Titanium thin film modified silica substrate to enhance the bonding properties of nanosilver

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Abstract
Nanosilver has intrinsic problem to adhesion on the surface of silica. To improve interfacial properties between nanosilver and silica substrate, a thin titanium film is introduced in this study. The titanium-coated silica substrates are prepared by sputter technique. The commercial silver nanopaste with size around 3-7nm is used in this study. The results indicate thin layer of titanium can improve the bonding properties of nanosilver and expect to be used in fabrication of TFT display panel.

1. Introduction
The traditional semiconductor fabrication process is used to fabricate the thin-film transistor liquid crystal display (TFT-LCD), including thin film, photo lithography and etching. In applications such as flat panel displays or imagers, the simplification or reduction of these processes and materials consumption would result in lessening the cost and complexity in fabricating large-area arrays. One approach to reducing this complexity is to replace the conventional photolithographic process by direct-writing methods to define devices or interconnect features on a substrate [1]. Ink-jet printing is a noncontact technique of imaging computer data by means of jetting the ink from a small orifice to a specified position on a substrate [2]. At present, the metal conducting wire was used traditionally in array of panel is usually the Cr, Al, Mo or alloy mixed structure. Therefore, based on the experience of IC system fabricated, the development of lower resistance conducting wire like Cu, Ag, Au, etc. are more important [3]. Silver as a best conductor is studied most intensively for metal deposition by ink jet printing. However, due to their low chemical stability and soft texture, silver with high hardness, good adhesion, and acceptable chemical stability are hard to obtain on a silica substrate without doing any improvements [4]. The purpose of this work is to develop novel processing technology for fabricate a well-adhesion silver conducting wire on a silica substrate by ink-jet printing device. Therefore, the adhesion between the silver and silica substrate is a key point in the research. In order to avoid the peeling of silver from the silica substrate, a thin Ti film was deposited on the silica as an intermediate layer. The adhesive quality of Ti on silica is good even at room temperature [5]. Thus, Ti is a good interfacial material to form good bonding between the glass and other metallic materials.

2. Experimental section
2.1 Characterization of silver nanopaste
The metallic conductor paste applied in the ink-jet printing was Harima silver nanopaste, manufactured by Daiichi Jitsucyo CO., LTD. The silver nanopaste consisting of 3-7 nm globular particles dispersed

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57.4% by weight in n-tetradecane. The viscosity and specific gravity of the silver nanopaste is 8.9 cps and 1.71 g/ml at 20℃.

2.2 The cleaning process of silica substrate

The silica substrates were cut by a diamond cutter to form the substrate size around 9cm x 5cm then cleaned in ultrasonic bath with DI water for 5 min. After that, substrates were soaked in a mixed solution with a ratio of H_2SO_4 to H_2O_2 = 3:1 and boiling at 80~100℃ for 15 min in order to remove the organic greases on silica substrates. Then, silica substrates repeated to clean in ultrasonic bath with DI water for 20 min, which was followed by drying with a stream of N_2.

2.3 The coating of titanium by sputtering

Ti target with the purity of 99.9% and size of ϕ 3”x 3 mm was used in the RF sputter system. In order to make the target has well electric and heat conduction; a Cu backing plate (size ϕ 3”x 3 mm) was fixed on the back of Ti target. Furthermore, in order to make the target can be fixed on the sputter gun; a small steel sheet (keeper) was also attached on the back of Cu backing plate. After cleaning and cutting, the silica substrates were put into working chamber. The chamber was first pumped to $5x10^{-3}$ torr by mechanical pump, further was pumped to $3x10^{-6}$ torr by cryo-pump. 30 sccm of Ar gas was introduced into chamber and set the vacuum at $1x10^{-2}$ torr. Turning on the RF power (100 W) and pre-sputter for 5 min to clean the glass substrate. After pre-sputter, removing the shutter and starting to deposit for 0.5hr, 1hr, 2hr, 2.5hr and 3hr to prepare different thickness of thin Ti film. The parameters of sputter were arranged in Table 1.

2.4 Adhesion test

In order to test the bonding properties between nanosilver and titanium-coated silica substrate, a silver drop (2μl) was ejected from a electronic pipettes on a unmodified and titanium-coated silica substrate. After curing at 250℃ for 1hr, the adhesion properties were tested by ASTM D3359.

2.5 Printer and process of printing

The ink jet printing system was composed of an ink jet print head, a CCD camera, a sample platform, an Apollo control system and a machine control system. The equipment used here is a drop-on-demand printer that prints with a piezoelectric print head. The print head was mounted onto a computer-controlled three-axis gantry system, and expelled droplets downward onto a horizontal substrate. The print head with 128 ink channels in a linear arrangement is able to deliver drop volumes of 80 pl/drop. The platform where the substrates were placed could move in two directions. A resistive substrate heating plate was mounted under the X-Y stage that can heat the substrate. The basic printing parameters, such as pulse amplitude, frequency, graphs of printing were controlled by an Apollo control system. The movement of the platform and a CCD camera were controlled by a machine control system. In the process of printing, experimental parameters of pulses frequency, amplitude of the controlling impulses and the drop separation were varied to optimize the quality of the printed lines. The optimal translation speed of the X-Y table had to be found in order to achieve well-shaped lines. Changing the translation speed of the stage changes the distance between the deposited drops. The gap between the nozzle plate and the printing surface was maintained at ~1mm by Z displacement. The substrates used were unmodified and titanium-coated silica substrates with different time of coating. The silica substrates were retained at room temperature in printing process. The printing parameters of pulse frequency and amplitude were 2.4 kHz and 100 V. The drop separation was set for 200 um. After printing and prior to microscope inspection the patterns were dried on a hot plate by gradually increasing the temperature from 25℃ to 250℃ and curing for 1 hr at 250℃.

2.6 Specimen analysis

Before the coating of titanium film, a dot of correction fluid was covered in the middle region of silica substrates to form a region without titanium coating. After coating, the region was cleaned by acetone. A step was formed between the coating and un-coating area. The thickness of printing lines and titanium film at different times of coating were measured by TENCOR alpha-Stepper 200. Alpha-step is mainly a tip that scans over the step and record the change of height. The shape and width of printing lines were observed by optical microscopy. The wet ability effect of titanium-coated silica substrates were measured by contact angle analyzer. The water contact angle on the modified silica substrates were measured by the sessile drop method with distilled water and observed using CCD at room temperature.

Table 1 The deposition parameters of titanium film

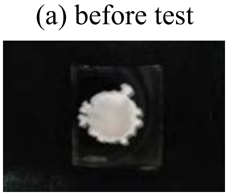
Group	Working pressure	RF power	Substrate temp.	Gas source	Sputter times	Thickness
1					0.5 hr	7.4 nm
2					1 hr	13.9 nm
3	1 x10^{-2} torr	100 W	no heating (room temperature)	Ar at 30 sccm	2 hr	28.2 nm
4					2.5 hr	35.1 nm
5					3 hr	44.2 nm

3. Results and discussion

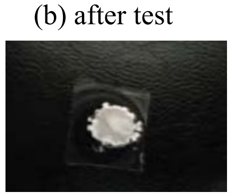
Figure 1 shows the photographs of the adhesion test of nanosilver between unmodified and titanium-coated silica substrate. After titanium-coated, an obviously promotion of the adhesion was appearance in Figure 1. The result indicated it is possible to form good bonding properties between silver and silica substrate. The thicknesses of titanium coating at different time of 0.5hr, 1hr, 2hr, 2.5hr and 3hr are 7.4 nm, 13.9 nm, 28.2 nm, 35.1 nm and 44.2 nm respectively. The sputtering rate was around 0.24 nm /min. At the coating for 2 hr to 3hr, the silica substrates were not present well transparency and shown a little color of brown. This phenomenon is unfavorable for the fabrication of TFT-LCD. The contact angle of water on unmodified and different thickness of titanium-coated silica substrates were investigated and observed using CCD, as shown in Figure 2. The contact angle shows the wettability of liquid on solid. The low contact angle means high wettability of water. With the increase of time of coating, there is a raise slowly of water contact angle.

(a) before test

(b) after test



(c) before test



(d) after test

Figure 1 The adhesion of nanosilver on (a)(b) unmodified and (c)(d) titanium-coated silica substrate cured at 250℃ for 1hr after ASTM D3359 test.

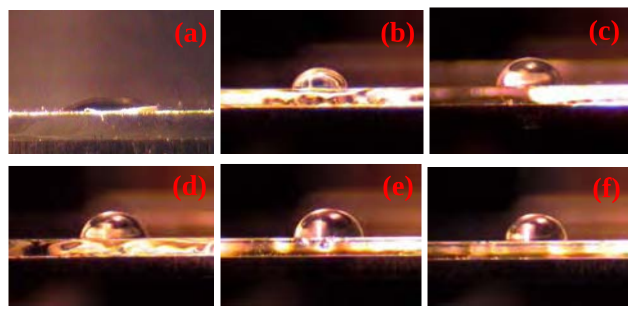


Figure 2 Contact angle of water with (a) unmodified, (b) 0.5 hr, (c) 1 hr, (d)2 hr, (e) 2.5 hr, and (f) 3hr titanium-coated silica substrates.

The contact of water reached to 82° for the 3 hr of titanium-coated silica substrate. The trend of the contact angle of water and the different thickness of titanium coating was shown in Figure 3. The silver conducting wires on unmodified and titanium-coated silica substrates by ink jet printing were observed by OM as shown in Figure 4.

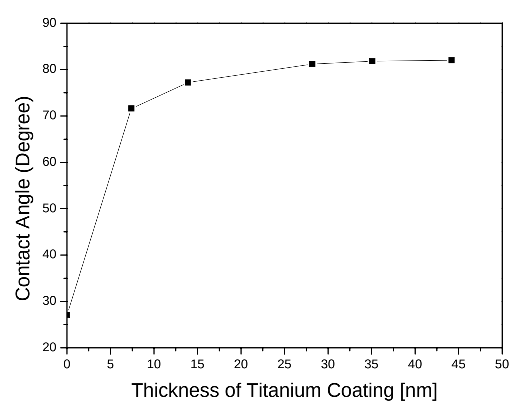


Figure 3 The relationship between contact angle of water and different thickness of titanium coating.

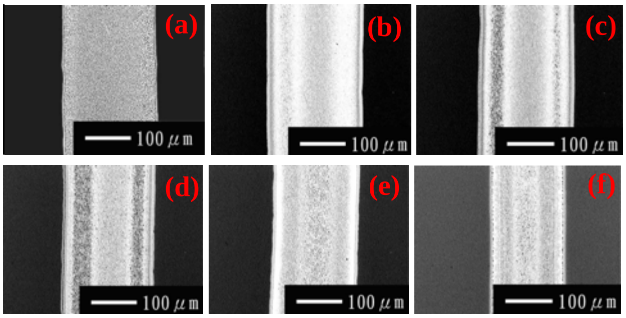


Figure 4 OM images of the silver conducting wires on (a) unmodified and (b) 0.5 hr, (c) 1 hr, (d) 2 hr, (e) 2.5 hr, and (f) 3 hr titanium-coated silica substrates.

The width of silver conducting wire on unmodified silica substrate was 209.4 μm. Because of the decrease of surface energy, the width of silver conducting wires on titanium-coated silica substrates were decreased to 162.7 um at the coating for 3hr in the same process conditions. It proves that it is helpful to restrain the spread of silver conducting wire. However, the thicknesses of silver conducting wires were opposite to the width. It was increased from 247 nm to 311 nm at the coating for 0.5hr and 3hr. The relationship between the widths and thicknesses of silver conducting wires on different times of titanium-coated silica substrates were shown in Figure 5.

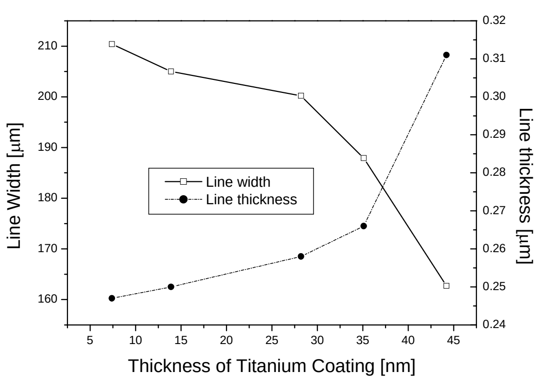


Figure 5 The relationship between the widths and thicknesses of silver conducting wires versus the different thickness of titanium-coated silica substrates.

4. Conclusion

1. An obviously promotion of the adhesion was enhanced between the nanosilver and titanium-coated silica substrate.
2. With the increasing of the thickness of titanium coating, there is a slow reduction of wettability of titanium-coated silica substrates and reached a maximum at 35nm of titanium coating.
3. At the same parameters of ink jet printing, the widths of silver conducting wires on the titanium-coated silica substrates are narrower than that on unmodified silica substrate. Besides, with the increasing of titanium thickness, the widths of silver conducting wires were reduced.
4. The thicknesses of silver conducting wires are increase with increasing thickness of titanium coating silica substrates.

5. Acknowledgements

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6. References

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