37.4: *Late-News Paper:* Integration of Carbon Nanotube Transparent Electrodes into Display Applications

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Abstract

Carbon nanotube (CNT) thin films for transparent, conducting electrodes are introduced for display device applications. We have vertically integrated the CNT thin films from synthesis to integration on devices. Here we report the brief characteristics of the CNT network thin film and process feasibility of the CNT films for TFT pixel and common electrodes in TFT-LCDs.

1. Introduction

During the last decade, amorphous-Si based TFT-LCDs changed the notebook PC and desktop monitor markets and has recently shown rapid growth in market share for television segments. An increased adoption of large size a-Si TFT–LCD has also been forecast for various display applications such as digital information display (DID), small-sized portable devices such as GPS system and even for some non-display applications such as X-ray detectors and sensing devices.[1] Compared to CRTs, TFT-LCDs offer advantages of thin widths, lower power consumption, and higher resolution up to 1080p. Although TFT-LCDs offer higher display quality than CRT and others, high equipment and manufacturing costs and low yield remain major obstacles for more widespread usage of TFT-LCDS.

Regarding manufacturing costs in current, matured TFT-LCD FABs, the only way to lower manufacturing costs is by increasing productivity/yield and reducing the number of process steps. Many TFT-LCD panel makers have tried to develop optimized TFT-array fabrication processes with reduced mask counts. In SID 2000, a novel slit photolithography technology for a four-mask-count array fabrication process was introduced and adopted in mass production although it has some process difficulty.[2]

The other approach to overcome process and architectural limitations of TFT array design to reduce process steps in the TFT Fab is to make a change of materials. There are practical limitations since there exists material compatibility issues between materials used in TFTs such as insulator, conductor and semiconductor. For instance, an ITO pixel electrode can not directly contact to aluminum gate/SD buslines due to high contact resistance at the interface from interfacial Al_2O_3 formation and electrochemical reaction under bias. In order to overcome this, one can use a multilayer structure such as Mo/Al/Mo or Mo-clad Al or new material such as IZO.[3]

Solution-based transparent CNT thin films have been developed as a novel material and applied in various devices applications, including organic light emitting diodes, organic photovoltaic devices, simple displays among many others.[4-6] It has been demonstrated that such transparent and conducting nanotube electrodes lead to competitive performance compared to traditional ITO in lab scale devices. Sheet resistance of 100~2000 Ohm/sq with 85% transmittance has been reported and the variety is mainly due to the quality of materials and the dispersions. Although the demonstrations of applying nanotube thins films have been done for various devices, the vertical integration of this novel material involves complicated device issues such as patterning, metal-nanotube electrode contact resistance, conformal coating on uneven structures among many others.

In this article, we introduce carbon nanotubes thin films as new material for pixel and common electrodes in TFT-LCD and discuss the critical aspects of random CNT networks as applied to their integration into electronic devices. We will share performance of our scaled CNT from synthesis to film fabrication highlighting the importance of vertical integration at this stage of CNT technology development. In the end, we shows proof-of concept for current device architecture and future flexible display technology.

2. Experiment

The CNT material is synthesized by thermal CVD system in Unidym-Houston. After the CNT synthesis, purification and formulation processes are done for the CNT ink. SDS, TX and other surfactant systems are considered to optimize solubilization with DI water. The concentration of the CNT is ranged from 0.2 mg/ml to 1.5 mg/ml. The detail process is shown in ref.4. The CNT thin films are coated by using conventional roll-to-roll–type coater at room temperature on PET, passivation SiNx:H surface and glass. Wet thickness application is used to control final dried CNT film thickness. The overall process flow for the CNT film is (1) CNT synthesis, (2) Purification, (3) Formulation, (4) Coating and (5) Patterning

In order to test feasibility of the CNT thin film as the pixel and common electrodes, conventional top ITO back channel etch 5 mask process is used. Photolithograph step including PR coating, bake, strip and etching is performed using conventional method using contact mask. Gate and SD lines are Al (200 nm) and gate dielectric (300 nm) and passivation (200 nm) are PECVD-SiN:H deposited at 150 ^{o}C. Active layer is skipped in this process feasibility test. For common electrode feasibility tests, the CNT film is coated on non-planarized color filters. The coated CNT films are characterized with 4 point probe, UV-visible-NIR spectrophotometer, optical profilometer, optical microscopy (OM) and SEM.

3. Results and discussion

3.1 Optoelectronic property of Carbon nanotubes network films

For FPD applications, the performance specification for pixel and common electrode in TFT-LCD is recommended based on ITO performance (100 Ohm/sq and >90%). The performance of transparent CNT electrodes varies from different research

ISSN/008-0966X/08/3901-0537-$1.00 © 2008 SID

groups. Figure 1(a) shows the typical data from various research groups based on different types of nanotubes.[7]

It was believed that CVD produced nanotubes leads to poorer performance as for transparent electrodes. However, Unidym CVD nanotubes outperforms any other CVD tubes together with Laser and Arc tubes. AFM studies show that nanotubes actually formed bundles with bundle size of 2 ~ 4 nm and length of 3 ~ 5 µm. The large bundle length/size ratio could be one of the reasons for the high performance, among many others such as high material purity level, unique purification and coating process.

Figure 1(b) shows an SEM of the morphology of random-network CNT films. Compared to other groups reported SEM images, the nanotubes are straighter and more packed on the surface, which enhance the charge transport and decrease the junction number per area.[6] Based on the sheet resistance and thickness from AFM, the dc conductivity is ~ 4000 S/cm. Note this is the non-doped nanotube performance with the high yield purification process and roll-to-roll manufacture compatible process. The doping by HNO_3 could enhance the conductivity by at least of factor of 2, reaching 8000 S/cm.[8] This is the highest reported DC conductivity of nanotube thin films.

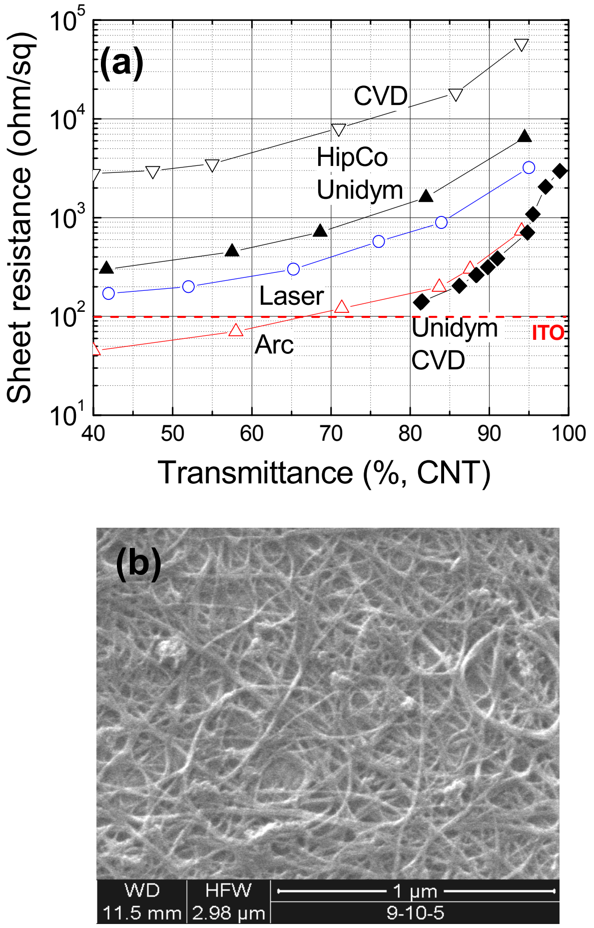

Fig. 1 (a) Tr and Rs value at 550 nm from reference [7] with Unidym data and (b) SEM image of the Unidym CNT film.

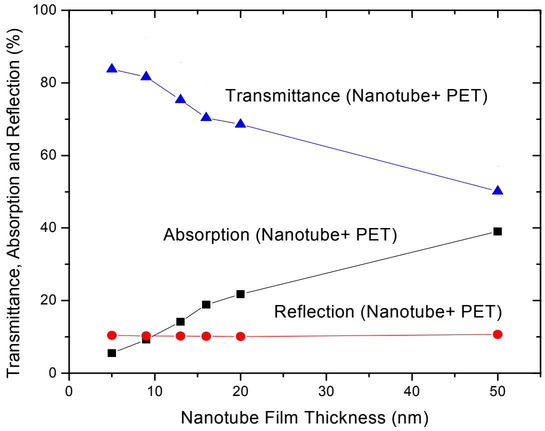

Figure 2 Transmittance, absorption and reflection of CNT nanotube thin films on PET substrates with various thickness. Most of the reflection for the CNT/PET comes from the PET substrate.

The optical properties of nanotube thin films on plastic substrates were studied using UV-Visible-NIR spectrometry. Figure 2 shows the reflection, absorption and transmittance of nanotube thin films on PET substrates. The thickness of nanotube thin films was measured by AFM and optical profiling the edge of patterned films. The thickness was confirmed by comparing the data from the two methods. Compared with ITO electrodes, the loss of the transmittance of nanotube thin films is due to the absorption of nanotubes. The optical loss from absorption is linearly related to the thickness. The absorption coefficient from absorption and thickness is 75000~110000 cm^{-1}. This value is compatible with the results from a previous study from reflection and Kramer-Kronig formula. The reflection of nanotube thin film is barely dependent on nanotube thickness, which is close to the reflection of bare PET. Therefore, the refractive index of nanotube thin films is close to PET substrates (n~ 1.6). The loss of transmittance for ITO is mainly due to the high reflection due to the high refractive index (~2.0).

3.2 Process feasibility

Fig. 3 shows the overall process architecture for 5 mask TFT-LCDs. The CNT film acts as a pixel electrode as well as top layer of contact PAD for IC bonding. We confirmed conventional 5 mask process architectures are compatible with CNT material as well as common electrode. For the device integration with new materials, process feasibility is an important issue. So far, direct growth of CNT layers on CMOS-based substrate for interconnect and channel for TFT has been reported. Here, we examined whether one can use conventional processes to integrate the CNT film on the TFT back plane. First, we tested the photolithograph process using contact mask and dry etching process. Fig. 4 shows optical microscope image of the strip patterned CNT film on PET using dry etching and line profiling result.

The CNT film can be rapidly etched by dry etch-based or laser ablation techniques. This result proves the process merit

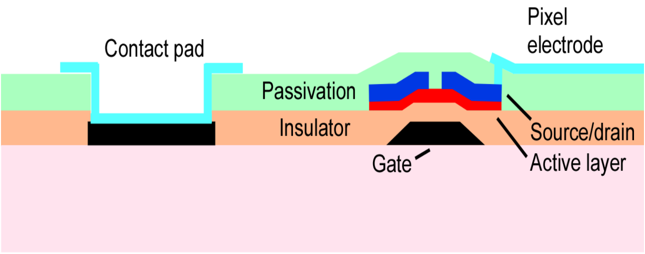

Fig. 3 Conventional 5 mask process architecture for TFT-LCD.

over ITO. Because, ITO wet etching generates significant amounts of chemical waste in TFT-LCD industry and it can be minimized with the CNT film. In this case, most etching processes (Gate dielectric/active/SD metal(Al and Mo) / passivation and pixel) can be done by dry etching.

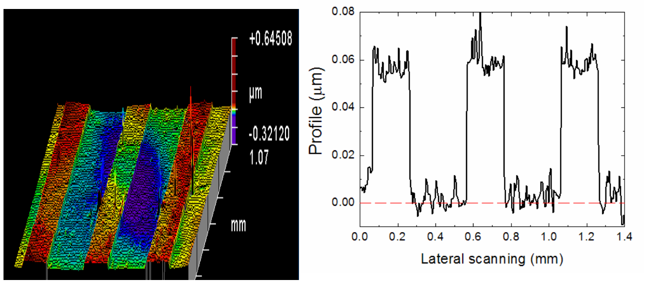

Fig. 4

(a) Optical profilometer image and (b) profile for the patterned CNT film on PET.

CNT pixel on passivation SiN:H surface. Using dry etching, the pattern edge is sharp and photo-resist on the CNT film shows good adhesion without any PR lift problem presumably because PR and CNT have strong interactions. RIE dry etch shows sharper pattern edge shapes without any significant pattern size change. In the middle of pixel, RMS roughness of the CNT film is about 5 ~ 10 nm. This is higher than ITO and may affect liquid crystal alignment. Roughness of the network films mostly comes from the micro-holes between the nanotubes. From optimizing coating process to form uniform lay-down and solubilization, we expect the roughness level to be lowered in the future.

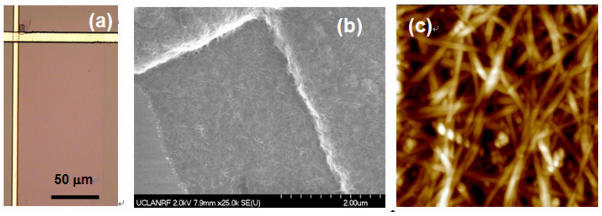

Fig. 5

(a) Optical microscope, (b) SEM and (c) AFM images (1x1 μm^2) for the patterned CNT pixel electrode.

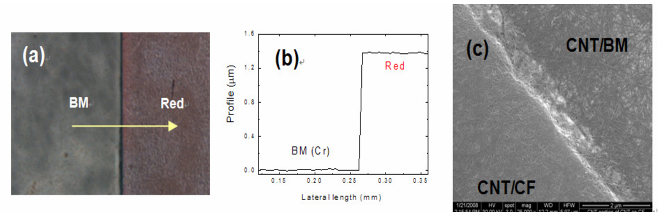

Fig. 6

(a) Optical microscope image for color filter BM/Red resin boundary, (b) line profile for the BM/color filter resin with CNT coating (c) SEM image.

The next challenge is the step coverage of the CNT film on high step height and via holes in the TFT and color filter substrates. Usually, step height in TFT backplane is 0.2 ~ 0.5 um and 1.5 um in color filter. Many efforts to minimize this step height to improve display quality have been investigated and the solution was planarization of overall uneven surface feature in both parts. But it requires additional processes and higher material cost. ITO can cover this step even being that it is deposited by physical vapor deposition (PVD). Still, there exists yield loss and reliability issues from overhang structures in via and contact PAD open regions. Here, we examine step coverage of the CNT film on various step and geometries. Fig. 6 shows step coverage on color filter side. Step height is 1.0~1.5 um high depending on color resin. The CNT films have adequate coverage across all step heights and surface topologies.

3.3 TFT Integration on plastic

The merit of optical property and process is mentioned above. For future displays with cost-effectiveness and flexibility, the CNT network film has additional advantages over ITO regarding mechanical robustness. As shown in Fig. 7, the CNT film on plastic substrates is very flexible and display no CTE or stress build-up issues during the coating process. After demonstrating the bending test 5000 times, electrical and mechanical properties do not change. Many groups are working on printed electronics for flexible devices. In the near future, the CNT film can be used for conductor and semiconductor layers in printed electronics via roll-to-roll coating or inkjet printing.

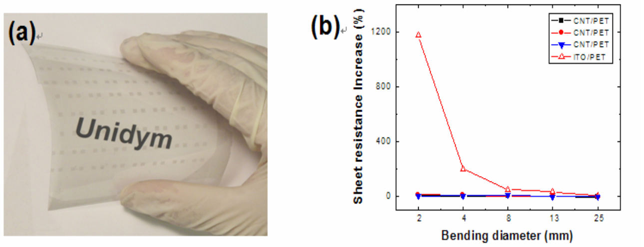

Fig. 7 (a) Proof-of concept of flexible device using CNT films on PET substrate. CNT film is used for SD, active and gate layers formed by wet-coating process. All processes are performed below 100°C. (b) Flexibility test result compared with ITO

4. Conclusion

In summary, we reported the opto-electronic properties of the CNT network thin films for the display applications. From CVD method, cost-effective CNT synthesis method, and formulation technique, we can obtain FPD-quality CNT network films. Using a TFT-LCD platform, we demonstrated process feasibility for coating on uneven surfaces, step coverage, patterning including photolithograph process and etching compared with conventional ITO process. In the end, we showed the proof-of concept of the CNT network for future display technology using flexible plastic substrates.

5. Acknowledgements

Authors thank to Unidym MP and Houston team members for their supporting this project.

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