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Hollow metallic pyramid plasmonic structures fabricated by direct laser writing and electron beam evaporation

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ABSTRACT

Here we report a method that enables the fabrication of hollow metallic pyramid plasmonic structures on free-standing copper grids, which were fabricated by direct laser writing lithography followed by noble metal deposition. Gratings on the faces of these pyramids can translate incident light into plasmons that propagate toward the apex of the noble metal coated pyramids. Surface Enhanced Raman Scattering (SERS) measurements confirm that these hollow metallic pyramid structures have superior properties to the planar metal surface and the degree of enhancement can be tuned by the size and geometry of the fabricated structures, which potentially could be used for better understanding of surface enhanced plasmonics on free-standing three dimensional structures as well as find application in the research field of SERS.

1. Introduction

Direct laser writing (DLW), a technique that based on two-photon polymerization (2PP), is a well established maskless technology for the realization of arbitrary three-dimensional (3D) micro-/nanostructures. Such a technique holds the promise of fabricating large-area structures rapidly and cheaply. Recently, various 3D structures have been fabricated by DLW, including photonic crystals [1,2], metamaterials [3], chip-scale interconnects [4], magnetic helical micromachines [5], cell-culture scaffolds [6] and so on.

Surface plasmons, a kind of electromagnetic surface waves, are coherent electron oscillations that exist and sustained by density fluctuations of free electrons at a metal interface. Sub-wavelength periodic metallic structures exhibit unique surface plasmon properties and have potential applications in nanophotonic devices, data storage, and biosensors [7–10]. Metallic pyramids, which can be used to concentrate electromagnetic field at the tip apex, have attracted particular interest as SERS substrate with excellent property [11]. Tapered metallic tapered waveguides were reported to be used as photonic–plasmonic device that are fully compatible with atomic force microscopy and Raman spectroscopy [12,13]. However, fabrication of metallic pyramids structures for SERS application has not been reported based on DWL technique.

In this paper, we develop a method to fabricate hollow metallic pyramids structures on copper grids utilizing direct laser writing lithography followed by electron beam evaporation of noble metal. Pyramid structures with various aspect ratios were fabricated followed by evaporation of Ag thin film with different thicknesses. p-thiocresol molecules were dispersed on different surface structures and the Ag coated pyramid structures showed much enhanced SERS properties. Moreover, it was found that the intensity of the Raman peaks can be tuned by the surface details of the pyramids and related mechanism has been discussed.

2. Experimental details

The schematic diagram of the fabrication process of metallic hollow pyramid structures on a free-standing copper grid is illustrated in Fig. 1(a), which includes two main steps, the fabrication of polymer 3D structures on TEM copper grid and the metal evaporation by electron beam evaporator. From Fig. 1(b), we can see the relationship between the achievable ultimate height (H) of the pyramid and the ratio defined by the layer distance over the line distance ($\Delta Z/\Delta X$). D denotes the side length of the pyramid structure. With increasing the ratio of $\Delta Z/\Delta X$, the height of the fabricated pyramid increased gradually, which could result a sharper pyramid top with a larger tapering angle. In this experiment, the laser beam was scanned in such a manner: firstly, the beam was set to travel a square line track at zero height (on the substrate/resist interface), then a second laser beam scanning was performed inside the first square line track with a shift distance of ΔX, and the side width was reduced $2\Delta X$, this is to avoid collapsing of the 3D structure which was very likely to happen if only one scanning was done.

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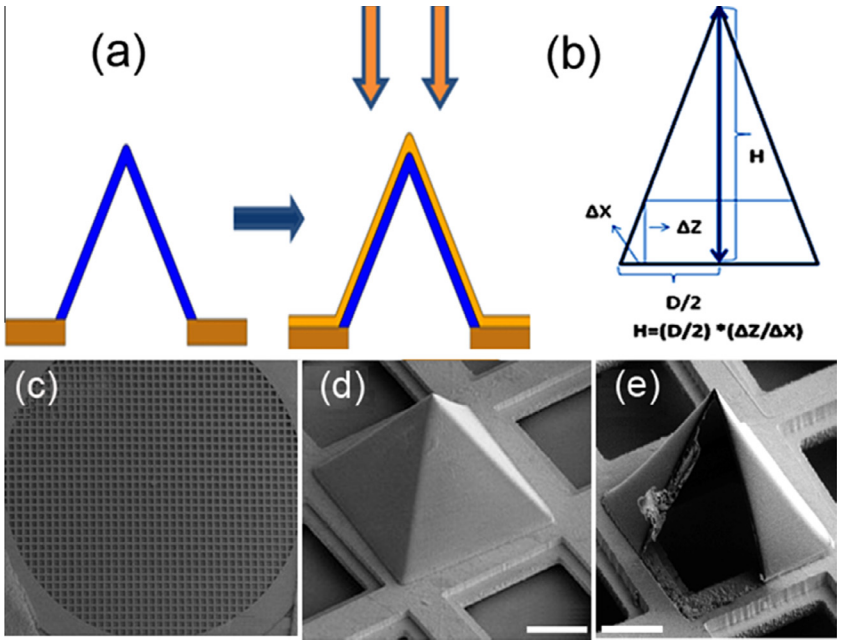

Fig. 1. (a), (e) The schematic diagram illustrates the main fabrication process of metallic hollow pyramid structures on a copper grid by direct laser writing; (b) the relationship between the ultimate achievable pyramid height (H) and the layer distance ΔZ and the line distance ΔX as shown in the diagram; (c) an SEM top-view image of a copper grid; (d) side-view SEM images of the fabricated hollow polymeric pyramids coated with a layer of 40 nm Ag and that with a broken wall to see inside of the pyramid, respectively showing its hollow nature. The scale bar is 20 μm.

Then, the beam focusing point was shifted over the substrate/resist interface with a distance of ΔZ, and another scanning was done just inside it with a shift distance of ΔX, and the side width further reduced $2\Delta X$. Thus on each layer, the beam was scanned along a square line track twice, with a line width reduced by $2\Delta X$, and between two neighboring layers, the focusing point of the beam was shifted away from the substrate/resist interface by ΔZ. For 3D hollow pyramid structure fabrication, firstly copper grid was stuck on the glass slide to serve as the supporting substrate (as shown in Fig. 1(c)) and the glass slide were fixed onto the sample holder, then a droplet of negative photoresist (IP-L) (supplied by Nanoscribe GmbH) was dropped on a copper grid followed by putting the sample holder to the piezo stage for exposure. A Direct Laser Writing (DLW) system (supplied by Nanoscribe GmbH) was employed, of which the fs laser has a center wavelength of 780 nm and the lateral fabrication feature sizes are achievable at 120 nm in 2D and 150 nm in 3D.

For surface enhanced Raman scattering (SERS) properties measurement, 10^{-4} M p-thiocresol was dispersed on Ag planer film, the IP-L photoresist pyramid and the Ag coated hollow pyramid structures with various heights, respectively. The wavelength of the excitation laser used for SERS measurements is 532 nm and the laser power on the sample is about 0.9 mW in the focus area, the spectra acquisition time is 10 s and a 50 X objective lens was used for focusing the laser on the top. The laser beam was normal incident onto the substrate, that is, parallel to the surface normal for SERS spectra collection.

3. Result and discussion

Fig. 1(d) and (e) shows the side view scanning electron microscope (SEM) micrographs of the fabricated hollow polymeric pyramids that coated with a layer of 40 nm thick Ag, sitting on a copper grid. From the break in the side wall of the pyramid shown in Fig. 1(e), it can be seen that the structure is actually hollow in nature as expected. The using of the copper grid is of great importance, for example it provides the advantage of no loss of the incident light when it enters or passes through the pyramid structures. Meanwhile, using copper grid as supporting substrate, charging effect can be easily avoided and no additional metal deposition is required in the later process of geometry and surface morphology examination by SEM, contrast to other transparent substrates, e.g. quartz and sapphire. Moreover, the use of hollow copper grids allows for the metallic coatings of the inner surface of the hollow structures; the transmission of light; and decorating the inside and outside surface. The reasons of choosing hollow rather than solid structures are twofold: firstly, polymerization of a solid structure could save much time than that required to make a solid structure; secondly, metal layers can be formed on both sides of the hollow structures, which could provide more opportunities for advanced studies of surface enhanced plasmonics [14,15].

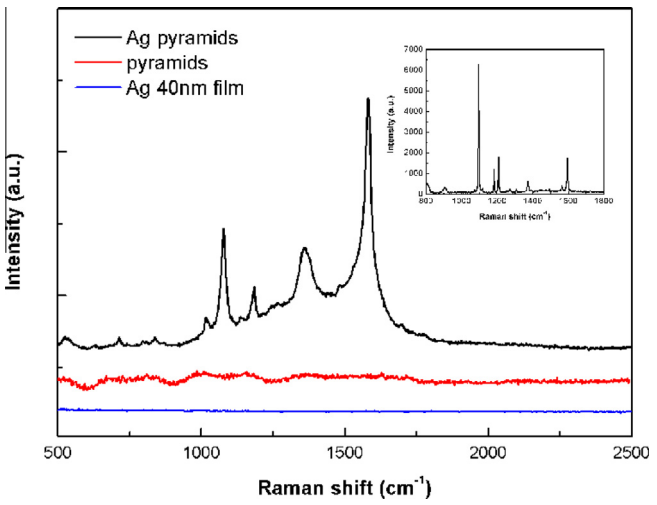

Fig. 2. Raman spectra of p-thiocresol (C_7H_8S) on planar Ag coated glass substrate (blue curve), polymer pyramid structure (red curve) and Ag coated pyramid (black curve). In the inset is the Raman spectrum of p-thiocresol (C_7H_8S) aquaous solution. (For interpretation of color in this Figure, the reader is referred to the web version of this article).

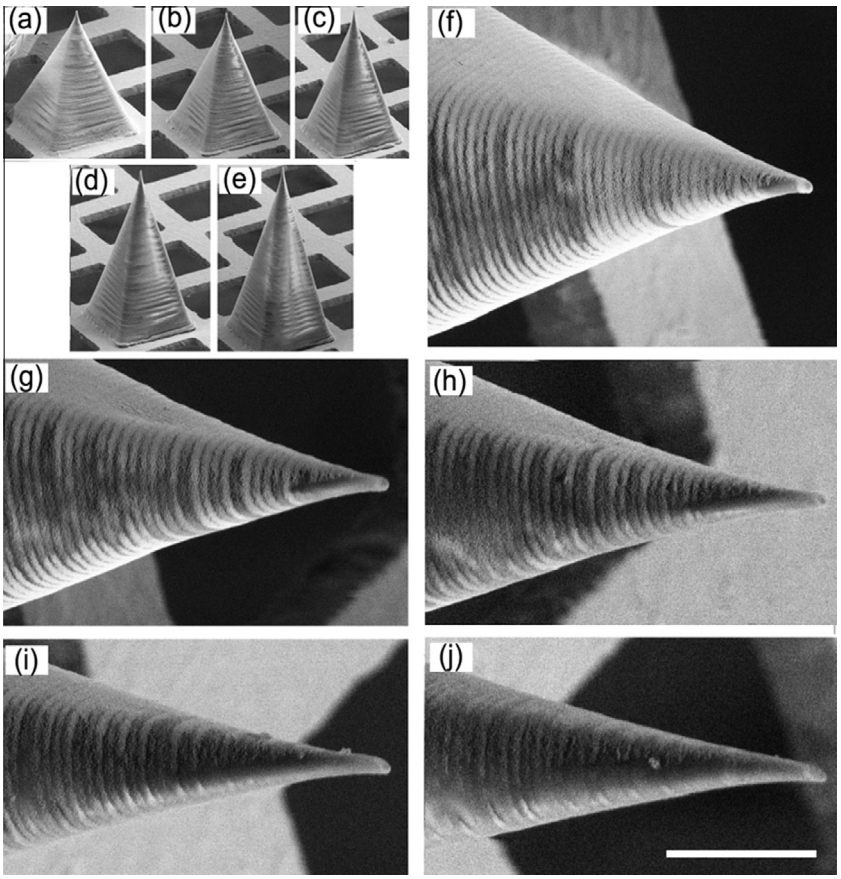

Fig. 3. The side-view SEM images of hollow silver coated pyramid structure that is 50, 60, 70, 80, and 90 μm in height for (a–e), respectively; (f–j) shows the corresponding top details of the pyramid structures shown in (a–e). The scale bar is 5 μm.

Fig. 2 shows the SERS spectra with the laser normal incident to the substrate surface, obtained from a planar Ag coated glass substrate, polymeric pyramid and Ag coated polymeric pyramid with a layer of p-thiocresol molecules. The planar silver film shows no SERS signal, the polymeric pyramid has slightly enhanced but very weak SERS intensity and the Ag coated polymeric pyramid shows significant enhancement. Such observation confirmed that there is excitation of surface plasmons from the incident light, occurring via the tapered surface of pyramid structures. In the inset is the Raman spectrum of p-thiocresol molecules with two strong characteristic vibration peaks at 1075 and 1585 cm^{-1}. The Raman peak positions on these obtained spectra indicate that the SERS spectra are truly from the p-thiocresol (C_7H_8S) molecules. Ag pyramid exhibit higher Raman enhancement effect, which could be attributed to the nature of the grating-shaped metal material itself. Ag was selected as the metallic surface layer is due to its relative strong combining strength with sulfur atom in the mercapto group of the p-thiocresol, compared with Au or Cu atoms. In addition, we would like to point out that the Ag pyramid structure has a periodic rough surface, which is conducive to the pyramid surface Plasmon bounding and coupling, further benefit to electromagnetic field enhancement around the pyramid.

Therefore, Ag pyramids showed better Raman enhancement effect, verifying that the pyramid structure can enhance molecular Raman signal intensity.

To explore the structural effect on the SRES behavior, the hollow Ag coated pyramids with height of 50, 60, 70, 80 and 90 μm, side length of 24 μm, were fabricated, the side-view SEM images of these structures are shown in Fig. 3(a–j). The geometric details of these values are listed in Table 1. As can be seem from the images

Table 1
Experimental parameters and geometry of the fabricated the pyramid structures.

H (μm)	ΔZ (μm)	ΔX (μm)	$\Delta Z/\Delta X$	$\Delta h_{exp.}$ (μm)	R_{tip} (μm)
50	0.365	0.08	4.56	0.29	0.20
60	0.441	0.08	5.14	0.30	0.22
70	0.515	0.08	6.43	0.33	0.21
80	0.584	0.08	7.30	0.35	0.22
90	0.658	0.08	8.27	0.39	0.21

that with increasing ΔZ, the surface roughness also increased. That is with a fixed ΔX and bottom side width of the pyramid, the actual height Δh between each layer also varied. The geometry at the tips of these pyramids is actually conical rather than pyramidal in shape. However, the radius of curvature is more or less the same, it is around 0.005 nm^{-1}.

Fig. 4 is the corresponding SERS spectra. It can be seen that the intensity of the Raman peaks increased dramatically with the height of the pyramid structures, which mainly affected by the periodicity of the "staircase" feature of the tapered sidewall of the pyramid as can be seen from the images in Fig. 3. The pyramid structures shown in Fig. 3 were achieved by setting different layer distance, which is the step size in Z direction with the side length of the pyramid fixed at 24 μm, thus the height were different, consequently, changing the surface morphology and periodicity of the Ag surface. It has been reported that analyzed molecules located in a close vicinity of the surface of a sharp metal tip could lead to obvious Raman enhancement [16,17], which can be interpreted that with increasing the height, the effect of focusing at the apes becomes more and more obvious, thus enhanced the SERS signal. The mechanism behind such phenomenon is mainly due to the

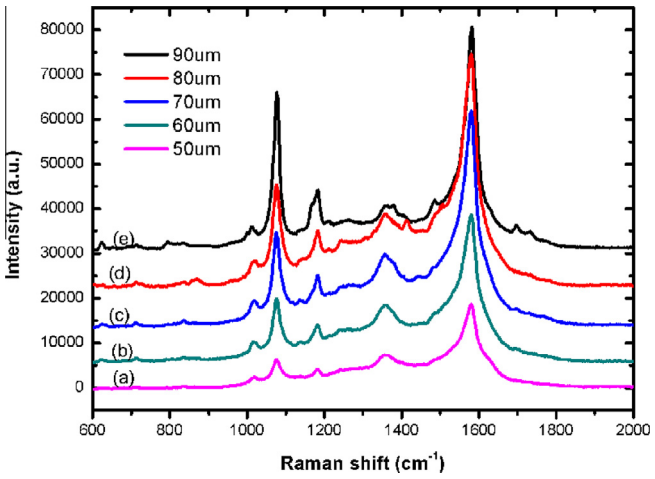

Fig. 4. The SERS spectra of p-thiocresol molecules adsorbed on Ag coated pyramid structure as shown in Fig. 3(a–e), respectively, showing the geometry related Raman peak intensity.

excitation of surface plasmons from incident light occurs via a grating-coupling mechanism [15]. Such phenomena have also been observed in tapered 3D structures, and photonic crystal cavity and tapered waveguide hybrid structures [10,12,13].

4. Conclusion

We reported the significant surface enhancement of hollow metal structures obtained via direct laser writing and electron beam evaporation. SERS spectra were obtained on samples with p-thiocresol adsorbed on planer silver films, IP-L photoresist pyramids and Ag coated hollow pyramids. Experiment results indicate that the pyramid structure can provide efficient generation of SERS. The extend of the enhancement can be modulated by structural details of the pyramids, here mainly tuned by simply changing the layer distance for pyramid fabrication, which resulted in surface modulated SPP for efficient coupling to molecules.

Acknowledgments

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