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Horizontally-aligned carbon nanotubes arrays and their interactions with liquid crystal molecules: Physical characteristics and display applications

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We report on the physical characteristics of horizontally-grown Single-Walled Carbon Nanotubes (h-al-SWNT) arrays and their potential use as transparent and conductive alignment layer for liquid crystals display devices. Microscopy (SEM and AFM), spectroscopic (Raman) and electrical investigations demonstrate the strong anisotropy of h-al-SWNT arrays. Optical measurements show that h-al-SWNTs are efficient alignment layers for Liquid Crystal (LC) molecules allowing the fabrication of optical wave plates. Interactions between h-al-SWNT arrays and LC molecules are also investigated evidencing the weak azimuthal anchoring energy at the interface, which, in turn, leads to LC devices with a high pretilt angle. The electro-optical responses of h-al-SWNT/LC cells demonstrate that h-al-SWNT arrays are efficient nanostructured electrodes with potential use for the combined replacement of Indium Tin Oxyde and polymeric alignment layers in conventional displays. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [doi:10.1063/1.3679155]

I. INTRODUCTION

Electronic displays are an integral part of many household and portable electronic devices such as televisions, laptop computers, touch screens or smartphones. These display devices currently make use of transparent electrodes mostly fabricated from glass panels coated with a thin layer of conducting Indium Tin Oxyde (ITO). Even though ITO is widely used, its high production cost and the limited supply of Indium require the development of new transparent conducting materials. Inherently conducting polymers are an efficient alternative to replace ITO in display applications1–4 but carbon nanotubes (CNTs) and graphene are now considered among the most promising substitutes for ITO due to their unique mechanical and electrical properties.5–8 In particular, Single-Walled Carbon Nanotubes (SWNTs) have great potential applications in electronic displays where energy-efficient, and/or lightweight materials are required.9 Random arrays of SWNTs were first produced either by direct growth on a catalyzed substrate or by deposition onto an arbitrary substrate from a solution of suspended SWNTs. For sufficiently high densities of SWNTs, the nanotubes interconnect and form continuous electrical paths allowing the fabrication of various devices like thin-film transistors,10, 11 sensors,12 transparent conducting electrodes for flexible OLED13 or optical switches.14

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Among display technologies, flat-panel liquid crystal (LCD) devices are the most widely used and they have a foreseeable future in communication systems. From a technical point of view, they are made of two glass substrates facing to each others covered with ITO and an alignment layer to orient the liquid crystal (LC) molecules in a given direction. The anchoring energy between LC molecules and the alignment layers allows the orientation of the entire slab, leading to antiparallel or twisted configurations. To align LC molecules, two main approaches have been developed: either by uniaxial rubbing of a polymeric film (PolyVinylAlcohol or PolyImide) or by using a phototalignment mechanism of specifically designed/synthesized polymers. During the device fabrication, processing of alignment layers is a critical step because orientation defects and/or rubbing-induced electrostatic charges lead to bad pixels and in turn to a deficient display. Recently, it has been demonstrated that soft nanoimprint lithography is an interesting and efficient method to align LCs, but numerous and sophisticated fabrication steps are required. Oriented carbon nanotubes are now also considered as a promising material to align mesogenic molecules. Self-assembly, dip-coating, spin coating of surfactant-based CNT dispersions or drawing process from a CNT forest have been reported lately. However, the use of surfactants usually leads to a non-homogeneous deposition of tubes providing non-uniform alignment as well as a low electrical conductivity of the CNT coating. In the case of transfer techniques, CNT films exhibit a low sheet resistance but a high roughness inducing numerous alignment defects. Therefore, besides the replacement of ITO, alignment layers are also a key point for next generations of LCDs.

In this paper, we demonstrate that horizontally-aligned single-walled carbon nanotubes (h-al-SWNTs) grown on transparent substrates can be used as both alignment and transparent conducting layers making a ‘two in one’ coating finding potential applications for liquid crystal display devices. h-al-SWNTs were first grown by CVD on quartz substrate and characterized by SEM, AFM, UV-Vis and Raman spectroscopies and four probe technique. Then the optical and electro-optical properties of LC h-al-SWNTs-based devices are presented and discussed. Finally, the anchoring energy of LC molecules on nanostructured SWNTs substrates is estimated providing interesting insights on the interactions between carbon nanotubes and rodlike molecules.

II. EXPERIMENTAL

A. Carbon nanotube arrays

The procedure used is based on a combination of the works of Huang et al. and of Kokabas et al. The quartz substrates (ST cut quartz single crystal wafers) were first dip-coated in an ethanol solution of cobalt acetate (0.1 wt%) and molybdenum acetate (0.05 wt%) followed by heating at 500°C for 0.5h to produce metal oxide nanoparticles. Then, the quartz substrates were heated at 850°C in an argon/H2 (500 sccm/50 sccm) flow for 10 min to reduce the metal oxide to metal nanoparticles. The chemical vapor deposition (CVD) of single-walled carbon nanotubes (SWNTs) using ethanol as a carbon feedstock was carried out in a 25 mm (o.d.)/22 mm (i.d.) quartz tube furnace at 850°C for 10-30 min by bubbling argon/H2 mixed gas (10:1 by volume, 150 sccm) into an ethanol pool (0°C). High density, aligned SWNTs were grown on the quartz substrates with variable tube densities depending on the catalyst concentration and the CVD duration time.

B. Characterization methods

Scanning electron microscopy images were taken on a Hitachi 4700 Field Emission SEM operated at 0.8 kV. AFM experiments were performed at room temperature in ambient air on a Veeco Multimode equipped with a Nanoscope IIIa controller and a Nanoscope Quadrex. Silicon tips (NCH, NanoWorld Ltd Co.) with a spring constant of 42 N m⁻¹ (Resonance frequency: 325 kHz) were employed. Topographic images were recorded in a non-contact mode (tapping) with a tip velocity of 2.5 μm s⁻¹, a scan rate of 0.5 Hz and a scan angle of 90°. Raman spectroscopy measurements were carried out on a Dilor XY using an Ar-Kr laser operating at λ=514.5 nm (2.41eV) with a power of 5 mW. The spectra were recorded in the back-scattering geometry under a ×100 objective. UV-Vis spectra were recorded with a Ocean Optics setup [deuterium/halogen light source...
(Mikropac DH-2000-BAL) combined with a USB2000+ spectrometer). Electrical conductivity measurements were performed on a Suss Microtec EP6 probe station equipped with a Keithley 2635 sourcemeter. Optical and electrooptical measurements were performed on a Olympus BH50 polarizing microscope. The LC cell was electrically driven by an amplified 1kHz square wave voltage (HP33220A waveform generator).

C. Optical device fabrication

The quartz substrates covered with h-al-CNTs were assembled in a parallel configuration such as h-al-SWNTs coatings were facing to each other (Figure 1). These plates were glued with calibrated spacers (Sikui, Japan) and the cell thickness was determined using the Fabry-Perot interferometric method. Then, the as-prepared cell was filled by capillary action with the nematic liquid crystal 4,4′-pentyl-cyanobiphenyl also known as 5CB (Frinton Labs, NJ, USA).

III. RESULTS AND DISCUSSION

A. Physical characteristics of carbone nanotube arrays

Figure 2 presents the morphological characteristics of the as-grown horizontally aligned carbon nanotubes. The SEM image (Fig. 2, left) shows that a nearly perfect alignment is achieved on large areas with a good homogeneity; the morphological anisotropy is also shown by the 2D power spectrum of the SEM image (Fig. 2, left, bottom inset). A tube density of ≈5.6 tubes µm⁻¹ was found (Fig. 2, left, top inset) illustrating the high coverage of the substrate. According to AFM images, the tubes are mostly individual single-walled with an average diameter of 1.1 ± 0.3 nm. Structures with diameters larger than 2 nm were assigned to bundles of nanotubes. A tube density of ≈6.1 tubes µm⁻¹ was found that is consistent with SEM observations.

In order to further investigate the CNT arrays, Raman spectroscopy was carried out. In the frequency range 100-250 cm⁻¹ (Fig. 3(a)), four peaks are observed. From numerical fitting of the experimental data (symbols) using lorentzians (lines), the two peaks at 126 and 204 cm⁻¹ were unambiguously assigned to the quartz substrate whereas the lines at 155 and 190 cm⁻¹ correspond to the radial breathing mode (RBM) of the carbon nanotubes. These two distinct contributions to the RBM show that the samples consist of single-walled carbon nanotubes but with different diameters. Using the relationship:

\[ \omega_{\text{RBM}} = \frac{227}{d_t}, \]

where \( \omega_{\text{RBM}} \) is the Raman frequency, the tube diameters were estimated at \( d_{t1} = 1.5 \) nm (\( \omega_{\text{RBM}} = 155 \) cm⁻¹) and \( d_{t2} = 1.2 \) nm (\( \omega_{\text{RBM}} = 190 \) cm⁻¹) which is in good agreement with the values retrieved from AFM investigations. According to the Kataura plot of SWNT deposited on quartz reported by Soares et al., the bands at 155 cm⁻¹ and 190 cm⁻¹ were assigned to the optical transition...
FIG. 2. Morphological characterization of horizontally-aligned Carbon Nanotubes: a) SEM image, insets: 2D spectrum (bottom) and section along the white arrow (top); b) $1.05 \times 1.7 \mu m^2$ AFM image (bottom), and section along the white arrow (top); the black arrows show catalytic nanoparticles whose size ranges from 1 nm up to 10 nm.

FIG. 3. Raman spectra of h-al-SWNTs (symbols represent experimental data points and lines are lorentzian fits assigned to a given vibrational mode\cite{26}); a) low frequency region (the dashed (blue) lines represent vibrational modes of the quartz substrate whereas the solid (green) lines correspond to the radial breathing mode (RBM) of the carbon nanotubes); b) tangential mode region (G bands); inset: polar diagram showing the G line intensity of SWNTs as a function of the angle between the polarization of the incident light and the nanotube axis (VV scattering configuration); symbols are experimental data whereas the solid line shows the twofold symmetry of the mode modeled by $I(G) \propto \cos^2 \theta$.

Energy $E_{33}^S$ corresponding to semiconducting tubes. Figure 3(b)) shows the Raman spectrum in the 1250-1700 cm$^{-1}$ region. The mode at 1342 cm$^{-1}$ is known as the disordered induced carbon peak (D band) and in the case of nanotubes it is generally attributed to symmetry lowering effects, e.g., defects, bending of the nanotubes, finite-size effects or amorphous carbon.\cite{5} The tangential mode of SWNTs consists of six lorentzians with two main contributions at 1565 and 1590 cm$^{-1}$. These peaks are attributed to TO mode ($G^-$ line) and LO mode ($G^+$ line) SWNTs, respectively.\cite{5,28} The lorentzian shape of the fitting curves indicate that the as-grown h-al-SWNT arrays consist mainly of semi-conducting nanotubes. The inset in Figure 3(b) displays a polar plot of the Raman intensity of the G band for various angles between the polarization of the incident laser light and the nanotube axis; the spectra were recorded in the VV configuration. When the polarization of the laser beam is parallel to the nanotubes axis ($0^\circ$, $180^\circ$) a maximum intensity is observed while near $90^\circ$ or $270^\circ$ the Raman signal reaches a minimum. The angular dependence of the experimental data can be accurately described by $I(\theta) \propto \cos^2 \theta$ confirming that the Raman signal reaches a maximum with the incident polarization parallel to the tubes axis and a minimum when perpendicular. These results stem from the one-dimensional nature of CNTs giving rise to highly anisotropic optical properties.\cite{30,31} In addition, it is important to note that the as-grown CNT film consists of an aligned array of SWNTs exhibiting a strong morphological anisotropy.
Figure 4 shows the evolution of voltage (V) versus intensity (I) retrieved from 4 probe measurements using two configurations: the probes were oriented either parallel or perpendicular to the SWNT array. A linear behavior is observed in both cases but the sheet resistivity is 4 times lower along the tubes ($R_{\parallel}^s = 2 \, \text{M} \Omega \, \text{sq}^{-1}$) than perpendicular to the tubes ($R_{\perp}^s = 8.5 \, \text{M} \Omega \, \text{sq}^{-1}$) showing the strong electrical anisotropy of h-al-SWNT arrays. The high value of $R_{\parallel}^s$ was assigned to the semiconducting properties of SWNTs as evidenced by Raman spectroscopy measurements, but, the finite value of $R_{\perp}^s$, instead of infinity, was more surprising and needed further morphological investigations of the h-al-SWNT arrays. Scanning Electron Microscopy and Atomic Force Microscopy experiments have been carried out and are presented in Figure 4(b)–4(d). Both SEM and AFM images show that some carbon nanotubes do not grow along the main axis of the array -defined by the atomic steps of the ST cut quartz substrate- but in various azimuthal directions even forming in a few cases serpentines. These misaligned carbon nanotubes can create locally interconnects or crosslinks between aligned SWNT. It should be also pointed out that these interconnects or crosslinks are mainly located around large catalytic nanoparticles (Fig. 4(c) and 4(d)). According to these morphological observations, it can be reasonably assumed that if the CNT growth took place on the top of these larger nanoparticles during the CVD process, the quartz substrate has much less influence on the direction of growth, i.e., the atomic steps of the ST cut quartz are obviously too far from the growing tubes to induce any efficient alignment. In addition, it is interesting to note that the nanotubes seem to grow from a catalytic nanoparticle to another leading to a catenation-like process. From the electrical point of view, the as-formed interconnects or crosslinks, resulting from misaligned nanotubes and serpentines, act as bypasses or shunts allowing to some extent the electrons to flow in a direction perpendicular to the SWNT array which in turn provide a finite value of $R_{\perp}^s$. Nevertheless, the as-prepared h-al-SWNT arrays exhibit a strong electrical anisotropy which is consistent with recent works. Indeed, it has been reported that in the case of SWNT-based TFTs, the alignment reduces the path lengths and hence improves the carrier mobility. Our observations confirm that alignment is an important parameter for SWNTs-based electronic devices.

The transmittance of the SWNT array is weakly dependent on the wavelength and above 85% in the range 300-900nm (inset of Fig. 4(a)). Recalling that the dc electrical conductivity $\sigma_{dc}$ is related to sheet resistance ($R_s$) and transmittance ($T$) by: \[ \sigma_{dc} = \frac{188 \sigma_{op}}{(R_s (\sqrt{T} - 1))}. \] where $\sigma_{op}$ is the optical conductivity ($\sigma_{op} = 200 \, \text{S} \, \text{cm}^{-1}$), $\sigma_{dc}$ was calculated to $\sigma_{dc}^{\perp} \approx 0.3 \, \text{S} \, \text{cm}^{-1}$ and $\sigma_{dc}^{\parallel} \approx 0.07 \, \text{S} \, \text{cm}^{-1}$, evidencing again the strong electrical anisotropy of h-al-SWNT arrays. From averaged values of $R_s$ and $\sigma_{dc}$, the film thickness ($t$) can be roughly estimated from $t = (R_s \sigma_{dc})^{-1}$.
without h-al-SWNT array:
Random Alignment
Topological defects
(Schlieren texture) =>
with h-al-SWNT array:
Uniform Alignment =>
LC monodomain (uniaxial)

FIG. 5. a) Optical micrograph (crossed polarizers) of a cell filled out with liquid crystal with and without h-al-SWNT coating. b) Normalized transmitted light intensity between crossed polarizers versus rotation angle $\theta$ of the LC cell; symbols are experimental data points and the solid line is a fitting curve (see text).

and was found to be $t \approx 10$ nm which is of the same order of magnitude to that of the features measured from AFM images.

B. Optical and electrooptical properties of h-al-SWNT based LC devices

In order to investigate the interactions between h-al-SWNT arrays and mesogenic molecules, devices were fabricated using the procedure described in section II C and studied by means of optical and electrooptical techniques. Figure 5(a) shows a polarized optical micrograph of a h-al-SWNT based cell filled with the liquid crystal 5CB. In the lower left corner, the h-al-SWNT array was locally removed from the quartz substrate by using scotch tape prior to cell assembly and LC capillary filling. In this region (delimited by a dash red line), a Schlieren texture is observed showing a randomly oriented nematic phase.$^{34}$ In the area at the upper right side of the image, a uniaxial monodomain is obtained demonstrating that a homogeneous alignment of the liquid crystal molecules is achieved when the substrate is covered with h-al-SWNT arrays. Figure 5(b) displays optical microscope pictures and the evolution of the transmitted light intensity between crossed polarizers versus rotation angle $\theta$ of h-al-SWNT based LC display devices. Rotation of the cell leads to bright (45$^\circ$ to the polarizer) and dark (0$^\circ$, 90$^\circ$ to the polarizer) states. In both cases, images exhibit spatial uniformity without Schlieren textures associated with randomly oriented nematic phases. These observations clearly indicate a good, homogeneous, in-plane alignment of the liquid crystal molecules within the cell. Experimental transmitted light intensity data points are represented by symbols (Fig. 5(b)) whereas the solid line is a simulated curve to the Malus equation ($I = I_0 \cos^2 \theta$). A good agreement was found demonstrating that the LC slab behaves as an optical wave guide. Recalling that the optical retardation is defined as,$^{16}$

$$\delta = \frac{\pi d \Delta n}{\lambda},$$

where $\Delta n$ is the birefringence ($\Delta n = 0.2$ for 5CB), $d$ is the LC film thickness ($d = 5 \mu m$) and $\lambda$ is the wavelength ($\lambda = 546$ nm), the calculation leads to $\delta \approx 2\pi$ meaning that the device behaves as a half-wave plate. This result clearly demonstrates that the LC molecules are aligned along the direction of the nanotubes and shows that h-al-SWNTs are efficient alignment layers for LC devices. The contrast ratio (CR) was measured from the light intensity passing through the cell between crossed polarizers at 45$^\circ$ (maximum) and 0$^\circ$ (minimum) to the polarizer. A CR of ca. 500:1 was found which is in the range of the values reported in the literature for conventional displays using polymeric alignment layers.$^{16, 18}$

To further investigate the interactions between h-al-SWNT arrays and LC molecules, the Berreman’s model, initially developed for a grooved periodic interface, has been used to estimate
FIG. 6. Transmittance versus applied electric field of a h-al-SWNT based LC display device: symbols are experimental data points and the solid line is a guide to the eyes. Cartoons are a schematic representation of the LC molecules reorientation process upon the application of an external electric field.

the azimuthal anchoring energy $W_B$ which can be calculated as:35

$$W_B = \frac{2\pi^3 a^2 K_{11}}{\zeta^3},$$

(4)

where $a$ is the amplitude of the groove, $K_{11}$ is the splay elastic constant of the LC ($K_{11} = 7 \times 10^{-12}$ N$^{-1}$), and $\zeta$ is the pitch of the groove. Assuming that the h-al-SWNT arrays exhibit a sinusoidal-like topography (inset Fig. 2, SEM image) with a tube density of 6 tubes $\mu$m$^{-1}$, i.e., $\zeta \approx 160$ nm, and where $a$ corresponds to the averaged tube diameter retrieved from AFM and Raman measurements $a = 1.3$ nm, one finds $W_B \approx 2 \times 10^{-7}$ N m$^{-1}$. It should be pointed out that SWNT arrays are not strictly speaking periodic and the groove amplitude is probably higher than the averaged nanotube diameter used for the calculation due to the presence of bundles. Taking into account these discrepancies between the model and the experimental data, it can be reasonably concluded that the overall azimuthal anchoring energy is weak, i.e., $W_B \leq 10^{-6}$ N m$^{-1}$ which is in agreement with molecular dynamic simulations demonstrating that $\pi-\pi$ interactions between CNTs and organic aromatic molecules are weak and only due to physisorption.37

Figure 6 shows the normalized light transmittance as a function of the applied electric of a h-al-SWNT based LC display device (see Fig. 1). The light beam was passed through the LC slab with its optic axis set at an angle of 45° with respect to the polarization direction of the incident beam. The emerging linearly polarized light (half wave plate) passes through the analyzer which is crossed with the polarizer. An alternating square wave voltage with a frequency of 1 kHz was applied with a function generator to the cell. The transmitted light is expected to oscillate like the square wave of the sine of optical retardation:16 $T_\perp = \sin^2(\delta/2)$. Upon application of an electric field, the nematic director rotates from planar to homeotropic due to the positive dielectric anisotropy of 5CB molecules and it aligns parallel to the electric field leading to a decrease of birefringence of the LC film. The light transmittance of the h-al-CNT based LC display device decreases monotonously with increasing electric field but measurements do not show an oscillatory regime. This observation can
be explained by a small change of the optical retardation with the director rotation because of a high pretilt angle of the LC molecules at the surface.\textsuperscript{38} A high pretilt angle value can be ascribed to low dipole-dipole interactions between the LC molecules and the nanotubes which, in turn, is associated to weak anchoring conditions. In other words, the electro-optical response of the h-al-CNT based LC device is consistent with the calculated azimuthal anchoring energy using the Berreman’s model. Eventhough h-al-SWNT arrays exhibit a high sheet resistivity, they are promising nanostructured electrodes which could be used as both alignment and conducting transparent coatings for display applications. For instance, it has been reported recently that the development of LC devices based on nonuniform anchoring energy might be used as tunable light deflecting systems or active lenses.\textsuperscript{39} Such a goal could be reach by tuning the density of nanotubes on the substrate during the CVD growth in order to induce a gradient of anchoring energy and of sheet resistivity.

IV. CONCLUSION

In summary, we have shown that h-al-SWNT arrays can be used as both alignment and conducting coatings which may find potential applications for liquid crystal display devices. The as-grown h-al-SWNT arrays exhibit strong morphological, optical and electrical anisotropy that demonstrate the nearly perfect alignment of these coating which were achieved on cm\textsuperscript{2} areas with a good homogeneity. Optical devices fabricated using these coatings allow in-plane alignment of liquid crystal molecules and then the development of optical wave plates. Using the Berreman’s model, it was found that the azimuthal anchoring energy between h-al-SWNT arrays and LC molecules is weak. This result can be explained by the weak interactions between CNTs and LC molecules which are mainly due to physisorption. The transmittance of h-al-SWNT/LC devices can be tuned between transparent and dark states upon application of an external electric field demonstrating that h-al-SWNT arrays are efficient nanostructured electrodes. From the electro-optical characteristics it was shown that the as-prepared cells exhibit high pretilt angle which is consistent with weak anchoring conditions at the interface between h-al-SWNTs and LC molecules. These findings open up promising possibilities for applications of h-al-SWNT arrays in the field of optical devices in particular for the combined replacement of ITO and polymeric alignment layers for next generations of LC displays.

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15 Observatory Nano: \url{http://www.observatorynano.eu/project/filesystem/files/ObservatoryNANO%20Briefing%20No.9%20Nanotechnology%20for%20Flat%20Panel%20Displays.pdf}
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