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Achieving Continuous Sub-100-nm Plasmonic Nanowires as Long as Centimeters

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Abstract

Gold nanowires with a width smaller than 100nm and a length in the order of centimeters have been fabricated using colloidal gold nanoparticles. The dewetting of the colloidal solution of gold nanoparticles on the photoresist master grating with a small duty cycle is utilized to limit the amount of gold nanoparticles that are confined into the grating grooves after spin-coating, which favors the achievement of narrow gold nanowires. During the subsequent annealing process, the sublimation of the ligands covering the gold nanoparticles, the melting of the gold nanoparticles, and the removal of the photoresist master grating take place sequentially as the annealing temperature is increased from room temperature to about 450ºC. Thus, high-quality gold nanowires are produced with excellent continuity in a large scale and excellent plasmonic response. These kinds of structures are important for sensitive biosensors with flexible dynamics in both the dimensions and the spectroscopic response.

Introduction

Plasmonic nanostructures have a variety of applications in sensors [1-3], spectroscopic [4,5] and optoelectronic [6,7] devices. Metamaterials [8-12] have developed into one of the most focused research fields in nanooptics and nanomaterials and attract extensive research interests. This is not only due to the rich physics in this kind of materials, but also because they are closely related to some new techniques in the control of terahertz radiation, solar power management, optical cloaking, antenna systems, etc. Thus, the controllable fabrication of the plasmonic nanostructures in a practically applicable scale and spatial resolution is essential for realizing their special functions, for example, in multi-channel biosensors and solar-cell devices.

Solution-processible techniques [13,14] using colloidal gold nanoparticles have shown a number of advantages of simplicity, low cost, high efficiency, and large-area homogeneity for the fabrication of plasmonic nanostructures over the conventional techniques that may involve electron-beam lithography, [15,16] ion-beam etching, [17,18] and nano-imprinting [19,20]. These techniques have evolved into a number of well-established fabrication schemes to realize various patterned [21,22] and unpatterned [23,24] metallic photonic structures.

However, annealing process has to be employed to remove the ligands covering the gold nanoparticles and the photoresist master grating, and to melt the gold nanoparticles to make them fused into nanowires or nanocylinders. The molten gold tends to spread on the surface of the substrate due to its wetting properties [13] and its self-gravity. Furthermore, higher annealing temperature is preferred to produce high-quality gold nanowires. However, the gold nanowires tend to be broken into segments when the annealing temperature is higher than 450°C. As a result, the width of each segment even becomes larger again, because the duty cycle of gold nanowire segments on each grating line becomes smaller. Thus, gold nanostructures with smaller widths or diameters than 150 nm have rarely been demonstrated in our previous reports on one- or two-dimensional patterned structures. This not only restricts the dynamic range of the dimensions of the fabricated nanostructures and the optical response of particle plasmon resonance, but also limits their applications in biosensors with small sensing volumes and the photonic devices requiring high spatial resolution.

In this work, we reduce the duty cycle of the photoresist master grating and make use of the dewetting of the colloidal solution of gold nanoparticles on the surface of photoresist in the fabrication of gold nanowire gratings. Continuous gold nanowires narrower than 100nm and longer than 1cm have been achieved. Reducing the width of gold nanowires is based on the following considerations: (1) In sensor applications, the narrower gold nanowires imply smaller sensing volume and higher sensitivity in the plasmonic response to the change in the environmental refractive index. (2) It is a challenge to apply gold nanostructures in organic solar cells to enhance light scattering or plasmon-induced localized field, because particle plasmon resonance of gold nanostructures shifts to the red-IR spectral range after being coated with organic semiconductors, whereas, the absorption of the organic semiconductors generally ranges from the UV to the green spectrum. Narrower gold nanowires may correspond to blue-shifted particle plasmonic resonance, enabling possible spectral overlap between particle plasmon resonance and the absorption spectrum of the active medium. (3) Higher spatial resolution implies possible miniaturization of the nanodevices, which is important for multi-channel sensors and optical integration.

Possible approaches to achieve high-resolution (<100 nm) gold nanostructures

Resolution of the gold nanostructures here refers to the width of the gold nanowires or the diameter of the gold nanocylinders (nanorods, nanoholes, nanodisks, etc.). Using smaller period or reducing the duty cycle are two straightforward approaches to achieve higher-resolution gold nanowires arranged in patterned structures using solution-processible fabrication techniques. However, reducing the period of the patterned structures is limited by the reliable resolution of the

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recording medium (e.g., photoresist) and by the laser wavelength used in interference lithography. In this work, S1805 photoresist is used as the recording medium and a He-Cd laser at 325nm is used as the UV light source. The grating period is limited to about 160nm by the laser wavelength provided that the photoresist has a higher resolution than this scale.

Figure 1 shows the procedures for the fabrication of patterned gold nanostructures using solution-processible gold nanoparticles. Gold nanoparticles are firstly synthesized chemically [25], which may be stored in the form of powders or dissolved in xylene with a concentration of 100 mg/ml and stored in the form of colloidal solution for later use. Then, the photoresist master grating is fabricated using interference lithography with designed period and optimized duty cycle. The colloidal solution of gold nanoparticles is spin-coated onto the finished master grating made of photoresist. Thereafter, the sample is heated in a Muffle furnace with the temperature increased from room temperature to 450°C at a speed of 0.25°C /s and the temperature is held at 450°C for about 20 minutes. In the final stage, the sample is cooled down to room temperature freely in the furnace.

Figure 2 shows the SEM image of the grating structures with a period of 180nm, where each grating line actually consists of isolated gold nanoislands with a diameter smaller than 50nm and the total area of the grating is larger than 1cm^2. The diameter of the gold nanoislands or the width of the grating lines is already close to the resolution limit of electron beam lithography. Furthermore, fabrication of such small plasmonic nanostructures into patterns larger than 1cm^2 in area is very difficult for the conventional techniques using electron-beam lithography or ion-beam etching. This indicates that the solution-processible method based on colloidal gold nanoparticles and interference lithography may be used to achieve high-resolution plasmonic nanostructures that cannot be realized by conventional techniques.

However, no continuous gold nanowires have been produced in the structures shown in Figure 2. This is because smaller period corresponds to smaller modulation depth and shallower grooves of the master grating structures, which have very limited capability to confine and hold sufficient amount of gold nanoparticles for the formation of continuous lines. Furthermore, the dewetting of the colloidal solution on the photoresist surface reduces further the amount of gold that

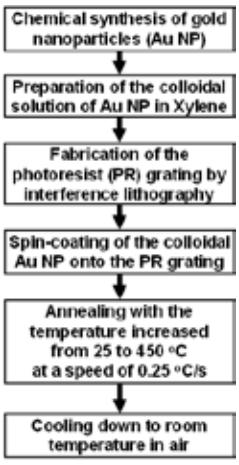

Figure 1: Experimental procedures for the fabrication of gold-nanostructured gratings using solution-processible gold nanoparticles.

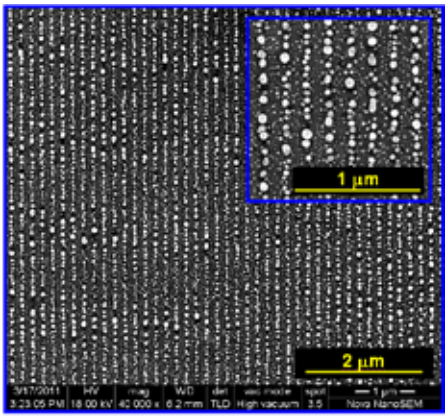

Figure 2: The SEM image of the patterned gold nanostructures with a grating period of 180 nm. Inset: an enlarged area.

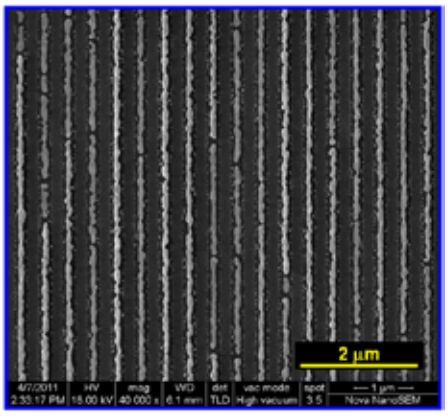

Figure 3: The SEM image of the grating of gold wires with high spatial resolution achieved through reducing the duty cycle.

remains on the grating surface and is available for being confined into the grooves. Therefore, in the annealing process the limited amount of gold is broken into islands due to the strong surface tension of the molten gold. Additionally, smaller grating period (Λ) implies larger separation angle (θ) between the two laser beams in the interference-lithography scheme for a given laser wavelength (λ) due to the relation of $\Lambda = \lambda / 2\sin(\theta / 2)$. However, a large separation angle not only results in an optical setup that is difficult to arrange for two-beam overlapping and for optical path length balancing, but also leads to seriously elongated laser spots in the overlapping area.

Thus, in the practical fabrication we actually adopted relatively larger grating periods in the range from 300 to 400nm and smaller duty cycles to achieve continuous gold nanowires with high spatial resolutions. The duty cycle can be easily changed by adjusting the exposure dose and the development time in the interference lithography process. A grating period larger than 300nm that can be easily realized makes easier and more reproducible the fabrication of the master grating.

Figure 3 shows a fabrication result of a gold-nanowire grating with a period of about 400nm and a duty cycle (grating line width over the period) of approximately 1:5. Thus, the gold nanowires have an average width of about 85nm. However, the homogeneity and continuity of each nanowire still need to be improved.

Actually, this kind of improvement may involve the optimization of a number of parameters: (1) the width and depth of the grating grooves, which is dependent on the grating period and the duty cycle; (2) the spin-coating speed of the colloidal solution; (3) the concentration of the colloidal solution of gold nanoparticles; (4) the annealing temperature and the temperature rising slope. For example, for the structures shown in Figure 3, a direct annealing temperature of about 450°C has been employed, which might be the main reason why the gold nanowires become irregular on the edges and tend to break into segments. Directing heating to about 450°C may evaporate the photoresist master grating and melt the gold nanoparticles almost simultaneously, the confinement of the molten gold suddenly becomes weak, leading to relatively more freely organization of the gold and reducing the regularity and homogeneity of the resultant nanowires. After a series of test experiments, the fabrication conditions have been optimized and a set of parameters as mentioned above have been obtained, as will be described in section 3.

Fabrication of sub-100nm gold nanowires with excellent continuity in centimeter scale

As have been mentioned above, a master grating written into the photoresist S1805 is firstly produced using the conventional scheme of interference lithography, where a He-Cd laser at 325nm is used as the UV laser source. The master PR grating is fabricated on the glass substrate that has an area of 20×20 mm^2 and is coated with a layer of indium-tin-oxide (ITO) as thick as 200nm. The same procedure as shown in Figure 1 is employed for this fabrication. The colloidal solution of gold nanoparticles with a concentration of 100mg/ml is then spin-coated onto the master PR grating at a speed of 2000rpm, where the chemically synthesized gold nanoparticles have a diameter ranging from 2 to 8nm and the ligands covering the gold nanoparticles are as long as 7nm [25]. The sample is annealed in a Muffle furnace with the temperature increased from room temperature to 450°C at a slope of about 0.25°C per second and the temperature is held at 450°C for more than 20 minutes. It should be noted that such a temperature-rising slope is essentially important for the precursor structures to experience a number of critical stages sequentially. Thus, the melting of the gold nanoparticles (at about 180°C) takes place after the sublimation of the ligands (at about 150°C). The photoresist is removed when the temperature is above 350°C. Gold nanoparticles larger than their original sizes after the above processes will be molten again completely when the temperature exceeds 400°C. Thus, homogeneous gold nanowires form after all of the molten gold fused together, as illustrated schematically in Figure 4. The temperature-holding at 450°C actually allows sufficient evaporation of the photoresist and sufficient melting of the gold nanoparticles with different sizes to be fused into high-quality nanowires.

However, to achieve high-resolution gold-nanowire structures, controlling the duty cycle and the depth of the grating grooves is of decisive importance. Under-exposure dose with short development time has to be employed in the interference lithography process, so that the resultant photoresist master grating is featured with small duty cycle (W/Λ) and small modulation depth (H), as shown in Figure 4. Obviously, the development does not necessarily reach the substrate. The following two mechanisms are essential for achieving continuous gold nanowires with a sub-100-nm width: (1) Under-exposure dose with short development time enables small volume of the grooves of the PR grating, leading to the small volume of the confined gold. (2) The dewetting of the colloidal solution on the photoresist reduces significantly the total amount of gold nanoparticles that are confined into the grating grooves. This can be understood by looking at the mechanisms illustrated schematically in Figure 4. Due to the narrow and shallow grating grooves and the dewetting of the colloidal solution on the PR surface, very limited amount of gold nanoparticles (Au NP) are naturally confined into the grooves, whereas, almost no gold nanoparticles remain on the top surface of the PR grating, as shown in Figure 4(a). In the first-stage annealing process, as the temperature increases the ligands sublimate first at about 150°C and the bare gold nanoparticles are left on the bottom of the grating grooves, as shown in Figure 4(b). The total volume of the gold nanoparticles is reduced to about 1/30 that before being annealed. This can be understood if assuming that the gold nanoparticles have an average diameter of 6 nm and they are covered with ligands as long as 7nm. Thus, the volume of the gold nanoparticles will be reduced to $\left(\frac{3}{10}\right)^3 \approx 1/37$ their original size before the ligands are removed, where the ligands shorter than 7 nm are assumed to be rigid. When the temperature is higher than 180°C, the gold nanoparticles begin to become molten and the smaller gold nanoparticles are fused into larger ones, as shown in Figure 4(c). This is based on the consideration that the gold nanoparticles have a size distribution and smaller ones are molten earlier at lower temperatures than the larger ones. It should be noted that the above mentioned mechanisms actually determine that very limited amount of gold are available for further processing, which actually determines the thickness of the gold nanowires. When the temperature exceeds 350°C, which is defined as the second-stage annealing, the photoresist begins to be evaporated and pure gold will be left on the substrate eventually. In the final stage, the sample is heated further to about 450°C, the photoresist is evaporated completely and the large gold nanoparticles become molten again, which are fused together to form continuous nanowires. At last, pure gold nanowires are obtained on the ITO glass substrate, as shown in Figure 4(d).

It should be noted that different mechanisms are utilized to achieve

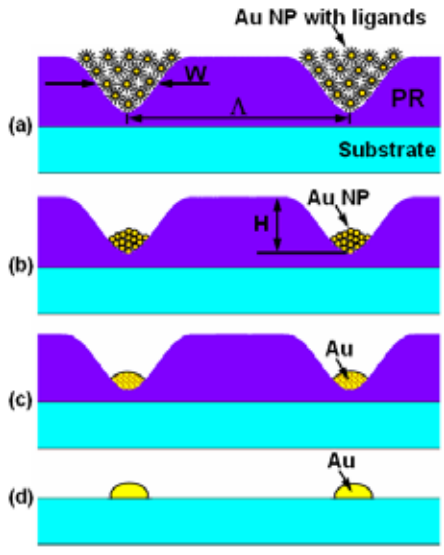

Figure 4: The schematic illustration of the principles for the fabrication of sub-100 nm gold nanowires: (a) Spin-coating of colloidal Au NPs onto the PR grating with a duty cycle of W/Λ and a modulation depth of H; (b) Annealing to above 150°C to remove the ligands; (c) Annealing to above 180°C to melt the Au NP into grating lines consisting of larger gold particles; (d) Annealing to above 350°C to re-melt the large Au particles and make them fused into homogeneous gold nanolines.

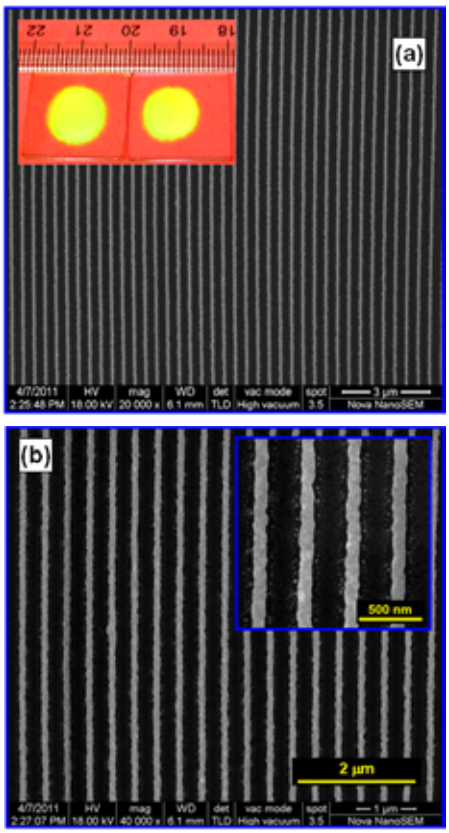

Figure 5: SEM images of the gold nanowire grating fabricated using the optimized parameters, where (a) demonstrates the large-area homogeneity of the structures and (b) shows in detail the high quality and excellent continuity of each gold nanowire.

this fabrication as compared with those described in Ref. [13]. Stronger aggregation of the colloidal gold nanoparticles to the ITO surface with higher surface energy than to the photoresist surface has been the basic mechanisms for the solution-processible fabrication in Ref. [13]. This inevitably requires development to the surface of the ITO substrate in the interference lithography process, leading to the wide and deep grooves of the photoresist master grating. Thus, narrow gold nanowires are difficult to achieve due to the large amount of gold confined into the grating grooves. However, in this work the amount of gold is controlled by reducing the duty cycle of the photoresist master grating. The development does not reach the ITO substrate, thus, very narrow and shallow grooves are produced in the master grating. Furthermore, the grating is entirely made of photoresist with much smaller surface energy than ITO [13], providing another mechanism for reducing the amount of gold left on the master grating. All of these favor the realization of narrow gold nanowires.

Microscopic and spectroscopic characterization of the sub-100 nm gold nanowires

The SEM image in Figure 5(a) demonstrates the large-area homogeneity and excellent continuity of the fabricated gold nanowires with the photograph of the device shown in the inset. The grating has an effective area as large as 1.2cm in diameter, implying that the longest gold nanowires have a length of approximately 1.2cm. The photograph of the device in the inset shows the large-area homogeneity and high quality of the gold nanowire structures by the strong diffraction with a pure color.

Figure 5(b) shows in detail the quality and the structural properties of the gold nanowires using enlarged SEM images. The gold nanowire grating has a period of about 400nm and a duty cycle slightly smaller than 1:4. The gold nanowires have an average width of 95nm with a stand deviation of about 3.8nm as measured using the Image-Pro® Plus software from Media Cybernetics Inc., Sharp edges can be observed with the gold nanowires and almost no gold remains outside the grating grooves, indicating excellent confinement of the gold nanoparticles and success of this fabrication technique.

Actually, the optical properties showing the strong coupling between the plasmonic and photonic resonance modes are the most convincing indication of the successful fabrication, where the periodically arranged gold nanowires on the ITO layer actually constitute the waveguide plasmonic grating structures [26]. Figure 6 shows the optical extinction spectroscopic measurements on the device shown in Figure 5, where the angle of incidence (θ) is increased from 0 to 20 degrees with the optical extinction defined as $\log_{10}\frac{I(\lambda)}{I_0(\lambda)}$. $I(\lambda)$ and $I_0(\lambda)$ are the transmission spectra through the gold-nanowire-structured and non-structured areas on the ITO glass substrate, respectively. In Figure 6(a), the waveguide resonance mode appears as narrow-band extinction peaks for the TE polarization with the light polarized parallel to the gold nanowires. However, for the TM polarization the waveguide resonance mode appears as extinction dips or enhanced transmission in narrow spectral bands due to the coupling with the particle plasmon resonance of the gold nanowires,

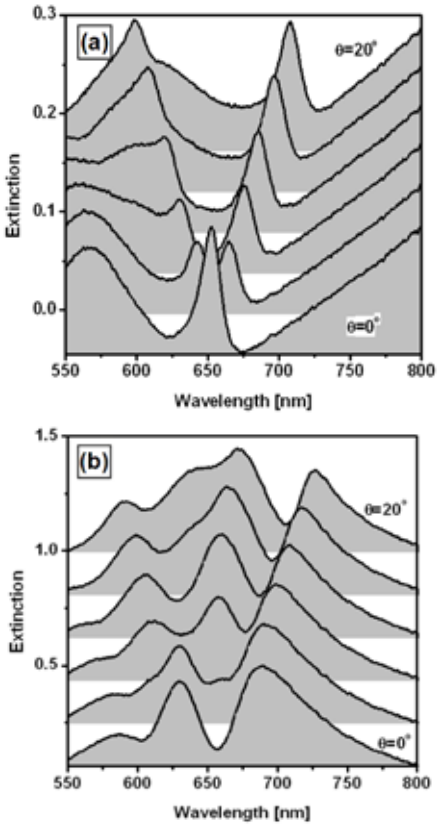

Figure 6: Angle-resolved tuning properties of the optical extinction spectrum measurements on the device shown in Fig. 5 for (a) TE and (b) TM polarizations of the incident light.

as shown in Figure 6(b). Particle plasmon resonance can be observed at about 660nm only when the light is polarized perpendicular to the gold nanowires, which is actually the peak position of the waveguide resonance mode at normal incidence, as can be seen clearly in Figure 6(a) and (b). Both the structural and the fabrication parameters have been optimized, so that at normal incidence the waveguide resonance mode overlaps almost exactly the spectral peak of particle plasmon resonance of the gold nanowires. The physics and principles of the waveguide gold nanowire structures can be found in a series of previous publications [13,26,27]. In this work, the strong waveguide resonance mode for TE polarization (Figure 6(a)), the strong coupling with the particle plasmon resonance for TM polarization (Figure 6(b)), and the excellent angle-resolved tuning properties of the coupled resonance modes are used to demonstrate the excellent spectroscopic and microscopic properties of the gold nanowires with high spatial resolution, indicating success of this fabrication.

Conclusions

We demonstrate fabrication of continuous gold nanowires that are narrower than 100nm and longer than 1 centimeter using solution-processible gold nanoparticles. This is believed to be so far the longest gold nanowire in the sub-100nm scale with excellent continuity and homogeneity. These kind of gold-nanowire photonic devices with high spatial resolution are very important for biosensors with small sensing volumes and high sensitivity. In particular, when cells are grown on the gold nanostructures for physiology studies and for drug screening techniques, this kind of high-resolution plasmonic photonic device will be of special importance. Furthermore, this kind of nanowire structures provide a platform for the investigation and development of plasmonic photonic devices for different applications in optical switching, optical filtering, and light-scattering or confinement in solar cells or lasers.

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