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Electron beam lithography-assisted fabrication of Au nano-dot array as a substrate of a correlated AFM and confocal Raman spectroscopy

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ABSTRACT

This paper documents a study of an Au nano-dot array that was fabricated by electron beam lithography on a glass wafer. The patterns that had features of 100 nm dots in diameter with a 2-μm pitch comprised a total area of $200 \times 200 \mu m^2$. The dot-shaped Cr underlayer was open to the air after developing Poly(methyl methacrylate) (PMMA). When dipped into the Cr etchant, the exposed Cr layer was eliminated from the glass wafer in a short period of time. In order to ultimately fabricate the Ti/Au dot arrays, Ti and Au were deposited onto the arrays with a thickness of 2 and 40 nm, respectively. The lift-off procedure was carried out in the Cr etchant using sonication in order to completely remove the residual Cr/PMMA layer. The fabricated Au nano-dot array was then immersed in an Ag enhancing solution and then into an ethanol solution containing (*N*-(6-(Biotinamido)hexyl)-3′-(2′-pyridyldithio)-propionamide (Biotin–HPDP). The substrate was analyzed using a correlated atomic force microscopy (AFM) and confocal Raman spectroscopy. Through this procedure, position-dependent surface-enhanced Raman spectroscopy (SERS) signals could be obtained.

1. Introduction

Surface-enhanced Raman scattering (SERS) has been widely studied as a method that can be used for various sensing applications [1–5]. While most chemical sensors rely on a single property to attain values for mass, fluorescence, or refractive index, the Raman sensor provides multiple molecular information. SERS results from molecules that have been absorbed on roughened metal surfaces [6]. The enhancement factor of SERS, compared with that of the normal Raman, is approximately 10^8 [7]. Typically, the substrates used for SERS are randomly roughened metal surfaces with a nano-size. However, the substrates have shown different Raman intensities depending on the position because of their random surface structure. In this study, a patterned SERS substrate was fabricated, assisted by electron beam lithography technology. An Au nano-dot array was created by electron beam lithography and was immersed in an Ag enhancing solution in order to specifically form a SERS-active surface on the Au nano-dot array. A position-dependent SERS was obtained by using this SERS-active substrate with a correlated AFM and confocal Raman spectroscopy system.

2. Experiment

2.1. Fabrication of Au nano-dot array

A Cr thin film of 10 nm was formed on a glass wafer using an E-beam evaporator. Poly(methyl methacrylate) (PMMA) was then spin-coated on the surface. By developing the PMMA, an electron beam lithography nanopatterning was carried out. The patterns that had features of 100 nm dots in diameter with a 2-μm pitch comprised a total area of $200 \times 200 \mu m^2$. The dot-shaped Cr underlayer was open to the air after developing the PMMA. The substrate was then dipped into the Cr etchant for 10 s in order to eliminate the exposed Cr layer from the glass wafer. Ti and Au were then deposited onto the substrate with a thickness of 2 and 40 nm, respectively. Lift-off procedure was carried out in the Cr etchant with sonication in order to completely remove the residual Cr/PMMA layer.

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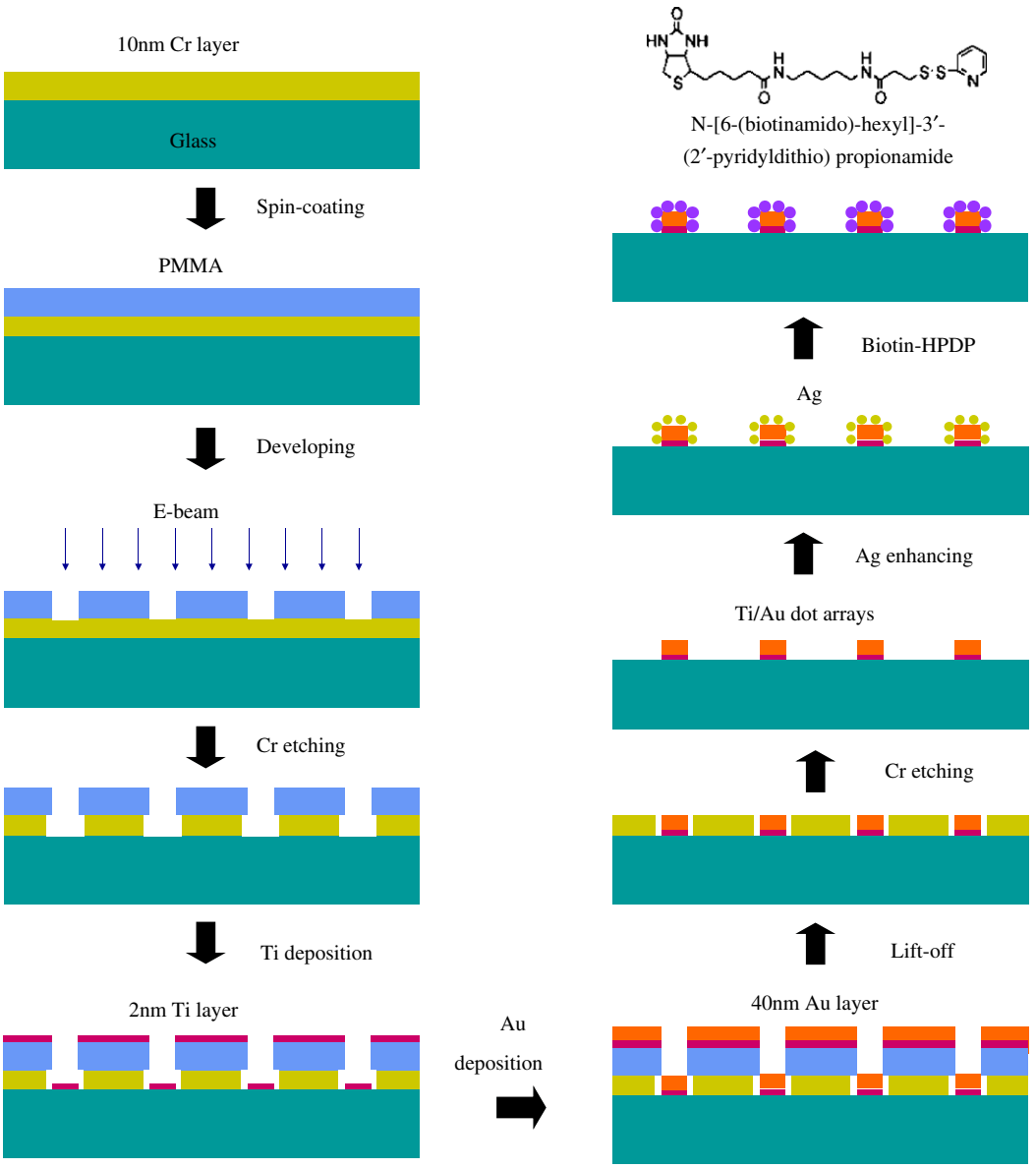

Fig. 1. Procedure for fabricating a surface-enhanced Raman scattering (SERS) substrate.

2.2. Preparation and characterization of a sample

The fabricated Au nano-dot array was immersed in an Ag enhancing solution (LI silver enhancement kit, Molecular Probe) for 30 min in order to form Ag nanoparticles specifically on the Au nano-dots. After being washed with de-ionized water and ethanol, the substrate was immersed in 0.04 mM of (*N*-(6-(Biotinamido)-hexyl)-3′-(2′-pyridyldithio)-propionamide (Biotin–HPDP) that had been solubilized in ethanol for 1 h. The substrate was then washed with ethanol and dried by blowing N_2 gas onto it. The prepared sample was analyzed using scanning electron microscopy (FEI NOVA nanoSEM 200) at an accelerating voltage of 10 kV.

2.3. A correlated AFM and confocal Raman spectroscopy analysis

The system configuration for the correlated AFM and confocal Raman spectroscopy analysis is basically the same as that of the report presented by Suh et al. [8]. Using a Nanoscope IV controller, the AFM (Bioscope, Digital Instruments Inc., Veeco Metrology Group), is mounted onto a micro-mechanical stage. The scanning confocal Raman microscope is based on an inverted optical microscope (Axiovert 200, Zeiss) and a piezoelectric *x*–*y* sample scanner (Physik Instrument) driven by an independent homemade scanning controller. The design, which uses two scanning controllers for the over–under positioned AFM scanner and the *x*–*y* sample scanner, ensures that the same sample areas in the nanoscale are measured consecutively. The precision of the in situ alignment between the two scanning measurements can be as close as 100 nm. Such precision has not as yet been achieved by using only one controller, due to the random offset shifting that occurs when the controller is switched from one scanner to the other.

The sample was loaded onto the correlated AFM and confocal Raman spectroscopy system. By using both the tip scanning and the sample scanning mode, AFM images were obtained. Raman spectroscopy was obtained at a predetermined position from the AFM image.