All-printed Liquid Crystal Display Devices Made from Sol-gel Indium Tin Oxide Ink

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ABSTRACT

In this paper, all-printed liquid crystal display (LCD) devices were fabricated from a sol-gel Indium tin oxide (ITO) ink. Ink-jet printing method was used to deposit ITO films and patterns on glass substrate for LCD devices. Different printing resolutions of ITO films were tested to find out the best combination of optical transmittance and electrical properties. The thickness of ITO films were controlled by the printing resolution and multiple printing layers. When building up to five layers, the ink-jet printed ITO films were highly transparent (95% transmittance) and had 588 ohms/sq sheet resistance. The surface morphology of these ITO films was relatively uniform and smooth, as inspected by confocal microscopy and SEM. As a result, the final LCD devices made with these ITO films were able to show clear images shift when connected to a dc voltage source.

Keywords: ITO, LCD, ink-jet, printing

1 INTRODUCTION

As important components in various devices like solar cells, touch screens and liquid crystal displays (LCD) [1-3], Indium tin oxide (ITO) is the most widely used transparent conducting oxide due to its high conductivity and transparency. Currently, the commercial ITO coating methods (e.g. sputtering, evaporation [4,5]) not only require strict vacuum conditions, high-cost equipments but also waste a large amount of ITO during the process. Therefore, easily scalable printing methods are under demand to coat ITO films on substrates without waste.

Recently, increasing attention has been paid to development of simple and easy solution processing of ITO films, including spin coating, dip-coating and spray pyrolysis methods [6]. Similar with these coating methods, ink-jet printing is also a cost-effective solution-based alternative for the ITO coating [6]. In addition, ink-jet printing can precisely deposit desired patterns on various substrates with almost no waste. This is a great improvement compared to the methods for commercial fabrication of ITO patterns which need photolighography and etching steps.

For ink-jet printing, the choice of ITO ink is the key factor to successful printing of ITO films with good properties. Commercial ITO nanoparticles (25nm) in ethanol dispersion [7] could be used for ITO ink. Although the final ITO films reached low sheet resistance, the optical transmittance was only 87% at 550nm wavelength. Small-size ITO nanoparticle (5nm) have also been synthesized for ITO ink [8], but the final resistance (10^5 Ω/sq) was too high for the real applications.

In this paper, we report on a sol-gel method to fabricate ITO ink for ink-jet printing which didn't require the steps to synthesize ITO nanoparticles. It was proved that ITO films and patterns could be ink-jet printed onto glass substrates controllably with this sol-gel ITO ink. We also demonstrated the good electrical and optical properties obtained for our ink-jet printed ITO films by fabricating an all-printed LCD device with a GT pattern.

2 EXPERIMENT

2.1 Fabrication of ITO films and pattern

Two precursors indium nitrate hydrate (99.99%, Aldrich) and tin(IV) chloride pentahydrate (98%, Aldrich) were dissolved into acetylacetone (99%, Aldrich) to prepare the sol-gel ITO ink. For the best of electrical property, the concentration for [In^{3+}] was made to 1M and dopant percentage of [Sn^{4+}] was 10% in atomic ratio. The detailed preparation method for this ink can be found in reference [9].

Borosilicate glass was used as substrate and cut into 0.5 × 0.5 inch^2 squares. To remove dust and contamination, all glass substrates were cleaned with acetone, isopropanol and then treated with UV-ozone cleaner. The ITO ink was filtered with 0.25 μm PTFE filter and deposited onto cleaned glass substrate through a 50μm-diameter jetting device in an ink-jet printer (JetlabII). Patterns were imported into the printer using Bitmap files. Different printing resolution was controlled by the spacing of two adjacent droplets. After printing, the ITO films were dried at 120°C for 10 minutes and annealed 450°C for another 10 minutes on a hot plate. To achieve good electrical property and desired thickness, five layers ITO films were deposited on the same substrate following the same annealing steps. All above procedures were conducted under air conditions. To further improve the electrical properties, all samples received a final anneal at 300°C for 3h under Ar gas before characterization.

2.2 Characterization of ITO films

There are no apparent property differences between ITO films and patterns except for the pattern. The optical transmittance of ITO films was collected by UV-vis

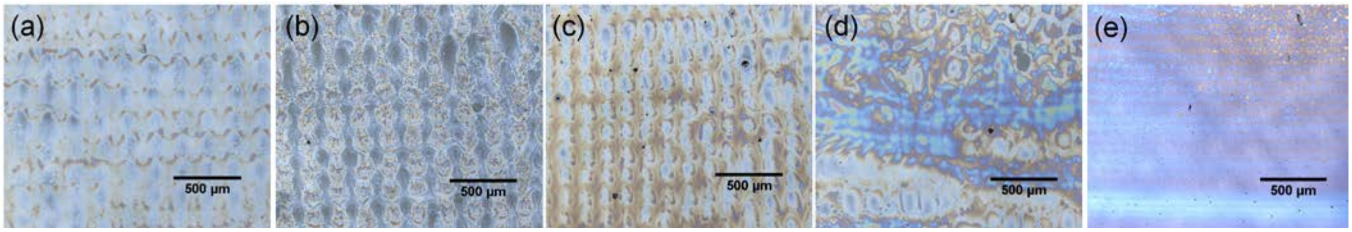

Figure 1: Optical micrographs of ink-jet printed ITO films with different printing resolution after annealing process. (a) 65 pixel (b) 72 pixel (c) 87 pixel (d) 100 pixel (e) 130 pixel

spectroscopy on a Cary 60 spectrophotometer. A pure glass substrate served as the 100% transmission baseline. The wavelength scan region was set as 400-800nm since glass has a strong absorption under 400nm. The electrical sheet resistance was measured by a Signatone four-point probe station connected to a Keithley nanovoltmeter and current source in delta mode. An Olympus Confocal microscope was used to inspect the surface morphology of the ITO films and patterns under low magnification. The surface morphology of ITO films was also investigated by a Hitachi SU8230 Cold field emission scanning electron microscope (SEM).

2.3 Assembly of LCD devices

PVA layers were coated onto ITO films by spin coater using 5wt% Polyvinyl alcohol (PVA) water solution. To make small reservoirs for liquid crystal, cotton cloth was used to rub the surface of PVA layer in one direction. One edge of the PVA layer was wiped by a damp tissue to expose ITO films. Then two pieces of these samples were combined by clips with liquid crystal in between. Next, two polarizer films were added with orthogonal optical axes [10]. Finally, the LCD devices were tested with a Keithley dc voltage source.

3 RESULTS AND DISCUSSION

To find out the best printing conditions, several one-layer ITO films were deposited onto glass with different printing resolutions by an ink-jet printer. Higher resolution meant shorter distance between two adjacent droplets. For example, the distance was 200μm for 65 pixel and 100μm for 130 pixel. First, an optical confocal microscope was used to inspect the surface of ITO films after annealing. From figure 1, it can be seen that the surface of the annealed ITO films show different surface morphology with various printing resolutions. With printing resolution less than 87 pixel, the regular printing marks could be found and the spacing between two spots matched the designed distance. The higher printing resolution gradually lost the printing marks because the droplets highly coincided on each other and ink started to flow on the surface. Finally, the surface of 130 pixel ITO film in figure 1e films show that the films became flat without apparent printing marks.

For ITO films, the two most important properties, optical transmittance and electrical resistance should also be taken into consideration. Table 1 shows the dc sheet resistance and corresponding standard deviation of ink-jet printed ITO films deposited with different printing resolution after an annealing step. The dc sheet resistance was measured by dc 4-point probe method when the film had less than 1×10^6 Ω. The ITO films printed with 87 pixel had the lowest sheet resistance of 4.03×10^4 Ω/sq with one layer. This value is around 2 orders of magnitude higher than commercial ITO-coated glass (100Ω/sq from Aldrich). However, the sheet resistance of 130 pixel ITO films exceeded the measurement set up limit and gave an insulating behavior. Then impedance spectroscopy was used to measure the sheet resistances of the 130 pixel ITO films and check the sheet resistance of the other samples as shown in figure 2. Impedance spectroscopy has a much larger measurement range than dc measurements. The 130 pixel ITO film was found to have a sheet resistance as high as 1.90×10^9 Ω/sq. All the other samples had similar sheet resistances as those obtained using the dc 4-point probe method.

	Sheet resistance R_1 (Ω/sq)	Stadard deviation σ_1 (Ω/sq)
65 pixel	8.64×10^4	3.09×10^3
72 pixel	2.48×10^5	1.08×10^4
87 pixel	4.03×10^4	1.09×10^3
100 pixel	2.78×10^5	1.15×10^4
130 pixel	Insulating	

Table 1. Sheet resistance and standard deviation of ink-jet printed ITO films made with different printing resolution after annealing process

The reason for the high resistance of the 130 pixel ITO films is believed to be related to having too much ink on the substrate during the ink-jet printing which gave better surface morphology but thicker films. Then the hot plate quick annealing process cannot fully remove all of the organics, chloride and nitric acid elements. Thus the conducting network of ITO nanoparticle was not well formed in the 130 pixel ITO films and the sheet resistance became very high.

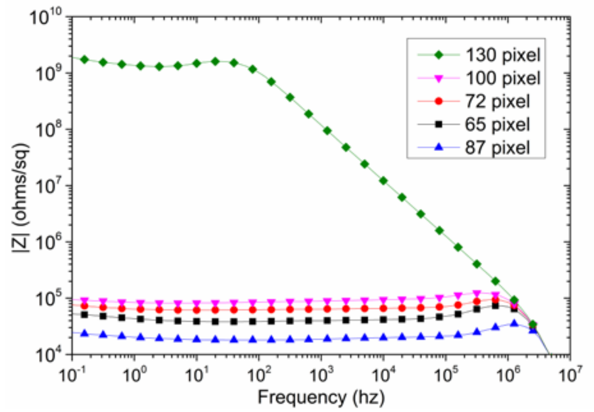

Figure 2. Impedance magnitude vs frequency of ink-jet printed ITO films with different printing resolution after annealing process

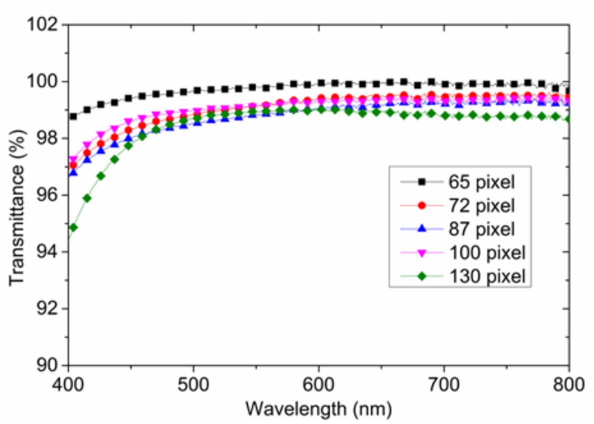

Figure 3. UV-vis spectroscopy of ink-jet printed ITO films with different printing resolution after annealing process

From UV-vis spectroscopy data in figure 3, we could discover that all the ink-jet printed ITO films had good optical transmittance (> 95% in the visible light region). The 65 pixel ITO films had the best transmittance in the visible light region whereas the 130 pixel ITO films were less transparent in most wavelength.

Considering the three factors of surface morphology, optical transmittance and sheet resistance, the 65 pixel and 87 pixel films were found to be two good printing resolutions for ink-jet ITO films. Indeed, the 65 pixel films might sometimes have voids on the surface because of the large spacing in between droplets. Since thicker ITO films could bring lower sheet resistance and resistivity [11], the 87 pixel printing resolution was used to build up to five layers of ITO films on the same glass substrate.

With increasing number of layers from one to five layers (5L), the surface morphology of the ITO films should be of concern. The top view surface of the 5L ITO films printed using 87 pixel resolution is shown in Fig. 4. The image was obtained by FE-SEM. With a relatively low magnification (100×) in figure 4a, the regular printing marks could also be found. The spacing between two marks was around 150 μm which matched the printing resolution of 87 pixel. This demonstrated that ink-jet printed ITO films still had a smooth surface even though they were deposited with five coating layers. The high magnification SEM picture (figure 4b) shows that the microstructure of the 5L ink-jet printed ITO films was very uniform without any big aggregates. This is a very important feature for electronic applications where the conducting network is expected to be uniformly distributed. In addition, the cross section of the 5L ITO films was also measured by SEM and the average thickness was around 400nm (not shown).

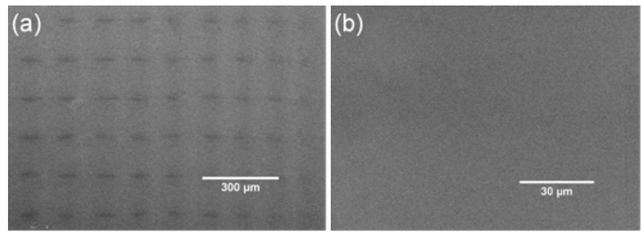

Figure 4. SEM pictures of five layers ink-jet printed ITO films after annealing process

	Sheet resistance R_2 (Ω/sq)	Stadard deviation σ_2 (Ω/sq)
1 layer	4.03×10^4	1.09×10^3
2 layers	4.65×10^3	94.3
3 layers	1.47×10^3	15.9
4 layers	8.56×10^2	7.83
5 layers	5.88×10^2	2.62

Table 2. Sheet resistance of ink-jet printed ITO films with different deposited layers after annealing.

For the electrical properties, ITO films with different printing layers after annealing were also measured by dc 4-point probe method and are listed in table 2. When the second ITO layer was printed on the 1L ITO film, the sheet resistance decreased by almost 1 order of magnitude from 4.03×10^4 Ω/sq to 4.65×10^4 Ω/sq. With increasing the number of printing layers, the sheet resistance continued decreasing to 5.88×10^2 Ω/sq for the 5L ITO films. This value is in the same order of magnitude with some commercial ITO-coated glass.

Another concern for multiple layers ITO films is the optical properties because increasing thickness usually decrease the transmitance of ITO films [11]. Figure 5 shows the transmittance at 550nm wavelength of ink-jet printed ITO films with different layers. All the samples had excellent transmittance higher than 97% at this wavelength which was really transparent without any color. Thus multiple layer ITO films still kept good transparency with increasing number of layers and thickness. One interesting phenomenon was that the two layer ITO film had a higher transmittance than the single layer ITO film. This may be a result from light interference between each layer of ITO films when the film thickness was comparable to the wavelength of incident light [12].

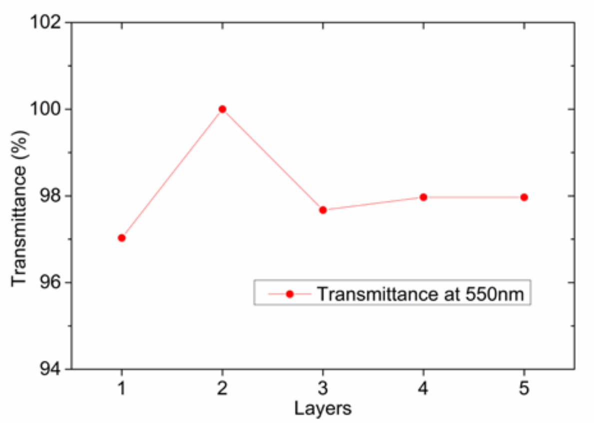

Figure 5. Optical transmittance at 550nm for ink-jet printed ITO films containing 1-5 layers after annealing

With smooth surface morphology, low sheet resistance and high optical transmittance, the 5L ink-jet printed ITO films can meet the requirements for several electronic applications. Simple LCD devices were fabricated to further prove the good properties of our inkjet printed ITO films. In order to show a "GT" pattern on the LCD devices, one should make a "GT" pattern on the ITO films. Thus, a 5L ink-jet printed ITO pattern was made using bitmap function when all the printing and annealing steps were the same with ITO films. All the steps didn't require any vacuum condition or photolighography steps. After assembly, the all-printed LCD devices show a clear image shift when connected to a dc voltage source in figure 6. A 3V dc voltage was enough to drive the device to show a "GT" pattern. Higher voltages could display better image contrast. Although some grey parts existed in the final pattern, all-printed fabrication was proved to be possible with our ink-jet printed ITO films and patterns.

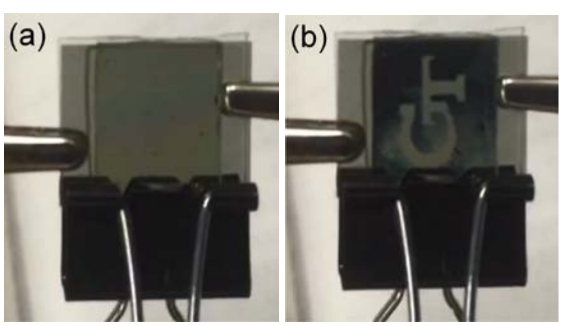

Figure 6. Visual images of All-printed LCD devices (a) before and (b) after connecting to voltage source

4 CONCLUSIONS

Highly conductive and transparent ITO films were successfully made by ink-jet printing method with a self-made sol-gel ITO ink. The transmittance for five-layer ITO films was higher than 95% at a wavelength of 550 nm and the sheet resistance was as low as 588Ω/sq. These ITO films also had very smooth and uniform surface morphology which is an essential feature needed for electronic devices. The properties of ink-jet printed ITO films could be further improved by better annealing process and increasing the number of coating layers.

Finally, all-printed LCD devices were fabricated with these ink-jet printed ITO films. The LCD devices displayed a clear image shift upon the application of a relatively low dc voltage. More complicated LCD devices and other applications requiring patterning will be fabricated with these inkjet printed ITO films in the future.

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