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Preparation of highly conductive gold patterns on polyimide via shaking-assisted layer-by-layer deposition of gold nanoparticles

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ABSTRACT

Shaking-assisted LBL deposition of gold nanoparticles (GNPs, 2.5 ± 0.5 nm) was carried out, along with the use of small non-toxic ethylenediamine (EDA) linker molecules for easy removal by sintering, in order to produce highly conductive gold patterns on polyimide substrates. First, shaking time were optimized by measuring the surface coverage of the first layer using large GNPs (12.8 ± 1.4 nm) since 2.5 nm GNPs are too small to be analyzed by FE-SEM. The concentration of EDA linker molecules and dipping time were also optimized by measuring the UV–vis absorption. Next, multilayer formation was demonstrated by measuring the NIR transmittance, multilayer thickness, and electrical conductivity, and compared with multilayer films prepared by conventional LBL deposition. Finally, gold patterns were prepared by patterning 20-layer film of small GNPs (line width of 10 μm) and subsequent sintering at 150 °C for 1 h. The shaking-assisted LBL deposition of GNPs produced clean gold patterns with very high electrical conductivity ($2 \times 10^5\ \Omega^{-1}\ \text{cm}^{-1}$) and short deposition time (~10 min) per layer.

1. Introduction

During the past decades, there has been a great amount of research on the fabrication of highly conductive metal patterns on polymeric substrate with gold nanoparticles (GNPs) since they can be easily converted to solid gold [1,2]. Techniques such as layer-by-layer (LBL) deposition [3–8], ink-jet printing [9], microcontact printing (MCP) [10], stencil printing [11], nanoimprinting [12], nanofountain probe [13] and dip-pen nanolithography [14] have been reported. Among these, MCP of spin coated GNPs provided very high electrical conductivity of $1 \times 10^5\ \Omega^{-1}\ \text{cm}^{-1}$ [10], which is slightly lower than that of bulk gold ($4 \times 10^5\ \Omega^{-1}\ \text{cm}^{-1}$) [16]. Moreover, this technique is known to be a simple, low-cost, and rapid process, but it is difficult to prepare thick GNP layers via spin coating, a pre-step needed for MCP.

On the other hand, the LBL deposition of GNPs is also known to be a easy and simple process, but it has the disadvantages of low electrical conductivity ($2 \times 10^3\ \Omega^{-1}\ \text{cm}^{-1}$) [3], poor patterning [4], and long deposition time of 60–90 min [4,8]. These drawbacks remained unsolved until we prepared clean gold patterns with high electrical conductivity of $4.1 \times 10^4\ \Omega^{-1}\ \text{cm}^{-1}$ [8], which were prepared by MCP of 3-aminopropyltriethoxysilane (γ-APS) on H_2O plasma etched polyimide substrates, followed by LBL deposition of GNPs. This value is still much lower than that of bulk gold ($4 \times 10^5\ \Omega^{-1}\ \text{cm}^{-1}$) [15].The reasons for the low electrical conductivity can be attributed to (1) residual linker/capping molecules remaining after sintering and (2) low surface coverage of GNPs which in turn leads to low packing density. In LBL deposition, large molecules [3,5–7] or polymers [16,17] that are used as capping/linker molecules are not completely removed during the sintering process due to their high degradation temperature, compared to the sintering temperature for small GNPs (~150 °C) [10–12]. Thus, an approach to solving this problem is using small molecules that can be evaporated at temperatures below ~150 °C [18]. Meanwhile, the low surface coverage of GNPs can be attributed to ionic repulsion forces, which interfere with side-by-side deposition [19], thereby providing 21–30% surface coverage [4,20,21]. These values can be compared to the theoretical jamming limit of 55% [22], indicating that surface coverage can certainly be improved if one can overcome the ionic repulsion forces. One way to do this is by imparting kinetic energy to GNPs, for example, by shaking the GNP solution. In fact, shaking has already been applied to gold solution for electroless plating by Musick et al. [23] and Brown et al. [24] at 120 rpm, but the method has yet to be utilized for GNPs.

In this study, therefore, LBL deposition of GNPs accompanied by shaking, called "shaking-assisted LBL deposition", was introduced to prepare highly conductive gold patterns by increasing the packing density. In addition, small linker molecules such as ethylenediamine (EDA) were utilized, instead of large molecules,

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in order to facilitate their complete removal during the sintering process and obtain high electrical conductivity.

2. Materials and methods

2.1. Materials

GNPs with citrate capping were synthesized by following the procedure published earlier [19,25]. Large GNPs (12.8 ± 1.4 nm) were prepared to optimize the shaking conditions since they are big enough to be analyzed by FE-SEM to estimate the surface coverage, while small GNPs (2.5 ± 0.5 nm) were used to prepare gold patterns because of their low sintering temperature [26]. Ethylenediamine (EDA, <Mn>: 60.1 g/mol, bp: 118 °C) was purchased from Sigma–Aldrich (St. Louis, USA) and used without purification as the linker molecule. The polyimide (PI) substrate was prepared by spin coating of PI solution on silicon wafer (1.5 cm × 1.5 cm), followed by water plasma etching and 3-aminopropyltriethoxysilane (γ-APS) monolayer coating via MCP to enhance the adsorption of GNPs. Flat and patterned PDMS stamps were utilized for the MCP of γ-APS. Further details on this can be found elsewhere [27].

2.2. Optimization of shaking conditions

The PI substrate (1.5 cm × 15 cm) was immersed in a vial of large GNP suspension (0.32×10^{-3}% v/v) and shaken using an orbital shaker (HB-203S, Hanbaek Scientific Co., Korea). Shaking speed of 120 rpm was utilized as reported earlier [23,24], while shaking time (1–15 min) was optimized by measuring the surface coverage of the first layer from SEM micrographs, as reported previously [19]. In addition, the EDA concentration (10–30 mM) and dipping time (3–7 min) in EDA solution were also optimized by measuring the absorbance by UV–vis spectrophotometer (Lambda 750, Perkin Elmer, USA) after depositing the second GNP layer under the optimized conditions for the first GNP layer.

2.3. GNP multilayer with large GNPs via shaking-assisted LBL deposition

The multilayer of large GNPs (4, 8, and 12 layers) was prepared by shaking-assisted LBL deposition under optimized conditions and then characterized by measuring the NIR transmittance by UV–vis spectroscopy, the layer thickness by alpha-step (α-step 500, Tencor Instruments, USA), and the electrical conductivity by Hall Effect Measurement System (7707A, Lake Shore Cryotronics Inc., USA) using a four-point probe method. For comparison, conventional LBL deposition using large GNPs was also attempted to prepare 8 and 12-layer GNP samples.

2.4. Gold patterns with small GNPs via shaking-assisted LBL deposition

Gold patterns were prepared from 20-layer samples of small (2.5 nm) GNPs, which were fabricated by patterning γ-APS on PI substrates via MCP with a patterned PDMS stamp (line width of 10 μm), followed by shaking-assisted LBL deposition. After sintering at 150 °C for 1 h, the samples were analyzed by optical microscope (BX51, Olympus, Japan) and FE-SEM (S-4700, Hitachi High-Tech, Japan). In addition, samples without patterning were also prepared in order to measure the NIR transmittance, UV–vis absorption, layer thickness, and electrical conductivity.

3. Results and discussion

3.1. Optimum shaking conditions

3.1.1. Optimum shaking time with large GNPs

As shown in Fig. 1, GNP aggregates of ~50 nm were observed at 1, 3, 5 and 7 min, but much bigger ones (~100 nm) at 10 and 15 min. Based on these FE-SEM micrographs, the surface coverage was calculated, as reported previously [19]. It increased sharply in the first min (44%) and then increased gradually up to 10 min (58%), before leveling off at 15 min (60%) (Fig. 2). In the first minute, the GNPs are virtually free to be adsorbed onto the γ-APS monolayer (on PI surface). As the shaking time increases, however, additional deposition of GNPs becomes difficult due to ionic repulsion forces, lowering the adsorption rate. Given the small difference between 58% and 60%, 10 min was selected as the optimum shaking time at 120 rpm, which is much shorter than the 60–90 min needed in the conventional LBL method [4,8]. This can be attributed to the enhanced diffusion of GNPs from shaking the GNP suspension. It is noted that the surface coverage at 10 min (at 120 rpm) is much higher than 21–30% obtained from the conventional LBL process [4,20,21], demonstrating the superiority of shaking-assisted LBL deposition over the conventional process. Moreover, the surface coverage at 10 min is higher than the theoretical jamming limit (55%) [22], being attributed to the aggregation of GNPs.

3.1.2. Optimum shaking conditions with EDA solution

As it is difficult to analyze the presence of EDA on the first GNP layer, the second GNP layer was deposited on the EDA layer and analyzed by UV–vis spectroscopy (Fig. 3). Two broad absorbance peaks at 522 and 695 nm were observed at the EDA concentration of 10 mM, compared to the single peak found at 521 nm in the one-layer GNPs (Fig. 3A), indicating a mixture of one and two layers [17]. At 20 and 30 mM, however, the samples exhibited no peaks and much higher absorbance, similar to the results reported by Fishelson and co-workers [28]. This can be attributed to the

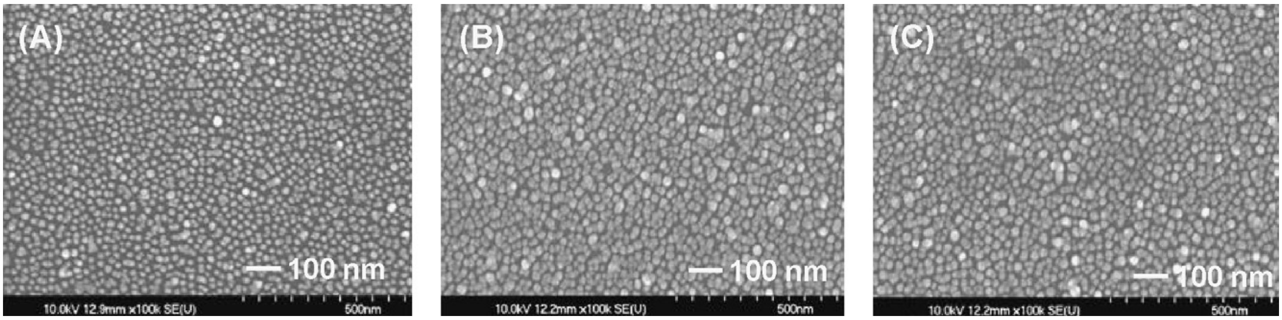

Fig. 1. FE-SEM micrographs of 1-layer GNPs prepared via shaking-assisted LBL deposition at 7 (A), 10 (B) and 15 min (C).