

Effect of Organic Additives on Electrochemical Reduction Assessment using SERS Analysis

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1. Introduction

Particles of noble metals such as Au, Ag, and Cu, resonate with optical electric fields, because the oscillation of the free electrons is suppressed in small particles. Free electrons oscillate and are polarized by the external electric field. This polarization effect is called localized surface plasmon resonance (LSPR). At the localized point, the intensity of the Raman spectrum is enhanced by LSPR; this phenomenon is known as surface-enhanced Raman scattering (SERS)¹. In SERS, significant electric field enhancement occurs, which enables the detection of unknown molecules as well as those in small quantities. In a previous study², we proposed plasmon sensors with a concentric circular relief structure; the centers of the sensors were designed to contain the highest electrical field. In the present study, the fabrication of these plasmon sensors using a UV nano-imprint process and the effect of organic additives such as poly(vinyl-pyrrolidone) (PVP) on electrochemical reduction focusing on the solid-liquid interface were investigated.

2. Experimental

The process of fabricating plasmon sensors is shown in Fig. 1. First, a periodic resist pattern was made on Si using electron beam lithography then Si was etched via reactive-ion etching. After spin-coating a UV resin onto glass, the nano-patterned Si stamp was pressed onto the glass and UV light was irradiated through the glass substrate. A 100-nm-thick Ag film was then sputtered onto the pattern. The plasmon sensor is shown in Fig. 1. The pitch varies from 400 to 700 nm while the depth is approximately 100 nm. The surface morphology was observed using scanning electron microscopy with a field-emission source (FE-SEM, S-4800, Hitachi High-Technologies Corp.). SERS measurements were performed using Raman microscopy (Nanofinder 30, Tokyo Instruments, Inc.)

3. Results

Fig. 2 shows in situ SERS spectra of a PVP solution at cathodic polarization potentials of 0, -0.2, -0.5, and -1 V vs. Ag/AgCl. The application of more negative potential to the samples, which are plasmon sensors, resulted in the appearance of a Ag-O peak at approximately 230 cm⁻¹. Based on these Raman spectra, it is assumed that PVP coordinates to the cathode through the addition of negative potential. Fig. 3 shows FE-SEM images of electrodeposited Cu films with and without PVP at a potential of -1.0 V vs. Ag/AgCl. The morphologies of the electrodeposited films with and without PVP are different; this is likely because of the coordination of PVP. The coordination of PVP to the samples suppresses the growth of the metals and results in the formation of uniform films.

Acknowledgments

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References

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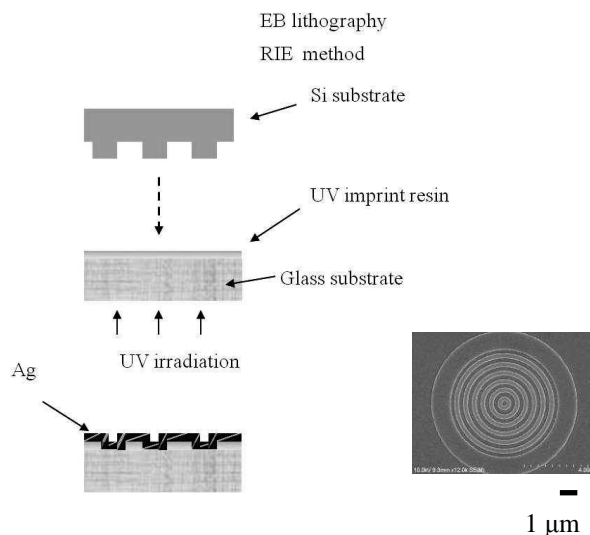


Fig. 1. Schematic of the fabrication of plasmon sensors and a picture of a plasmon sensor.

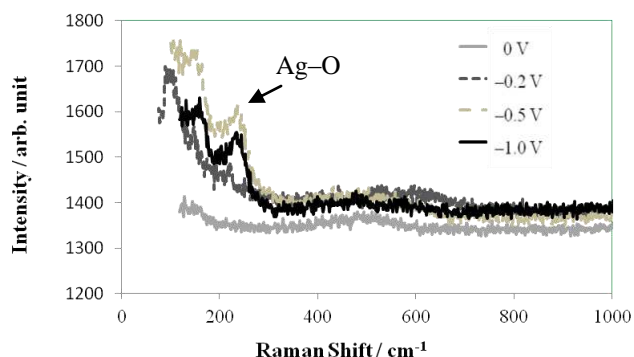


Fig. 2. In situ SERS spectra of PVP.

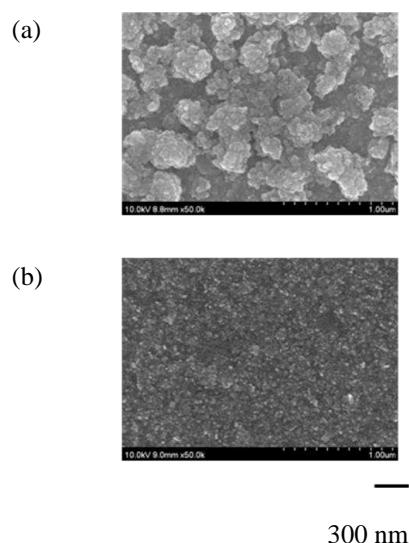


Fig. 3. FE-SEM images of electrodeposited Cu films (a) without and (b) with PVP.