Controllable plasmonic nanostructures induced by ultraviolet laser

Dongfang Li¹,², Yanping Yuan¹,²*, Chunlian Wang¹,², Jimin Chen¹,²

¹ Key Laboratory of Trans-scale Laser Manufacturing Technology (Beijing University of Technology), Ministry of Education, Beijing 100124 China
² Institute of Laser Engineering, Faculty of Materials and Manufacturing, Beijing University of Technology, Beijing 100124 China

* Corresponding author: ypyuan@bjut.edu.cn

Abstract. The plasmonic resonance express as strong extinction band and great enhancement of the electromagnetic field in the vicinity of the nanoparticles, which have been exploited in various applications such as data storage, super-resolution imaging, light collimation, solar cells, biosensors and absorbers. However, a simple and effective route to obtain uniform metal nanoparticles is still a challenge. Here, we have demonstrated a cost-efficient, lithography-free, and facile methods to obtain controllable gold nanoparticles (GNPs) for structure color by direct ultraviolet (UV) laser writing. The thermals dewetting process realized by UV laser direct writing, greatly simplifies the manufacturing process of plasmonic nanoparticles, lowers the bar for equipment, and realizes the structure color in selected areas. The direct laser writing process is performed on a 4 nm-thin island-like Au films atop dielectric-metal sandwiches. By local laser heating, the semi-continue gold film merges and reshapes into approximately spherical structure, generating brand colors. The structure color changes as a function of the laser energy density, low laser energy density to green and high laser energy density to red. Especially for larger laser energy density, the processed area shows a high saturation Numerical simulations confirm that the reflectance of the processed area is strongly affected by the absorption of the bottom metal layer and the local surface plasmon resonance of the top GNPs. In addition, the top GNPs play a major role in tuning the peak of reflection spectrum.

1. Introduction

In recent years, plasmonic generated by metallic nanoparticles has drawn enormous interest for routing and manipulating of light at nanoscales. The plasmonic resonance expresses as strong extinction band and a great enhancement of the electromagnetic field in the vicinity of nanoparticles, which has been exploited in various applications, such as data storage, super-resolution imaging, light collimation, solar cells, biosensors and absorbers. [1,2] To tune the plasmonic resonance properties, the nanoparticles have to be controlled over their geometry and separation as well as dielectric environment. [3] To date, ion-beam milling, multistage e-beam and nanoimprint lithography provide an accuracy and high resolution design and fabrication of plasmonic nanostructures for mass production. These processes generally exist the inevitable shortcomings of high cost, small area and time-consuming. [1] The dewetting process has been widely regarded as a cheap and simple method for large-area fabrication of nanoscale plasmonic structures. [4,5] Usually, the dewetting effect carried out on a hot plate or in annealing furnace, leads the entire area dewetting which limits the wide application. Therefore, a way to achieve nanostructures in selected areas with high efficiency and low cost is more desirable.
Here a cost-efficient, lithography-free, and facile method is proposed for fabricating plasmonic nanostructures with controllable arrays. The thermal dewetting process with UV laser direct writing extremely simplifies the fabrication process of gold nanostructures, and the GNPs can be easily obtained in desired area. The sizes and density of the GNPs can be tuned by changing the density of the laser energy. Thereby, producing structure colors span from green to red. Meanwhile, the metal-insulator-metal (MIM) configuration is adopted for enhance the color saturation.

2. Materials and Methods

2.1. Sample Preparation
The 4 nm-thick semicontinuous Au films on the top layer is deposited by ion beam sputtering system (Quorum Q150R Plus) at current of 8 mA. The 100 nm thick Au layer and 40 nm thick SiO2 layer are prepared using a commercial magnetron sputtering equipment DENTON Discovery 635.

2.2. Laser Writing
The sample is mounted on a computer-driven Nano-positioning platform. The UV laser with wavelength of 355 nm, pulse duration 5 ns and frequency 100 kHz is focused onto the sample surface by a NA = 0.43 objective lens (Nikon Engineering NUV 50×). The laser power is adjusted by the continuous attenuator in the optical path.

2.3. Morphology and optical Characterization
The morphology of laser-induced area is investigated by a field emission SEM (SU-8020, Hitachi). The optical image and reflection spectroscopy are conducted on a Ti-U microscope (Nikon) equipped with a halogen light source and spectrometer system (Andor SR-303i-B). The reflected light is collected using an objective with ×20 magnification (NA = 0.4).

2.4. Numerical Simulations
The optical response is calculated using a commercial FDTD solver available from Lumerical Solutions. The refractive indices of Au and silicon are taken from material library included in the software. The periodic boundary conditions are defined along the x-axis and y-axis and perfectly matched layer is applied for top and bottom boundaries. The plane waves are set half a wavelength away from the nanostructure and incident along the -z direction.

3. Results and discussion
Generally, the semi-continuous Au films can be melt and aggregated, forming larger GNPs under annealing process. The Rayleigh instability is identified as the main mechanism for the dewetting process. The size and shape of GNPs can be adjusted by controlling the annealing temperature and time, leading to the modulating of the optical resonance. Figure 1a schematically depicts the processing principle of GNPs based on direct laser writing. A UV laser beam is tightly focused on semi-continuous Au films by a UV objective (NA=0.43) with a diameter of ~1 μm. The sample has a MIM configuration composed by a 4 nm-thick semicontinuous Au films (as shown in Figure 1b), 30 nm-thick silica spacer and a 100 nm-thick gold reflective layer. The Au back-reflector is set to be 100 nm thick to prevent light transmission in the entire visible spectrum. The focused laser has a high energy density, giving a possibility of locally realizing the dewetting process in selected areas. As shown in Figure 1b-c, after the laser irradiation, the island-like gold films transforms into regular Au nanoparticles with an average diameter of 40 nm, which can greatly change the reflectance of the processed area. The new formed GNPs and bottom Au film constitute a gap-surface plasmon (GSP) resonators, which is pivotal for improving the color saturation.
Figure 1. a Schematic illustration of plasmon structure fabricated by UV laser direct writing on the surface of the MIM structure. b SEM image of the semi-continuous Au films on the top layer. c SEM image of the area exposed by the laser beam.

Under irradiation of various laser powers, the semi-continuous gold films form nanostructures with different particle densities and particle sizes. Firstly, the scanning speed of 10 μm/s and an incident power of 40-70 μW are used for direct laser writing, and the corresponding reflection images are shown in Figure 2a. According to previous research for the processed area, low laser power corresponds to green, and high power exposure corresponds to red. However, in Figure 2a, the processed area remains to be a red reflection color, as the laser power decreases. To expand the structural color range of the processed area, the different scanning velocity is adopted. The simplified laser energy density $E$ ($E = P/V$, where $P$ is laser power and $V$ is scanning velocity) is used to evaluate the energy irradiating on Au film. As shown in Figure 2b, with the increase of $E$, the color uniformity is improved and the optical image shows the color that span from slightly green to bright red. The SEM image in Figure 2c shows that the GNPs have an average particle size of 150nm, and a particle density of 88/μm². The GNPs with a diameter of less than 10 nm account for a large proportion. This phenomenon may be related to the merge and explosion of the gold film under laser exposure. As shown in Figure 2d-f, with the increase of $E$ (from 1.65 to 41.6 J/m), the GNPs result an increase of particle density and decrease of particle size. Meanwhile, the particle morphology and color purity shows a tendency to be uniform, especially in high laser energy density.
Figure 2. a Optical images with laser power 42, 52, 55, 64 μW. b-c Optical images of area induced with E 1.44, 1.65, 4.8, 41.6 J/m. Scale bar: 20μm(a,b). c-f The SEM images and particle size distribution for the area in (a).

Figure 3a depicts the reflection spectrums measured on a home-built micro-spectroscopy. The reflectance of the unexposed area is presented by a black curve, showing a reflection peak at 630 nm and reflectance smaller than 40% in the entire spectrum. For the sample exposed at laser energy density of 1.44 and 1.65 J/m, the reflection peaks are blue-shifted to 570nm and 550nm respectively. For samples with laser energy density 4.8 and 41.6 J/m, the corresponding reflection peaks are almost disappeared. While new reflection peaks appear in the 700-800 band, and the reflectance are greatly increase to ~80%. To further understand the physical mechanisms involved in the optical response caused by the morphology of GNPs, numerical simulations are performed with commercially available software (FDTD Solutions) based on the Finite-difference time-domain (FDTD) method. The schematic model is illustrated in Figure 3b I, where the Au nanoparticles are assumed spherical and have plane contact with the SiO2 layer. The geometric parameters of the simulated model are based on the particle distribution and particle size statistics in Figure 2. The simulated reflectance spectra for the sample with brightly saturated red are plotted in Figure 3a by red dash line, which shows a good agreement with the measured reflectance spectra. For detecting the physical origin of the spectral characteristics and corresponding colors of the processed architecture, we explored the optical response of the two additional model II and model III in Figure 3b. These two models are used to calculate the independent absorption spectral of the GNPs and the bottom gold layer, which is set same geometric parameters in model I. As shown in Figure 3c, in the entire wavelength range, the absorption spectrum characteristics of the f-p model are jointly affected by the top GNPs and the bottom gold layer. For the wavelength 500-600nm, the spectrum of the top GNPs is a major contributor for affecting the absorption spectrum of the f-p model. The absorption peak around 520 nm of the top GNPs is associate to the localized surface plasmon resonances. [8] This peak is corresponding well to that of the f-p model, indicating that the top GNP s plays an important role in the entire model. Hence, the optical characteristic of the MIM structure can be effectively controlled by adjusting the laser-induced GNPs.
Figure 3. a The experimental and simulated reflectance spectra of the film in Figure 2. b The simulated absorption spectra in for different combination of architecture. The model II is combined by GNP and silica spacer. The model III is composed by perfect electrical conductor (PEC) material, silica spacer and gold reflective layer. c The corresponding simulated absorption spectra in (b).

4. Conclusion

In conclusion, we have demonstrated a simple and effective route to obtain uniform GNPs for structural color by direct UV-laser writing. By laser-heating-induced, the semi-continue gold film transform into the GNPs with different morphologies and particle densities, showing brand structure colors. The structure color varies from green to red, especially showing a high saturation in the red spectrum band. The structure color changes as a function of the laser flounce, low laser energy density to green and lager laser energy density to red color. Numerical simulations confirm that the reflectance of the processed area is main affected by the absorption of the bottom metal layer and the local surface plasmon resonance of the top Au nanoparticles. In addition, the top Au nanoparticles play a major role in tuning the peak of reflection spectrum. This facile direct writing method allows us to prepare GNPs in arbitrary graphics, which is prospective for various applications including data storage, security marking, biosensor and color printers.

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