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Shelf time effect on SERS effectiveness of silver nanorod prepared by OAD technique

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ABSTRACT

Recent developments in silver nanorods, fabricated by oblique-angle deposition (OAD) technique, have provide a great ability to produce high gain enhancement, reproducible, uniform response, and low-cost surface-enhanced Raman scattering (SERS) substrates. However, shelf-time stability, while not well studied, of this type of the substrates has been a primary concern for future SERS applications. Therefore, this work aimed to provide a better understanding of the shelf-time effect, within a normal laboratory storage condition, on the stability of SERS effectiveness for the OAD-based silver nanorods. For this purpose, SERS substrates consisting of the silver nanorods were prepared by an electron-beam metal evaporator, based on the OAD technique. The prepared substrates were systematically kept in laboratory storage for an experimental period of one month in order to represent their shelf life. When methylene blue molecules, previously exposed on the SERS surface, were used as probing reference, SERS spectra of such molecules were periodically recorded. Subsequently, gain enhancement factors were calculated from the measured spectra to monitor the change in effectiveness of the SERS substrates under prolonged storage time. Auger electron spectroscopy (AES) was performed to investigate degradation in the SERS effectiveness from an accumulation of residual contaminants from ambient air onto the substrate surface. In addition, an effect of ion etching was further investigated in an attempt to remove the adsorbed molecules. Our discovery confirmed that the SERS effectiveness was recovered by the ion treatment, which efficiently extended the SERS shelf life for practical applications.

1. Introduction

Raman spectroscopy, based on an inelastic scattering of photons, has been commonly used to identify a wide variety of chemical and biological molecules by their fingerprint spectra. Nevertheless, a conventional Raman spectroscopy suffers small scattering cross section, which results in low signal intensity and sensitivity. Such drawbacks had hindered Raman spectroscopy from several real-life applications for a long time. The advent of the surface-enhanced Raman scattering (SERS) technique, which greatly enhances the sensitivity from the conventional Raman spectroscopy by six or more orders of magnitudes, was successfully proved for its potential to overcome the inherent problem. Indeed, this powerful technique has drawn a great attention in research and development for over three decades [1–3].

SERS is mainly based on huge electromagnetic and chemical enhancements of the Raman emission from certain molecules when they are physically or chemically adsorbed in the proximity of specific nanostructure of noble metallic surface. Many existing surface techniques have been reported to allow ideal conditions required for a certain level of SERS enhancement. Most frequently reported methods include colloids, nanopatterned array and electrochemically modified electrodes [4–6]. Despite successful demonstration in a laboratory scale, these techniques inconveniently fail in many practical applications. To date, metal colloids provide the best SERS enhancement factor, nonetheless, they suffer from aggregation states. Different analytes produce different aggregation states; they equally impose unreliable Raman intensity and difficulty for standardization. In another method, nanopatterned array, produced by electron-beam lithography, is ideal for reproducibly uniform SERS substrates, but very expensive in a large-area production caused by tedious preparation step. On the other hand, roughed metal surface fabricated by electrochemically modified electrodes can be used as low-cost SERS substrate, although the effectiveness is normally poor. Until recently,

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self-assembled silver nanorod has gained much attention due to the invention of a convenient fabrication method, called oblique-angle deposition (OAD). The OAD method is based on a conventional physical vapor deposition principle that can be used to fabricate metal nanorod array on large substrate areas. Silver, due to its broad Plasmon resonant in the visible to near-infrared region and a large imaginary part of dielectric constants, provide the most effective SERS surface for such structure and has been used intensively in previous studies [7–10]. In fact, silver nanorod array fabricated by the OAD method have been well proved for its ability to produce high gain enhancement, reproducibly uniform response, and low-cost SERS substrates. Despite of several merits, at the present time, this type of substrate is still not widely utilized, which is most likely due to the issue with its short shelf-life stability of the SERS effectiveness, as mentioned by C. Song et al. [11]. Although silver surface is considered stable in pure air and water, it can accumulate with small fraction of hydrogen sulfide, hydrocarbon, and ozone, thus resulting in degradation of the SERS effectiveness over a period of time. Apparently, this is one of the most serious issues for the application of SERS as a routine technique, which would require a predictable effectiveness at the time the measurement takes place. Determining stability of the substrate after exposed to the ambient environment is of great importance for practical applications in both laboratory and field-detection system. However, at the present time, there is no systematic study of shelf-time effect on the SERS effectiveness of the OAD silver nanorods found in the literature. Understanding the effect has been therefore necessary for future works toward both commercialization and standardization.

This work aims to contribute to the effect of ambient air exposure, within a normal laboratory storage condition, on the shelf-time stability of the SERS effectiveness for the silver nanorods. For this purpose, the SERS substrates consisting of silver nanorods utilized by the OAD technique were prepared by an electron-beam metal evaporator. The SERS spectra of the reference molecules were periodically recorded for an experimental period of one month. SERS enhancement factor were calculated and used to monitor the changes in SERS effectiveness. Auger electron spectroscopy (AES) was performed to investigate an accumulation of residual molecules, causing degradation of the SERS effectiveness, from ambient air onto the silver nanorod array. Finally, we performed ion etching to remove the adsorbed molecules and investigate its potential to recover the SERS effectiveness. Although it has been previously reported by P. Negri et al. [12] that argon plasma treatment can eliminate background contamination, the SERS efficiency of such experiment was found to be decreased by approximately a factor of 2 even with a short exposure time. In this work, we investigate ion source treatment which offers the advantage of tightly controlled energy of extracted argon ions rather than a broad range of kinetic energies from ions, electrons and neutrals, as provided in a standard plasma cleaning system. The ion treatment might be able to recover the SERS effectiveness and therefore could be important for future applications.

2. Experimental details

2.1. Preparation of SERS substrates and surface characterization

All SERS substrates were prepared by a PVD evaporator (Denton Vacuum), based on oblique-angle deposition (OAD) technique. Silicon (100) wafers were used as substrates, where they were sonicated in de-ionized water and then in isopropanol at 30 min each. Prior to the deposition, the c-Si substrates were loaded into the evaporation chamber and immediately cleaned in argon plasma environment for 5 min. With an End-Hall ion source (Hanil), an argon flow was constantly supplied at 13.0 sccm at 120 V and 1.0 A of emission current. Such ion source offered high-density ion flux at small energy per atoms in order to ensure that the plasma cleaning would not damage the surface of the c-Si substrates. During the SERS preparation, we deposited silver nanorods on the prepared substrates based on an OAD technique at 85° of the substrate holder. We used an electron-beam evaporation on 99.99% pure silver pellets, with approximately 7.80 kV and 1.00 A of the electron-beam power supply. Note that base and operating pressures were maintained at lower than 0.4 mPa. The deposition of such silver nanorods was designed such that, an array of the nanorods were constantly spaced out for high porosity. The rod length and width were approximately 1 μm and 80 nm, respectively. Immediately after the deposition, the fabricated SERS samples were handled with great care and stored in standard desiccators for future studies.

The nanorod structure was verified by a Hitachi's s-5200 field emission scanning electron microscope (FE-SEM).

2.2. SERS spectral measurements

In order to evaluate SERS activities, we cut the fabricated substrates into small pieces of 5×5 mm^2 and conduct SERS spectral measurements with a field-type Raman spectrometer (EZRaman-M; Enwave Optronics). This Raman instrument was of a portable type with 4.0 inch × 6.5 inch × 8.5 inch in size and approximately 10 pounds in weight including a built-in computer. The instrument utilized a 785-nm diode laser, which passed through an optical fiber to a Raman probe. With a 0.30 NA focusing lens, the laser was focused to a probing area of 100 μm in diameter. Laser power was adjustable within a range of 0–400 mW. The resulting backscattered light was then collected and collimated by the same lens before being filtered and focused into the collecting optical fiber. In the study, aqueous solution of methylene blue (MB) was used as probing molecules, where we periodically and systematically conducted the SERS measurements over an experimental period of one month. Prior to each measurement, a tiny drop of MB solution, with a volume of 2.5 μl and a concentration of 5×10^{-6} M, was deposited on each SERS surface and left to dry at room temperature in an air atmosphere. During measurement, the laser power output was maintained at 50 ± 5 mW. Each scan had an integration time of 10 s and each output spectrum was obtained from only a single scan. In addition, for the purpose of gain enhancement calculation, a traditional Raman scattering spectrum was also collected from the MB molecules in aqueous solution at the concentration of 10^{-2} M.

2.3. Auger electron spectroscopy (AES) and ion etching

After being stored within a normal laboratory storage condition for one month, an elemental composition of the fabricated SERS substrate was analyzed by an Ulvac-Phi PHI-700FE auger electron spectroscopy (AES) system. Next, argon ion etching was carried out under the same system with energy of at 2 kV, for 2 min, on 1 mm × 1 mm surface area. Later, the elemental composition of the area after ion treatment was recorded. Finally, the sample was unloaded from the system and the SERS measurement of the probe molecules was performed on the ion etched area.

3. Results and discussion

3.1. Surface morphology of silver nanorods

The FE-SEM images of the fabricated silver nanorods are shown in Fig. 1. The overall morphology of the fabricated film was