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Plasmon resonant Au nanospheres and nanorods in anodic alumina matrix

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Abstract

This paper discusses theoretical studies of optical properties of gold nanospheres and nanorods with various aspect ratios, embedded in porous anodic alumina matrix. We show in this study that when the alumina template is made under certain conditions, nanostructures with diameters in the 15–25 nm range can be synthesized. Embedding gold particles of nanometer dimensions into a dielectric matrix provides a simple way to study the optical properties of the particles. Plasmon resonance wavelength for gold nanospheres and nanorods with different aspect ratios embedded in porous anodic alumina matrix are computed and discussed in this study. Recently, the plasmons in porous anodic alumina matrix have been considered for quasi-non-diffractive nano-optics applications. Other potential applications of the noble metal nanoparticles include optical filters and sensors.

Keywords: Nanospheres; Nanorods; Plasmons; Porous anodic alumina

1. Introduction

In recent years, the interaction of light at a metal/dielectric interface that leads to the formation of surface plasmon waves at specific frequencies has been the focus of intense research. The structures of interest for plasmonics are small metallic particles, wires, rods, and thin films that act as dipole oscillators and whose plasmon frequencies are in or near the visible spectral range. The interesting cases are usually those where the plasmon lines incur minimal interference from interband optical transitions. In these cases, the surface plasmon resonances are usually dependent on the size, shape, and degree of particle-to-particle coupling; furthermore, they are also dependent on the dielectric properties of the metal from which the nanoparticles are made, and the dielectric properties of the matrix into which the nanoparticles are embedded [1].

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We study here plasmon resonant gold nanometer size particles embedded in porous anodic alumina (PAA) matrix. We are particularly interested in studying gold nanoparticles with diameters below 50 nm. In the following section, we show that such particles can be fabricated by electrodeposition of gold in a PAA matrix obtained under certain anodization conditions.

Highly ordered PAA is a well-established material [2,3] that has been used by several groups over the past decade as a template for fabricating metal [4,5] and semiconductor [6,7] nanostructures of various materials. The structure of these PAA films is characterized as a closely packed regular array of hexagonal columnar cells. Each cell contains an elongated cylindrical nanopore normal to the aluminum surface, extending from the surface of the oxide to the oxide/metal interface where it is sealed by a thin barrier oxide layer with approximately hemispherical geometry. In addition to the above-mentioned structural features, the pore diameters and pore densities of PAA film can be finely controlled by appropriately varying the electrochemical process parameters.

Maxwell–Garnett (MG) effective medium theory is often used to describe the optical properties of metallic nanoparticles [1,8]. MG theory computes the complex effective dielectric function of the system consisting of the metallic nanoparticles and the surrounding medium. From this dielectric function the refractive index and the absorption can be calculated. The shape of the particles can be included in the theory via a screening parameter. However, since the MG theory assumes that the nanoparticles are infinitesimally small relative to the wavelength of visible light, the calculated resonance wavelengths calculated using MG theory are always smaller than the experimental ones in the absorption spectra. A modified version of the MG theory that takes into account the finite size of the nanoparticle was developed [9].

We discuss the applicability of the MG theory in its original and modified form, for describing the optical properties of gold nanospheres and nanorods with different dimensions (size and aspect ratio), embedded in a PAA matrix.

2. Fabrication of the porous anodic alumina template

Ordered nanoporous alumina films have mostly been fabricated using oxalic [10–12] and phosphoric [13,14] acid solutions. To our knowledge, only a few papers exist on the use of sulfuric acid as an electrolyte for the manufacture of well-ordered nanoporous alumina [15–18]. Values of interpore distances obtained by anodizing aluminum in oxalic and phosphoric acid solutions are in the range of 100–200 nm [13,19–21] and 400–500 nm [13,20,21], respectively; the pore diameters, however, vary between 50 and 100 nm for oxidation in oxalic acid solutions [13,19–21], and between 200 and 250 nm in phosphoric acid solution [13,20,21].

A one-step anodization process has been commonly used in the past for manufacturing nanopore arrays of aluminum oxide [16,17]. The ability to create highly periodic pore structures was greatly enabled as a result of the development of a two-step anodization technique by Masuda and Fukuda [19].

In the present study, high-purity (99.999%) circular aluminum coupons were anodized using the two-step anodic process described by Masuda et al. [19]. Prior to anodization, the aluminum sheets were electropolished at a constant electrostatic potential of 60 V for 30 s. These conditions produce an atomically smooth surface with a hexagonal pattern of quasi-periodic arrangement of nanopits [22]. Anodization was performed in a constant temperature bath, while the electrolyte solution was stirred. An Al plate was used as a counter electrode. The samples were anodized using various conditions.

In order to obtain anodic aluminum oxide with lattice constants of 40 and 60 nm, a 20% by weight sulfuric acid solution was used as an electrolyte, with the anodization voltage of 15 and 22 V, respectively. The evolution of surface morphology of the PAA film was characterized by scanning electron microscopy (SEM). The interpore distances and the pore diameters were evaluated and compared from the SEM photomicrographs of PAA obtained at different cell potentials. Fig. 1 shows the experimental and calculated values of