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ABSTRACT

Nanoimprint lithography is conventionally used to transfer a pattern from a mold to a deformable and curable resist layer. Here we report a nanoimprinting technique to selectively transfer components of a pre-assembled nanostructure to a new substrate, while retaining the advantages of nanoimprint lithography such as low cost and high throughput. We use this technique to study metal particle roughness in Au "nanofinger" substrates, along with the effects of annealing to reduce roughness, and the impact of annealing on the Surface Enhanced Raman Scattering (SERS) signal. The nanofinger substrates consist of Au-coated polymer pillars arranged to collapse into a designed assembly. Upon exposure to a volatile liquid and subsequent drying, microcapillary forces pull the pillars and their metal caps together into the designed structure. Successful transfer was achieved using the concept of template stripping via cold welding using a normal nanoimprinting process with no resist layer but under appropriate pressure to ensure even and complete transfer of all the nanostructures. Particle roughness was not found to be a significant factor in SERS from naonfinger substrates as annealing did not increase the observed Raman intensity.

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1. INTRODUCTION

Nanofabrication is a rapidly expanding field, with new techniques and applications being discovered at an amazing pace in diverse fields such as plasmonics,[1,2] data storage[3-5] and biology.[6,7] A variety of methods are available to generate nanoscale patterns and particles, which can be split into two main categories, top-down and bottom-up approaches. Resolution limits of top-down approaches such as EUV and electron-beam lithography are continually improving,[8] but still face some fundamental limits.[4] In addition, direct write processes like e-beam lithography are expensive and time consuming. This limits there general application to mold or mask fabrication, and the incorporation of additional processes such as nanoimprint lithography is necessary to achieve economic mass production.[9] Bottom-up approaches are often capable of rapidly generating patterns with nanometer scale features, sometimes over large areas, by relying on self-assembly.[10,11] However, it can be difficult to tailor these processes to form the exact spacing and geometric structure desired.[12]

Even when fabrication of structures with appropriate dimensions is achieved, some important considerations remain. For example, the roughness and grain size of metals can play an important role in their plasmonic performance.[13,14] However, some studies have suggested that surface roughness may not play an important role in some plasmonic applications, such as Surface-Enhanced Raman Spectroscopy (SERS).[15] Other SERS research has focused on the intense electromagnetic field enhancement found when two or more metal nanoparticles are brought together with gaps on the order of a few nanometers.[16-20] On this scale, the roughness of the particles can have a considerable impact on the actual gap between two particles, so it would be surprising if this has no effect. However, the discussion of roughness effects has so far been largely theoretical, so experimental studies are needed to resolve the issue.

In this paper, we discuss the further development of a fabrication technique for generating metal particle assemblies resting on polymer pillars with designable symmetry and nanometer scale features using a combination of top down and bottom up fabrication approaches.[21] These arrays have proven to be flexible[22] and powerful SERS substrates,[23] suggesting the name "nanofingers" due to their tendency to trap molecules in SERS hot spots. However, there is still much to be learned about their performance, such as the effects of surface roughness. The surface roughness of the metal particles remains difficult to resolve in the SEM because they sit on top of non-conducting polymer pillars. While we can assume that is similar to that of the underlying film, which appears to have significant roughness and a relatively small grain size, we can observe the metal particle structure more directly by transferring them off of the pillars onto a conducting substrate. This transfer technique is an expansion on a previous study on template stripping by cold welding.[24] While template stripping is often used to generate ultra-flat surfaces,[25] expanding this technique to the transfer of patterned metal particle assemblies opens up new possibilities for incorporating plasmonic particles into devices. Finally, we will examine the effects of reducing metal roughness in Au nanofinger substrates through low temperature annealing.

2. EXPERIMENTS AND RESULTS

The starting point for the experiments described in this report is an array of flexible polymer pillars fabricated using a combination of e-beam lithography, reactive ion etching, and nanoimprint lithography in a process described previously.[21] An array of metal particles is formed on top of these pillars by depositing a thin film in an e-beam evaporator. The pillars have a height and diameter ranging from 400-700 nm and 100-170 nm, respectively and are composed of the UV resist used in the nanoimprint process.[26] This high aspect ratio is achieved due to the siloxane backbone formed during the curing process,[27] but enough flexibility remains that these metal-capped pillars collapse into predefined geometries when exposed to an evaporating liquid due to microcapillary forces.[28] Furthermore, when molecules such as *trans*-1,2-bis(4-pyridyl)ethylene (BPE) are included in this solution, they can become trapped between the particles.[22] This is particularly interesting for SERS applications, where locating analyte molecules precisely at the "hot spots" that occur when metal particles are brought into close proximity is important but often challenging. It is also interesting to note that this molecular trapping can be used to modify the gap size, as has previously been reported for DNA[29,30] and cucurbit[n]urils.[16]

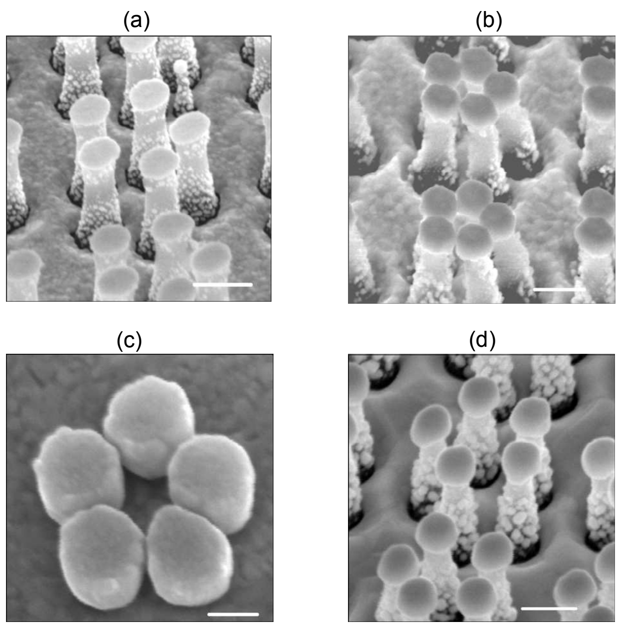

Figure 1. SEM images taken at a tilt of 35° of (a) Au-capped polymer pillars before closing, (b) Au capped polymer pillars after closing by exposing to ethanol and drying, (c) Au metal particles transferred to an Au-coated Si substrate and (d) Au-capped polymer pillars after annealing at 300 °C for 35 minutes. The scale bars are 200 nm in (a), (b) and (d) and 100 nm in (c).

The surface roughness of Au particles is examined in an FEI Sirion XL30 SFEG scanning electron microscope (SEM) and shown in Figure 1, but is difficult to resolve in the as fabricated state shown in Figure 1a. However, the roughness of the underlying film implies that there is significant roughness in the metal caps themselves. To confirm this, metal particles were transferred off of the polymer posts onto a conducting substrate. A thin Au film was deposited onto a Si substrate in an e-beam evaporator. The Au-capped pillar template and Au-coated substrate are then pressed together in a nanoimprinting tool for about 12 hours, as shown in the schematic in Figure 2. While cold welding has been demonstrated at extremely low pressure in ultra-high vacuum (UHV) conditions, our nanoimprinting does not achieve UHV conditions,[31] so a pressure of 150 psi was applied to the backside of the pillar template to ensure transfer. The image shown in Figure 1c confirms that the particle roughness is similar to that observed in the underlying film.

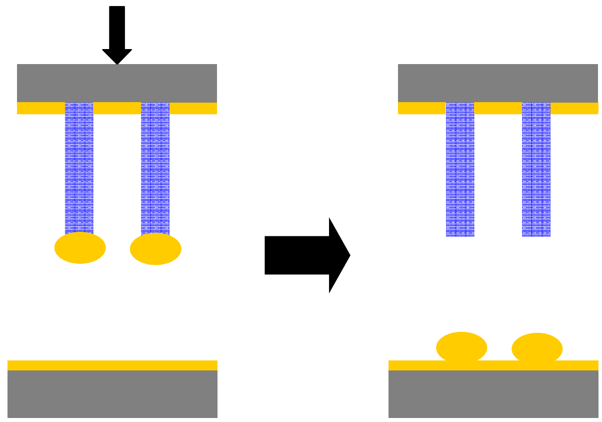

Figure 2. Illustration of method to transfer metal nanoparticles to a new substrate using metal-metal cold welding.

To reduce the Au particle roughness, the pillar template was annealed in a furnace with a nitrogen flow rate of 25 sccm. As shown in Figure 1, annealing at 300 °C for 1 hr was sufficient to significantly reduce the Au roughness in the nanofinger samples. Annealing for longer time or at higher temperature causes the underlying film to bead up, making comparison to the original geometry more difficult. Some further examples of the negative effects of annealing on the polymer pillars are shown in Figure 3. Annealing at elevated temperatures of 390 °C or more led to significant shrinkage and instability of the polymer pillars, as can be seen in the narrow necks and tilting of the pillars in Figure 3a. Even annealing at lower temperature can lead to increased polymer stiffness, leading to unreliable pillar closing when exposed to ethanol in the normal experimental procedure.

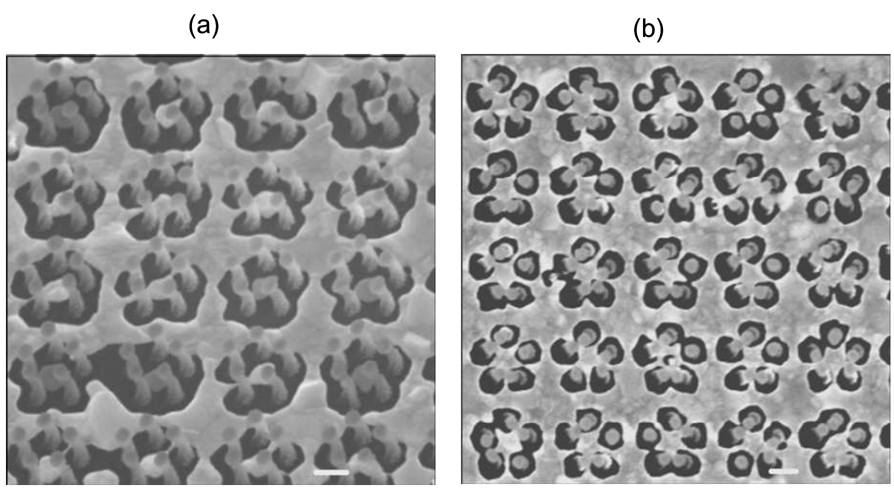

Figure 3. SEM images of Au-capped polymer pillars (a) annealed at 390 °C for 100 minutes and (b) 306 °C for 35 minutes followed by finger closing. Scale bars are 200 nm.

The effect of annealing to reduce roughness of the Au particles is assessed by measuring their SERS performance using a standard raman active molecule, *trans*-1,2-bis(4-pyridyl)ethylene (BPE). As described previously, BPE is an ideal molecule for these pillar structures as the two pyridine rings at either end of the molecule bind well to Au, often bridging the gap between two particles in the closed state, locating them optimally for SERS enhancement.[22] For the SERS measurements presented in Figure 4, the pillar templates were soaked in 1 mM BPE in ethanol for 10 minutes, allowed to air dry causing the nanofinger closing, and then rinsed with ethanol to remove physically adsorbed molecules. The annealed pillars show significantly reduced performance as compared to unannealed structures, at least in part due to suboptimal closing behavior. Since the annealed nanofingers close in a dimer pattern, the results of unannealed dimer nanofingers are displayed in in Figure 4 and show more than double the Raman intensity of the annealed nanofingers. There are a number of factors that could explain this change. For example, it is possible that a small degree of roughness enhances the local SERS hot spots, and annealing to remove this roughness is detrimental to performance. Another possibility is that changes to the underlying Au film during the annealing process, such as the enlarged voids due to Au diffusion see in Figure 3 and Figure 4, play an important role in the plasmon resonance that is central to the SERS enhancement effect. Finally, the size and shape of the metal particles is observed to change in the annealing process, which can modify the plasmonic response of the nanofinger substrate. Further study would be necessary to determine the true cause of the reduced performance, but we can conclude that the as deposited Au roughness does not substantially degrade SERS performance.

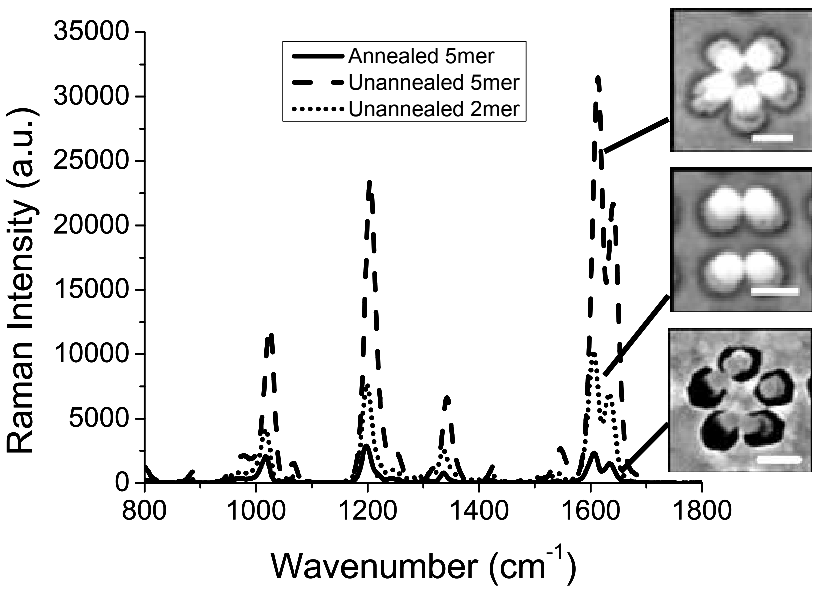

Figure 4. SERS spectra of Au nanofinger pentamers annealed at 306 ^{o}C for 35 minutes compared with unannealed Au nanofinger dimers and pentamers. Scale bars are 200 nm.

4. CONCLUSIONS

We studied the effect of Au roughness on SERS performance in nanofinger substrates by low temperature annealing. Particle roughness was not found to play a significant role in the SERS intensity of metal particles in close proximity, while annealing had a number of unexpected effects on the substrate. Furthermore, a transfer technique similar to template stripping by cold welding was presented as a method to study metal particle roughness. This transfer technique has potential for wide ranging applications, as it represents a system for incorporating plasmonic nanoparticle assemblies in an arbitrary new environment with no chemical modifications.

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[1] Stewart, M.E., Anderton, C.R., Thompson, L.B., Maria, J., Gray, S.K., Rogers, J.A. and Nuzzo, R.G., "Nanostructured plasmonic sensors," Chem. Rev**.** 108, 494-521 (2008).
[2] Atwater, H.A. and Polman, A., "Plasmonics for improved photovoltaic devices," Nat. Mater. 9, 205-213 (2010).
[3] Strukov, D.B., Snider, G.S., Stewart, D.R. and Williams, R.S., "The missing memristor found," Nature 453, 80-83 (2008).
[4] Yang, X.M., Xiao, S., Wu, W., Xu, Y., Mountfield, K. and Rottmayer, R., "Challenges in 1 Teradot/in.^{2} dot patterning using electron beam lithography for bit-patterned media," J. Vac. Sci. Technol. B 25, 2202-2209 (2007).
[5] Yang, X., Wan, L., Xiao, S., Xu, Y. and Weller, D.K., "Directed block copolymer assembly versus electron beam lithography for bit-patterned media with areal density of 1 Terabit/inch^2 and beyond," ACS Nano 3, 1844-1858 (2009).
[6] Xu, C., Mu, L., Roes, I., Miranda-Nieves, D., Nahrendorf, M., Ankrum, J.A., Zhao, W.A. and Karp, J.M., "Nanoparticle-based monitoring of cell therapy," Nanotechnology 22, 494001 (2011).
[7] Guo, P.X., "The emerging field of RNA nanotechnology," Nature Nanotechnology 5, 833-842 (2010).
[8] Gronheid, R., Younkin, T.R., Leeson, M.J., Fonseca, C., Hooge, J.S., Nagus, K., Biafore, J.J. and Smith, M.D., "Extreme-uvltraviolet secondary electron blur at the 22-nm half pitch node," J. Micro/Nanolith. MEMS MOEMS 10, 033004 (2011).
[9] Yang, XM., Xu, Y., Seiler, C., Wan, L. and Xiao, S., "Toward 1 Tdot/in.2 nanoimprint lithography for magnetic bit-patterned media: opportunities and challenges," J. Vac. Sci. Technol. B 26, 2604-2610 (2008).
[10] Jiang, P. and McFarland, M.J., "Wafer-scale periodic nanohole arrays templated from two-dimensional nonclose-packed colloidal crystals," J. Am. Chem. Soc. 126, 3710-3711 (2005).
[11] Cui, L., Zhang, Y., Wang, J., Ren, Y., Song, Y. and Jiang, L., "Ultra-fast fabrication of colloidal photonic crystals by spray coating," Macromol. Rapid Commun. 30, 598-603 (2009).
[12] Duan, H., Hu, H., Kumar, K., Shen, Z. and Yang, J.K.W., "Direct and reliable patterning of plasmonic nanostructures with sub-10-nm gaps," ACS Nano 5, 7593-7600 (2011).
[13] Logeeswaran, V.J., Kobayashi, N.P., Islam, M.S., Wu, W., Chaturvedi, P., Fang, N.X., Wang, S.-Y. and Williams, R.S., "Ultrasmooth silver thin films deposited with a germanium nucleation layer" Nano Lett. 9, 178-182 (2008).
[14] Yuan, H.-K., Chettiar, U.K., Cai, W., Kildishev, A.V., Boltasseva, A., Drachev, V.P. and Shalaev, V.M., "A negative permeability material at red light," Opt. Express 15, 1076-1083 (2007).
[15] Hao, E. and Schatz, G.C., "Electromagnetic fields around silver nanoparticles and dimers," J. Chem. Phys. 120(1) 357-366 (2004).
[16] Taylor, R.W., Lee, T.-C., Scherman, O.A., Esteban, R., Aizpurua, J., Huang, F.M., Baumerg, J.J. and Mahajan, S., "Precise subnanometer plasmonic junctions for SERS within gold nanoparticle assemblies using Cucurbit[n]uril "glue"" ACS Nano 5, 3878-3887 (2011).
[17] Xu, H., Aizpurua, J., Kall, M. and Apell, P.; "Electromagnetic contributions to single-molecule sensitivity in Surface-Enhanced Raman Scattering," Phys. Rev. E 62, 4318-4324 (2000).
[18] Wustholz, K.L., Henry, A.-L., McMahon, J.M., Freeman, R.G., Valley, N., Piotti, M.E., Natan, M.J., Schatz, G.C. and Van Duyne, R.P., "Structure-activity relationships in gold nanoparticle dimers and trimers for Surface-Enhanced Raman Spectroscopy," J. Am. Chem. Soc. 132, 10903-10910 (2010).
[19] Campden, J.P., Dieringer, J.A., Wang, Y.M., Masiello, D.J., Marks, L.D.,, Schatz, G.C. and Van Duyne, R.P., "Probing the structure of single-molecule Surface-Enhanced Raman Scattering hot spots" J. Am. Chem. Soc. 130, 12616-12617 (2008).
[20] Danckwerts, M. and Novotny, L., "Optical frequency mixing at coupled gold nanoparticles," Phys. Rev. Lett. 98, 026104-1-4 (2007).
[21] Hu, M., Ou, F.S., Wu, W., Naumov, I, Li, X., Bratkovsky, A., Williams, R.S. and Li, Z., "Gold nanofingers for molecule trapping and detection," J. Am. Chem. Soc. 132, 12820-12822 (2010).
[22] Kim, A., Ou, F.S., Ohlberg, D.A.A., Hu, M., Williams, R.S. and Li, Z., "Study of molecular trapping inside gold nanofinger arrays on Surface-Enhanced Raman Substrates," J. Am. Chem. Soc. 133, 8234-8239 (2010).
[23] Ou, F.S., Hu, M., Naumov, I., Kim, A., Wu, W., Bratkovsky, A., Li, X., Williams, R.S. and Li, Z., "Hot-spot engineering in polygonal nanofinger assemblies for Surface Enhanced Raman Spectroscopy," Nano Lett. 11, 2538-2542 (2011).
[24] Blackstock, J.J., Li, Z. and Jung, G.-Y., "Template stripping using cold welding," J. Vac. Sci. Technol. A 22, 602-605 (2004).
[25] Hegner, M., Wagner, P. and Semenza, G., "Ultralarge atomically flat template-stripped Au surfaces for scanning probe microscopy," Surf. Sci. 291, 39-46 (1993).
[26] Jung, G.-Y., Ganapathiappan, S., Ohlberg, D.A.A., Olynick, D.L., Chen, Y., Tong, W.M. and Williams, R.S., "Vapor-phase self-assembled monolayer for improved mold release in nanoimprint lithography" Langmuir 21, 1158-1161 (2005).
[27] Jung, G.Y., Ganapathiappan, S., Ohlberg, D.A.A., Olynick, D.L., Chen, Y., Tong, W.M., and Williams, R.S., "Fabrication of a 34 x 34 crossbar structure at 50 nm half-pitch by UV-based nanoimprint lithography," Nano Lett. 4, 1225-1229 (2004).
[28] Segawa, H., Yamaguchi, S., Yamazaki, Y., Yano, T., Shibata, S. and Misawa, H., "Top-gathering pillar array of hybrid organic-inorganic material by means of self-organization," Appl. Phys. A 83, 447-451 (2006).
[29] Alivisatos, A.P., Johnsson, K.P., Peng, X., Wilson, T.E., Loweth, C.J., Bruchez Jr., M.P. and Schultz, P.G., "Organization of 'nanocrystal molecules' using DNA," Nature 382, 609-611 (1996).
[30] Lim, D.-K., Jeon, K.-S., Kim, H.M., Nam, J.-M. and Suh, Y.D., "Nanogap-engineerable Raman-active nanodumbbells for single molecule detection," Nat. Mater. 9 60-67 (2010).

[31] Pethica, J.B. and Tabor, D., “Contact of characterized metal surfaces at very low loads: deformation and adhesion,” Surf. Sci. 89, 182-190 (1979).