Ultrathin films of homeotropically aligned columnar liquid crystals on indium tin oxide electrodes

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We report the achievement of very thin films (thickness of about 50 nm) of thermotropic columnar liquid crystal in homeotropic (columns normal to the interface) orientation on indium tin oxide (ITO) electrodes. The face-on alignment of the discotic compound has been obtained by thermal annealing without any intermediate coating between the mesophase and the ITO substrate. Such a columnar mesophase alignment is thus shown on a substrate of technological interest in open supported thin film reaching the thickness range suitable for organic photovoltaic devices. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2831009]

Organic solar cells, consisting typically of at least two electronically complementary materials that form a heterojunction, have recently reached power efficiencies of several percent,[1] which is a considerable improvement compared with the first photovoltaic devices published by Tang in 1985 (Ref. 2) that had an efficiency of slightly less than 1%. Nevertheless, organic solar cells, with their intrinsic advantages of flexibility, absorption tunability, and cost-efficient production, have still to be considerably improved before being competitive with conventional silicon solar cells.[3] Since most organic photovoltaic materials are molecular amorphous solids or polymer glasses that feature, in general, very limited charge mobilities and exciton diffusion lengths, an approach to achieve the necessary jump in efficiency is the use of self-assembled materials into large domains of crystalline or liquid crystalline order. In particular, columnar liquid crystals (colLC), made of aromatic disks assembled into columnar stacks,[4] have been shown to exhibit excellent charge and exciton transport properties along the columns,[5,6] which has led to very promising proof-of-principle photovoltaic cells.[7] Recently, we have shown that the necessary uniform vertical orientation of the columnar axis on the substrate, i.e., homeotropic anchoring (or equivalently face-on alignment of the discotic molecules; see Fig. 1) can conveniently be achieved in submicron thick open films by controlling the growth kinetics of the columnar domains during thermal annealing.[8] When the film thickness is further reduced to the typical value required in organic solar cells, i.e., 50–100 nm considering the light absorption coefficients versus the exciton diffusion length and the charge carrier mobility,[6] the homeotropic alignment is increasingly disfavored over the planar orientation, and dewetting may occur during annealing leading then to strongly inhomogeneous films. Whereas thin homeotropic colLC films have been obtained on polytetrafloroethylene layers that show appropriate interactions with some columnar materials,[9] such insulating alignment coatings are prohibited in photovoltaic devices where good charge transport throughout the device is essential. In this work, we show that by using two different indium tin oxide (ITO) surface treatments associated with a thermal annealing of the discotic compound, ultrathin films (≈50 nm) of a columnar mesophase can be stabilized in homeotropic orientation on an ITO elctrode.

The discotic material benzo [g,h,i]perylene 1,2,4,5,10,11-hexacarboxylic 1,2-di-(2-ethylhexyl)ester 4:5,10:11-di-(4-heptyl)imide (Fig. 1) was synthesized according to Ref. 10. Its absorbtion range is in the green part of the visible light. Its phase behavior features a hexagonal columnar liquid crystalline phase from the isotropic liquid phase (iso) at $T_{\mathrm{colLC-iso}}=225\ ^\circ\mathrm{C}$ down to ambient temperature. The ITO coated glass was purchased from VisionTek Systems Ltd. (UK) with an ITO sheet resistance of about 20 Ω/□, an ITO thickness of 150 nm and a glass thickness of 0.17 mm.[11] The ITO substrates were preliminarily cleaned with three successive ultrasonic baths of 10 min each, of acetone, methanol, and isopropanol. A surface treatment was then applied on the ITO electrode, either by UV ozone or by nitrogen plasma. The former procedure consisted of a commercial ultraviolet ozone cleaning system (UVOCS, USA) during a period of 30 min; the latter was a homemade cold atmospheric pressure plasma method applied during 2 min.[12] Note that the ITO resistivity remains constant after the two surface treatments, and no change of the ITO surface mor-

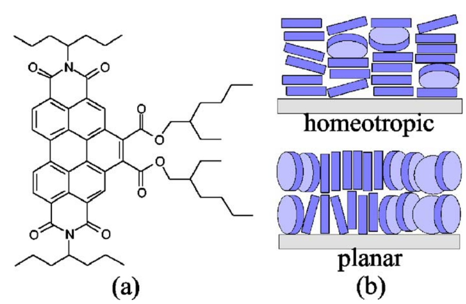

FIG. 1. (Color online) (a) Molecular structure of the benzoperylene derivative. This compound exhibits a hexagonal columnar phase from $T_{\mathrm{colLC-iso}}=225\ ^\circ\mathrm{C}$ to ambient temperature. (b) Schematic representation of the homeotropic (face-on) and planar (edge-on) orientations of a columnar mesophase.

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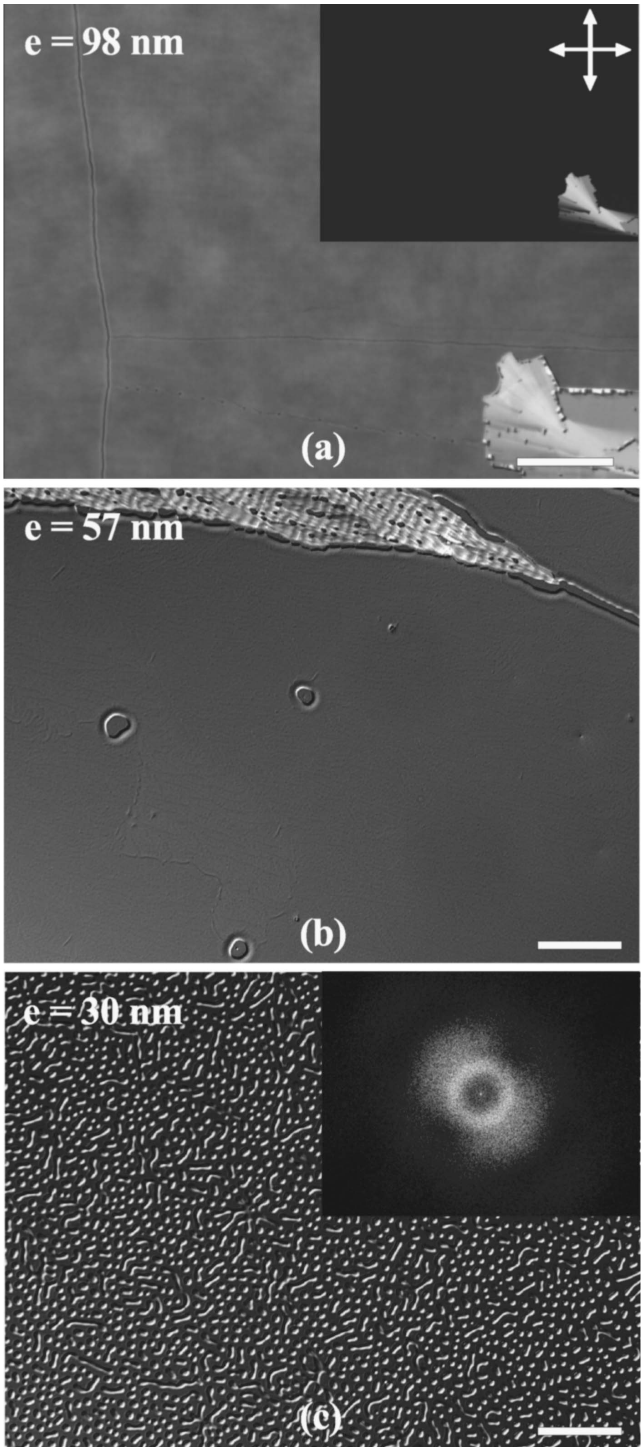

FIG. 2. Dependence with the film thickness of the colLC orientation and wetting behavior observed after thermal annealing by DIC microscopy. The scale bar indicates 50 μm in (a) and 10 μm in (b) and (c), respectively. (a) For film thicknesses above 80 nm, the uniform homeotropic orientation of the columnar mesophase extends over several mm^2. A small highly birefringent planar region is shown for contrast. Inset: the same image between crossed polarizers. (b) By decreasing the layer thickness down to 50 nm, the sample exhibits large homeotropic regions in coexistence with a few planar domains. Small circular dewetted zones also appear around defects on ITO surface. (c) A complete dewetting is found for colLC films thinner than 40 nm. Inset: the same image after a fast Fourier transform.

phology has been observed by atomic force microscopy (AFM). The substrate was then stored under inert argon atmosphere before coating with colLC films, either by spin coating or by vacuum deposition. The discotic compound is heated up to the isotropic liquid phase and subsequently

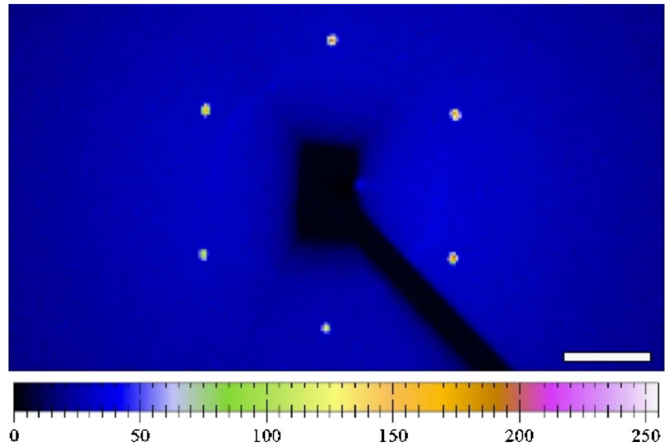

FIG. 3. (Color online) X-ray diffraction pattern of a single colLC domain observed in the geometry of an open supported film. The sixfold symmetry is the signature of homeotropic alignment of the hexagonal columnar mesophase, investigated in transmission with the x-ray beam normal to the plane of the substrate. The white scale bar indicates 2 nm^{-1}.

cooled down to ambient temperature at 10 °C/min. The film thicknesses were measured by using an atomic force microscope in tapping mode acting as a mechanical profilometer. The orientation of the columnar liquid crystal film was mainly studied by polarizing and differential interference contrast (DIC) microscopy. The DIC optical technique is sensitive to the refractive index gradient, and therefore improves the contrast of all interfaces such as grain boundaries between colLC domains, dewetted zones, etc. Transmission x-ray diffraction has been used to investigate the colLC anchoring in thin films. In order to increase the x-ray transmittance through the glass substrate which is weak at 8 keV (the x-ray energy of the anode generator), the coverslips have been etched by hydrofluoric acid to locally obtain a glass thickness of about 50 μm (instead of 170 μm initially).

A few studies have previously shown that contact angles, from which surface tensions can be deduced, decrease after different surface treatments of ITO electrodes. For the case of complex fluids such as liquid crystals where surface tensions are *anisotropic*, a characterization of the ITO only performed with isotropic liquid phases,[13,14] turns out to be insufficient. That is why we decide to focus our work on both the phase orientation and the wetting behavior of the discotic film in the columnar liquid crystalline state: the optimization of the surface treatments have been performed in terms of wetting efficiency and degree of homeotropic alignment compared to the planar one. By applying the thermal process described above, the spontaneous formation of a homeotropically aligned layer is observed for colLC film thicknesses above 80 nm, as displayed Fig. 2(a). The homeotropic anchoring is demonstrated either by the lack of birefringence [inset of Fig. 2(a)] or by the typical hexagonal pattern obtained by x-ray scattering (Fig. 3).[9,15] Such an alignment extends over macroscopic distances, and prevails down to film thicknesses of about 50 nm [Fig. 2(b)]. In this thickness range, both regions with planar orientation and dewetted zones appear, the latter often induced by the presence of some heterogeneities on the ITO surface (Fig. 4). Mechanical scrubbing may be applied to remove these surface defects and to improve the ITO roughness.[13,16] For colLC films thinner than 40 nm, complete dewetting is observed, stemming from a spinodal instability as shown by the typical length

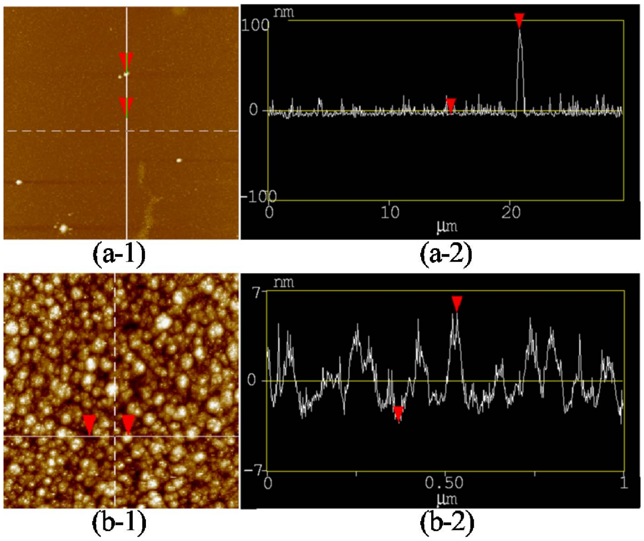

FIG. 4. (Color online) ITO substrate studied by AFM. (a-1) The region of interest has a square side of 30 μm and the white bright spots are surface defects of about 100 nm high, as shown by the corresponding profile in (a-2). (b-1) Zoom in of 1 μm square side showing the average roughness of the ITO surface of about 5 nm (b-2).

scale given by the fast Fourier transform of the image [Fig. 2(c)]. The best results in terms of the lowest film thickness exhibiting an uniform homeotropic anchoring have been obtained by using nitrogen plasma surface treatment associated with colLC coating by vacuum deposition. In the case of spin coating, some impurities may be introduced by the use of solvent, which leads to surface contamination. Any weakening of the surface energy has to be avoided and the sooner the colLC film is prepared after the ITO surface treatment, the better the wetting behavior is. The presence of imide and ester polar groups in the discotic compound (Fig. 1) may explain the affinity toward molecular face-on anchoring on the ITO surface, as such groups are likely to decrease the surface tension between the colLC and the substrate interface.[8] However, any theoretical approach of colLC wetting and orientation only based on surface tension considerations is not valid here: for films thinner than 100 nm, the disjoining pressure, involving van der Waals interactions, has to be taken into account.[17]

In conclusion, we have shown, in this letter, the achievement of uniform ultrathin films (down to 50 nm thick) of a columnar liquid crystal in homeotropic orientation. Such a control of the mesophase alignment and wetting in this range of film thicknesses on ITO electrodes opens the way toward efficient solar cells based on self-organized discotic materials.

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