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A bio-inspired method to inkjet-printing copper pattern on polyimide substrate

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ABSTRACT

In this work, we propose a mussel-inspired method to fabricate copper pattern on polyimide substrate by an inkjet printing method. A new type of catalytic ink containing polydopamine (PDA) and silver ammonia solution was developed, which can induce the formation of electroless copper coating. As a result, we successfully prepared copper pattern which has good adhesion by inkjet-printing. Due to the unique property of PDA that is able to adhere to almost every kind of material, this method may be applied to diverse substrates in the future.

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1. Introduction

Conductive patterns find widespread application, such as in molded interconnect devices (MID), radio frequency identification (RFID) electronic tags and integrated circuits (IC). For this reason, the preparation of conductive patterns is gaining increasing importance in the microelectronics industry. Conventional methods of preparing conductive patterns include photolithography and printing techniques. Photolithography to make conductive patterns is very complex and inefficient, resulting in over 70% of the copper used in the process being wasted. On the other hand, conductive patterns obtained by printing, such as with electronic pastes and nano-metal inks [1], rely on a sintering process that limits the types of substrates that can be used, and causes issues with ink stability. Thus, to avoid these challenges, the electroless plating using catalyst seed particles has been proposed by the laser-induced method [2], silver nitrate method [3] and polyacrylic acid (PAA) adsorption method [4,5]. The silver ion will be always reduced by a reductant in order to get the catalytic seed of electroless copper. In this paper, we try to find a new kind of reductant and surface modifier, which can adhere to polyimide substrate, adsorb silver ion by nitrogen atom of amino groups and reduce the silver ion to Ag nanoparticles (Ag NPs) that can be as the catalytic seed to induce the formation of electroless copper coating. So we can develop a new kind of ink, which can ensure good adhesion between the substrate and the copper pattern and the Ag NPs of ink can be as the catalytic seed of

the electroless copper to easily prepare the copper pattern at the same time. Finally, dopamine has attracted our attention.

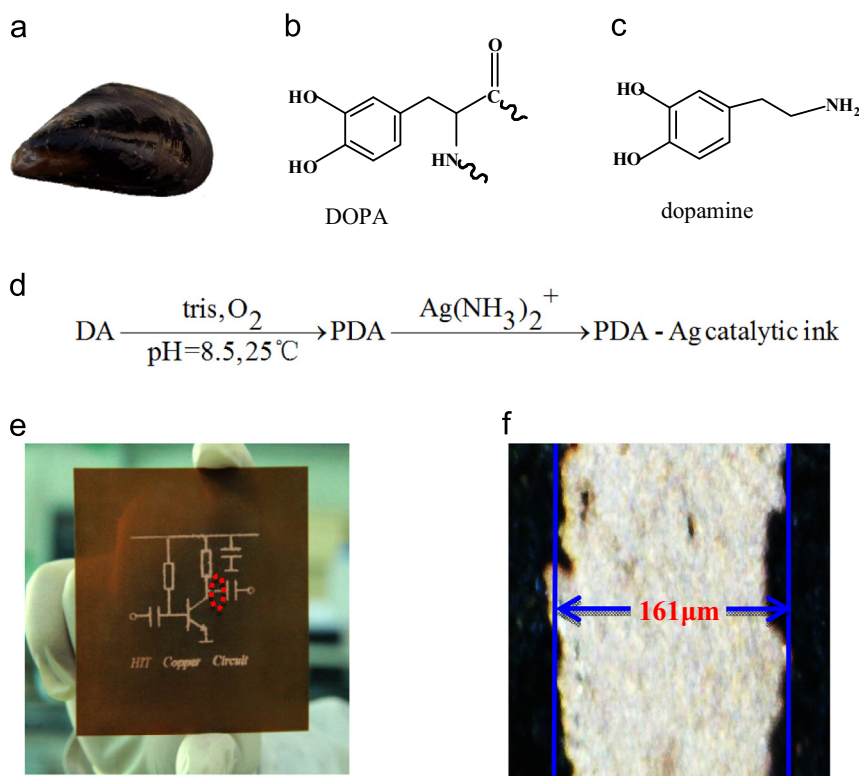
Lee et al. [6] proposed the use of dopamine as a biomimetic adhesive protein, inspired by the structure of the *Mytilus edulis* (i.e. the common mussel) foot protein-5 (mefp-5) that allows these saltwater residing creatures to attach to almost any surface. This pioneering work inspired related investigations in metal deposition [7], and preparation of sensors [8], superhydrophobic materials [9], anti-corrosion coatings [10], and micro-contact printing [11], whereby it has been demonstrated that the oxidized polymers of dopamine (PDA) can adhere to almost any substrates. At the same time, PDA provides hydrophilic and redox-active properties, including the ability to reduce silver (Ag) ions [12]. Recognizing these fascinating properties, we have developed a unique method of preparing conductive copper patterns on polyimide substrate, using an innovatively designed PDA-Ag catalytic ink coupled with inkjet printing. The typical procedure for preparing the PDA-Ag catalytic ink is shown in Scheme 1d. In a basic environment, dopamine is able to spontaneously polymerize into PDA, after which a 0.1 M silver ammonia solution is added dropwise and the PDA-Ag catalytic ink is prepared at last.

2. Experimental section

Materials: Polyimide film (UBE INDUSTRIES, LTD, Upilex 500S, $80 \times 80 \times 0.125 \text{ mm}^3$), Dopamine hydrochloride (ACROS, 99%), TRIS (Aladdin, ACS, $\geq 99.8\%$), Silver nitrate (Aladdin, 99.8%), Ammonia solution (Aladdin, AR), IMT 8760 (Highnic Group in Guangdong) (Electroless copper solution), IMT 8715 (Highnic Group in Guangdong)

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Scheme 1. The preparation of mussel-inspired PDA-Ag catalytic ink (d) and the copper pattern (e) by inkjet-printing on polyimide substrate (HIT is the abbreviation of Harbin Institute of Technology). (f) the linewidth measurement image of the red zone of (e) (400 × enlarged).

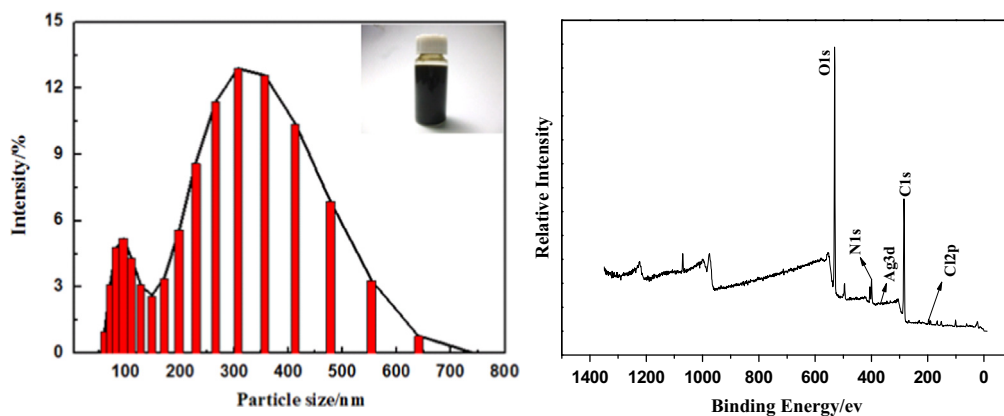


Fig. 1. The particle size distribution (including two kinds of plot types: line black) and column/bar (red) and XPS full spectrum of the (inset) PDA-Ag catalytic ink. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(Degreasing and hydrophilic treatment solution), Inkjet Printer(canon, ip1180).

Preparation of PDA-Ag catalytic ink: The 0.1 M silver ammonia solution was prepared by dissolving silver nitrate in deionized water, followed by the dropwise addition of an ammonia solution until the precipitate disappeared. To prepare the PDA mixture, a 2 mg/mL dopamine solution was dissolved in 10 mM Tris (pH 8.5), and polymerization allowed to proceed for 24 h with constant stirring at 25 °C. After completion, the silver ammonia solution was added dropwise into the as-prepared PDA solution with a volume ratio of 1:4, and the PDA-Ag catalytic ink was allowed to stir for 15 min.

Inkjet-printing copper pattern: The polyimide film were physically roughened by sandblasted treatment (280# Al₂O₃). The substrate was then subjected to a degreasing and hydrophilic treatment by immersion in IMT-8715 solution(Alkali equivalent 0.19–0.26 N

for 10 min at 60 °C, followed by rinsing with deionized water and drying with a hair dryer. The as-prepared PDA-Ag catalytic ink was printed onto the treated polyimide substrate by inkjet printing technology. After completion, the PDA-Ag catalytic ink pattern was dried in vacuum for 10 min at 65 °C. Finally, the printed substrate was immersed in IMT-8760 solution(a kind of commercialized electroless copper solution, Cu²⁺ 1.8–3.0 g/L, Formaldehyde 2.5–3.5 g/L) for 24 h at 40 °C. To obtain the fine copper pattern, a few copper particles which were produced around the pattern or in the electroless plating solution due to all kinds of reasons would be removed with the help of corrosion solution(NH₄S₂O₈ 100 g/L, H₂SO₄ 100 mL/L) at room temperature in time during the electroless copper plating process. The copper pattern was successfully obtained at last.

Characterization: The average particle size distribution of the PDA-Ag particles was measured by a Zeta-sizer Nano ZS90 (Malvern). The wettability of polyimide film before and after pretreatments

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