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Surface-enhanced Raman scattering from a hexagonal lattice of micro-patterns of vertically aligned Ag nanorods

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ABSTRACT

Aligned Ag nanorods were prepared by glancing angle deposition on micro-patterns of silicon fabricated by electron beam lithography, forming hexagonal lattices. Excited by a 633 nm He–Ne laser, Raman scattering of Rhodamine 6G molecules on the hexagonal lattices has been investigated. The enhancement of the Raman signals by the hexagonal lattices was found to be dependent on the separation distance of the micro-patterns, i.e. it reached the maximum when the patterns are separated by ~200 nm or closely packed, suggesting a coupling effect at the micro-nano scales. This study also provides an idea to further enhance the Raman scattering.

Surface-enhanced Raman scattering (SERS) is one of the powerful tools in detection at trace level of pollutants and biochemicals, due to its ultrasensitivity, convenience and cheapness [1–4]. SERS was discovered in 1987 so that the intensity of Raman spectra from organic molecules can be magnified when molecules are adsorbed on the surface of Ag electrode [1,3]. This effect has been verified in many kinds of metals such as Ag, Au, Cu, Li, Na, K, etc. [1,5]. The magnification of the Raman intensity can be mainly attributed to the enhancement of localized electric field from resonance with localized surface-plasmon frequency of metal structures, which is closely related to the roughness of metal surface and thus excites Raman signal with a higher intensity [1,5]. SERS seems to be outstanding on surface that contains many coupled metal domains, referred to as SERS-active surface [6], thus devising ways to improve the performance of the SERS substrates has been a focus in this field, in order to enhance the effectiveness of SERS.

A number of structures have been found to be SERS-active and are of good sensitivity, e.g., the electrode surface formed by metals' solution and re-deposition into clusters is found to be SERS-active surface [6]; periodically arranged Au particles with hierarchical rough surface by electrochemical deposition exhibited good SERS performance [7]; metal colloid is also SERS-active and is of great sensitivity [5,8–10], etc. A powerful means worthwhile mentioning in creating excellent SERS substrates is the glancing angle deposition (GLAD) technique, which is capable of producing one-dimensional nanostructures with various morphologies [11–14]. Lots of efforts have thus been directed to creating morphologies of nanostructures by GLAD to improve the performance of SERS substrates. For example, one can deposit by GLAD slanted or vertically aligned Ag nanorods on planar substrates, which acted as excellent SERS substrates to detect organic molecules [3,11–14,16].

So far most studies have been focused on controlling the morphology of individual nanostructures to maximize their performance as SERS substrates, without consideration of the effect of the ordered arrangement of the nanostructure(s). Obviously, periodically arranged nanostructures might result in an enhancement in the localized electrical field due to the resonance with the localized surface Plasmon [2,15] different from that of randomly arranged nanostructures, providing a possibility to improve the performance of SERS substrates. Therefore, it is of great interest to investigate the surface-enhance Raman scattering from those nanostructures periodically arranged at a micro-nano scale.

In this paper, we report our investigation on the Raman scattering of Rhodamine 6G (R6G) molecules on hexagonal lattices of micro-patterns consisting of vertically aligned Ag nanorods as the SERS substrates.

The substrates used in this study were pristine silicon substrates with an orientation of (0 0 1). Hexagonal lattices (200 μm × 200 μm) of silicon patterns (~1 μm in diameter) were fabricated on the substrates by electron beam lithography, where the separation distance of the patterns was controlled to be 0 (closely-packed), 50 nm, 100 nm, 200 nm, 300 nm, 400 nm, 500 nm and 600 nm. They were cleaned in sequence in acetone, ethanol and de-ionized water baths supersonically, and were mounted on the substrates holder (cooled by liquid nitrogen) in a high vacuum e-beam deposition system (with a background vacuum level better than 2×10^{-5} Pa). Vertically aligned Ag nanorods were deposited on these substrates by the glancing-angle deposition (GLAD) technique described elsewhere

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[11]. During deposition, the substrate was cooled down to −20 °C, rotated at a speed of 2 rpm/min and its surface normal was set ~88° off the incoming vapor flux and the deposition rate was monitored to be ~0.5 nm/s using a quartz crystal microbalance.

The morphology of Ag nanorods deposited was characterized by scanning electron microscopy (SEM). The performance of the Ag nanorods as SERS substrate was evaluated by Raman spectrometer using R6G as the probing molecule, and a 633 nm He–Ne laser as the excitation source. Before the Raman scattering measurements, all SERS substrates were dipped in the different aqueous solutions of R6G (concentration ranging from 10^{-6} to 10^{-14} M) for 30 min, and dried by a gentle continuous nitrogen blow. The Raman

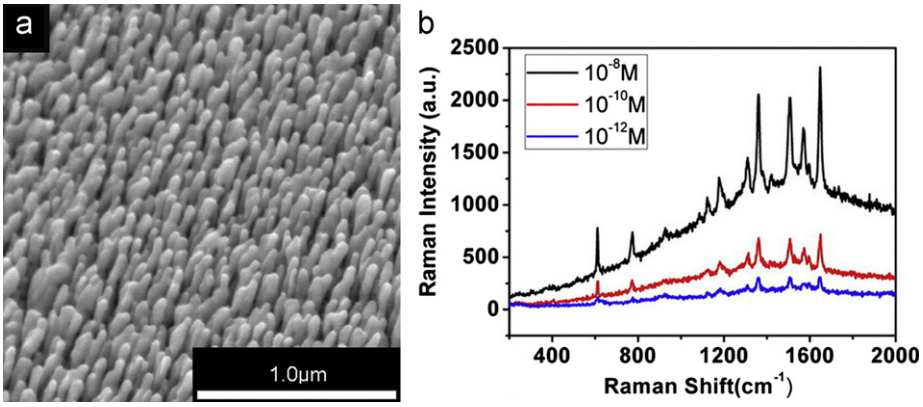

Fig. 1. (a) SEM image of vertically aligned Ag nanorods deposited on planar silicon substrates; and (b) Raman spectra of R6G on these Ag nanorods as the SERS substrate, at concentrations of 10^{-8} M, 10^{-10} M and 10^{-12} M.

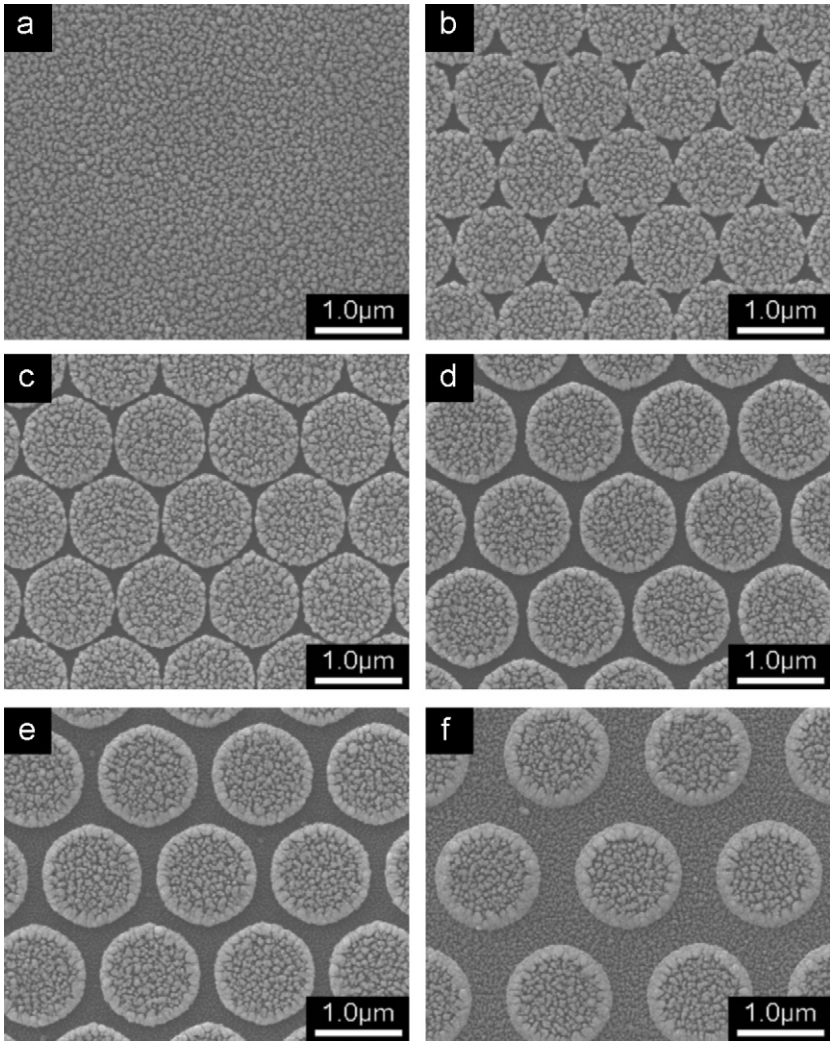

Fig. 2. Top-view SEM images of vertically aligned Ag nanorods deposited on (a) planar silicon; and on hexagonal lattices of micro-patterns of silicon that are separated by (b) 0 nm (closely-packed); (c) 50 nm; (d) 200 nm; (e) 300 nm; and (f) 600 nm.