Fe.[12] Based on these results, we deduce that the Fe element is sputtered

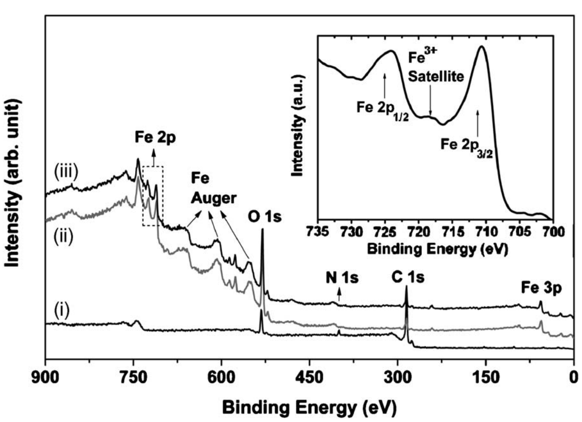

FIG. 2. Measured Mg *K*α-excited core-level spectra of (i) as-deposited PI film, (ii) IB-etched PI film, and (iii) ITO films with conditions of 1120 V, 255 μA/cm², 60°, and 5 min. Inset: the measured Fe 2*p* spectrum in multiplex mode of film (ii).

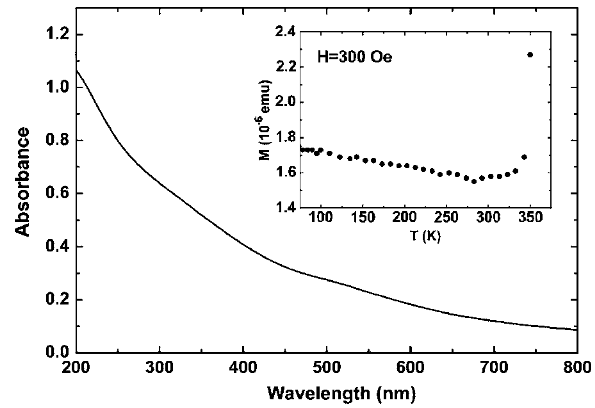

FIG. 3. UV/Vis absorbance spectrum of iron oxide thin film with ion condition of (1120 V, 255 μA/cm², 0°, and 20 min). Inset: temperature dependence of the magnetization for the iron oxide film with ion conditions of 1120 V, 255 μA/cm², 0°, and 30 min in an applied field of 300 Oe.

from the electrode while the ion sputter is operated with HEIB.

For a detailed study of the Fe peaks, the multiplex mode scanning of Fe 2*p* region on HEIB-etched PI film is carried out with a step size of 0.2 eV and analyzer pass energy of 23.5 eV. The result is shown in the inset of Fig. 2. According to the literatures,[13,14] the shake-up satellite line at 718.2 eV is a characteristic of Fe^{3+} in Fe_2O_3. Further, the narrow peak at 710.4 eV of the Fe 2*p* spectrum indicates that no Fe^{2+} iron oxidation state exists. In other words, the possibility of forming Fe_3O_4 (magnetite) in the film can be excluded. The film should be composed of the Fe^{3+} oxides, Fe_2O_3 only. The spectrum of the HEIB-etched ITO film reveals the same profile. Structurally, however, there are four possible types of Fe_2O_3. Two of them, α-Fe_2O_3 (hematite) and γ-Fe_2O_3 (maghemite), are common and widespread in soils.[15] Of the two, only the γ-Fe_2O_3 has permanent magnetic moments.

The XPS Fe $2p_{3/2}$ signals of HEIB-etched PI and ITO films have been analyzed quantitatively with deconvolution technique.[16–18] The results also conclude that the treated substrate is coated with a film of γ-Fe_2O_3. We have also coated a substrate without PI using the ion sputter in coating mode with the beam parameters of 1120 V, 255 μA/cm², 0°, and 20 min. The XPS spectrum is almost the same as that for films sputtered in etching mode.

Moreover, the UV/Vis absorbance spectrum of the film sputtered with coating mode is also measured and plotted in Fig. 3. The spectrum shows that this sample exhibits better transparency in the visible spectral region and does not have the typical absorption peak for α-Fe_2O_3 in the UV region from 300 to 380 nm.[19–22] These results also support our assertion that the coated iron oxide films are of the particular allotropic form, i.e., γ-Fe_2O_3.

Since γ-Fe_2O_3 is a magnetic material, we have also measured the magnetic dipole moments of the films sputtered in the coating mode to verify its magnetic property. A SQUID (MPMS-XL7, Quantum Design) equipped with a superconducting magnet with maximum strength of 70 kOe has been used for this measurement. The typical sensitivity of the magnetization measurement is better than 1×10^{-8} emu (H <2.5 kOe). The total magnetization (M) of the sample prepared in the coating mode with ion conditions of 1120 V, 255 μA/cm², 0°, and 30 min is measured as a function of temperature (T) from 75 to 350 K in an applied field of 300 Oe. The measured *M*-*T* curve is shown in the inset of

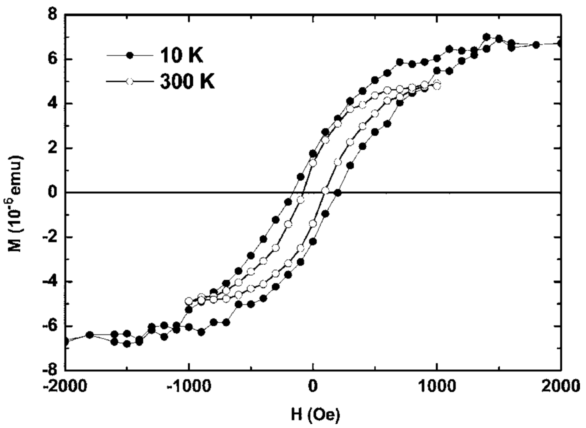

FIG. 4. Magnetization curves for an iron oxide thin film sputtered in coating mode with ion conditions of 1120 V, 255 $\mu A/cm^2$, 0°, and 30 min at T = 10 K and 300 K in the magnetic field parallel to the film surface.

Fig. 3. This curve shows a minimum that corresponds to the compensation temperature, a typical feature of ferrimagnetism.[23] The Curie temperature reported in the literature for γ-Fe_2O_3 is in the range from 820 to 986 K.[15] This is well above our measuring temperature and the operating temperature of common LC devices. The characteristic hysteresis loops expected for ferrimagnetic films are obtained at 10 and 300 K. These are shown in Fig. 4 after correction for the diamagnetic component at high field due to the quartz substrate. We note that the magnetization of our sample is measured with the magnetic field parallel to the film surface. More studies about the domain structure and magnetic properties of the coated iron oxide thin film are in progress.

Through systematic measurement and analyses as described above, we have confirmed that the sputtered films are iron oxides composed of ferrimagnetic γ-Fe_2O_3. Moreover, because of aromatic rings on the molecular axis of typical nematogenic molecules such as the 5CB, such LC molecule exhibits positive anisotropy in the diamagnetic susceptibility χ_a. Therefore, the magnetic field $\boldsymbol{H}$ due to the ferrimagnetic film can exert a torque $\Gamma = \chi_a(\boldsymbol{n}\cdot\boldsymbol{H})\boldsymbol{n}\times\boldsymbol{H}$ on the LC molecule, where $\boldsymbol{n}$ is the unit vector for average molecular orientation and the direction of optical axis.[1] As a result, homeotropic alignment of 5CB is achieved on a HEIB-treated substrate.

Since the torque on LC molecules is proportional to the square of magnetic field, the film may consist of small domains having magnetic dipole mainly perpendicular to the surface but with alternating signs. The magnetic field is strong enough at the surface to align the LC molecules but decreases rapidly away from the surface. The surface bonding due to the molecular-orbital interactions between the Fe atoms and cyanobenzene of 5CB should also contribute to the alignment mechanisms.[24]

We have also studied the surface anchoring energy and the electro-optical performance of a LC cell using the HEIB-sputtered film as the alignment layer. The surface anchoring energy for 5CB is about 2.0×10^{-4} J/m^2 better than 3.4×10^{-5} J/m^2 of commonly used surfactant, N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP). Furthermore, the magnetic thin films can also be used to achieve homogeneous alignment after some treatments. We have also found out that the sputtered films are composed of nanoscaled clusters of γ-Fe_2O_3 particles by using the atomic force microscope.

In conclusion, we unambiguously demonstrate that ITO coated glass substrates with or without PI films, after bombardment using the dc diode sputter with ion energy of 1120 V and current density of 255 $\mu A/cm^2$, can achieve excellent homeotropic alignment of the LCs. We show that the homeotropic alignment is achieved due to orientation of the diamagnetic nematogenic molecules by the magnetic field from the γ-Fe_2O_3 ferrimagnetic thin films created on the substrates by ion beam bombardment. The films exhibit a high Curie temperature well above 300 K and a compensation temperature which is the typical feature of ferrimagnetism. This is a simple, noncontact, and reliable alignment method for LC devices. It can be easily scaled for manufacturing of large-size LC television panels.

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