

## Resonant surface enhancement of Raman scattering of Ag nanoparticles on silicon substrates fabricated by dc sputtering

Yingcui Fang, Xiayi Li, Kevin Blinn, Mahmoud A. Mahmoud, and Meilin Liu

Citation: *J. Vac. Sci. Technol. A* **30**, 050606 (2012); doi: 10.1116/1.4742967

View online: <http://dx.doi.org/10.1116/1.4742967>

View Table of Contents: <http://avspublications.org/resource/1/JVTAD6/v30/i5>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

---

### Additional information on J. Vac. Sci. Technol. A

Journal Homepage: <http://avspublications.org/jvsta>

Journal Information: [http://avspublications.org/jvsta/about/about\\_the\\_journal](http://avspublications.org/jvsta/about/about_the_journal)

Top downloads: [http://avspublications.org/jvsta/top\\_20\\_most\\_downloaded](http://avspublications.org/jvsta/top_20_most_downloaded)

Information for Authors: [http://avspublications.org/jvsta/authors/information\\_for\\_contributors](http://avspublications.org/jvsta/authors/information_for_contributors)

## ADVERTISEMENT

# Instruments for advanced science

**Gas Analysis**



- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

**Surface Science**



- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

**Plasma Diagnostics**



- plasma source characterization
- etch and deposition process reaction kinetic studies
- analysis of neutral and radical species

**Vacuum Analysis**



- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

contact Hiden Analytical for further details

**HIDEN ANALYTICAL**

[info@hideninc.com](mailto:info@hideninc.com)  
[www.HidenAnalytical.com](http://www.HidenAnalytical.com)

CLICK to view our product catalogue 

# Resonant surface enhancement of Raman scattering of Ag nanoparticles on silicon substrates fabricated by dc sputtering

Yingcui Fang<sup>a)</sup>

Vacuum Section of Hefei University of Technology, Hefei, Anhui, 230009, China and School of Materials Science and Engineering, Center for Innovative Fuel Cell and Battery Technologies, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

Xiayi Li and Kevin Blinn

School of Materials Science and Engineering, Center for Innovative Fuel Cell and Battery Technologies, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

Mahmoud A. Mahmoud

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Meilin Liu<sup>b)</sup>

School of Materials Science and Engineering, Center for Innovative Fuel Cell and Battery Technologies, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

(Received 21 June 2012; accepted 24 July 2012; published 9 August 2012)

Ag nanoparticles (AgNPs) were deposited onto silicon substrates by direct current (dc) magnetron sputtering. The influences of sputtering power and sputtering time on the AgNP film morphology were studied using atomic force microscopy. The particle size was successfully tuned from 19 nm to 53 nm by varying the sputtering time at a dc power of 10 W. When Rhodamine 6G (R6G) was used as the probe molecule, the AgNP films showed significant surface enhanced Raman scattering effect. In particular, it is found that larger particles show stronger enhancement for lower concentrations of R6G while smaller particles display stronger enhancement for higher concentrations of R6G. © 2012 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4742967>]

## I. INTRODUCTION

Ag nanoparticles show such a high surface enhanced Raman scattering (SERS)<sup>1</sup> effect that single molecule detection was reported under some conditions.<sup>2</sup> Most SERS substrates are based on colloidal chemistry methods<sup>3</sup> or monolayer assembly by Langmuir-Blodgett technique.<sup>4</sup> These methods involve surfactants or chemical compounds, which could interfere with the absorption of the probe molecules. Magnetron sputtering in vacuum is a very common technology not only in laboratory research but also in industry. Sputtering a silver target in vacuum can produce very clean Ag nanoparticle (AgNP) substrates. Such substrates would enable probe molecules to be chemically adsorbed on their surface so that both electromagnetic and chemical enhancements can take place simultaneously, endowing the AgNP substrates with very high SERS efficacy. To date, quite a few groups have studied the properties of AgNPs on various substrates. Ruffino *et al.* investigated the nano-morphology of Ag on SiC substrates by radio-frequency sputtering,<sup>5</sup> Charton *et al.* studied the optical properties of thin Ag films on polyethylene terephthalate deposited by magnetron sputtering,<sup>6</sup> and Kato *et al.* researched the influence of low voltage sputtering on the microstructure of AgNP films on glass substrates.<sup>7</sup> In 1998, Kunduy *et al.* reported Ag thin films grown by direct current (dc) sputtering on Si (001) that were composed of silver islands.<sup>8</sup> In 2007, You *et al.* utilized sputtered AgNP films on silicon substrates to study the optical properties of ZnO thin films and found that the local surface plasmon of AgNPs

could enhance UV emission of ZnO greatly.<sup>9</sup> Our group has previously produced AgNP substrates by dc sputtering that provided high SERS activity and were successfully applied to detect carbon deposition and cathode thin films in solid oxide fuel cells.<sup>10</sup> For the current work, AgNP films were deposited on silicon substrates using different dc power levels and sputtering times to study the effect of these variations on the nanostructure of the substrate and SERS effects. Due to the three-dimensional AgNP structure, high SERS effects were obtained. Further, we found an interesting phenomenon: larger particles have larger enhancement for lower concentrations of Rhodamine 6G (R6G) and smaller particles have stronger enhancement for higher concentrations of R6G.

## II. EXPERIMENT

The AgNPs were deposited onto silicon substrates in a high vacuum system by dc magnetron sputtering at different power levels (4, 10, and 15 W) using a high purity Ag target (99.995%) with a plasma generated by ultra-high purity Ar (99.999%) at different exposure times (60, 180, 240, 540 sec). The base pressure in the vacuum chamber was about  $2 \times 10^{-6}$  mbar. During sputtering, the flow of Ar was 80 sccm and the working pressure was maintained at  $2.5 \times 10^{-2}$  mbar. The substrates were not heated during sputtering. Following deposition, the samples were removed from the vacuum chamber and immersed into R6G solution with concentrations of  $10^{-5}$ ,  $10^{-6}$ ,  $10^{-7}$ , and  $10^{-9}$  M for 3 h. The samples were then dried naturally in air. Raman spectra were collected with a Raman spectromicroscopy system (Renishaw RM 1000). The excitation wavelength was 514 nm from an Ar ion laser with 5 mW power, and the

<sup>a)</sup>Electronic mail: yingcui.fang@mse.gatech.edu

<sup>b)</sup>Electronic mail: meilin.liu@mse.gatech.edu

collection time for each spectrum was 10 s. The morphologies of the films were characterized by atomic force microscopy (AFM).

### III. RESULTS AND DISCUSSION

#### A. AFM analysis

SERS effects mainly depend on the particle size and the inter-particle distance<sup>11</sup>; thus, tuning and optimizing these parameters is important. We first tried to tune the dc power. The morphologies of the samples made at  $2.5 \times 10^{-2}$  mbar for 60 s at dc power of 4 W, 10 W, and 15 W are shown in Figs. 1(a)–1(c), respectively. The particles deposited at 4 W were much smaller compared with the other two samples due to the smallest amount of Ag sputtering yield from 1 min of sputtering. The average size of the particles obtained by sputtering at 10 W was near and even a little larger than that of particles obtained by sputtering at 15 W. At higher dc power, the amount of atoms from the Ag target sputtered by  $\text{Ar}^+$  per unit time was larger, and the excess of atoms may not have been given sufficient time to migrate across the surface to join with the formed Ag particle nuclei and promote their growth. Instead, more nuclei were formed. Hence, the Ag nanoparticle population density was higher when the sputtering power was 15 W. Since a higher density of nuclei would result in a higher population density of AgNPs, the maximum size of the individual particles becomes limited. The histograms of

Figs. 1(a)–1(c) are shown in Figs. 2(a)–2(c), respectively, and the corresponding average sizes are about 14, 19, and 17 nm, respectively. From these results, it is apparent that controlling the morphology by dc power is not feasible due to this constraint. We chose 10 W as the sputtering power and tried to tune the particle size by varying sputtering time. The AFM images are shown in Figs. 1(d) for 180 s, Fig. 1(e) for 240 s, and Fig. 1(f) for 540 s. The corresponding histograms are shown in Figs. 2(d)–2(f), respectively, and the average sizes were about 29, 31, and 53 nm, respectively. Therefore changing the sputtering time is an effective way to tune the particle size.

#### B. Raman spectroscopy

The Raman spectra collected from samples with different concentrations of R6G are shown in Fig. 3. Several spectra were collected from different points on the same sample, and these are shown in the same color or symbol. The spectra showed some Raman intensity dispersion but the trends of the Raman intensity evolution with the sputtering time were clear. According to Figs. 3(a) and 3(b), as the sputtering time was successively increased, the intensity increased until a maximum was reached and then decreased. The optimal sputtering time to obtain the highest Raman enhancement was 180 s for  $10^{-5}$  M and 240 s for  $10^{-6}$  M concentration. For the  $10^{-7}$  M and  $10^{-9}$  M cases [Figs. 3(c) and 3(d), respectively], the 540 s samples showed the strongest SERS effect.

There are mainly three types of enhancement mechanisms responsible for the high SERS enhancement<sup>12</sup>: electromagnetic (EM),<sup>13</sup> chemical,<sup>14</sup> and resonant enhancement.<sup>15</sup> The chemical enhancement factor generally ranges between about  $10^1$ – $10^4$ , but its effects only occur between the first layer of the adsorbed molecules and the AgNPs,<sup>16</sup> so it is seldom observed. That said, we remain confident that chemical enhancement took place in the case of our samples for multiple reasons. First, the Ag nanoparticles produced by dc sputtering were very clean without any of the common surfactants left on the surfaces of AgNPs made by colloidal synthesis. Surfactants could interfere with the adsorption of R6G and prevent the molecules from being chemically absorbed on the AgNP surface, which would weaken chemical enhancement. Second, we observed that samples with low concentrations of R6G absorbed on large Ag particles yield some differences in Raman spectra collected at different spots on the same sample. More detailed investigation of chemical enhancement is a subject of our ongoing work.<sup>17</sup>

EM enhancement has been reported to reach up to  $10^8$ .<sup>18</sup> This type of enhancement is related to several factors: the particle size, inter-particle distance, and dielectric environment surrounding the particles.<sup>11</sup> For example, Stampelcoskie *et al.* reported that 40–60 nm was the optimal size range to obtain the strongest SERS enhancement,<sup>19</sup> while the particle size for single molecule detection was found close to 100 nm.<sup>20</sup> Most likely, the strongest determining factor for electromagnetic enhancement is sufficiently short interparticle distance. If two AgNPs are at the right distance from one another, a local

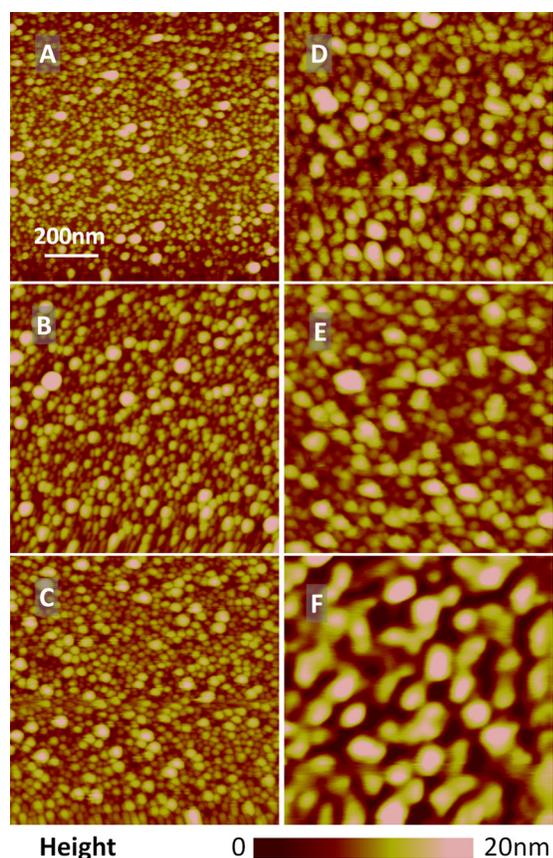


Fig. 1. (Color online) AFM images of AgNP samples made at  $2.5 \times 10^{-2}$  mbar by sputtering for 60 s at (a) 4 W, (b) 10 W, (c) 15 W, and 10 W for (d) 180 s, (e) 240 s, and (f) 540 s.

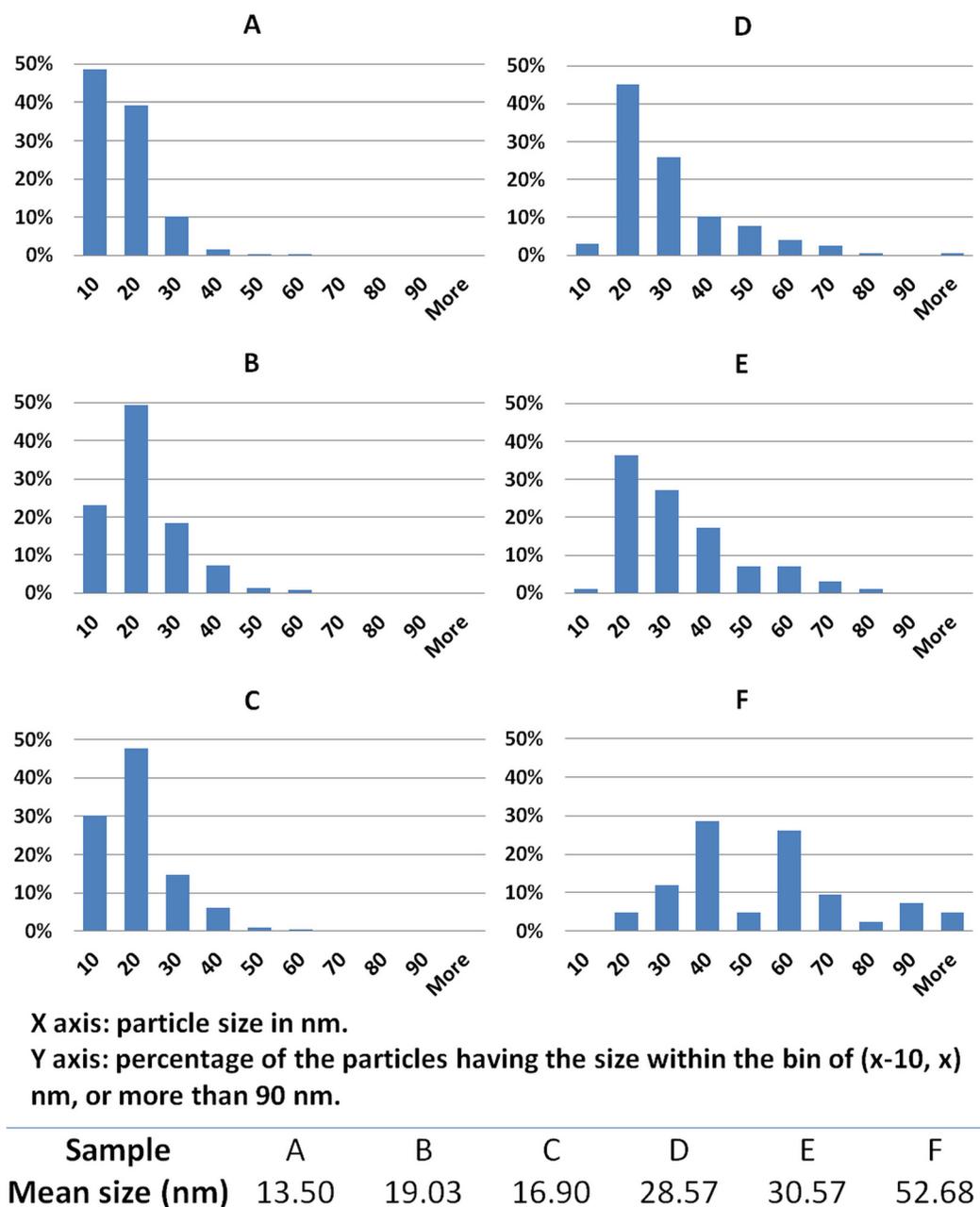


Fig. 2. (Color online) Histograms of the particles distribution from AFM images of samples made at  $2.5 \times 10^{-2}$  mbar by sputtering for 60 s at (a) 4 W, (b) 10 W, (c) 15 W, and 10 W for (d) 180 s, (e) 240 s, and (f) 540 s.

surface plasmon resonant coupling can take place causing a field enhancement and subsequently a Raman signal enhancement. These gaps are referred to as hotspots.<sup>21</sup> Further, if probe molecules were only located within these gaps, the signal from each individual molecule would gain huge enhancement from SERS. According to Fig. 1, the AgNP films in the current work grew discontinuously into particle “islands” that were mostly isolated from each other. This type of structure possesses a very strong local EM field and “hotspots” were easy to form.<sup>22</sup> Hence, the samples showed strong SERS effects.

The samples were excited by 514 nm laser, so R6G was also resonantly excited since R6G has a strong absorption near this wavelength.<sup>23</sup> Under resonant excitation, the SERS

enhancement factor is proportional to the number of R6G molecules.

We found that Raman intensity did not necessarily increase with AgNP size or R6G concentration. For a fixed R6G concentration, as particle size increases, two effects occur. First, the EM field contribution from each particle increases, which is also partially due to decreasing interparticle distance; second, the specific area of the nanoparticle film is reduced, especially when the interparticle gaps become pinched off. The increase of the EM field contribution from each particle will promote SERS effects. However, the reduction of a specific surface area will result in a decrease of the number of R6G molecules in each detection area and at the same time a possible increase in dimer

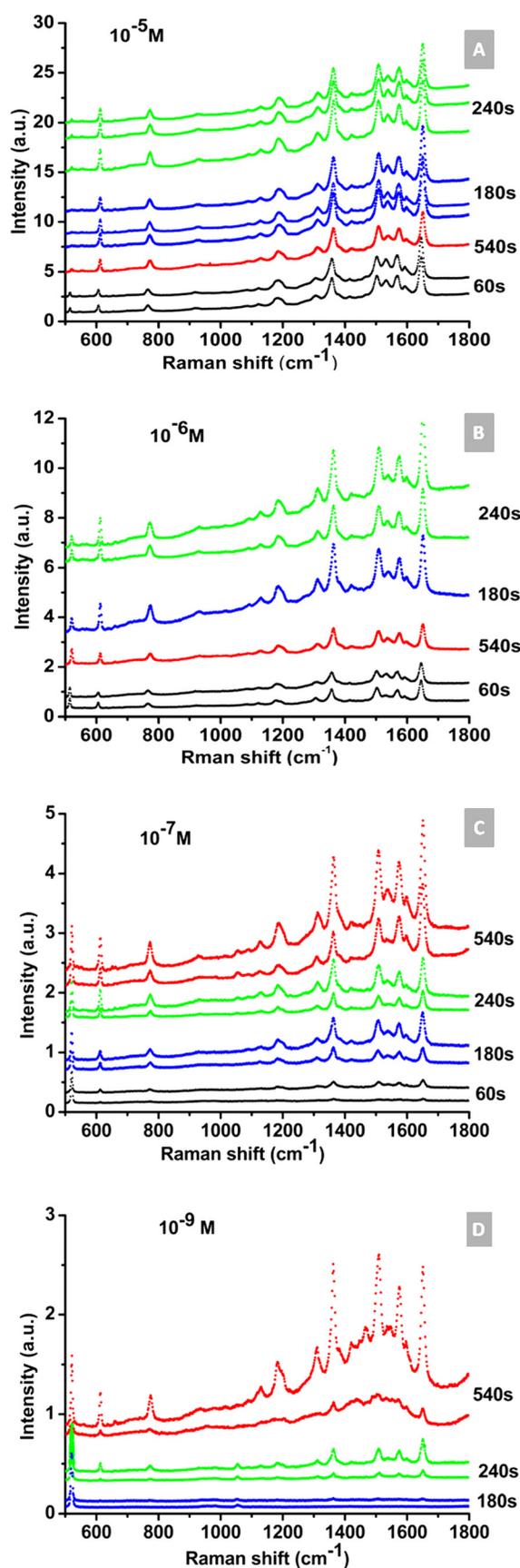


Fig. 3. (Color online) Raman spectra evolution with sputtering time at R6G concentrations of (a)  $10^{-5}$  M, (b)  $10^{-6}$  M, (c)  $10^{-7}$  M, and (d)  $10^{-9}$  M. It should be noted that the bottom-most spectrum in (c) is mostly flat noise through the  $600\text{--}1000\text{ cm}^{-1}$  as the signal is very near the sensitivity threshold.

formation. A reduction in the number of R6G molecules will cause the total Raman signal decrease due to the proportional loss in resonant excitation. Thus, the reduction in a specific area hurts the SERS effect. In other words, the two effects decide an optimal size for obtaining the strongest enhancement for a specific concentration of R6G. For  $10^{-5}$  M concentration, the optimal particle size came from a sputtering time of 180 s. When the concentration was decreased to  $10^{-7}$  M, the total number of R6G molecules in solution was reduced, as was the amount of R6G adsorbed on the AgNP surface. The corresponding particle size at which dimers began to form increased. Therefore, the optimal size increased to that obtained from a 540 s sputtering time. For the  $10^{-9}$  M concentration case, the largest particles would give the strongest enhancement. At this concentration, the number of R6G molecules was small, so the resonance contribution was also small. Even with the large EM enhancement of each particle, the Raman signal was still weak. However, if the molecules happened to be at the hotspots between two nanoparticles, the Raman signals from these molecules potentially experienced huge enhancement.<sup>24</sup> For this reason, the Raman spectrum collected from the  $10^{-9}$  M sample had remarkably high intensity in some cases.

On the other hand, when particles were small, though the electromagnetic field of each particle was weak, more gaps existed. More molecules could be accommodated at these gaps. When the particle sizes were larger, each particle's EM contribution was larger but the number of gaps between particles was reduced, so fewer molecules could be hold at these gaps. That is, smaller particles showed larger enhancement for higher concentrations R6G.

#### IV. CONCLUSIONS

Sputtering in vacuum is a facile method to fabricate very clean AgNPs. The AgNPs size can be tuned from 19 to 53 nm by changing dc sputtering time at a sputtering power of 10 W. These three dimensional AgNPs showed a high and stable SERS effect. The SERS effect was related to morphology of AgNPs and R6G concentration. Larger particles have stronger enhancement for lower concentration R6G while smaller particles have stronger enhancement for high concentration R6G. Substrates with these kinds of structures and properties can provide huge Raman enhancement for low concentration R6G or other molecules for detection by Raman spectroscopy. The mechanisms described herein were only analyzed qualitatively for this work. More exploration into a quantitative model of this behavior is ongoing.

#### ACKNOWLEDGMENTS

This material is based upon work supported as part of the HeteroFoam Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC0001061. We also thank the China Scholar Council.

- <sup>1</sup>M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 163 (1974).
- <sup>2</sup>S. Nie and S. R. Emory, *Science* **275**, 1102 (1997).
- <sup>3</sup>M. A. Mahmoud and M. A. El-Sayed, *Nano Lett.* **9**, 3025 (2009).
- <sup>4</sup>M. A. Mahmoud, B. Snyder, and M. A. El-Sayed, *J. Phys. Chem. C* **114**, 7436 (2010).
- <sup>5</sup>F. Ruffino and M. G. Grimaldi, *J. Appl. Phys.* **110**, 044311 (2011).
- <sup>6</sup>C. Charton and M. Fahland, *Surf. Coat. Technol.* **174–175**, 181 (2003).
- <sup>7</sup>K. Kato, H. Omoto, and A. Takamatsu, *Thin Solid Films* **520**, 4139 (2012).
- <sup>8</sup>S. Kunduy, S. Hazray, S. Banerjee, M. K. Sanyal, S. K. Mandal, S. Chaudhuri, and A. K. Pal, *J. Phys. D: Appl. Phys.* **31**, L73 (1998).
- <sup>9</sup>J. B. You, X. W. Zhang, Y. M. Fan, S. Qu, and N. F. Chen, *Appl. Phys. Lett.* **91**, 231907 (2007).
- <sup>10</sup>X. X. Li, K. Blinn, Y. C. Fang, M. F. Liu, A. M. Mahmoud, S. Cheng, and M. L. Liu, *Phys. Chem. Chem. Phys.* **14**, 5919 (2012).
- <sup>11</sup>E. Ringe, J. M. McMahon, K. Sohn, C. Cobley, Y. Xia, J. Huang, G. C. Schatz, L. D. Marks, and R. P. Van Duyne, *J. Phys. Chem. C* **114**, 12511 (2010).
- <sup>12</sup>M. D. Malinsky, K. L. Kelly, G. C. Schatz, and R. P. Van Duyne, *J. Phys. Chem. B* **105**, 2343 (2001).
- <sup>13</sup>M. Moskovits and J. S. Suh, *J. Phys. Chem.* **88**, 5526 (1984).
- <sup>14</sup>M. G. Albrecht and J. A. Creighton, *J. Am. Chem. Soc.* **99**, 5215 (1977).
- <sup>15</sup>G. H. Gu and J. S. Suh, *J. Phys. Chem. A* **113**, 8529 (2009).
- <sup>16</sup>A. Otta, I. Mrozek, H. Grabhorn, and W. Akemann, *J. Phys.: Condens. Matter* **4**, 1143 (1992).
- <sup>17</sup>Y. C. Fang, K. Blinn, X. X. Li, A. M. Mahmoud, and M. L. Liu, “Localized surface plasmon and strong coupling with R6G of Ag nanoparticles fabricated by DC sputtering,” *ChemPhysChem* (submitted).
- <sup>18</sup>K. A. Willets and R. P. V. Duyne, *Annu. Rev. Phys. Chem.* **58**, 267 (2007).
- <sup>19</sup>K. G. Stamplecoskie, J. C. Scaiano, V. S. Tiwari, and H. Anis, *J. Phys. Chem. C* **115**, 1403 (2011).
- <sup>20</sup>J. P. Camden, J. A. Dieringer, Y. Wang, D. J. Masiello, L. D. Marks, G. C. Schatz, and R. P. Van Duyne, *J. Am. Chem. Soc.* **130**, 12616 (2008).
- <sup>21</sup>A. Campion and P. Kambhampati, *Chem. Soc. Rev.* **27**, 241 (1998).
- <sup>22</sup>J. Dong, S. Qu, Z. Zhang, M. Liu, G. Liu, X. Yan, and H. Zheng, *J. Appl. Phys.* **111**, 093101 (2012).
- <sup>23</sup>H. Tang, G. Meng, Q. Huang, Z. Zhang, Z. Huang, and C. Zhu, *Adv. Funct. Mater.* **22**, 218 (2012).
- <sup>24</sup>J. Jiang, K. Bosnick, M. Maillard, and L. Brus, *J. Phys. Chem. B* **107**, 9964 (2003).