Journal of
Materials Chemistry

Cite this: *J. Mater. Chem.*, 2012, **22**, 23012

www.rsc.org/materials

PAPER

One step synthesis of uniform organic silver ink drawing directly on paper substrates†

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Received 2nd July 2012, Accepted 17th September 2012
DOI: 10.1039/c2jm34264b

A new uniform organic silver ink, for writing directly on paper, was synthesized by a one step method using ethanolamine as the complex agent of silver acetate and ethylene glycol (EG) and ethanol (EA) as a complex solvent. The patterns or lines drawn with the as-prepared organic silver ink easily formed a favorable conductive connection on a sulfuric paper substrate at 200 °C. Interestingly, the coffee ring and solvent contraction effects, which often go with the drawn lines by silver inks, could be effectively improved. The magnitude, intercontact of particles and residual organic species are mainly responsible for the conductivity of the silver patterns.

1. Introduction

Printed electronics have gained considerable research interest in recent years. Thanks to its high potential in the development of innovative applications such as flexible displays,[1] photovoltaics,[2] transistors,[3] antennas,[4] batteries[5] and sensors,[6,7] an amazing impact on the consumer electronic market is expected. However, many technological challenges have to be solved first, in order to build production platforms. Among these challenges, one of the biggest current challenges lies in the materials used for printing, such as the proper inks and flexible substrates. Another challenge is developing the processes themselves for real mass-manufacturing.

Traditionally, photolithography has been widely adopted in the microfabrication of conductive patterns in electronics.[8–10] However, this method involves many steps such as etching, electroplating, *etc.*, so it is time consuming, complicated and expensive. Therefore, many researchers started to pay more attention to the new manufacturing techniques, including inkjet printing,[11] sputter coating,[12] airbrush spraying,[13] and so on. However, these deposition methods are still costly for the printed electronics industry.

The pen-on-paper paradigm offers a unique approach to fabricate flexible devices by a patterning instrument such as gel-ink, which is ubiquitous and portable.[14] In addition, the defects in the production process of electronic devices, which are hard to repair by a traditional approach, could be solved easily by this method. Moreover, using paper as substrates has many advantages over others with special properties like low cost, relative abundance, flexibility, light weight, less environmental impact, and full recyclability.

Upon the pen-on-paper approach, the design and fabrication of conductive inks have become a hot point, currently. An optimal ink design should meet the following requirements. First, the ink's synthetic procedure should be simple and high-yielding. Second, the ink should have low viscosity, be easy to flow through the gel-ink pen during writing and should not leak from, dry out, or coagulate within the pen. Third, the patterned features should achieve bulk conductivity upon annealing at a lower temperature.

Up to now, conductive polymers,[15] carbon,[16,17] and metallic nanoparticle inks[18–24] have been used in the formation of conductive lines. However, organic inks typically exhibit low conductivity, whereas metallic nanoparticle inks with high solid fractions generally result in the clogging of inkjet nozzles or pen points.

The solvent composition used in the ink also has decisive effects on the quality of the printed patterns. The design of solvent composition, which could meet various requirements, such as stability, uniform surface morphology of the silver lines formed by the ink, and high conductivity, is crucial. However, very little research has been done on this, especially in paper-based ink.

In this paper, we report a new organic silver ink system synthesized by a one step method. Our approach is demonstrated with the following advantages: using silver acetate instead of silver nitrate, avoiding the formation of explosive silver azide and creating a non-explosive silver precursor ink; ethanolamine as a complex agent for silver acetate, forming silver organic complexes of Ag(acetate)(ethanolamine)$_2$, which is liquid at room temperature, and does not clog the pen point or transform into metallic silver at a lower sintering temperature; and ethylene glycol (EG) and ethanol (EA) mixed solvent to prevent the coffee ring and solvent contraction effects, to some degree; the as synthesized ink is composed of 20 wt% silver, comparable to other silver-precursor-based inks; and last, the ink could be

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2jm34264b

written directly on sulfuric paper by a pen-on-paper paradigm and formed accredited electronic patterns by sintering at a lower temperature.

2. Experimental section

2.1 Materials

All chemicals (silver acetate, ethanolamine, ethylene glycol, ethanol and oleic acid) were purchased from Beijing Chemical Factory of China and were used as received without further purification. Sulfuric paper was obtained from Sunrise (Wuxi) Paper Products Co. of China and used without further surface treatment. The physical properties of the various solvents used in this study are listed in Table 1.

2.2 Synthesis

Silver acetate (0.01 mol) was first dissolved completely in a mixed solvent of ethanol, ethylene glycol and oleic acid under vigorous stirring, and then ethanolamine (0.02 mol) was titrated into the above solution dropwise over 60 s. After strongly stirring for 60 min, the mixture was filtered through a 0.45 μm filtering membrane, and then yielded a uniform light brown ink for direct writing.

2.3 Patterning and metallization

A gel-ink pen, which is composed of a hollow cylinder 12.3 cm in length and 3.8 mm in diameter, and a pen-head 1.2 cm in length and 0.5 mm in line-width was purchased from Beijing Lotus Stationery Co. For the application, the pen was washed with deionized water and ethanol, and then the as-prepared ink was injected into the empty pipe of the pen. The pen filled with the organic silver ink could be used to draw patterns or lines directly on sulfuric paper, just like writing on ordinary paper. The paper with patterns or lines drawn was sintered at 200 °C for some time in air to get conductive silver lines or patterns.

2.4 Characterization

The viscosity and surface tension of the ink were obtained on a Brookfield DV-III+ rheometer and a Kruss K10ST tensiometer, respectively. The measuring temperature was maintained at 25 °C. The crystalline structure was determined by X-ray diffraction (XRD) using Cu Kα and λ = 0.15418 nm; Fourier transform infrared spectra in the range of 400–4000 cm^{-1} were recorded on an FTIR Tensor 27 spectrometer using KBr pellets. The morphology and chemical composition of the silver lines after sintering was investigated by SEM (S-4300, Hitachi, Japan), surface profilometer (Dektak 150, Veeco, America) and EDX spectra. The specific electrical resistance was measured by a multimeter.

3. Results and discussion

3.1 Synthetic mechanism

In this study, the inks were prepared through the complexation between silver acetate and ethanolamine. The lone pair of electrons on the nitrogen of ethanolamine can coordinate with silver acetate and form silver organic complexes, Ag(acetate)(ethanolamine)$_2$, according to the reaction below:

$$CH_3COOAg + 2NH_2CH_2CH_2OH \rightarrow CH_3COOAg(NH_2CH_2CH_2OH)_2$$

In the organic silver complex compound, each complex contained two –OH groups, which increased solubility, as the hydrophilic OH group readily forms hydrogen bonds with water and particularly, the complex maintains a liquid state with a higher viscosity at room temperature.

FT-IR spectroscopy was used to investigate coordinative interactions between silver ions and ethanolamine. Fig. 1a shows the IR spectrum of pure ethanolamine. The absorption peaks at 3353 and 3297 cm^{-1} were the asymmetric and the symmetric stretch of NH_2 groups. Two bands at 2936 and 2871 cm^{-1} were assigned to the asymmetric CH_2 stretch and the symmetric CH_2 stretch. The peak at 1575 cm^{-1} and 1483 cm^{-1} indicated a coupling of C–N stretching and in-plane bending of NH groups. The C–O stretching vibration is at 1071 cm^{-1}. Fig. 1b shows the spectrum of Ag(acetate)(ethanolamine)$_2$. It is worth noting that the in-plane bending of the NH group peak at 1483 cm^{-1} became weaker. In addition, a new COO$^-$ symmetrical stretching vibration peak appeared at 1409 cm^{-1} and the O–C–C in-plane bending vibration at 652 cm^{-1} became stronger, respectively. These differences mean that the ethanolamine was coordinated to silver acetate and donated an electron from the amino group

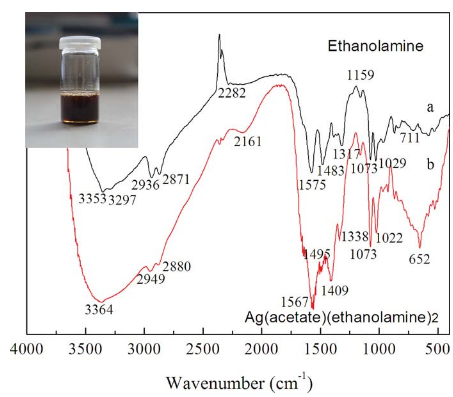

Fig. 1 The FT-IR spectra of ethanolamine and Ag(acetate)(ethanolamine)$_2$ (inset: a digital photo of Ag(acetate)(ethanolamine)$_2$).

Table 1 Physical properties for various solvents

Reagent	Viscosity (η, mPa s)	Surface tension (γ/mN m^{-1})	Boiling point (T_b/°C)	ρ/g cm^{-3}	Possible negative effect
Ethanol (EA)	1.20	22.27	78.32	0.7894	Coffee ring effect
Ethylene glycol (EG)	25.66	46.49	197.85	1.1115	Solvent contraction effect
Ethanolamine (MDEA)	24.14	39.70	170.30	1.0180	Solvent contraction effect
Oleic acid (OA)	26	32.50	286.00	0.891	/

to the silver atom, which decreased the electron density of the amino group and resulted in a weaker NH group peak.

It should be mentioned that to easily obtain Ag(acetate)-(ethanolamine)$_2$ for the measurement of FT-IR spectra, the relating ink was prepared here using only ethanol as the solvent and removal of the solvent was achieved *via* rotary evaporation.

3.2 Properties of the organic silver ink

During the preparation of the ink, the design of solvent composition is crucial. The surface tension and viscosity of the ink should be low to prevent the formation of satellites,[25] and the evaporation rate of the ink in the pen in use needs to be controlled to prevent clogging the head, due to solvent evaporation along the pen-end orifice. In the present work, ethylene glycol was used as a co-solvent to suppress the evaporation rate, ethanol used to adjust the surface tension of the ink and oleic acid used to improve the continuity and conductivity of the resulting silver ink films (Fig. S1†).

In order to find the optimal mixing ratio of the co-solvent (EG–EA), the inks with different solvent compositions were prepared. Fig. 2 shows the digital photos of the as-prepared organic silver ink with different solvent compositions. It can be seen that the stability of the inks decreased with the increase of EG content. Especially, large amounts of precipitation appeared when the solvent ratio of EG–EA was 8 : 0 (the first sample in Fig. 2).

The parameter of the silver ink and property of the sintered silver patterns are listed in Table 2 and Fig. 3. It can be seen that the viscosity and the surface tension of the ink decreased with the increase of EA content. Additionally, the sintered patterns of the silver ink mainly exhibit two kinds of surface morphology: camel hump (EA as a main solvent), and bread hump (EG and EA as co-solvent). The specific morphology may be induced by two flows in an ink droplet during heating; convective flow (also called coffee ring effect) and Marangoni flow.[26,27]

Generally, a droplet of the ink containing a solvent with a lower boiling point, such as EA, can easily form an outward convective flow in the area contacting with a substrate during heat treatment and the flow would make the small particle formed in the ink droplet shift to the edge region. As a result, the coffee ring effect (Fig. 3a) appeared. In the case of a mixed solvent of high (EG: $T_b = 179$ °C) and low boiling points (EA: $T_b = 78$ °C), the differences of the evaporation rates would cause an additional Marangoni flow[26,27] from the outer rim to the center of the ink droplet, resulting in a solvent contraction effect (the digital photo in Fig. 3b). In the mixed solvents with a proper rate (EG–EA = 1 : 1), Marangoni flow helps to create an inward flow and balances the outward convective flow, thus the coffee ring effect was avoided (Fig. 3c). Fig. 4 is the schematic illustration of the ink droplet evolvement during the drying process.

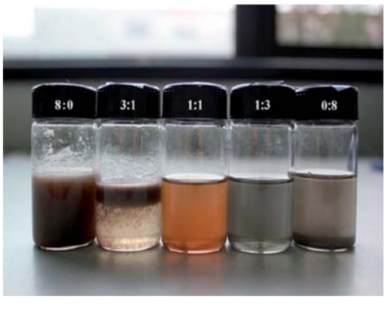

Fig. 2 The digital photos of the prepared inks with different solvent ratios of EG–EA = 8 : 0, 3 : 1, 1 : 1, 1 : 3 and 0 : 8.

Due to the ratio with 1 : 1 of EG–EA providing the best properties of the ink, this ratio was used as a constant solvent composition in the later study.

3.3 Preparation and microstructure of the silver lines

Silver lines were directly drawn on the sulfuric paper by a pen-on-paper paradigm using the as-prepared conductive ink. Fig. S2† is the schematic illustration for the preparation of conductive lines.

In the present research, the contact angle between the ink and sulfuric paper is about 23.8° (Fig. S3†), due to the low surface tension of the ink, exhibiting a hydrophilic wetting behavior, which is good for the spread of the ink on paper. The line-width, length and thickness were controlled by the same writing conditions, including the times, speed and force (Fig. S4†).

It should be mentioned that the as-prepared ink can be also drawn on ordinary paper. The choice of sulfuric paper as a substrate here is due to its low permeability, low surface roughness, good graphomotor property, excellent heat resistance and fatigue resistance, in comparison to ordinary paper.

Considering the boiling point of ethanolamine and EG, we used 200 °C as the thermal treatment temperature. The XRD patterns of the silver lines sintered at 200 °C for different times are shown in Fig. 5. The prominent peaks at 38.2°, 44.4°, 64.5°, 77.5° and 81.6° are all in good agreement with the characteristic values for metallic silver crystalline. The reflection peaks are indexed as the (111), (200), (220), and (311) crystal planes, indicating that silver is well crystallized. No diffraction peaks from any other impurities were detected, indicating that the silver ions are transformed to silver crystals according to the following reactions:

$$\mathrm{CH_3COOAg(NH_2CH_2CH_2OH)_2(l) \xrightarrow{\Delta} Ag(s) + NH_3(g) + H_2O(l) + CH_3CO_2H(l)}$$

$$\mathrm{2HOCH_2CH_2OH(l) + O_2(g) \xrightarrow{\Delta} 2HOCH_2CHO(l) + 2H_2O(l)}$$

$$\mathrm{Ag(NH_3)_2^{+} + CH_3CHO(l) \xrightarrow{\Delta} CH_3COONH_4(s) + Ag(s) + H_2O(l) + NH_3(g)}$$

Clearly, the intensity of the reflection peak increased with the sintering time, indicating that more metallic silver formed.

Surface microstructures of the produced silver lines after sintering at 200 °C for different times were evaluated by SEM (Fig. 6). After a sintering time of 10 min, though silver nanoparticles connected with each other, many holes still existed and the connection was loose (Fig. 6a and d). With the increase of the sintering time, more silver particles were generated, and the original silver particles grew quickly (Fig. 6b and e). Meanwhile, the holes among them reduced obviously and the interface became vague. After 60 min, more silver nanoparticles had grown and formed a dense structure (Fig. 6c and f).

Table 2 The ink parameter and line quality from the organic silver ink with different solvent ratios after sintering

No.	Solvent composition (OA = 0.15 ml, MDEA = 2.44 ml, 25 °C), EG–EA	Viscosity (mPa s)	Surface tension (mN m^{-1})	With or without precipitation	Coffee ring or solvent contraction effect of sintered lines
1	8 : 0	25.32	44.98	With	/
2	3 : 1	20.72	40.33	With	/
3	1 : 1	16.05	35.61	Without	Without (Fig. 3c)
4	1 : 3	11.29	30.79	Without	Mild coffee ring effect (Fig. 3b)
5	0 : 8	6.45	25.89	Without	Coffee ring effect (Fig. 3a)

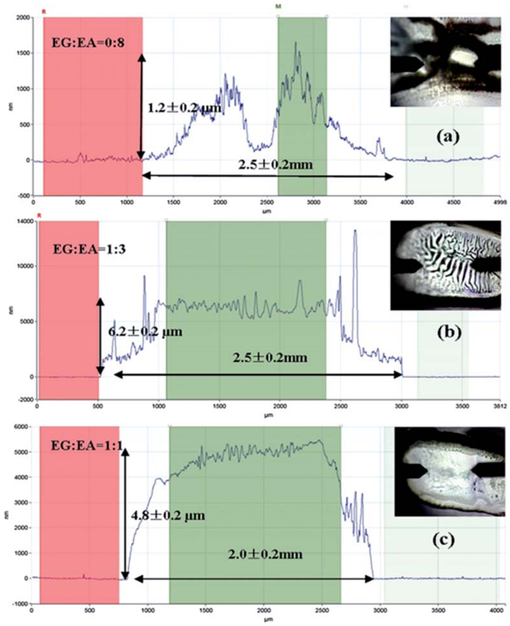

Fig. 3 Surface profiles of silver lines drawn by gel-pen on glass after sintering at 200 °C for 60 min; (a) camel hump; (b and c) bread hump (inset: corresponding digital photos of silver lines).

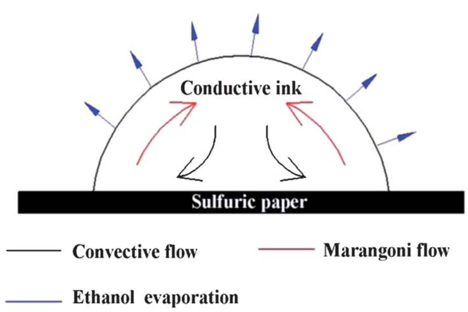

Fig. 4 Schematic illustration of the ink droplet evolvement during the drying process.

The chemical composition of the produced silver lines after sintering at 200 °C for 10 min, 30 min and 60 min was identified by EDX surface energy and point spectra (the sample taken from the area 1, 2 and 3 in Fig. 6). As Fig. 7 showed, two elements (C, Ag) were detected on the surface of the deposited silver lines and the white phase and grey phase in the line are basically silver particles. With the increasing of the sintering time, the content of Ag increased from 99.30 wt% to 99.79 wt% and the content of C

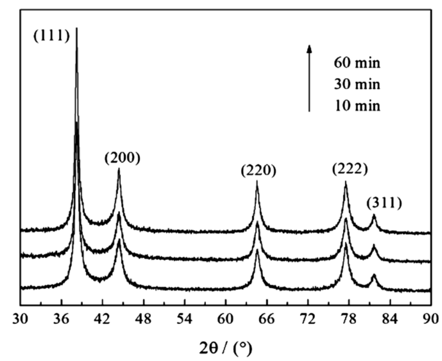

Fig. 5 The XRD patterns of the silver line prepared with the organic silver inks after sintering for 10 min, 30 min, 60 min.

decreased from 0.7 wt% to 0.21 wt%, indicating that Ag(acetate)(ethanolamine)$_2$ has almost completely decomposed to silver and very small amounts of organic residue existed, such as OA (T_b = 286 °C).

3.4 Electrical performance of the silver ink lines

The resistivity of the silver ink lines was calculated using the following equation:

$$\rho = Rab/l$$

where ρ is resistance, a, b and l are the cross-sectional width, thickness and length of the silver line, respectively. As all the

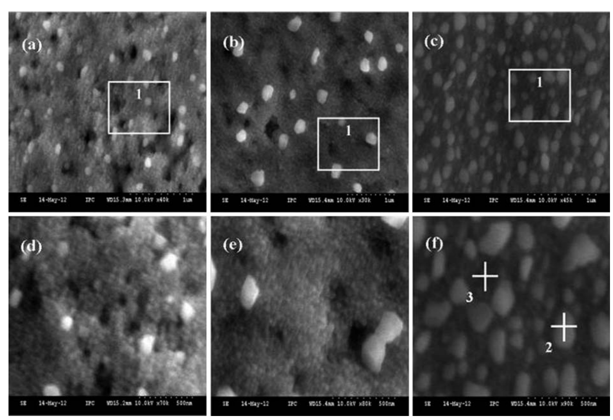

Fig. 6 SEM images of the drawn lines on the sulfuric paper after sintering at 200 °C for 10 min, 30 min, 60 min (a–c) and corresponding magnified images (d–f).

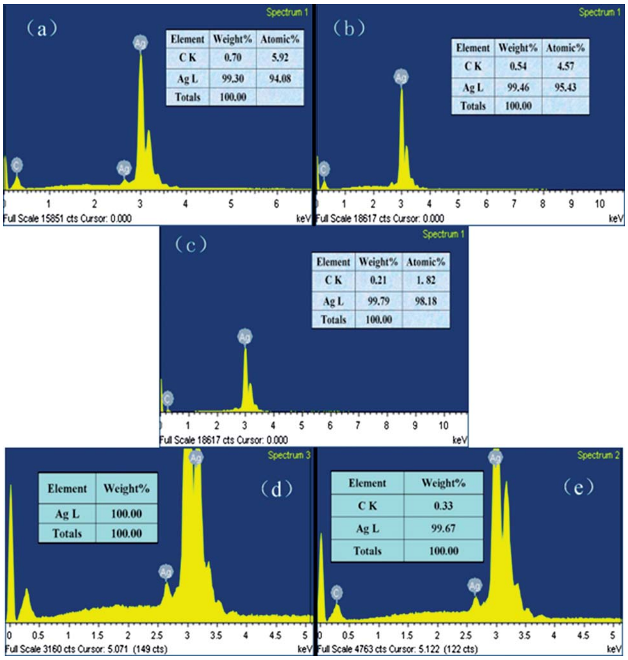

Fig. 7 The EDX spectra of the drawn lines sintered at 200 °C for 10 min, 30 min and 60 min on the sulfuric paper (a–c, surface energy spectra; d and e, point spectra).

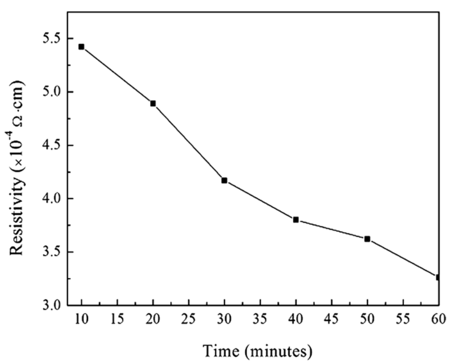

Fig. 8 Resistivity variation of the silver lines on the sulfuric paper sintered at 200 °C.

conductive lines have relatively non-uniform surface structures, according to the results of surface profilometer observation, the average thickness 5.0 ± 0.2 μm was taken for the calculation. As Fig. 8 showed, with the increase of the sintering time, the resistivity decreased gradually. When the time came to 60 min, the resistivity was down to 3.26×10^{-4} Ω cm.

Based on the microstructure observations and analysis, it is concluded that three dominating factors are responsible for the conductivity of silver after sintering; they are particle sizes, remnant degree of organic species at the interface of silver particles and the stacking density of metallic silver. The improvement of the properties of the organic silver ink is still under study.

4. Conclusions

In summary, using ethanolamine as a protecting agent, the uniform organic silver ink with a relatively high concentration of silver ions has been prepared. Using an optimal ratio of a mixed solvent (EG and EA), the coffee ring and solvent contraction effects can be effectively improved. The experiments showed that the application of organic silver compound ink can reduce heating temperature and improve the morphology of the lines. The sizes, contact area of particles, as well as the elimination degree of organic species are three dominating influence factors on the conductivity of the nanosilver lines.

Acknowledgements

The author thanks National Natural Scientific Foundation of China (no. 21273256 and 21103209) for the financial support.

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