Screen Printed Aluminum Cathode for Flexible Devices

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ABSTRACT

All-printed electronic devices are rapidly emerging due to its great potential for large area, flexible and low cost products such as organic light-emitting diodes (OLED) and organic photovoltaic (OPV). Aluminum (Al) electrodes are widely used in these devices as the cathode due to the high conductivity and matched work function with organic active materials.

In this study, AlH_3 {O $(C_2H_5)_2$} was used as the Al precursor ink and $TiCl_4$ as the catalyst to pattern Al electrodes by screen printing. The printed Al films, which were sintered at low temperature of 80℃, have excellent electrical conductivity, mechanical flexibility and high stability, and are almost the same as those deposited by vacuum thermal evaporation. The work function of Al thin film prepared by screen printing is about 3.72eV and well suited as cathodes, which paves the way for development of all-printed flexible OLEDs and OPV devices.

Keywords: Al precursor ink, low temperature sintering, printing Al cathode

1 INTRODUCTION

Printed electronics stands for a revolutionary, new type of electronics: thin, lightweight, and flexible, produced at low cost, enabling single use, ubiquitous electronic devices and new applications. Intelligent packaging, OLED (organic light emitting diode) lighting, low cost RFID (radio frequency identification) transponders, rollable displays, flexible OPV(organic photovoltaic) devices, and printed batteries which prepared by printed electronic technology are just a few examples [1].

Aluminum (Al) electrodes are used almost exclusively as the cathode materials in OLED and OPV devices due to its high conductivity, matched work function, easy preparation and low cost. The matched work function is considered to be the most important property for organic electronic devices in order to improve the electron injection process. Currently, the mainstream technology for depositing Al electrodes is either thermal evaporation or sputtering with a shadow mask, which is of high cost in terms of energy consumption and equipment usage.

It have been reported that nanoparticle-based Al inks can be thermally cured in air to form conductive Al electrodes for solar cells [2]. However, the required sintering temperature is as high as 550-940℃. Such high temperature is unbearable for both organic active layers and plastic substrates. In addition, due to the high oxidative behavior during the preparation of Al nanoparticles or ink in air, there is always a 3-10 nm thick Al_2O_3 shell on the surface of Al particles, causing reduction of electrical conductivity [3].

Recently H.M. Lee [3, 4] proposed a solution process to stamp Al cathodes using AlH_3 {O $(C_4H_9)_2$} precursor ink which can decompose into Al at 150℃ with Ti (O-i-Pr) $_4$ vapor as a catalyst in an argon (Ar) environment. However, the sintering temperature is still too high for OLED, OPV and devices on flexible substrate such as PET.

In the present study, Al films were patterned by screen printing and cured at 80℃ using the AlH_3 {O $(C_2H_5)_2$} ink with $TiCl_4$ as the catalyst. The prepared Al films exhibited excellent electrical and mechanical properties, and can be used to fabricate cathodes for flexible OLED and OPV devices.

2 EXPERIMENT

2.1 Preparation of Al precursor ink

Al precursor ink was prepared by an ethereal reaction of aluminum chloride ($AlCl_3$) and lithium aluminum hydride ($LiAlH_4$) in anhydrous diethyl ether (O $(C_2H_5)_2$). Here, $AlCl_3$ and O $(C_2H_5)_2$ were purchased from Aladdin Chemical, and $LiAlH_4$ was purchased from Aldrich Chemical. O $(C_2H_5)_2$ was further dried by sodium (Na). All reactions were carried out in the glove box under argon (Ar) atmosphere, with the oxygen and water level less than 0.1ppm.

$AlCl_3$ was used as a precursor for preparing the Al precursor ink, while $LiAlH_4$ was used as both a precursor and a reduction agent. O $(C_2H_5)_2$ was used as the solvent for the reaction of both chemicals. In the experiment, 500mg $AlCl_3$ and 427.5 mg $LiAlH_4$ were added to 50ml O $(C_2H_5)_2$ at room temperature. The mixed solution was magnetically stirred for 24 hours then filtrated to remove solids and precipitate. The clear solution was concentrated to 10% and used as an Al precursor ink for screen printing, following an adjustment of viscosity.

2.2 Preparation of Al films

Fig.1 shows a schematic diagram of the screen printing process for fabricating conductive Al films on target substrate using the Al precursor ink. Firstly, the target substrate was bathing in catalyst ($TiCl_4$) vapor in a covered glass bowl with a drop of 100ul $TiCl_4$ (1wt% concentration) on a hotplate at 80 ℃ for 30s.

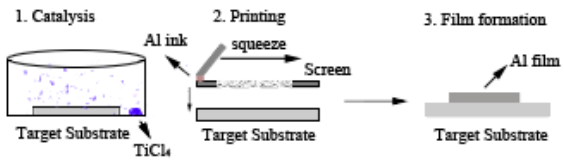

Figure 1: Schematic diagram of screen printing process for preparing Al film

Then the Al precursor ink was printed on the surface of the pretreated target substrate by screen printing. Finally, the target substrate with patterned Al ink was sintered at 80 ℃ for 1 minute, resulting in a high quality Al films.

2.3 Characterization

The surface morphology and work function of Al films were measured by Kelvin probe force microscopes (KFM) measurements (Dimension 3100, Veeco). The 400-MHz ^1H Nuclear Magnetic Resonance (NMR) spectra were tested by Varian MR-400 spectrometer with THF-D_8 as solvent and TMS as internal standard. X-ray diffraction spectra of the prepared Al films were recorded with a Bruker AXS D8 Advance X-ray diffractometer using nickel filtered Cu Kα radiation (40 kV, 40 mA). The measurements were performed within a 2θ range of 30-90°. Electrical sheet resistances of Al films were measured by four-point probe method (Keithley 4200).

3 RESULTS AND DISCUSSION

3.1 Mechanical and electrical properties of Al films

Prepared Al films at sintering temperature of 80 ℃ on different substrates were shown in Fig.2. It can be seen that all films were shiny metallic on substrates such as photopaper, glass, PET, and P3HT layer (active layer for OPV). However, some corrosion is observed on P3HT film. It is suggested that direct printing of Al ink on top of P3HT should be avoided. Pre-deposition 5nm thickness Al_2O_3 films on P3HT surface by atomic layer deposition (ALD) then screen printing Al ink can effectively solve the corrosion problem. The insertion of such ultra-thin Al_2O_3 will not harm electron injection [5].

Photo paper Glass PET P3HT layers

Figure 2: Prepared Al film at sintering temperature of 80 ℃ on different substrates

Table 1 lists the electric resistance, roughness and work function of Al films. All samples show conductivities similar to the Al film prepared by thermal evaporation. The surface morphology suggested that the Al surface grain size by screen printing process is about 200 nm while it is about 80 nm by thermal evaporation. It is also found that the surface of Al film on glass substrates becomes smoother as the sintering temperature was decreased from 150 to 80 ℃. It is believed that the reaction of decomposition of Al ink into H_2 and Al gets more drastic at higher temperature and forms tiny porous in Al film. Furthermore, the Al films sintering at 80 ℃ show lowest work function of 3.72eV. It can be explained that Li elements contained in $LiAlH_4$ precursor in Al film results in a decrease in work function, and it has been reported that the work function of Al substrates with a native oxide layer is 3.3eV. This indicated that the Al film prepared at 80 ℃ by screen printing can be used as cathode for OLEDs and OPVs.

Al-Fabrication Method	Surface Morphology	R (Ω·cm)	Ra (nm)	W_F (eV)
Thermal Evaporation		2.79	2.63	4.15
Screen printing/80 ℃ (Glass substrate)		3.90	5.51	4.08
Screen printing/80 ℃ (PET substrate)		2.31	26.0	3.72
Screen printing/100 ℃ (Glass substrate)		3.10	11.0	4.11
Screen printing/150 ℃ (Glass substrate)		2.00	7.33	4.47

Table 1 Mechanical and electrical properties of Al films under different fabrication methods

3.2 Structural analysis and mechanism

The Al films are formed by the decomposition of Al precursor ink in a catalytic reaction. There are two steps of reaction processes. The Al precursor ink is formed according to the equation (1) [6-8].

$$AlCl_3 + LiAlH_4 \xrightarrow{O(C_2H_5)_2} AlH_3\left\{O\left(C_2H_5\right)_2\right\} + LiCl\downarrow \quad (1)$$

Decomposition of Al precursor ink into Al film follows reactions in equations (2) and (3). First, AlH_3 {O $(C_2H_5)_2$}is decomposed into Al{O$(C_2H_5)_2$} and H_2 and then Al{O$(C_2H_5)_2$} is decomposed into Al and O$(C_2H_5)_2$ [3,10]. In both reactions, the catalyst $TiCl_4$ and sintering play the key role. Once the decomposition of Al precursor ink is initiated, it will be self-sustaining and form a continuous layer covering the whole surface of target substrate.

$$AlH_3\left\{O\left(C_2H_5\right)_2\right\} \xrightarrow{TiCl_4} Al\left\{O\left(C_2H_5\right)_2\right\} + 1.5H_2\uparrow \quad (2)$$

$$Al\left\{O\left(C_2H_5\right)_2\right\} \xrightarrow{TiCl_4} Al + O\left(C_2H_5\right)_2 \quad (3)$$

Fig. 4 shows the NMR spectrum of Al precursor that dissolved conducted in THF-D_8 solvent. It can be seen that H atoms attached to Al atom of AlH_3 group appear in the 3.20 ppm. The signals of -CH_2- fragment in ether group with 4 peaks appear in the 3.35 ppm to 3.45 ppm range. The -CH_3 fragment in ether group with 3 peaks appear between 1.10 ppm and 1.145 ppm. Compared with the peak area of AlH_3 and O $(C_2H_5)_2$, this result could be clearly confirmed that the chemical structure of Al precursor ink is AlH_3·0.3{O $(C_2H_5)_2$}.

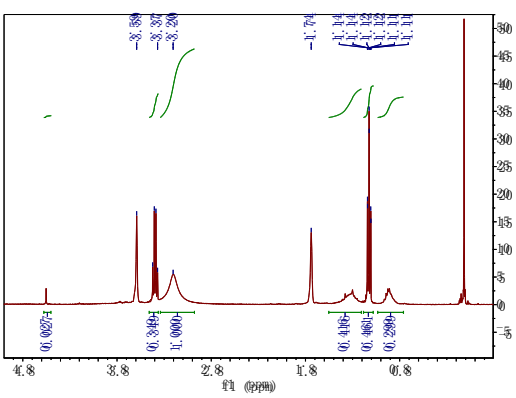

Figure 4: NMR spectrum of Al precursor dissolved in THF-D_8 solution with internal TMS

Fig. 5 compares the XRD measurements of crystal structure of Al films by thermal evaporation and by printing. XRD patterns of these films are in good agreement with a face-centered-cubic aluminum metal. Though the intensity of printed Al film is slightly weak, the electrical conductivity shows no sign of weakening. The measured sheet resistance of printed Al films sintered at 80 ℃ is lower than 2.29 Ω/□.

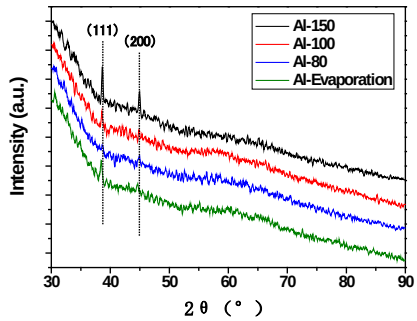

Figure 5: XRD patterns of Al films synthesized at different temperatures.

The stability of printed Al film is also good, as shown Fig.6. After exposure to ambient air for 5 days, the electric resistance of printed Al films still maintained at 3.63Ω, indicating that the Al film is very stable.

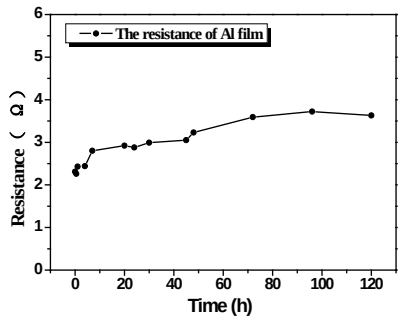

Figure 6: The resistance stability of Al film in air

4 CONCLUSION

We have successfully prepared Al precursor ink, AlH_3·0.3{O $(C_2H_5)_2$}, which can be patterned by screen printing and decomposed into high quality Al films through catalytic reaction of $TiCl_4$ at low sintering temperature of 80 ℃. Compared with traditional thermal evaporation, printed Al films demonstrated high conductivity (2.29 Ω/□) and low work function (3.72eV), which can be used as cathode electrode in flexible OLED and OPV devices with low fabrication cost.

ACKNOWLEDGEMENT

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