Applied Surface Science 459 (2018) 249–256

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Fabrication of highly conductive and flexible printed electronics by low temperature sintering reactive silver ink

Yun Mou[a], Yuru Zhang[b], Hao Cheng[a], Yang Peng[a,*], Mingxiang Chen[a,c,*]

[a] School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
[b] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China
[c] State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Keywords:
Reactive silver ink
Low temperature sintering
Highly conductive
Flexible
Printed silver film

ABSTRACT

To solve the problems of high sintering temperatures (~200 °C), particle aggregation, nozzle clogging, and poor shelf life of silver nanoparticle inks, we prepared a transparent and stable reactive silver ink for fabricating printed electronics. The ink mainly consisted of ammonia and formic acid ligands, silver acetate, and hydroxyethyl cellulose (HEC) adhesive agent. The highly conductive and flexible silver films were fabricated by printing and low temperature sintering the reactive silver ink, and the effects of sintering temperature and sintering time on the electrical properties of the printed silver films were investigated. Consequently, the printed silver film sintered at 70 °C exhibits good electrical properties with a resistivity of 12.1 μΩ·cm, which is only seven times higher than that of bulk silver (1.65 μΩ·cm). Moreover, the silver film also displays excellent adhesive strength and mechanical flexibility in terms of bending and twisting.

1. Introduction

Owing to their cost-effective and eco-friendly fabricating process and unique properties such as light-weight, bendable, and foldable, the printed electronics have attracted great attentions in various fields, such as flexible electrodes, low temperature bonding, solar cell arrays, radio frequency identification (RFID) tags, thin film transistors, and organic light emitting diodes (OLED) [1–7]. Conductive ink can be patterned by printing process to achieve robust tracks with high conductivity, which is a critical component for the printed electronics [8–10]. Currently, most conductive inks are based on silver nanoparticle inks because of their excellent electrical conductivity and good oxidation resistance [11–13]. Unfortunately, most of the reported silver nanoparticle inks require high sintering temperature above 200 °C to remove the organic stabilizers and sinter nanoparticles [14–17], which limits their practical applications on heat-sensitive flexible substrates. In order to decrease the sintering temperature, the chemical sintering of silver nanoparticle inks has been proposed to prepare the highly conductive silver tracks at room temperature [9,18,19]. However, the special sintering or destabilize agents and stabilizers are needed to achieve the coalescence and sintering of the nanoparticles, and the agglomeration of silver nanoparticles still is a severe issue to be solved, which results in clogging the nozzles and shortening the shelf life of the inks [20,21].

Aiming to solve these problems, the particle-free silver reactive inks have received significant attentions because of their facile synthesis processes and low sintering temperature. More importantly, neither additional stabilizers nor reducing agents are required, which plays an important role in enhancing the performances of printed electronics [22,23]. At present, many researchers have synthesized different reactive silver inks to fabricate highly conductive silver tracks with the order of 10^{-5}-10^{-6} Ω·cm [24–30]. However, most of the reported inks are less stable, and multi-component solvents in the inks have negative effects on the conductivity, which require relatively high sintering temperature (150–200 °C) to form highly conductive silver tracks. Although the lower sintering temperature and higher conductive silver tracks have been achieved by adjusting the ligands and silver precursors [31–34], the sintering process is too time-consuming (> 12 h) to be desirable for the actual production. Recently, the developed reactive metalorganic (ROM) inks can prepare silver tracks at room temperature by chemical reaction, which provide a lower thermal budget and faster route for fabricating the flexible printed electronics [35–37]. But this approach needs the reducing agents to trigger the chemical reaction, and the additional cleaning or curing process is essential to remove the residual organics. In addition, the advanced sintering technique (photonic and microwave-plasma) is a good alternative for decreasing sintering temperature and improve sintering efficiency [26,38,39], but thermal sintering is a preferred choice for fabricating conductive tracks

* Corresponding authors at: School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China (M. Chen).
E-mail addresses: pengyang656@126.com (Y. Peng), chimish@163.com (M. Chen).

https://doi.org/10.1016/j.apsusc.2018.07.187
Received 30 May 2018; Received in revised form 7 July 2018; Accepted 27 July 2018
Available online 29 July 2018
0169-4332/

because of their low cost and simplicity. More importantly, the adhesion with substrate and printing stability is either not provided or discussed in most of the reported inks.

Herein, we prepare a transparent and stable reactive silver ink, wherein ammonia and formic acid act as the ligands of silver acetate precursor. The highly conductive and bendable printed silver films on flexible substrates using the reactive ink were fabricated at 70 °C, and displayed good adhesion and stability. The effects of the sintering temperature and sintering time on the electrical properties of the printed silver films were systematically investigated, and the adhesive strength and mechanical flexibility of the printed silver films were discussed.

2. Materials and methods

2.1. Materials

Silver acetate (98%) and ammonia (25–28%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydroxyethyl cellulose-water solution (HEC, 4% in water) and Formic acid (88%) were purchased from Aladdin reagent Co. All chemical reagents were used without any further treatment. Polyimide (PI) substrates (thickness: 100 μm) were purchased from Toray Industries, Inc.

2.2. Preparation of reactive silver ink

Fig. 1 illustrates the preparation process of reactive silver ink. Ammonia (2.0 g) and formic acid (0.36 g) were mixed at 5 °C in a glass vial. Subsequently, under magnetic stirring, silver acetate (1.0 g) was slowly dissolved in the mixing solution to prepare reactive silver ink, and the color of the solution changed from colorless to light brown. Finally, the obtained reactive silver ink was filtered by the filter syringe (200 nm), and stored at 3 °C in the refrigerator. Acting as the adhesive agent, HEC-water solution (0.6 g) was added to adjust the adhesion and wettability of the reactive silver ink.

2.3. Low temperature sintering process

PI films were used as the flexible substrate in this work. To remove organic contaminations on the surfaces, the substrates were successively ultrasonic cleaned by in deionized water and ethanol for 10 min. Subsequently, the reactive silver ink was uniformly printed on the substrates by mask-printing method. The thickness of the mask was 50 μm. Finally, the printed reactive silver inks were sintered in the air from 50 °C to 100 °C for 0.5 h to 8 h.

2.4. Characterization and measurement

The thermal behaviors of the reactive silver ink and silver acetate were investigated by thermogravimetric analyzer (TG, TG 209 F3 Tarsus) at a heating rate of 5 °C/min in the air. The crystal structures and surface compositions of the printed silver films were analyzed by X-ray diffractometer (XRD, PANalytical PW3040/60) and X-ray photoelectron spectroscopy (XPS, Escalab 250Xi), respectively. The morphological features of the printed silver films were observed by transmission electron microscope (TEM, FEI Tecnai G2 20 U-TWIN) and field-emission scanning electron microscope (SEM, FEI Nova Nano SEM 450), together with energy dispersive spectroscopy (EDS). Atomic force microscopy (AFM) was utilized to examine the 2D and 3D morphology of the printed silver films. The resistivity (ρ) of the printed silver films was calculated as $\rho = R_s \times W$, where R_s is the sheet resistance and W is the thickness of the film. The sheet resistance and thickness of the film were measured by four-point probes resistivity measurement system (Probes Tech RTS-8) and step profiler (ET4000 Series), respectively. The resistance of the printed silver film was measured by the simple 2-point I-V measurement method (Digital milliohmmeter, VC480C) during the peel-off and bending tests.

3. Results and discussion

TG analysis was carried out to evaluate the thermal decomposition behaviors of the ink and silver acetate, as depicted in Fig. 2(a). The TG curve of the ink shows that the mass starts to decrease at room temperature, and the mass becomes constant at 130 °C. The weight loss of silver acetate starts at 225 °C and finishes at about 280 °C. The difference between the complete decomposition temperatures of silver acetate and the reactive silver ink is approximately 150 °C, which is attributed to the formation of silver ammonia complex and reduction of formic acid [40]. Besides, the remaining solid weights of the ink and silver acetate correspond to their silver weights, indicating that the organics are absolutely removed during the thermal sintering process. Moreover, when the reactive silver ink is hermetically stored in the refrigerator, it is stable and transparent, but the particles begin to form at room temperature with the evaporations of formic acid and ammonia. To analysis the crystal phases of the particles, XRD analysis was conducted after drying the ink at room temperature for 12 h, as shown in Fig. 2(b). Four diffraction peaks of the printed silver film are detected at 38.10°, 44.37°, 64.18°, and 74.16°, which represent the (1 1 1), (2 0 0), (2 2 0)and (3 1 1) planes of silver crystal. These characteristic peaks confirm that the printed silver film is face-centered cubic (FCC) silver phase without silver oxide or silver acetate. Therefore, TG and XRD analysis indicate that the reactive silver ink can be thermally decomposed to form silver particles at low temperature.

To analyze the surface compositions of the printed silver film in depth, XPS analysis was performed after sintering the ink on PI substrate at 50 °C for 2 h. As shown in Fig. 3(a), carbon and oxygen elements are detected on the surface of the printed silver film, and may originate from silver acetate or HEC. Fig. 3(b) presents the peak fitting of Ag3d spectrum of the printed silver film. The characteristic Ag3d peaks at 367.5 eV and 373.6 eV are assigned to silver crystal, and no significant peaks of silver oxide or silver salt are separated, which demonstrates that the ink is completely thermal decomposed to silver at 50 °C. Fig. 3(c) shows the peak fitting of C1s spectrum of the printed silver film. The characteristic peaks appear at 284.8 eV and 286.6 eV, which correspond to the C-O group and C-C group of HEC, respectively. Fig. 3(d) shows the XPS spectra of O 1s peak of the printed silver film. The major peak is divided into two peaks at 531.2 eV and 533.0 eV, corresponding to the O1s peak of the adsorbed oxygen and C-O group of

Fig. 1. Schematic preparation process of the reactive silver ink.