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Fabrication of one-dimensional alumina photonic crystals by anodization using a modified pulse-voltage method

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ABSTRACT

The alumina nanolayer structure with alternating high and low porosities is conveniently fabricated by applying a modified pulse voltage waveform with constant high and low voltage. This structure shows the well-defined layer in a long-range structural periodicity leads to a strong photonic band gap (PBG) from visible to near infrared and brilliant film colors. Compared with the previous reported tuning method, this method is more simple and flexible in tuning the PBG of photonic crystals (PCs). The effect of duration time of high, low and 0 V voltages on PBG is discussed. The first PBG could be modulated easily from the visible to near infrared region by varying the duration time of constant high or low voltages. It is also found that the 0 V lasting for appropriate time is helpful to improve the quality of the PCs. The formation mechanism of multilayer is also discussed.

1. Introduction

Photonic crystals (PCs) are a class of spatially periodic dielectric composites with a photonic bandgap (PBG) in which the propagation of the incident light is inhibited [1,2], and have received considerable interest for their great potential applications, such as light filters [3], photo energy conversion [4], reflecting mirrors [5], LED light extraction [6], sensors [7], optical analysis [8] and others [9]. Therefore, various methods have been explored to fabricate photonic band gap structures. Generally, PCs could be prepared by mainly two methods, one is by "top-down" approach, such as lithography including holographic lithography [10], electron beam lithography [11,12] and soft lithography [13], which provide the required structural accuracy but are generally expensive, complex, and limited to small area. The other is by "bottom-up" approach, such as inverse opal templating [14], layer-by-layer (LBL) deposition [15] and sol–gel process [16], although they are more convenient and cost-effective. Recently, Park et al. [17] firstly prepared the 3D plasmonic photonic crystals by using a DNA-programmable assembly technique, which also provide control over the assembly of nanoparticles into complex structures. But the inverse opal templating method is prone to structural irregularities, the LBL method involves multistep procedures which are prone to human errors, and the sol–gel method lacks precise structural control. All of these factors hinder the possible application and commercialization of PCs. However, the preparation of PCs, especially two- and three-dimensional PCs with photonic band gap positioned on the short wavelength, are still difficult, complicated and expensive. Therefore, it is still a challenge to find a simple and effective preparation technique to produce a large area PC with a PBG in the visible spectral region.

The anodic growth technique shows a potentially promising method for photonic crystal fabrication due to its cheap equipment and high controllability of the process and capability of large-area photonic crystal fabrication at low cost. Especially, the porous anodic alumina oxidation (AAO) nanostructures by directly anodic oxidizing Al foils for building one-dimensional photonic crystals have aroused great interest. Firstly, AAO is a transparent insulator with a wide electronic band gap, a relatively high refractive index (~1.7), and excellent mechanical and chemical stability. Then more importantly, the pore geometry and the effective refractive index are easily modified in depth by anodization using a periodical voltage or current profile. Therefore, since Masuda, et al. [18] first reported that AAO with highly ordered pore arrays had a PBG in the visible region in the direction parallel to the membrane surface in 1999, and intensive efforts have been made to fabricate PCs by electrochemical anodic oxidation of aluminum. For example, Wang et al. [19] fabricated an anodic alumina PC with a strong PBG by adjusting the anodizing cell voltage periodically in the process of

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electrochemical oxidation and the PBG position could be easy to control in the following chemical etching time process. Zheng et al. [20,21] modulated anodic alumina PCs with a strong PBG by adjusting anodic oxidation temperature and the duration of cell voltage. These results were all obtained with a pulse voltage waveform controlled method including an identical sinusoidal rising edge of 30 s and a linear falling edge. To effectively control each layer of pore structure, pulse and cyclic anodization methods were also developed by Losic et al. [22] and Lee et al. [23], although these works did not focus on the optical properties of the obtained nanostructures. More recently, Shang et al. [24] successfully obtained a high quality PC by applying a sine-wave voltage with a step voltage compensatory mode in a period. Yan et al. [25] fabricated PCs by applying a sine-wave current in the anodic anodization of aluminum. Obviously, the PBGs position was tuned by the periodic time, and the higher and lower dielectric layer cannot singly control, respectively. However, AAO-based PCs is introduced in which refractive index variation is achieved with an in-depth varying porosity obtained with cyclic voltage profiles or cyclic current profiles. Unfortunately, all the voltage profiles applied to preparing PCs is in one cycle consisting of a sinusoidal increasing voltage phase and subsequent a linear decreasing voltage phase or directly a sine-wave voltage, therefore the thickness and porosity of each layer are difficult to be delicately controlled in a large of range and the corresponding delicate tuning on the PBG is difficult. In addition, AAO membranes are widely used as extremely flexible templates for fabrication of various one-dimensional nanostructured materials [26]. Especially, periodic or non-periodic variations of the nanowire diameter within the nanowire length were synthesized successfully by diameter-modulated AAO membrane [27], which exhibits some special properties different from those observed for straight and smooth nanowire. So it is imperative to find a method to further develop and optimize the fabrication procedure.

In this paper, the facile anodization approach of generating nanoporous multilayered alumina by anodizing aluminum foils is obtained, which applied a modified voltage waveforms including a constant high and low voltage. Thus, the AAO nanolayer structure alternating high and low porosities is effectively controlled by the value and duration time of constant high and low voltage, respectively. The PBGs are more effectively and flexibly tuned than previous reported method. Also the mechanism of the multilayer formation is discussed intensively, and the key factor of formation multilayer is to reduce the barrier to an appropriate value when the voltage varies from high to low. It is more important that when the nanopore array on the AAO is modulated to distribute highly ordered in large area and the nanopore size is uniform through further optimizing the technique parameters of pulse-voltage anodization method, the three dimensional alumina PCs would be prepared.

2. Experimental

For fabrication of AAO membranes with multilayer structure, high purity aluminum (99.999%, 25 mm × 15 mm × 0.25 mm) samples were used as the starting material. Before anodization the aluminum ultrasonically cleaned in acetone, ethanol, and deionized water successively. Then, the surface of aluminum samples was electropolished in a mixed solution of perchloric acid and ethanol (1:4 in volume) under a constant voltage of 18 V for about 30–60 s to achieve a smooth surface, and was thoroughly rinsed in deionized water and transferred to a nitrogen environment to reserve for anodization. After the pretreatment, a first anodization was performed on the electropolished Al surface using a 0.3 M oxalic acid ($H_2C_2O_4$) solution at a room temperature. The process was carried out at a constant voltage of 50 V for 2 h, which was dissolved by wet chemical etching at 70 °C in a solution of chromic and phosphoric acid (0.4 M H_3PO_4 and 0.2 M H_3CrO_3) stirred slightly for 6 h. Anodic alumina films were generated in a two-electrode electrochemical cell, with graphite as the counter electrode and an Al foil as the working anode. A computer-controlled programmable AC/DC Power Sourcemeter (APS-1102) was used to apply the anodization voltage.

After the first anodization step, the second anodization step was carried out using the same acid electrolyte (0.3 M $H_2C_2O_4$) and the same temperature. In this way, a self-ordered layer of vertical pores is obtained. To obtain the PC structure, the cyclic anodization process starts immediately at 50 V by cycle voltage waveforms with four voltage steps per period to generate alumina multilayer, and each cycle consists of four phases: (i) an interval of constant voltage at 50 V last for t_1 s, (ii) a linear decreasing ramp from 50 to 20 V for t_2 s, (iii) subsequently, an interval of constant voltage at 0 V last for t_3 s, and (iv) an interval of constant voltage at 20 V last for t_4 s. During the second oxidation, a voltage waveform was shown in Fig. 1. After anodization, the back Al substrate of sample was removed. This process was carried out in a saturated mercury chloride solution.

The alumina films were characterized by field-emission scanning electron microscopy (FE-SEM, Zeiss Neon 60). Direct transmittance measurements were carried at room temperature in the range from 200 to 2500 nm by a spectrophotometer (Lamada 900) with the incident light perpendicular to the alumina-based PC.

In order to study the formation mechanism of the porous AAO multilayer, a series of control experiments by using different anodization voltage waveforms were carried out, which is indicated in Table 1.

3. Result and discussion

3.1. Morphology and mechanism studies

A typical anodization voltage consisted of 50 periods and each period of the voltage waveform composed of a high voltage of 50 V for t_1 (=30 s), then a linear decreasing ramp from 50 to 0 V for t_2 (=120 s), followed by 0 V for t_3 (=10 s), and 20 V for t_4 (=270 s) was used to anodize Al foils, as illustrated in Fig. 1. A type of multilayered nanostructures (Fig. 2a) which differ significantly from the commonly observed self organized nanotubular morphology is successfully achieved using pulse anodization voltage waveforms, as revealed by the SEM study. The AAO film shown in Fig. 2a has 50 layers with well-defined interfaces between neighboring layers. Such an excellent long-range structural

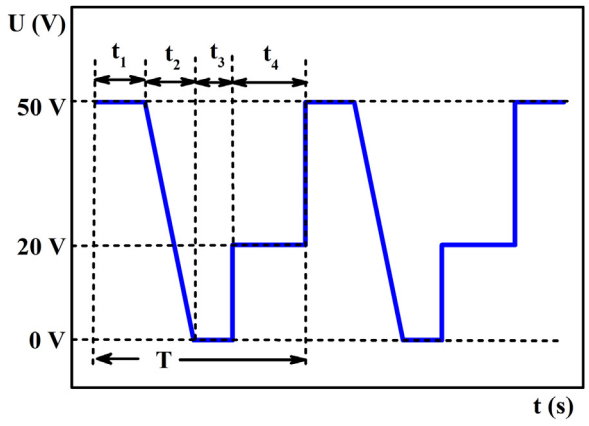

Fig. 1. Anodization voltage waveform mode applied during the anodization. And the duration of one period is *T*.