Fabrication and Characterization of Tin nanostructures based on porous anodic alumina membranes.

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ABSTRACT

In this paper, a simple method to fabricate two-dimensional (2D) Sn nanostructures is demonstrated. Sn nanostructures are deposited on porous anodic alumina membrane (PAA) by using thermal vapor deposition technique. According to SEM images the deposited Sn nanostructures have two different morphologies; thin nanoporous film of Sn with height 64 nm and average pore diameter 44 nm, and hexagonal arrays of Sn nanoparticles on the PAA surface with small particles diameter of 80 nm and large particle diameter of 146 nm. According to reflection spectra, the interference of the Sn/PAA nanostructures is enhanced relative to interference of the blank PAA. In addition, the effective refractive indices of PAA and Sn/PAA nanostructures were calculated based on Maxwell- Garnett effective medium approximation.

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1. Introduction

Metallic nanostructures are attracting increasing interest as an important class of photonic components that control and manipulate light at nanometer scale [1]. It is generally accepted that 2D nanostructures are ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of structure properties for potential applications [2]. 2D nanomaterials are also expected to play an important role as functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions [3]. Among them, Sn nanostructures, especially 2D nanoporous arrays have received substantial interest due to their outstanding electrical, optical, and mechanical properties. This is in part due to their low melting temperature, ductility, excellent wetting properties, high electrical conductivity, and electrical reliability [4,5]. Also, Sn nanostructures were used as substrates for metal-enhanced fluorescence (MEF) applications which make Sn nanostructures have applications in medical diagnostics and biotechnology [6,7]. Porous anodic alumina (PAA) membranes with nanoporous structure have been widely used as membranes in the fabrication of various nanostructures because of the cheap equipment, easy technology and high controllability of the process [8-11]. In order to extend the applications of porous membranes, metal particles are usually loaded [12], so the conducting, mechanical and optical properties of porous membranes could be improved [13]. The position of metal nanoparticles on the membranes shows a significant influence on the properties of the structures, especially with respect to sensor applications. For instant, the metal particles on the outer surface of the structure have more possibility to touch with the reactant than those inside. Thus, it is meaningful to load the Sn nanoparticles up on the outer surface of the PAA membrane. Therefore a controlled methodology to coat a PAA membrane with well defined Sn nanostructures is required. One of the most promising options, due to its simplicity, low-cost, and high-throughput technique, is the thermal evaporation of Sn into a porous anodic aluminum (PAA) template. However, this method has faced certain challenges, such as achieving uniformity in the height and diameter of the nanoarrays and their uniform alignment without deformation. On other hand, many studies have been done on reflection spectroscopy of PAA membranes [14-17]. It showed a bright color in the visible light range due to the interference of light [14]. The color is bright but its saturation is very low. To make the color pure and highly saturated, colored substances always have to be sealed into the PAA membrane nanopores [14,18].

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By contrast, research on Sn nanostructures using reflection spectroscopy were very limited in spite of its simplicity in sample fabrication and optical characterization [6,19]. However, there are a number of factors that complicate the study of the optical properties of Sn nanostructures based on PAA template, including the presence of a supporting substrate, dielectric host, and electromagnetic coupling between nanoparticles. All of these factors make it important to clarify the relationships between optical response and surface morphologies of the fabricated samples.

In this study, tin nanostructures of two different morphologies were deposited using thermal vapor deposition onto PAA / Al substrate, which were characterized by optical reflection and field emission scanning electron microscope (FE-SEM) techniques. Enhanced optical interference from PAA coated with nanoporous hexagonal array of tin nanoparticles was observed, suggesting that both an enhanced electric field and a plasmon-coupling underpin the mechanism for interference enhancement.

2. Experimental procedure

For the fabrication of uniform Sn nanostructures, the preparation of a uniform PAA membrane is very important. High purity (99.999%) aluminum foils of 0.25 mm thickness were used as a starting material. The foils were electropolished to mirror finish in an electrochemical solution of volume mixture of 3:1:1 H₃PO₄: H₂SO₄:H₂O at 50°C under constant stirring for 3 min. The PAA templates were prepared by a two-step anodization process. In the first anodization step, the electropolished aluminum foil was anodized in a 0.3 M C₂H₂O₄ solution at 40 V and at 9°C for 3 h. After first anodization, the alumina membrane was immersed in an etching solution of H₃PO₄, H₂SO₄, and CrO₃ (100 mL: 10 mL: 1 gm) at room temperature for 3 h to remove the alumina layer. We carried out the second anodization under the same conditions for 5 min. Finally, pore widening was carried out at 6 wt% H₃PO₄ for 45 min.

Tin nanostructures were deposited using thermal vapor deposition technique (Evaporation plant, Edward, mode 6E) at room temperature and pressure of 10⁻⁵ torr on the top surface of porous anodic alumina membrane. The fabricated structures were characterized by a field emission scanning electron microscope (FE-SEM). The optical properties of the PAA and Sn/PAA nanostructures were characterized by reflection spectroscopy (Jascko, UV-Visible range) from 200 to 900 nm.

3. Results and discussion

3.1 PAA morphology

Fig.1 shows SEM images of the PAA membrane. As shown in Fig. 1(a), PAA has highly ordered hexagonal arrangement of the pores with thickness approximately equal to 300 nm. The average pore diameter and interpore distance are 54 nm and 120 nm, respectively. Porosity of the PAA is approximately 17% and pore density approximately equal 1.15x10⁹cm².

In order to check the chemical composition of the fabricated sample, the PAA/Al film was analyzed by EDX and XRD as shown in Fig. 1(b and c). The EDX pattern in Fig.1 (b) shows the signals of Al and O elements. The quantitative results were 52% Al and 48% O.

Figure1 shows SEM images of (a) PAA with thickness 300nm and pore diameter 70nm and (b) EDX spectrum of alumina membrane.

Figure 2 shows top-view SEM images of (a) ultrathin nanoporous film of Sn with height 64 nm and average particle diameter 44nm and (b) Sn nanoparticles arrays with average particle diameters of 80 and 146 nm.

3.2 Sn/PAA nanostructures Morphologies

When Sn deposited on PAA, two different morphologies of Sn nanoarrays are observed in Fig.2. At low deposition rate nanoporous hexagonal array of Sn nanoparticles of height 64 nm and average diameter of 44 nm are formed on the walls between the pores and to some degree cover the pores, hence the pore diameter decrease but not blocked completely as shown in Fig.2(a). In addition, Porosity of the nanostructure is decreased to be ~ 21%. When the deposition rate increased, two different arrays of tin nanoparticles with different sizes are observed. The sizes of small and large Sn particles were measured to be 80 nm and 146 nm. The large size particles are resulted from the aggregation of small tin nanoparticles around the active points on the top-surface of the membrane and the particle diameter alternating from 93 nm to 199 nm. Whereas the small nanoparticles array spread around the pores and blocked the pores surface of the PAA membrane as shown in Fig.2 (b). Around there are six small nanoparticles with a hexagonal arrangement, which is consistent with the hexagonal packing structure of the pores.
3.3 Optical Characterization.

Reflection spectra as a function of the wavelength between 200 and 900 nm were measured at a normal incident. The recorded spectra were normalized with respect to a reflection from an Al mirror. These reflectance spectra are characterized by well resolved peaks and valleys originating from the interference between the reflected light from the top and bottom interfaces. There are interesting features in the reflectance spectra over the wavelength investigated. First, it is clear that the reflectivity of the porous Sn/PAA membrane is relatively low compared to that of blank PAA membrane and change smoothly with wavelength. Second, the reflectance of the Sn/PAA membranes strongly depends on the coating time and surface morphology. Thirdly, the oscillation strength (difference between the maximum and minimum of interference fringes) of the coated PAA membranes increases compared with that of the blank PAA membrane.

![Figure 3](image)

**Figure 3** Reflection spectra of blank PAA and Sn-coated PAA with thickness 64nm and 91nm.

A possible reason is as follow: From the schematic diagram 4(a) which illustrated the reflection of light rays from the PAA, we found that a ray of light (ray 1) whose amplitude is $A_1$ penetrates into PAA template and reflection takes place at both the top(Air/Alumina) and bottom (Alumina/Aluminum) interfaces. The two reflected rays (ray 2 and 5) with amplitude of $A_2$ and $A_5$ have the same frequency and fixed phase difference, so interference happens. The resultant amplitude ($A$) is given by

$$A = (A_1^2 + A_2^2 + 2A_1A_2\cos\Delta\theta)^{1/2}$$

(1)

Where $\Delta\theta$ is the phase difference. For constructive interference, $\cos\Delta\theta$ is equal to 1 and $A_{\text{max}} = A_1 + A_2$. For destructive interference, $\cos\Delta\theta$ is equal to -1 and $A_{\text{min}} = A_1 - A_2$. When Sn deposited on the top-surface of PAA template to form ultrathin nanoporous film as shown in schematic diagram 4(b), the two reflected rays (ray 2 and 5) with amplitudes $\hat{A}_2$ greater than $A_2$ and $\hat{A}_5$ smaller than $A_5$ are coherent and the interference occur with resultant amplitude $\hat{A}$ calculated by

$$\hat{A} = (\hat{A}_2^2 + \hat{A}_5^2 + 2\hat{A}_2\hat{A}_5\cos\Delta\theta)^{1/2}$$

(2)

When $\cos\Delta\theta = 1$, $\hat{A}$ becomes maximum and given by $\hat{A}_{\text{max}} = \hat{A}_2 + \hat{A}_5$ and when $\cos\Delta\theta = -1$, $\hat{A}$ becomes minimum and given by $\hat{A}_{\text{min}} = \hat{A}_2 - \hat{A}_5$. $A_{\text{max}}$ approximately equal $\hat{A}_{\text{max}}$ and $A_{\text{min}} > \hat{A}_{\text{min}}$. Then the difference between the maximum and minimum of interference fringes increases. For Sn/PAA sample that has two different arrays of Sn nanoparticles with different sizes and due to the non-homogenous surface morphology, this sample has oscillation strength less than that of the ultrathin nanoporous Sn sample. In addition, the effective refractive index of PAA template is defined by the porosity and the refractive index of the medium inside the pores. The measurement of the PAA reflectance enables us to determine the effective refractive index $n_{\text{eff}}$ by using the following relation

$$n_{\text{eff}}^2 = \frac{\lambda_2^2 - \lambda_1^2}{4d(\lambda_2 - \lambda_1)^2} + \sin^2\theta$$

(3)

Where $\theta$ is the incident angle, and $\lambda_1$, $\lambda_2$ are the wavelengths of two adjacent maxima or minima. By suing equation (3) and Figure 3, the effective refractive index $n_{\text{eff}}$ of the blank PAA is equal to 1.69. When Sn deposited on the PAA the porosity decreased this means that the effective refractive index of the sample increases and by using equation (3), $n_{\text{eff}}$ of the Sn/PAA nanostructure is 1.8 and 1.85 for ultrathin nanoporous film of Sn and Sn nanoparticles, respectively.

4. Conclusions

In conclusion, we have successfully coated the the surface of PAA membrane with Sn nanoporous layer and Sn nanoparticles by thermal evaporation technique. The coated PAA membrane exhibits strong interference patterns with much higher saturation compared to that of the blank PAA membrane. The fabrication approach used in this study is simple, rapid, economical, and reproducible. Therefore, we expect that the proposed structures can serve as building blocks for nanophotonic and nanoelectronics devices in the near future.
References