Surface-Enhanced Raman Spectroscopy Using Self-Assembled Silver Nanoparticles on Silicon Nanotips

Surojit Chattopadhyay,*,† Hung-Chun Lo,† Chih-Hsun Hsu,‡ Li-Chyong Chen,‡ and Kuei-Hsien Chen†,‡

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan, and Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan

Received May 9, 2004. Revised Manuscript Received September 7, 2004

A new substrate for surface-enhanced Raman spectroscopy has been developed in the form of silicon nanotips, by electron cyclotron resonance plasma chemical vapor deposition, with apex diameters of ∼2 nm, lengths of 1000 nm, and densities of 10^{11}/cm^2. The surface areas of the nanotips are ∼150 m^{2}cm^{-3}, comparable with the best-quality porous silicon. Ion-beam-sputtered silver self-assembles on these substrates as nanoparticles of 4−10 nm diameter and these metallic nanoparticles act as surface enhancement centers for Raman spectroscopy. Standard molecules such as Rhodamine 6G and *trans*-1,2-bis(4-pyridyl)ethylene (BPE) of concentrations in the range of 10^{-6} to 10^{-10} M have been studied on these substrates and enhancements in the range of 10^6 to 10^8 were observed. These dry etched substrates, unlike those conventionally prepared by wet chemistry, are compatible with silicon device technology and are remarkably stable and reproducible.

I. Introduction

Surface-enhanced Raman spectroscopy (SERS) has evolved as a powerful and sensitive tool for detection and identification of a wide range of adsorbate molecules down to the limit of single molecule detection.[1−3] Due to the low scattering cross section (10^{-30} cm^2/molecule), Raman spectroscopy was much inferior to fluorescence spectroscopy, which had a larger cross section (10^{-16} cm^2/molecule), for trace detection. Using specially prepared rough metallic surfaces the otherwise weak Raman signals can be enhanced by several orders making detection possible.[4] This enhancement can be as large as 10^{14}.[1] Hence, SERS has the capability to unite the sensitivity of fluorescence with the rich structural content inherent to Raman spectroscopy. This extraordinary enhancement is believed to be predominantly due to two mechanisms: a long-range classical electromagnetic (EM) effect and a short-range chemical effect.[5] The respective contributions of these mechanism to the overall SERS enhancement are debated, but the EM effect is believed to be a few orders more than that due to the chemical effect. Nie and Emory[1] showed that the commonly observed enhancement of the order of ∼10^6 may have been only an ensemble average over several hundred nanoparticles, whereas a few of these SERS active metallic particulates, called hot particles, can actually give an enhancement of about 10^{15}. At this level of enhancements, SERS, with the richness of molecular information, supersedes laser-induced fluorescence experiments that carry molecular information only at low temperatures.

Even as we lack a complete quantitative understanding of the fundamentals of SERS, the progress in application developmental research has been remarkably fast and successful. Probing single molecules[6−8] or nanostructures[9,10] and development of nanoscale chemical sensors[11,12] utilizing SERS independently or in conjunction with liquid chromatography was made possible. The first step for achieving such advanced stages of application development was the fabrication of proper substrates which are SERS active and provide high enhancement factors. The first substrate on which SERS was observed was electrochemically roughened silver (Ag) electrode.[4] Since then Ag films produced by Tollens reaction[13] or by vapor-deposition methods[14,15] have been commonplace. Nitric-acid-etched Ag foils,[16] or Ag photodeposited on anatase TiO$_2$ substrates[17] are also relatively easy to prepare. Self-assembled Ag or Au colloid particles on

---

* To whom correspondence should be addressed. E-mail: sur@diamond.iams.sinica.edu.tw. Tel: +886 2 33665231. Fax: +886 2 23655404.
† Institute of Atomic and Molecular Sciences, Academia Sinica.
‡ Center for Condensed Matter Sciences, National Taiwan University.

(1) Nie, S.; Emory, S. R. *Science* **1997**, *275*, 1102.
(2) Kneipp, K.; Yang, Y.; Kneipp, H.; Parleman, L. T.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Phys. Rev. Lett.* **1997**, *78*, 1667.
(3) Xu, H.; Bjerneld, E. J.; Kall, M.; Borjesson, L. *Phys. Rev. Lett.* **1999**, *83*, 4357.
(4) Fleishmann, M.; Hendra, P. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, *26*, 163.
(5) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.
(6) Betzig, E.; Chichester, R. J. *Science* **1993**, *262*, 1422.
(7) Xie, X. S.; Dunn, R. C. *Science* **1994**, *265*, 361.
(8) Gessner, R.; Winter, C.; Rösch, P.; Schmitt, M.; Petry, R.; Keifer, W.; Lankers, M.; Popp, J. *Chem. Phys. Chem.* **2004**, 5, 1159.
(9) Higgins, D. A.; Kerimo, J. K.; vanden Bout, D. A.; Barbara, P. F. *J. Am. Chem. Soc.* **1996**, *118*, 4049.
(10) Birnbaum, D.; Kook, S. K.; Kopelman, R. J. *J. Phys. Chem.* **1993**, *97*, 3091.
(11) Tan, W.; Shi, Z. Y.; Smith, S.; Birnbaum, D.; Kopelman, R. *Science* **1992**, *258*, 778.
(12) Petry, R.; Schmitt, M.; Popp, J. *Chem. Phys. Chem.* **2003**, *4*, 14.
(13) Ni, F.; Cotton, T. M. *Anal. Chem.* **1986**, *58*, 3159.
(14) Van Duyne, R. P.; Hulteen, J. C.; Treichel, D. A. *J. Chem. Phys.* **1993**, *99*, 2101.
(15) Schlegel, V. L.; Cotton, T. M. *Anal. Chem.* **1991**, *63*, 241.
(16) Miller, S.; Baiker, A.; Meier, M.; Wokaun, A. *J. Chem. Soc., Faraday Trans.* **1984**, *I80*, 1305.
(17) Sudnik, L. M.; Norrod, K. L.; Rowlen, K. L. *Appl. Spectrosc.* **1996**, *50*, 422.

10.1021/cm049269y CCC: $30.25

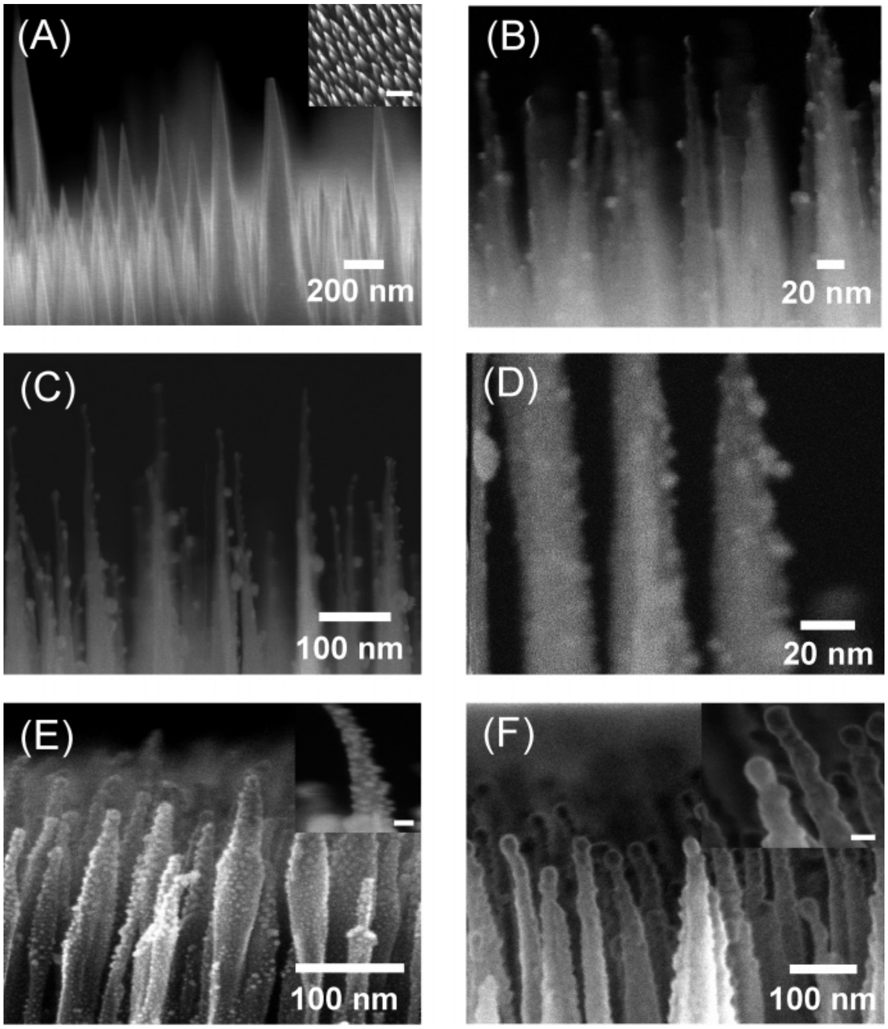

Figure 1. Scanning electron micrographs showing (A) cross-sectional view of the as-grown silicon nanotips (inset shows the top view of the as-grown nanotips; scale bar 200 nm); cross-section images of silicon nanotips covered with silver sputtered for (B) 1 min, (C) 3 min, (D) 5 min, (E) 10 min (inset showing a single tip with the silver nanoparticles; scale bar 20 nm), and (F) 20 min (inset showing a magnified image of the silicon tip covered in a silver film; scale bar 20 nm) in IBS.

polymer-coated substrates and silver particles layered onto etched polymer substrates has also been used as SERS active substrates.[14] These substrates demonstrate enhancement factors of 10^3-10^6 which can be further enhanced by resonance effects. However, most of these techniques, apart from photolithography,[18] involve wet chemical etching and thus cannot be readily integrated into existing silicon device technologies. Achieving nanometer-size metal prints is several years down the line even for lithographic techniques.[18,19] However, a special tip-induced SERS aiding in nanoscale chemical analysis has been demonstrated which does not require a substrate fabrication.[20] SERS active substrate generation techniques compatible with silicon device technology are important since only then can it have a wider scope in applications such as micro−electro−mechanical systems (MEMS). In this paper we report a dry-etched nanostructured substrate on which silver nanoparticles, with less than 10-nm diameter, can be self-assembled at an extremely high density that readily exhibits the surface enhancement. The dry-etching technique is compatible with the existing silicon device technology and requires no chemical modification. Moreover, these substrates are stable and reproducible as far as SERS signals of analytes are concerned.

II. Experimental

A high-density electron cyclotron resonance (ECR) plasma discharge of silane (SiH_4), methane (CH_4), hydrogen (H_2), and argon (Ar) gas mixture was used to etch out these silicon nanotips from a bare untreated crystalline silicon wafer. A detailed description of the nanotip formation can be found elsewhere.[21] In short, severe plasma (Ar and H_2) etching of the silicon substrate partially masked by silicon carbide nanoparticles, originating from CH_4 and SiH_4 plasmas, resulted in a uniform array of aligned silicon nanotips. The aspect ratio and the packing density of these nanotip arrays can be controlled by adjusting the etching parameters such as substrate temperature, microwave power, etc. Each silicon tip had a cap at its apex that was characterized to be silicon carbide (SiC) by auger electron spectroscopy (AES) and high-resolution transmission electron microscopy (HRTEM). The high-resolution scanning

---

(18) Gunnarsson, L.; Bjerneld, E. J.; Xu, H.; Petronis, S.; Kasemo, B.; Kall, M. *Appl. Phys. Lett.* **2001**, *78*, 802.
(19) Green, M.; Liu, F. M. *J. Phys. Chem. B* **2003**, *107*, 13015.
(20) Zenobi, R.; Deckert, V. *Angew. Chem., Int. Ed.* **2000**, *39*, 1746.
(21) Hsu, C. H.; Lo, H. C.; Chen, C. F.; Wu, C. T.; Hwang, J. S.; Das, D.; Tsai, J.; Chen, L. C.; Chen, K. H. *Nano Lett.* **2004**, *4*, 471.

electron microscope (HRSEM) images shown in Figure 1 were taken using a JEOL JSM-6700 FESEM.

The nanotips were coated with silver by the ion-beam sputtering (IBS) process. A base pressure of 1×10^{-6} Torr was achieved in the sputtering chamber that contained a high-purity silver target, mounted on a rotating stage, and the silicon nanotip substrates were held about 10−15 cm away from the target. An argon (Ar) ion beam (Ar flow rate of 2 sccm) was accelerated toward the silver target using a Commonwealth Scientific (CS) IBS controller. The sputtered silver was collected on the substrate, kept at room temperature, for different durations of time. The working pressure was about 5×10^{-4} Torr. Flat crystalline silicon substrates were also coated with silver by IBS and used for comparison purposes. These silver-coated flat silicon substrates were scanned with a Solver line P-47 SPM−MDT to image the resultant silver islands and particles.

Commonly used molecules for SERS experiments such as Rhodamine 6G and *trans*-1,2-bis(4-pyridyl)ethylene (BPE) (TCI, Tokyo, Japan) were then dispersed by drop coating onto these substrates, in measured quantities, from their solution (in methanol) and dried. They were then used for the Raman measurements using a Renishaw-2000 micro Raman spectroscope. Single accumulations with integration times of 5s were used to collect the spectra in a backscattered mode. A 532-nm laser with a source intensity of 100 mW was used with a probe beam diameter of 1 μm. Different concentrations (10^{-6} to 10^{-10} M) of Rhodamine 6G and BPE were used and their Raman spectra were taken on these specialized substrates.

III. Results and Discussion

The formation of silicon nanotips, by a process named self-masked dry etching (SMDE), has been depicted schematically elsewhere.[21] Arrays of aligned silicon nanotips with a tip diameter typically in the range of ∼2 nm, base diameter of 100 nm, and tip length of ∼1 μm can be obtained using the electron cyclotron resonance (ECR) plasma chemical vapor deposition (CVD) technique.[21] Figure 1A shows the cross-section scanning electron micrograph (SEM) of the as-grown silicon nanotips[21] without any metal particles on them. The inset shows a plane view SEM of the as-grown nanotips. The tip density could be as high as 10^{11} cm^{-2}, as shown in Figure 1A. Assuming all the nanotips are touching each other at the bottom, the surface area can be quantified at 150 m^{2}cm^{-3}, which is as good as the high-porosity porous silicon.

These substrates were then coated with silver (Ag) by Argon ion beam sputtering (IBS) using silver target at room temperatures. Due to the surface energy difference between the silicon nanotips and that of silver they self-assembled to form nanoparticles on these nanotips. The size of these nanoparticles was always between 4 and 10 nm with a rather small departure from the mean value. The density of these particles, under optimized IBS time, was also very high and could be found throughout the entire surface of the nanotips. Figure 1B−F depict the SEM images of the silicon nanotips coated with different ion beam sputtering times using silver targets. As evident from the pictures, with lower silver sputtering times, between 1 and 5 min, the silver nanoparticles were scattered near the apex of the nanotips only with a random low-density distribution (Figure 1B−D). From the sputtering time of 5 min onward the nanoparticles developed throughout the entire surface of these nanotips with a higher and uniform density (Figure 1E). In the optimized condition, for 10 min IBS time, high density of monodispersed Ag nanoparticles could be obtained throughout the entire surface of these nanotips. This ensured a rather high density of nanoparticles that could be packed over a unit area of the substrate in comparison to the flat silicon or other polymer substrates normally used for SERS. Such high packing density of these nanoparticles would help maintain the reproducibility levels since the probability of attachment of an analyte molecule in unit probe area would increase manifold. Longer Ag sputtering time will, however, encourage agglomerated clusters leading to the formation of a conformal thin film of Ag on these silicon nanotips (Figure 1F) instead of the well-separated monodispersed nanoparticles. The density of the metallic nanoparticles could be controlled easily by the sputtering time only, allowing a small dispersion of the particle size. This renders these substrates ideal systems for verifying theoretical modeling of SERS.

The effect of silver coating time on the surface-enhanced signal is demonstrated in Figures 2 and 3. Surface-enhanced Raman signals of Rhodamine 6G (Figure 2) and BPE (Figure 3) were collected from silicon nanotip substrates coated with 0 min (uncoated), 1, 3, 5, 10, and 20 min of silver using IBS. Different concentrations of Rhodamine and BPE were dispersed on these differently coated substrates. Figure 2A shows the Raman spectra collected from uncoated silicon nanotips for three different concentrations of Rhodamine 6G adsorbed on these substrates. A broad fluorescence band and only the silicon signal from the nanotips at 520 cm^{-1} could be observed with all three different concentrations of Rhodamine 6G used. However, with the silver coating on these silicon nanotip substrates, the surface-enhanced Raman signals were readily observed on a fluorescent background. It is to be noted that one of the analytes used in this study, namely Rhodamine 6G, has electronic resonance in the visible and our probe laser (532 nm) may excite resonance effects contributing to the Rhodamine signals. But to maintain a uniform terminology over the entire text, the term SERS has been retained. The enhancement factors were calculated from the ratio of the SERS cross-section of adsorbed analytes to the RS cross-sections of bulk analytes[1] through the calculation of the total number of Raman photons (N_R) from the recorded count. N_R is calculated as follows:

$$(N_R) \times (\text{collection efficiency}) \times (\text{optical throughput}) \times (\text{CCD efficiency}) \times (\text{gain}) = \text{recorded count}$$

where collection efficiency (in %) is that of the objective of the microscope, optical throughput is the total transmission (in %) of the optical path involved in the detection, which, along with the detector efficiency and gain can be calculated for a particular Raman spectroscope. The recorded count being known from the Raman spectrum, N_R, is estimated.

The number of analyte molecules (N_M) can be calculated as follows: since the number density (10^{11}/cm^{2}), the base radius (50 nm) and length (1 μm) of the nanotips are all determined from HRSEM measurements, we can calculate the number of nanotips, approximately 1000, in the probe area. The surface area of the nanotips can be found out assuming the nanotips as regular cones of fixed height (1μm

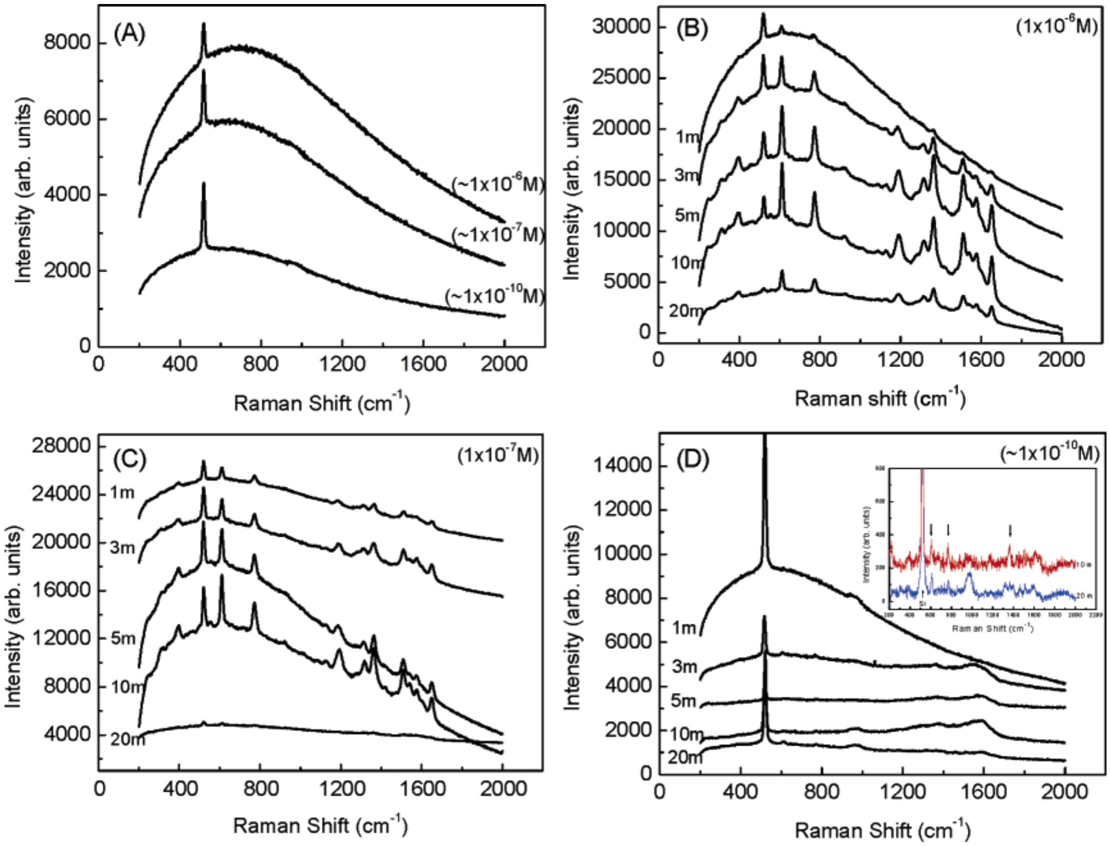

Figure 2. (A) Raman spectra of Rhodamine 6G drop-coated on as-grown silicon nanotips (the concentration of Rhodamine 6G is marked on each curve); SERS spectra of different concentrations of Rhodamine 6G drop coated on silicon nanotips covered with different amounts of self-assembled silver nanoparticles (B) 1 × 10^{-6} M, (C) 1 × 10^{-7} M, (D) ~1 × 10^{-10} M (the numbers mentioned on each curve in Figure 2B−D denote silver sputtering times). Inset in Figure 2D shows the background-subtracted Raman spectra for Rhodamine 6G dispersed on silicon nanotips covered silver coating for 10 and 20 min by IBS. Silicon signal and the three most intense Rhodamine 6G Raman lines are marked by arrows.

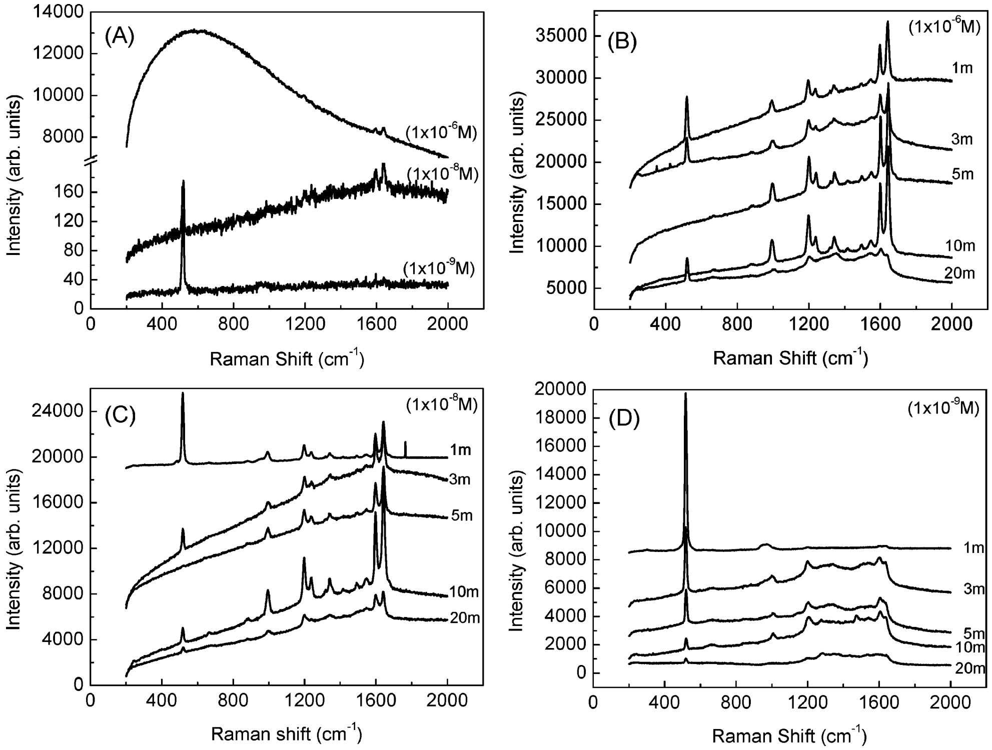

Figure 3. Raman spectra of BPE drop coated on as-grown silicon nanotips (the concentration of BPE is marked on each curve); SERS spectra of different concentrations of BPE drop coated on silicon nanotips covered with different amounts of self-assembled silver nanoparticles (B) 1 × 10^{-6} M, (C) 1 × 10^{-8} M, and (D) ~1 × 10^{-9} M (the numbers mentioned on each curve in Figure 3B−D denote silver sputtering times).

long) and base radius of 50 nm. Using a fixed volume of analyte solution (10 μL) of fixed concentration, N_M in the probe volume can be estimated by assuming homogeneous dispersion (the assumption of homogeneous distribution is supported from the fact that our nanotips were hydrophilic having very low water contact angles) of the molecules over the entire sample area (5 mm × 5 mm). This has been estimated to be $\sim 2 \times 10^5$ molecules in the probe volume for an analyte concentration of 1×10^{-6} M. We assumed 100% dye molecules taking part in the SERS process to estimate the "minimum" enhancement factor in our case using

$$(F(\text{photons/cm}^2\text{•sec})) \times (N_\text{M}) \times (\sigma_\text{R}{}^*) = N_\text{R}$$

where F is the incident photon flux and $\sigma_\text{R}{}^*$ is the SERS cross section. Basically, this methodology of enhancement factor calculation is identical to what was reported by Nikoobakht et al.,[22] assuming 100% adsorption. A lower adsorption (less than 100%), will give rise to a lower N_M taking part in the Raman process and hence, a higher enhancement. An estimation of the enhancement factors using careful geometrical analysis and consideration of surface coverages and adsorption isotherms have produced large errors of 30−50%.[19,23] Here the quoting of a "minimum" enhancement by considering 100% adsorption seems more reasonable.

The intensities of the Raman signals were markedly higher for higher concentrations (10^{-6} M) of Rhodamine 6G used (Figure 2B) and merely visible for lower concentrations approaching 10^{-10} M (Figure 2D). However, unambiguous signals of the three most intense Rhodamine 6G Raman frequencies can be found even at the lowest concentrations (inset, Figure 2D) which may not be too obvious in Figure 2D itself.

Similarly when BPE was used as the analyte, there was no SERS signal from the uncoated silicon nanotip substrates, with only a broad fluorescence and the silicon signal at 520 cm^{-1} being observed (Figure 3A). For the highest concentration of BPE used ($\sim 1 \times 10^{-6}$ M) even the silicon signal was suppressed. However with silver coating on the substrates, the SERS signals could be readily obtained for all three concentrations of analytes used in this study (Figure 3B−D).

Figures 2 and 3 both show the Raman signals on a broad fluorescent background. The fluorescent background observed in most spectra indicates that a fraction of analytes were adsorbed on bare silicon instead of the metallic sites which would have quenched the fluorescence. The nanotips coated with silver for 10 min yielded the largest SERS signals independent of the concentrations. Several groups have investigated the variation of the SERS intensity with analyte concentrations and inferred a linear dependence.[22,24] However, they differ on the range of this linear regime, spanning 10^{-10} to 10^{-6} M in concentration in some case[24] and only 10^{-5} to 10^{-4} M[19] in some. This indicates a system-dependent variation of the SERS intensity with analyte concentration. We observed that the integrated intensity, say, of the 1650 cm^{-1} line of Rhodamine 6G does not increase linearly with its molar concentration. An increase of 4 orders in concentration saw an increase of 5×10^2 in the SERS intensity (plot not shown). Intuitively, a linear variation of the SERS intensity with the analyte concentration is expected assuming that the SERS active sites increase linearly with the analyte concentration, and the SERS active and inactive sites all have the same adsorption energy (consistent with the Langmuir isotherm).[19] But SERS active sites have higher affinity for adsorbates than the inactive sites.[23] This is the reason for the blinking of SERS signal probably arising out of the thermally activated diffusion of analyte molecules between SERS inactive and active sites.[25] A nonlinear increase in SERS active particles, hence SERS intensity, was also observed with molecular concentration by Michaels et al.[26] The sub-linearity in our case may be a result of (i) nonlinear increase in SERS active sites with the increase in analyte concentration,[26] (ii) the rough morphology of our substrate scattering (over a much larger solid angle than that projected by our objective lens) or re-absorbing the Raman photons predominantly at the higher concentrations, or (iii) the extremely low surface coverage[19] regimes in our experiments.

It has been mentioned that a silver coating time around ∼10 min produced the best enhancements. At longer silver coating times, since they produced a continuous thin film on the nanotips, the enhancements were relatively small. Again at small silver coating times, say 1 min, the density of the nanoparticles was not sufficiently high to guarantee a strong and reproducible SERS signal. This can be interpreted from the modeling of Garcia-Vidal and Pendry.[27] They showed from a model study that the efficiency of an SERS active substrate is maximum when the separation, d, between the metallic particles is equal to their diameter, $2R$, (assuming half cylindrical particles), i.e., the particles just touching each other. To satisfy this modeling condition, we need to have a high density of nanoparticles on our substrate. This condition is close to what we have for the nanotips covered with silver sputtered for 10 min in the IBS system. With lesser silver coating times, we observed scattered nanoparticles which simulates the modeling condition of $d > 2R$, and with higher silver coating times (20 min or more) we approach the modeling condition of $d < 2R$, both of which will amount to reduced SERS activity of the nanoparticles. Gunnarsson et al.[18] also demonstrated through their electron beam lithographically prepared substrates that SERS activity increases manifold with decreasing particle separation. This could be related to the electromagnetic coupling effects between the silver nanoparticles.[28] However it should be mentioned here that the silver particles used by Gunnarsson et al.[18] are of the size 200 nm, much larger than what was used in this study. Although in that study they mentioned that the effect of interparticle separation far outweighs the effect of particle size itself. Talking of interparticle coupling, a situation very similar to the present case was reported by Maxwell et al.[29] where the SERS intensity was shown to

---

(22) Nikkobakht, B.; Wang, J.; El-Sayed, M. A. *Chem. Phys. Lett.* **2002**, *366*, 17.
(23) Hildebrandt, P.; Stockburger, M. *J. Phys. Chem.* **1984**, *88*, 5935.
(24) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R.; Sun, Y.; Xia, Y.; Yang, P. *Nano Lett.* **2003**, *3*, 1229.
(25) Maruyama, Y.; Ishikawa, M.; Futamata, M. *Anal. Sci.* **2001**, *17*, i1181.
(26) Michaels, A. M.; Nirmal, M.; Brus, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 9932.
(27) Garcia-Vidal, F. J.; Pendry, J. B. *Phys. Rev. Lett.* **1996**, *77*, 1163.
(28) Otto, A. In *Light Scattering in Solids*; Cardona, M., Guntherodt, G., Eds.; Springer: Berlin, 1984; Vol. IV, Chapter 7.

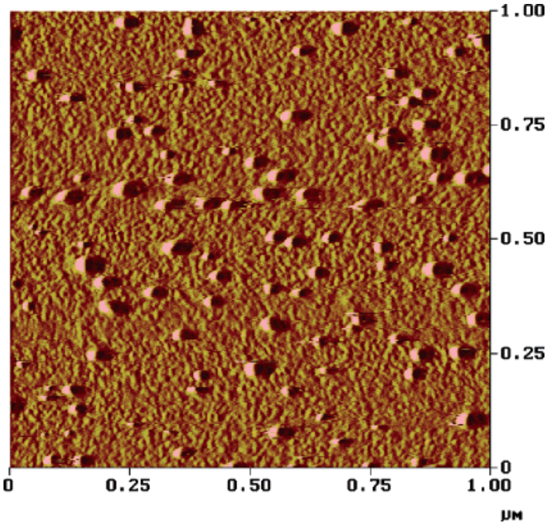

Figure 4. Atomic force microscope image of a flat crystalline silicon surface covered with silver sputtered in the ion beam system for 10 min.

increase as a function of “particle coverage” and ultimate saturation of SERS signal above 1 monolayer. The lack of particle−particle interaction as a result of longer interparticle separation implying lower particle coverage (substrates shown in Figure 1B and C), produced relatively weak SERS intensities, but with increasing particle coverage (Figure 1E), stronger SERS intensity was observed. However, with increased sputtering times, the 3-dimensional particle formation breaks down promoting a 2-dimensional film (Figure 1F), our observation is a decreased SERS intensity that matches well with the reported SERS intensity normalized to the particle coverage.[29] The current technique of Ag particle generation, apart from being friendly to silicon technologies, can also produce substrates on which such models[27] can be verified.

There are several reports[30,31] on the growth of silver on flat crystalline silicon that generally demonstrates a Stranski-Krastanov or a modified Stranski-Krastanov growth mode, where 3-dimensional Ag islands grow on a thin 2-dimensional Ag wetting layer. However, we are less cognizant about the growth of silver on rough silicon surfaces, such as these nanotips. To identify the advantage of using a rough silicon nanotip morphology to generate SERS-active Ag nanopaticles, flat crystalline silicon substrates and silicon nanotips both were identically coated with silver for 10 min (that yielded the best SERS signals) using IBS technique and matched for the surface enhancement effects using Rhodamine 6G as an analyte. The silver-coated flat silicon surfaces had larger silver nanoparticles of >20 nm diameters sparsely (interparticle distances of ∼100 nm) distributed on agglomerated Ag islands (Figure 4) as expected for a Ag coverage exceeding 1 monolayer.[30] This is both qualitatively and quantitatively different to the high density of nearly monodispersed Ag nanoparticles observed for the nanotip substrates. An effort to mimic the effective thickness or the surface coverage of the Ag layer as observed on silicon nanotips, by decreasing the Ag sputtering time on flat silicon substrates, will produce a 2-dimensional wetting layer[30] (for a coverage below 1 monolayer) devoid of particle formation required for SERS.

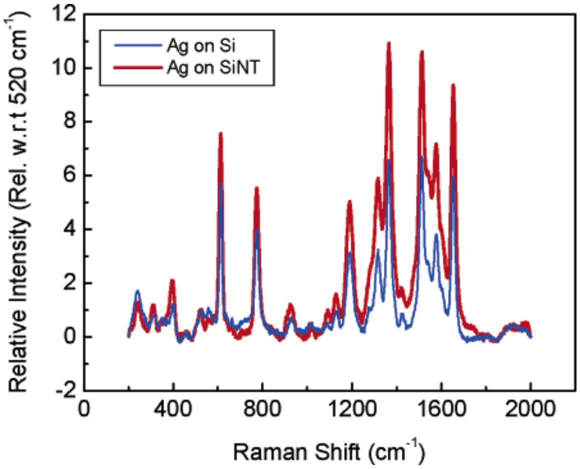

Figure 5. Background-subtracted SERS spectrum of Rhodamine 6G, normalized with respect to the 520 cm^{-1} signal from silicon, on (blue line) flat crystalline silicon covered with sputtered silver (as in Figure 4), and (red line) silicon nanotips covered with self-assembled silver nanoparticles (as in Figure 1E). Estimated number of analyte molecules in unit SERS probe area is higher by several tens in the case of flat crystalline silicon.

Figure 5 shows the background fluorescence subtracted SERS spectrum, normalized to the intensity of silicon signal at 520 cm^{-1}, for Rhodamine 6G on flat crystalline silicon (as in Figure 4) and silicon nanotips coated with 10 min of silver by IBS (as in Figure 1E). The background removal was done by pixel imaging of the spectrum or alternatively by using mathematical software to fit the background with a polynomial and using a suitable scaling factor to match the SERS spectrum and generating the particular background after specifying the Raman peak positions of the analytes. Figure 5 only distinguishes the SERS activity of differently self-assembled Ag morphologies generated on silicon nanotips against a control sample of flat silicon. Clearly the silicon nanotip substrates showed higher enhancements ($\sim 1 \times 10^8$), by about 2 orders of magnitude, in comparison to the silver-coated flat silicon substrates (3×10^6). This is attributed to several factors. The silicon nanotips with silver particles were found to be hydrophilic, whereas the silver-coated flat silicon substrates were found to be hydrophobic in our experiments. Such difference in the wettability of these substrates definitely arose due to the difference in surface roughness in these two substrates apart from other possible chemical contributions. The removal of any surface hydrogen from the nanotip surface during the plasma etching may be one such chemical contribution. The same volume of analyte molecules dispersed uniformly over the whole surface area of the nanotip substrate reproducibly produced SERS spectra, whereas the same volume of analyte on the flat silicon substrate was confined to a small area only, outside which no SERS spectra could be obtained. This resulted in an excess population of analyte molecule per unit probe volume on the flat silicon substrate. This, apart from the difference in SERS count (Figure 5), was taken into account while calculating the enhancement factors. Other than this, the larger particle size and interparticle separation of silver

---

(29) Maxwell, D. J.; Emory, S. R.; Nie, S. *Chem. Mater.* **2001**, *13*, 1082.
(30) Glueckstein, J. C.; Evans, M. M. R.; Nogami, J. *Phys. Rev. B* **1996**, *54*, R11066.
(31) Müller, T.; Nienhaus, H. *J. Appl. Phys.* **2003**, *93*, 924.

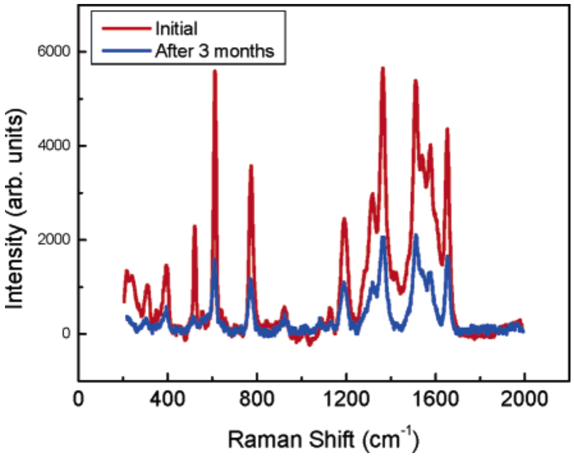

Figure 6. Aging of SERS spectra (background subtracted) of Rhodamine 6G (1×10^{-6} M) on silicon nanotips covered with self-assembled silver nanoparticles (as in Figure 1E).

particulates on the flat silicon substrate in comparison to the silicon nanotips would affect SERS activity.

The stability of these substrates was tested by measuring the Raman activity with time. These substrates can give Raman signals even three months after they were drop coated with the analytes. Figure 6 shows the aging of SERS spectrum for Rhodamine 6G (1×10^{-6} M) on silicon nanotip substrates coated with silver (as in Figure 1E). There is a reduction in the SERS intensity over a period of 3 months but still the analyte detection is clear and unambiguous, which is required for analytical studies.

Electrochemically roughened silver electrodes are not stable for SERS; their activity started decreasing after the preparation itself and the activity may last for few days.[32] Silver foil roughened with nitric acid etching generally stays active for a week, whereas the silver film produced by Tollen's reaction is not stable. Photodeposited silver films are stable over few weeks.[32] Such instabilities may result from desorption of analytes from the SERS active sites or a decay in the activity of the metal nanoparticles in the scattering process, among other probable reasons such as photobleaching. However, from the high density of the silicon nanotips and resultant high packing density of the monodispersed metal nanoparticles on them, an initial explanation of the stability may be statistical in nature whereby a significant fraction of active analytes on active SERS centers still exist. However, further studies are required to know the reason for such stability in this case, or rather the root cause for instabilities in all the SERS active systems. Viewed in the wider perspective these new SERS active substrates can be termed quite stable.

In conclusion, self-assembled silver nanoparticles monodispersed on silicon nanotips, formed by self-masked dry etching of crystalline silicon substrates, demonstrated high activity for surface-enhanced Raman scattering. These macroscopic substrates possess the attributes such as uniform particle size (4−10 nm), controllable interparticle distance, large enhancement factors (10^6−10^8), and remarkable stability. The high density of the silicon nanotips (10^{11}/cm^2) and a consequent uniform density of the metal nanoparticles, which can be controlled by the ion beam sputtering time of the metal targets, ensures high levels of inter- and intrasubstrate reproducibility. Molecules with concentrations as low as 10^{-10} M could be detected in a reproducible and stable fashion with the help of these substrates. These substrates can be useful systems for fundamental modeling as well as analytical studies, especially in devices such as MEMS which is not accessible to conventional wet chemical techniques.

Acknowledgment. This work was carried out with financial support from the National Science Council and Ministry of Education, Taiwan. (S.C. acknowledges the award of a postdoctoral fellowship from Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan.

CM049269Y

---

(32) Norrod, K. L.; Sudnik, L. M.; Rousell, D.; Rowlen, K. L. *Appl. Spectrosc.* **1997**, *51*, 994.