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Printing Al Cathode with Low Sintering Temperature for Organic Lighting Emitting Diodes

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Printed aluminum (Al) cathode was achieved with low sintering temperature by Al precursor ink, $AlH_3 \bullet O(C_3H_7)_2$, which can be pattern by printing and decomposed to Al micro-like films under catalyst of $TiCl_4$. Sintered at 80 °C for 30 s, the Al cathode with thickness of 50 nm shows a sheet resistance of 2.09Ω/□ and work function of 3.67 eV. The low sintering temperature and low work function of printing film, along with its high conductivity and stability, is well suited for OLED cathode as proved in this work. This study also paves the way to the all-printed flexible devices.

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Introduction

Printed electronics stand for a revolutionary, new type of electronics, production of which presents characteristics of large area, thin, lightweight, flexible and low cost, promoting further developments of technics in paper batteries, radio frequency identification (RFID), organic light- emitting devices (OLED) and organic photovoltaics (OPV), etc.[1] For all-printed electronic devices, printable conductive electrodes are attractive technology because of their simple processing technology and low cost in terms of energy consumption and equipment useage. The preparations of anode by printing condctive materials such as indium tin oxide (ITO),[2] IZO (ZnO-doped In_2O_3),[3] nano-silver,[4] carbon nanotubes (CNTs)[5] and some conductive polymers[6,7] were widely reported. However, the printed cathode is still a big challenge because of the lack of suitable ink material with low work function. Suitable work function of the cathode is considered to be one of the most important factors for organic electronic devices, which determines the efficiency of the charge carrier injection from the cathode.[8-12]

For cathode materials in organic devices, aluminum (Al) electrodes are almost exclusively used due to its high conductivity, matched work function,and low cost. Currently, the mainstream technology for fabricating Al electrodes is either thermal evaporation or sputtering with a shadow mask.

It has been reported that nanoparticle-based Al inks can be patterned by printing and thermally cured in air to form conductive Al electrodes for solar cells.[13] However, the sintering temperature is very high, ranging from550°C to 940 °C. Such a high temperature is detrimental to 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, a Al_2O_3 shell with a thickness of 3-10 nm would always appear on the surface of Al particles, causing the low electrical conductivity. [14]

Recently, H.M. Lee[14,15] proposed a solution process to stamp Al cathodes by using $AlH_3\{O(C_4H_9)_2\}$ ink. Then the ink can turn into Al film at 150 °C with the caralyst of Ti $(O\text{-}i\text{-}Pr)_4$ in an inert atomsphere. However, the sintering temperature is still too high for OLED and OPV functional layers and flexible substrate such as PET. Therefore, a suitable Al ink is necessary for printing Al cathode with lowsintering temperature.

In this work, we have explored series of Al organometallic compound precursor ink and suitable catalyst for printing Al cathode to lower the sintering temperature without reducing the premise stability.

Experimental sections

Typically, Al precursor ink was prepared by an ethereal reaction of aluminum chloride ($AlCl_3$) with lithium aluminum hydride ($LiAlH_4$) in anhydrous ethers, such as diethyl ether ($O(C_2H_5)_2$),[16] isopropyl ether ($O(C_3H_7)_2$), and butyl ether ($O(C_4H_9)_2$)[14,15] respectively, as shown in equation (1).[14-18] $AlCl_3$ and ethers were purchased from Aladdin Chemical and the latter was further dried by sodium (Na) before usage, $LiAlH_4$ was purchased from Aldrich Chemical. All synthesis and Al cathode printing process were carried out in the glove box with the oxygen and water level both less than 0.1ppm.

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

We found that $O(C_3H_7)_2$ ink is especiallyeffective in achieving compact Al films at a low temperature. And it is more secure than $O(C_2H_5)_2$, which is highly flammable and explosive even at a low temperature (-5 °C), as mentioned by Schmidt *et al.*.[16] However, the Al films successfully achieved by $AlH_3\{O(C_4H_9)_2\}$ are performed at 110-150 °C.[14,15] However, this temperature is higher than the endurance of some flexible substrates and organic active layers, as discussed above. So we chose high volatile and easy manipulated solvent $O(C_3H_7)_2$ as the candidate precursor to realize a low sintering temperature (80 °C) to print Al cathode.

Accordingly, a high quality Al conductive films was achieved by screen printing under lower sintering temperature of about 60-80 °C from the as-synthesized $AlH_3\{O(C_3H_7)_2\}$ ink under the catalyst of $TiCl_4$ vapor. The electrical and mechanical properties of the printedAl film was investigated, and the printing process of Al cathode for OLED was also described. Al precursor ink was first perpared with $AlCl_3$ as precursor, while $LiAlH_4$ was used as both precursor and reduction agent in $O(C_3H_7)_2$. Typically, 0.50 g

$AlCl_3$ and 0.43 g $LiAlH_4$ were added into a flask with 50 mL $O(C_3H_7)_2$ solvent at room temperature. The mixed solution was magnetically stirred for 24 hours and then filtrated with a .045 µm filter. The clear solution was concentrated to 10wt% and used as an Al precursor ink for printing process, following adjustment of viscosity.

The fabrication process of conductive Al films which were prepared through the following procedures. Firstly, the target substrate was bathed in the catalyst ($TiCl_4$) vapor in a covered glass bowl with a drop of 100 µL $TiCl_4$ (1wt % concentration) on a hotplate at 80 °C for 30 s. Then the Al precursor ink was printed on substrate by means of drop casting, stamping or screen printing. Finally, the target substrate patterned with Al ink was sintered at 80 °C for 1 minute, which resulting in high qualityAl films. Here, stamping process is a little complicated while it can ensure the good quality of Al films. Here, this process needs two substrates, target substrate and source glass. Target substrate need to be bathed in the $TiCl_4$ vapor as mentioned above. The Al precursor ink was coated on the source glass by drop casting and then dried for 5-10 min at room temperature. While contacting the source glass and the target substrate at 80 °C for 1 minute, thermal energy and catalyst within the target substrate activates the decomposition of Al precursor ink into Al film.

The decomposition follows reactions in equations (*2*) and (*3*). Firstly, $AlH_3\{O\,(C_3H_7)_2\}$ is decomposed into $Al\{O(C_3H_7)_2\}$ and H_2, then $Al\{O(C_3H_7)_2\}$ is decomposed into Al and $O(C_3H_7)_2$.[14, 19] In both reactions, the $TiCl_4$ catalyst and sintering conditions play the key roles. 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.

$$AlH_3\{O(C_3H_7)_2\} \xrightarrow{TiCl_4} Al\{O(C_3H_7)_2\} + 1.5H_2\uparrow \qquad (2)$$

$$Al\{O(C_3H_7)_2\} \xrightarrow{TiCl_4} Al + O(C_3H_7)_2 \qquad (3)$$

The chemical structure of synthesized organometallic compounds were confirmed through 400 MHz ^{1}H Nuclear Magnetic Resonance spectra by Varian MR-400 spectrometer using the THF-D_8 as solvent.

The crystal structure of Al films was measured with a Bruker AXS D8 Advance X-ray diffractometer. Their sheet resistance with the size of 1×1 cm^2 were investigated by a four-probe set-up with a Keithley 4200 parameter analyser, and the measurement size of four-probe was 6mm with 2 mm distance by each other. The surface potential were measured by Kelvin probe force microscopes (KFM).

Results and discussion

The 400-MHz ^{1}H Nuclear Magnetic Resonance (NMR) spectra were tested by Varian MR-400 spectrometer with THF-D_8 as the solvent. Figure 1 shows the NMR spectrum of the prepared Al precursor ink. It can be seen in the NMR spectrum that H atoms attached to Al atoms of AlH_3 group appear in the 3.17 ppm. The signals of $O\ (C_2H_5)_2$ appear around 1.1 and 3.3 ppm. And the peaks in 1.72 and 3.57 belong to the solvent of THF-D_8. The signal around 4.53 ppm is the assigment of hydrogen (H_2), which was generated by the reaction of Al precursor exposuring to the atmosphere. Besides these signals, there are not any other significant peaks. The result clearly showed the purity of the Al precursor, and also could confirm that the chemical structure of the prepared Al precursor ink is $AlH_3\cdot x\{O\ (C_2H_5)_2\}$.

Crystal structure analyses were also carried out using XRD (Bruker AXS D8 Advance X-ray diffractometer), and the acquired diffration patterns of the obtained samples show only patterns of Al metal (Fig. 2). The diffraction peaks attributed to pure Al with a face-centered cubic structure (JCPDS No. 01-089-2769) were clearly detected from all samples under different preparation process, which slightly deviates from the standard value. We believe that the small deviation from standard value is tolerable considering that the nanostructures are somewhat different from bulk materials in properties, which is a common phenomenon in nanostructures, rather than test errors 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 °C is lower than 2.09 Ω/□.

The stability of printed Al film was also tested, again we obtained good results as our previous report on $AlH_3\{O(C_2H_5)_2\}$,[20] shown in Figure 3. After exposure to ambient air for 5 days, the electric resistance of printed Al films still maintained at 3.61Ω/□, indicating that the Al film is relatively stable. In the intial stage of exposure to air, the change of resistance is obivious. This is due to the oxidation of Al nano-particles as mentioned before, a 3-10 nm Al_2O_3 shell would form on the surface of Al particles, causing the reduction of electrical conductivity.[14]

Figure 4 shows the performance of the prepared Al films. It can be seen that all the films are shiny metallic on substrates such as photopaper, glass, PET, and P3HT layer (active layer for OPV). However, some corrosion is observed on P3HT film, which is caused by the polar solvent (ethers) in Al precursor ink and the acid by the decompostion of $TiCl_4$. It is suggested that direct printing of Al ink on top of P3HT should be avoided. Pre-deposition 5 nm thickness Al_2O_3 films on P3HT surface by atomic layer deposition (ALD) followed by printing Al ink can effectively solve the corrosion problem, although the insertion of such ultra-thin Al_2O_3 may decrease the electron injection.[21] We will attempt to some new methods to avoid the corrosion in our future research, for example, selecting new protective layers or chemical cross-linking organic layers.

Table 1 lists the electric resistance, roughness and work function of Al films. All samples show conductivities similar to Al films prepared by thermal evaporation. The surface morphology suggested that the Al surface grain size by stamping process is about 220 nm while it is about 80 nm prepared 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 °C. It is believed that the reaction of decomposition of Al ink into H_2 and Al becomes more violent at higher temperature and forms tiny porous holes in Al film. Furthermore, the Al films sintered at 80 °C showed the lowest work function of 3.67 eV. It can be explained that Li elements contained in $LiAlH_4$ precursor in Al film leading to a decrease in work function. It has been reported that the work function of Al substrates with a native oxide layer is 3.3 eV, which indicated that the Al films prepared at 80 °C by stamping process can be used as cathode for OLEDs and OPVs.

Accordingly, we applied the stamping processed Al films to the cathode of an OLED，the OLED structure is shown in Figure 5. The architecture of the device consist of a indium tim oxide layer (ITO), N,N’-di(naphthalene-l-yl)-N,N’-diphenyl-benzidine (NPB) layer (40 nm), tris(8-hydroxyquinoline) aluminum (Alq_3) layer (60 nm), lithium fluoride (LiF) layer (1 nm), and aluminum oxide (Al_2O_3) layer (5 nm) with cathode of Al film (50 nm) prepared by the solution-stamping process. It is well known that the insertion of Al_2O_3 for interfacial modification of cathodes would enhance the electron injection, and the thickness is ca. 1 nm.[21] While 1 nm Al_2O_3 is not enough to protect organic layers against the corrosion of solvent and acidic gases in the solution-stamping process of preparing Al cathode. In the proces of fabrication OLED device, 5 nm Al_2O_3 layer was deposited by ALD proces in 80 °C with trimethylaluminum (TMA) as precursor and water (H_2O) as oxidizing gases. It was clearly observed that the green light was emitted from the prepared OLED. This indicates that the Al film prepared by stamping process can be used to prepare cathodes of OLED and OPV devices.

Conclusion

In conculsion, we have successfully synthesized the Al precursor ink, $AlH_3 \cdot x\{O(C_3H_7)_2\}$, which can be patterned by printing and decomposed into high quality Al films through catalytic reaction of $TiCl_4$ at low sintering temperature of 80°C. Compared with traditional thermal evaporation, printed Al films demonstrated high conductivity (2.09 Ω/□) and low work function (3.67eV), which can be used as the cathode with low fabrication cost in flexible OLED and OPV devices.

Acknowledgements

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References

1. OE-A roadmap for organic and printed electronics. Organic Electronics Association OE-A, Frankfurt, (2008).

2. M. Gross, N. Linse, I. Maksimenko, and P.J. Wellman, *Adv. Eng. Mater.* 2009, **11**, 295-301.

3. K.K. Han, *Surf. Coat. Technol.* 2008, **203**, 652-656

4. T.M. Lee, J.H. Noh, C.H. Kim, J.Jo, and D.S. Kim, *Thin Solid Films* 2010, **518**, 3355-3359.

5. Y.M. Chien, F. Lefevre, I. Shih, and R. Izquierdo, *Nanotechnology* 2010, **21**, 134020 (1)-(5).

6. K. Fehse, K. Walzer, K. Leo, W. Lovenich and A. Elschner, *Adv. Mater.* 2007, **19**, 441-444.

7. H. Kajii, Y. Ohmori, H. Maki, Y. Sekimoto, Y. Shigeno, N. Takehara and H. Nakagawa, *J. J. Appl. Phys.* 2008, **47**, 460-463.

8. Y. Kurosaka, N. Tada and Y. Ohmori, *J. Appl. Phys.* 1998, **37**, L872-L875.

9. J. Lee, Y. Park and D.Y. Kim, *J. Phys. D* 2002, **35**, 3171-3175.

10. J. Lee, Y. Park, D.Y. Kim, H.Y. Chu, H. Lee, and L.-M. Do, *Appl. Phys. Lett.* 2003, **82**, 173-175.

11. H. Park, H. Kim, S.K. Dhungel, J.Yi, S.Y. Sohn and D.G. Jung, *J. Korean Phys. Sco.* 2007, **51**, 1011.

12. J. Lee, J.S. Lim, H.J. Shin, and Y. Park, *Appl. Phys. Lett.* 2007, **91**, 261902 (1)-(3).

13. J.P. Novak, Y.J. Li, J. Li, et al., “Direct Print of Metal Nanoparticle Inks for Si Solar, ” 2012 *NIP26: International Conference on Digital Printing Technologies and Digital Fabrication*, 124.

14. H. M. Lee, S. Y. Choi, K. T. Kim, J. Y. Yun, D. S. Jung, S. B. Park, J. Park, *Adv. Mater.* 2011, **23**, 5524-5528.

15. H. M. Lee, H. B. Lee, D. S. Jung, J. Y. Yun, S. H. Ko, S. B. Park, *Langmuir* 2012, **28**, 13127-13135.

16. D.L. Schmidt, C.B. Roberts, P.F. Reigler, *Inorganic Syntheses* 1973, **14**, 47-52.

17. A.E. Finholt, A.C. Bond Jr., and H.I. Schlesinger, *J. Am. Chem. Soc.* 1947, **69**, 1199-1203.

18. F.M. Brower, N.E. Matzek, P.F. Reigler, H. Rinn, *J. Am. Chem. Soc.* 1976, **98**, 2450-2453.

19. J.A. Haber, W.E. Buhro, *J. Am. Chem. Soc.* 1998, **120**, 10847-10855.

20. F. Fei, W.M. Su, Z. Cui, *NSTI-Nanotech* 2013, **2**, 96-99.

21. S.T. Zhang, Y.C. Zhou, J.M. Zhao, Y. Q. Zhan, Z. J. Wang, Y. Wu, X. M. Ding, X. Y. Hou, *Appl. Phys. Lett.* 2006, **89**, 043502 (1)-(3).

Title content

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

Figure captions

Figure1. NMR spectrum of Al precursor, $AlH_3 \cdot x\{O(C_2H_5)_2\}$, dissolved in THF-$D_8$ solution.

Figure 2. XRD patterns of Al films synthesized by different process at different temperatures.

Figure 3. The resistance stability of Al film prepared by stamping process in air.

Figure. 4. Al film Prepared by stamping process at sintering temperature of 80 °C on different substrates.

Figure. 5. (a) schematic structure of OLEDs with a cathode of Al thin film prepared by stamping process and (b) its light emission photos.

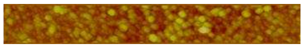
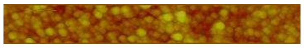
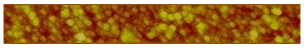
Al-Fabrication Method	Surface Morphology	R (Ω·cm)	Ra (nm)	W_F (eV)
Thermal Evaporation		2.79	2.63	4.15
Stamping/80 °C (Glass substrate)		3.10	4.56	4.05
Stamping /80 °C (PET substrate)		2.09	24.5	3.67
Stamping /100 °C (Glass substrate)		2.49	10.5	4.07
Stamping /150 °C (Glass substrate)		2.20	6.03	4.28

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

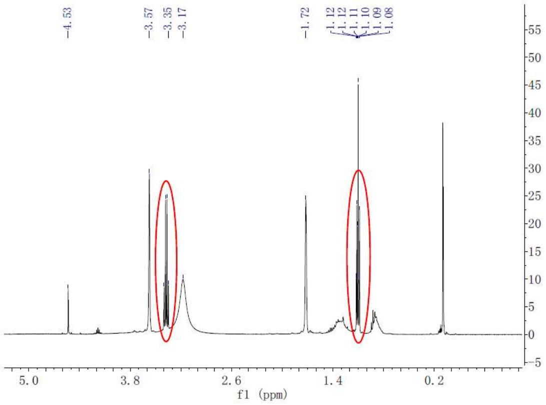


Figure 1. NMR spectrum of Al precursor, $AlH_3 \cdot x\{O(C_2H_5)_2\}$, dissolved in THF-$D_8$.

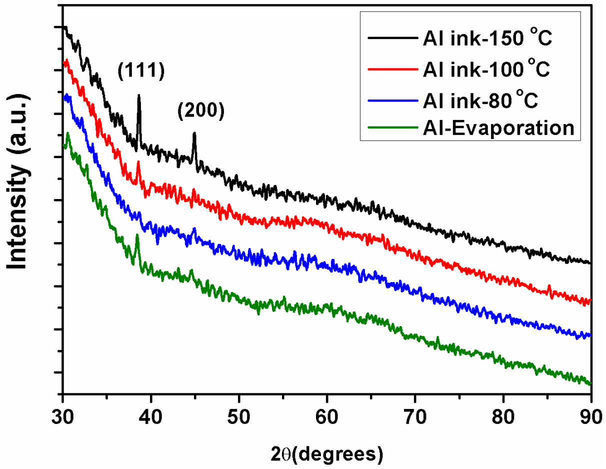


Figure 2. XRD patterns of Al films synthesized by different process at different temperatures.

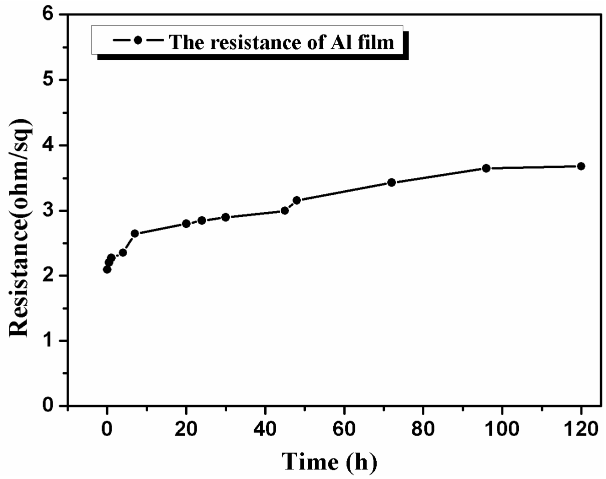


Figure 3. The resistance stability of Al film prepared by stamping process in air.

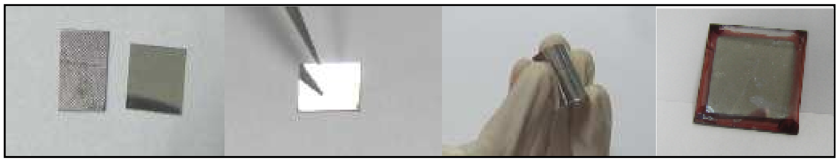
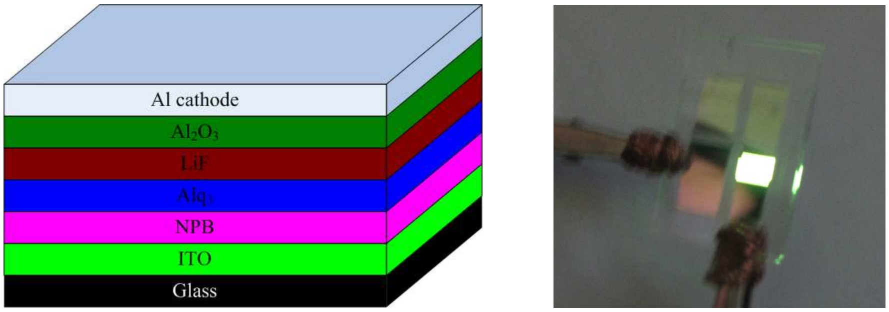


Photo paper Glass PET P3HT layers

Figure 4. Al film Prepared by stamping process at sintering temperature of 80 °C on different substrates.



(a) (b)

Figure 5. (a) schematic structure of OLEDs with a cathode of Al thin film prepared by stamping process and (b) its light emission photos.