Thermally Stable Nanoporous Gold-Alumina Core-Shell with Tunable Optical Transmission

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Tuning localized surface plasmon resonance (LSPR) of nanoporous metals is crucial to manipulate light within tiny volumes for the implementation of optical devices at the nanoscale. Herein, nanoporous gold-alumina core-shell films with constant gold skeleton and variable alumina sheaths are fabricated by means of chemical corrosion and subsequent atomic layer deposition. Optical transmission properties of these composite films can be tailored due to LSPR excitations of the three-dimensional gold skeleton and alterable alumina shells as the surrounded dielectrics. The widely tunable light transmission and significantly improved stability are thus suggested to incorporate nanoporous gold-alumina core-shells into promising nano-devices with reliable performance.

Introduction

Controllable synthesis of nanoporous metals has recently attracted much attention due to interest in fundamental optics and their immense applications in miniaturized optical devices, chemical sensors and optical filters.\(^1\)\(^-\)\(^2\) Unique response to light is characterized by localized surface plasmon resonance (LSPR) due to surface corrugation at the sub-wavelength scale, which is significantly different from surface plasmon polaritons (SPPs) of planar surfaces. So far, many scientific and technical concerns are to tailor the LSPR bands of nanoporous metals finely, which can guarantee to select the suitable entity with requisite properties and fabricate optical devices with minor units.

Besides the dependence of LSPR location on geometrical features that is broadly investigated, optical properties of nanoporous metals strongly depend on the surrounding dielectrics.\(^3\)\(^-\)\(^4\) Most attempts have investigated optical transmission of nanohole patterns surrounded by a liquid solution of dissolved molecules, due to their applications as chemical sensors.\(^5\) Essentially, the molecular scale is much finer than the decay length of the electromagnetic field (tens of nm), which originates from LSPR excitation of interconnected metallic ligaments. So far, few investigations have attempted to tune the optical properties by filling the hollow spaces with solid dielectrics, primarily due to difficulties in fabricating thin solid films at the nm scale by conventional processes, especially for the precise deposition of ultrathin films into three dimensional channels of nanoporous metals.

Atomic layer deposition (ALD) is widely used for the synthesis of ultrathin solid films including metals, metal oxides, and semiconductors with sub-nanometer thickness. The layer-by-layer growth mode allows the control of film thickness at atomic scale. Gaseous precursors during ALD can facilely penetrate into hollow channels in three dimensions together with a sequential self-terminating gas-solid reaction, and this
procedure has the capability to coat extremely complex shapes with a conformal material layer of high quality. Herein we report the fabrication of three-dimensional nanoporous gold-alumina core-shell films by the controlled ALD of alumina film onto nanoporous gold. Their optical properties are tunable by changing the shell thickness.

**Experimental Procedures**

Nanoporous gold films with a thickness of 100 nm were synthesized by chemically etching a Ag<sub>65</sub>Au<sub>35</sub> leaf in a 70 wt.% nitric acid (HNO<sub>3</sub>). The etching process was performed for 8 hours at room temperature, and the pore size was around 35 nm. Nanoporous gold films supported by glass slides were used for optical properties measurements, and samples on copper grids were used for transmission electron microscope (TEM) characterization.

Alumina thin films were deposited on nanoporous gold substrates by ALD using a Savannah 100 series ALD system. Trimethylaluminum (TMA) and distilled H<sub>2</sub>O vapors were alternately pulsed through the viscous flow reactor utilizing high purity N<sub>2</sub> (99.999%) at a mass flow rate of 20 sccm as carrier gas. The deposition was carried out at a growth temperature of 80 °C.

Nanoporous gold-alumina core-shell films were characterized by a TECNAI G2 F30 transmission electron microscope (TEM). Pore size and shell thicknesses were determined by the morphologies. Ultraviolet-visible (UV-VIS) spectra of the nanoporous gold-alumina core-shell films were measured by a Perkin-Elmer Lambda 750 spectrophotometer.

**Results and Discussion**

Figure 1 shows a TEM image of a nanoporous gold-alumina core-shell film. Gold ligaments exhibit the interconnected skeletons with dark contrast, which are significantly

![Figure 1. TEM image of nanoporous gold-alumina core-shell. The interconnected network in the dark region is nanoporous gold. Thin layer with grey color is the alumina coating.](image-url)
distinct from the nanopores with elliptical shapes. Both the ligament widths and the pore have the identical scale of $35\pm 5$ nm. Alumina films partially fill into all the pores as evidenced by different contrast between the alumina coating and the vacuum background. It is clear that the alumina is uniformly coated onto any exposed surfaces of the gold ligaments, and the thickness of alumina shell does not rely on the local geometries of gold ligaments with the evidence of the identical thickness almost everywhere.

Well controllable surface morphologies of alumina shell offer an efficient route to tailor the optical properties of the nanoporous gold film reliably.\textsuperscript{6} Figure 2(a) shows transmittance spectra of nanoporous gold and nanoporous gold-alumina films. The transmittance spectrum of nanoporous gold reveals a platform between 490 and 540 nm, which can be considered to be a convolution of two isolated bands. The first band is located at 492 nm, and the other band is at 537 nm. It is interesting to note that the two bands show completely distinct behaviors to dielectric environments. The first one does not shift with the oxide layer thickening even if the pores are completely filled. This feature which is independent of the dielectric medium is also detected in dense gold films (without the pores), which exhibit one band that is not sensitive to the dielectric oxide (the figure is not shown). In comparison, the band at 537 nm is well related to LSPR excitation of gold ligament at nm scale, which is confirmed by the significant red-shift with the increasing thickness of the alumina coatings. 90 nm shifts can be attained after the nanopores are almost filled with alumina (at a thickness of 17 nm).

It is well-known that LSPR excitation enhances local electromagnetic fields normal to the surface of metal nanostructures, which decay exponentially in the normal direction. The LSPR location significantly depends on the decay length, the thickness, and the refractive index of the dielectric coating. Based on the surface plasmon response of the metal film to the dielectric medium, the LSPR band shift of nanoporous gold induced by dielectric coatings in this work can be roughly estimated using:\textsuperscript{7-8}

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\Delta \lambda (d) = m (n_m - n_a)[1-\exp[(-2d/\delta)]
$$

(1)

where $n_m$ is the refractive index of the oxide coating with a thickness $d$, $n_a$ is the refractive index of the surrounding air; and $m = \partial \lambda / \partial n$ is the shift per refractive index unit.

Figure 2. (a) Transmittance spectra of nanoporous gold and gold-alumina films with variable alumina shell thicknesses. (b) LSPR band position versus thickness of alumina coating. The solid line is fitted following Equation (1).
for bulk dielectrics (it is about 239 nm for nanoporous gold with a pore size of 35 nm). \( \delta \) is the characteristic decay length correlating with the detailed geometries of metal nanostructures. The data in Fig. 2(b) were fit using equation (1) while varying \( \delta \) and the best fit yielded \( \delta = 25 \) nm.

In addition to the well-tunable optical transmission, nanoporous gold-alumina core-shell films developed in this study have another attractive advantage: their excellent thermal stability. Figure 3 shows transmittance spectra of nanoporous gold-alumina structures with 1.6 nm shell thickness annealed at different temperatures. The shapes of the two plasmon bands in the transmittance spectra do not change after annealing to 200 \(^\circ\)C (less than 5 nm shift in the LSPR band position). In contrast, more than 25 nm shifts can be obtained for pure nanoporous gold without alumina coating.

![Figure 3](image-url)

**Figure 3.** Transmittance spectra of nanoporous gold-alumina films with 1.6 nm alumina shell thicknesses annealed at 100 \(^\circ\)C and 200 \(^\circ\)C for one hour, respectively.

**Conclusions**

Nanoporous gold-alumina core-shell films consisting of the gold core and alumina shell with distinct thicknesses are fabricated by chemical corrosion and subsequent atomic layer deposition. The transmission properties of these nanoporous composite films can be tailored due to LSPR excitations of the three-dimensional gold skeleton and the alterable thickness of the alumina dielectric shells. 90 nm red-shifts of the LSPR band are obtained due to the dielectric medium dependence of the LSPR. The widely tunable light transmission and significantly improved thermal stability are thus suggested to incorporate nanoporous gold-alumina into promising nano-devices with reliable performance. Low temperature surface decoration (<100 \(^\circ\)C) provides a universal route to tune the optical properties while retaining the spatial geometries of metallic nanostructures.
References