Length Dependent Surface Enhanced Raman Scattering Obtained from Copper nanorod array substrates *

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***Abstract*—The length dependence of surface enhanced Raman scattering has been investigated in Copper nanorod array substrates fabricated using an oblique angle deposition technique in this paper. The surface enhanced Raman scattering intensity of trans-1,2-bis(4-pyridyl) ethene was found to be proportional to the length of the nanorod.**

Keywords—Copper nanorod array; surface enhanced Raman scattering; length; trans-1,2-bis(4-pyridyl) ethene; oblique angle deposition

I. INTRODUCTION

Surface-enhanced Raman scattering (SERS) has received considerable attentions in recent years as it exhibits tremendous detection capability. It has applications in the detection of food, drugs, explosives, and environment pollutants[1]. Unlike chemical sensors based on electrochemical mechanisms, SERS identifies molecules based on a specific Raman fingerprint of a specific species. Previous studies have demonstrated that coinage metals, including Au, Ag, and Cu, usually provide much stronger SERS enhancements than alkali metals or transition metals because the surface-plasmon resonance of these free-electron metals can be effectively excited by visible light. Thus, nanostructured Au, Ag, and Cu are important candidates for practical SERS applications. Extensive investigations have demonstrated that the SERS enhancements of nanostructured Au and Ag strongly rely on their morphology, size, and assembly, and various nanostructured Au and Ag have been developed as sensitive SERS substrates. However, amongst the three coinage metals, the SERS effect of nanostructured Cu is much less investigated[3][4]. This is probably due to their insignificant SERS effects and poor thermal and chemical stability[5].

Tremendous efforts have been made in the past decade to develop various effective SERS substrates[6]. Using numerous fabrication methods, a wide range of metallic nanostructures can be produced, DNA-conjugated nanoparticle clusters, nanoparticle arrays formed through molecular self-recognition, and nanoparticle self-assembly within a matrix. Alternatively, metallic films of various structures have also been created for use in SERS applications. In particular, aligned Ag nanorod arrays created by oblique angle deposition (OAD) have recently been demonstrated to be highly effective SERS substrates[7]. Producing strong SERS with high sensitivity, these arrays also show good reproducibility in signal strength and can be fabricated with substantial uniform areas for applications such as sensing. In addition, the OAD approach is relatively straight forward compared with other methods employed to generate nanostructured arrays, such as photolithography or electron beam lithography (EBL), and avoids the time-consuming, complex, and expensive steps inherent in those methods[8][9].

To establish SERS as a routine analytical tool, however, it is essential to produce powerful, reproducible SERS-active substrates in a cost-effective way[2]. In this work, we demonstrate the application of copper nanorod (CuNR) process during OAD and, in turn, the subsequent growth of ordered metallic nanorod arrays for SERS.

II. EXPERIMENTS

A. Materials

Trans-1,2-bis(4-pyridyl) ethene (BPE), methanol acetone and ethyl alcohol are purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Copper (99.999%) was obtained from Kurt J. Lesker Co., Ltd. (USA). Ultra-pure water (≥18.2 MΩ) was used in all experiments.

B. Fabrication of CuNR substrates

Silicon substrates were cut into 1 cm × 1 cm as the supporting substrate for growing CuNR arrays. The Si substrates were successively cleaned in acetone, ethyl alcohol and deionized water, and then dried with nitrogen gas. Then, the cleaned Si substrates were mounted at deposition angle of 0 ° inside deposition chamber. Under the pressure of 1×10^{-6} Torr, 20 nm Cu film was deposited with the rate of 0.2 nm/s by using an electron beam evaporation equipment (DE500 electron beam evaporation deposition system, DE instrument technology, Beijing). Subsequently, the substrate holder rotated

at a deposition angle of 84°, and another 100 nm ~700nm Cu film were deposited with the rate of 0.2 nm/s (Fig. 1(a)). The top-view and cross-section SEM images of the CuNRs with another 700 nm Cu film deposited were obtained as shown in Fig. 1 (b) and (c). The measured nanorod length L=(600±90) nm, the rod diameter D=(150±70) nm, the average rod-to-rod spacing S=(130±40) nm, and the nanorod tilting angle was 65±2°.

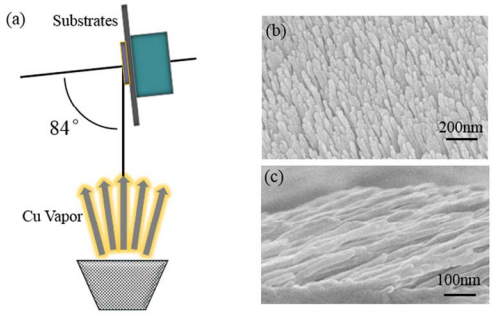

Fig.1. (a)Schematic diagram of the CuNR array fabricated by OAD. (b) The top-view SEM image of the CuNR array substrate. (c) The cross-section SEM image of the CuNR array substrate.

C. SERS measurements

A commonly used probe molecule BPE was dissolved with methanol and reached the final concentration of 10^{-4} mol/L solution sample was applied to the CuNR substrate to detect the Raman signals after air-dried. For SERS detection, samples were detected by the portable Raman Spectrometer (BWS465, B&WTEK, USA). Before testing, CuNR array substrates were put on the platform of the instrument to obtain the background signals. The excitation wavelength was 785 nm, the spot size of laser was 85 μm and the scanning range was from 350 cm^{-1} to 1800 cm^{-1}. All of the spectra were acquired from nine randomly selected spots with a laser power of 100 mW and integration time of 10 s.

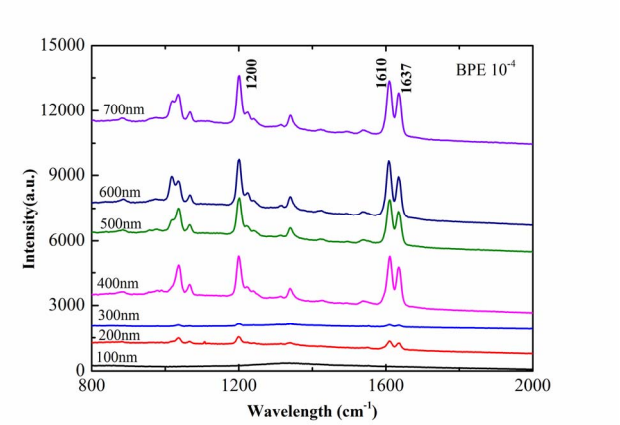

Fig.2. The SERS signal of 10^{-4} mol/L BPE solution on CuNR substrate deposited with different length.

III. Results and Discussion

Figure 2 shows typical SERS spectra of BPE for Cu nanorod arrays of 100nm-700nm length on silicon substrates. All of the spectra show the following Raman characteristic peaks of BPE: $\Delta\nu$ = 1200 cm^{-1} (C=C stretching mode), 1610 cm^{-1} (aromatic ring stretching mode), and 1637 cm^{-1} (in-plane ring mode). As shown in the figure, the characteristic peaks intensity of BPE were in proportional to the length of the nanorods.

Acknowledgments

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