Applied Surface Science 389 (2016) 67–72

Contents lists available at ScienceDirect

Applied Surface Science

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

A facile fabrication of Ag-Au-Ag nanostructures with nanogaps for intensified surface-enhanced Raman scattering

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ARTICLE INFO

Article history:
Received 8 June 2016
Received in revised form 7 July 2016
Accepted 8 July 2016
Available online 14 July 2016

Keywords:
Nanogap
Surface-enhanced Raman scattering (SERS)
Electrodynamics simulation

ABSTRACT

Nanogap between two metallic nanostructures has been demonstrated to be able to efficiently concentrate an incident electromagnetic field into a small space. As a result, the formed strong field localization could extraordinarily enhance the surface-enhanced Raman scattering (SERS). In this study, controllable plasmonic nanogaps are formed by separating two layers of plasmonic Ag nanoparticles (50–100 nm) with small Au nanoparticles (2.5–6 nm). The size of the nanogaps can be readily tuned by altering the size of the Au nanoparticles. Utilizing an SERS substrate with such nanogaps, the SERS performance can be significantly improved. Such improvement could be attributed to the strongly enhanced electric field within the nanogaps, which is demonstrated by the Finite-difference time-domain simulations. The present work provides a facile strategy to rationally fabricate SERS substrates with controllable nanogaps and intensified SERS signals.

1. Introduction

Surface-enhanced Raman scattering (SERS) is an optical spectroscopic technique which amplifies the sensitivity of classical Raman spectroscopy. Owing to its high identification and sensitivity, SERS has attracted increasing attention in diverse areas, including chemistry, biology, food safety and biomedical diagnostics [1,2]. The dramatic variations in the SERS intensification have been attributed to the formation of localized plasmons or the so-called “hot spots” [3]. The electromagnetic “hot spot” is a location with strongly enhanced local field, which occurs near sharp asperities or forms at the nanoscale gaps between the metal nanostructures [4]. Short-range electromagnetic interactions at “hot spots” could lead to enormous Raman enhancement factors, even realize the single-molecule detection [5,6]. It is well known that the “hot spots” strongly depend on the shape of metal nanoparticles (NPs) as well as the interparticle distance [2,7]. Metallic nanostructures with various morphologies and interparticle spaces, such as nanocubes, nanospheres, nano-octahedrons, nanostars, nanowires and nanopyramids, have been explored to produce the “hot spots” and enhance the Raman signals [6,8–12].

Since the nanogaps in SERS substrates can provide abundant “hot spots” and improve the SERS performance, the structures with controllable nanogaps have been given much of interest [13,14]. Various methods have focused on the fabrication of SERS substrates with nanogaps. Several sophisticated lithographic methods, such as electron-beam lithography, nanosphere lithography, focused ion-beam patterning and soft lithography are commonly used to produce tightly spaced plasmonic geometries [15]. Other methods, such as physical/chemical vapor deposition, atomic layer deposition and template technique, are also developed to fabricate nanogap structures [16]. However, although lithographic methods can accurately control the inter-particle distance from tens of nanometers to ∼1 nm, highly specialized lithographic facilities are complex and expensive [17,18]. The other methods are relatively inexpensive, but the tedious preparation and implementation steps require accuracy and time consumption [16,18,19]. It is still a challenge to establish a rational and facile method for the fabrication of high-quality SERS substrates with reliable nanogaps.

In this study, we develop a promising strategy to fabricate Ag-Au-Ag SERS substrates with deliberate nanogaps. In the present strategy, the reductive Si-H bonds on the surface of Si were utilized to reduce Ag^+ ions into Ag nanoparticles (Ag NPs) on the surface of Si wafer. Then the uniform Au nanoparticles (Au NPs) with tunable sizes were sputtered onto the Ag NPs-coated Si wafer. Finally, a second layer of Ag NPs prepared by reducing

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http://dx.doi.org/10.1016/j.apsusc.2016.07.066

$AgNO_3$ with ethylene glycol (EG) was spin-coated onto the Si wafer with Ag and Au nanoparticles. As a result, the nanogaps were deliberately formed between the two layers of Ag NPs by the inset of Au NPs. The nanogaps could be reliably tuned by altering the size and distribution of the Au NPs, which were controlled by the sputtering process. The as-fabricated Ag-Au-Ag SERS substrate with deliberate nanogaps exhibits an improved performance in the detection of 4-Mercaptopyridine (4-MPY) molecules. Finite-difference time-domain (FDTD) simulations indicate that the improved SERS performance could be attributed to the strongly enhanced electric field within the nanogaps.

2. Experimental details

2.1. Preparation of the Ag-Au-Ag SERS substrate

The Ag-Au-Ag SERS substrate consists of the first layer of Ag NPs, the interlayer of Au NPs and the second layer of Ag NPs. The fabrication processes are schematically illustrated in Fig. 1a (the 3-dimensional schematic) and Fig. 1b (the cross-sectional schematic). The first layer of Ag NPs was prepared by immersing the cleaned Si wafer into an aqueous solution consisting of 5 mM $AgNO_3$ and 4.8 M HF for 10 s. Si reacted with HF to form the reductive Si-H bonds on the surface of Si wafer [20]. Then, the Ag^+ ions were reduced by the Si-H bonds and Ag NPs were formed on the surface of the Si wafer. After rinsing thoroughly with deionized water, the obtained Ag NPs on Si wafer were annealed at 180 °C for 20 min in the Ar atmosphere and the first layer of Ag NPs was obtained. Then the Au NPs were deposited onto the Si wafer with Ag NPs for a determinate time by ion sputter equipment (Hitichi E-1010) with the vacuum at 10 Pa and discharge current at 10 mA.

Finally, the second layer of Ag NPs was spin-coated onto the Si wafer with Ag and Au nanoparticles. The Ag NPs used for spin-coating were synthesized by reducing $AgNO_3$ with ethylene glycol (EG) in the presence of Poly (N-vinylpyrrolidone) (PVP-K30, Mw & 40,000, the concentration was calculated in terms of the repeating unit). Briefly, a 10 mL EG solution of 0.1 M PVP was injected into 10 mL of a magnetically stirred EG solution of $AgNO_3$ (0.1 M).

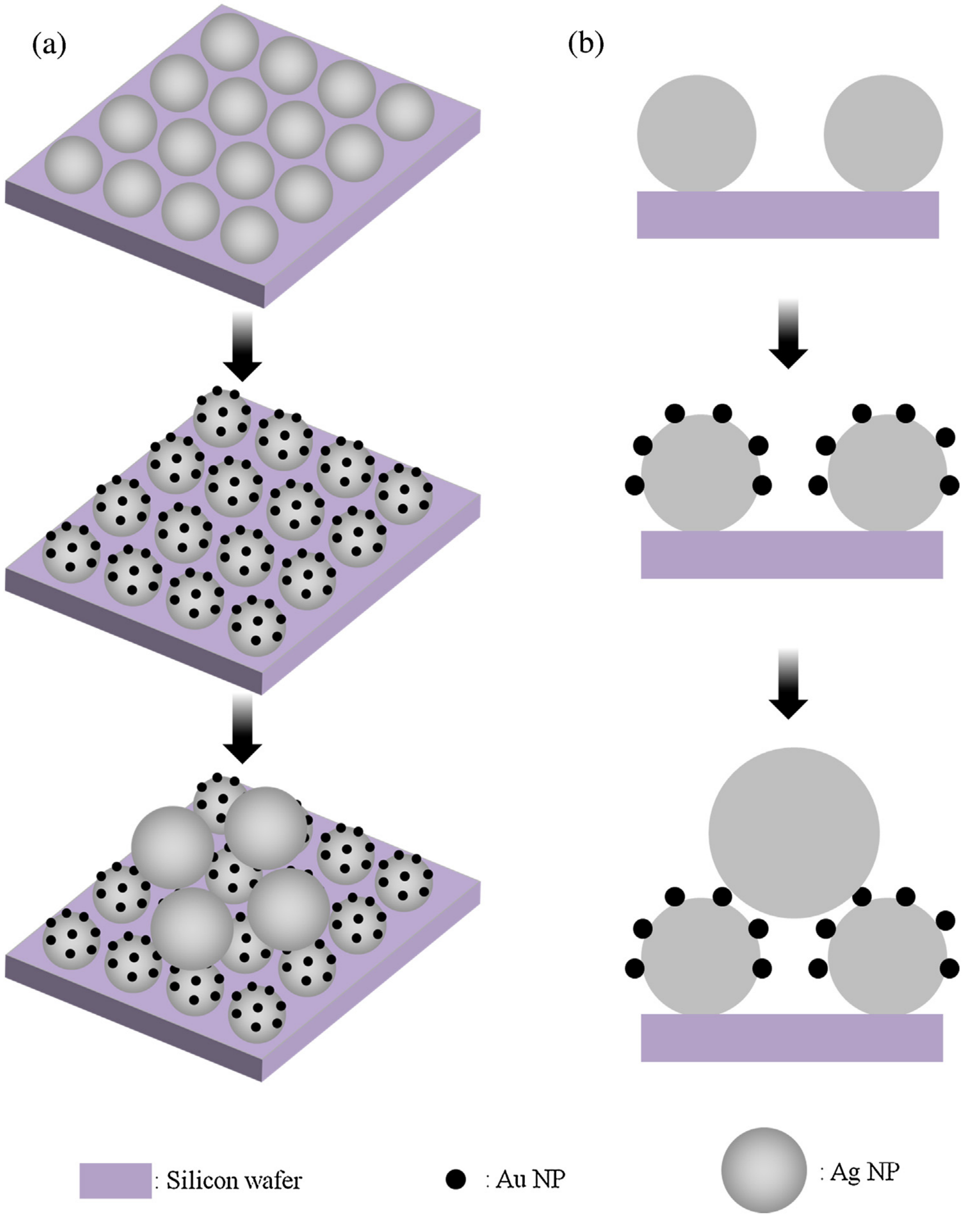

Fig. 1. (a) 3-dimensional and (b) cross-section schematic illustration of the sample preparation process for the Ag-Au-Ag substrate.