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Distributed Bragg reflector based on porous anodic alumina fabricated by pulse anodization

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Abstract

In this paper, we demonstrate a distributed Bragg reflector (DBR) based on nanoporous anodic aluminum oxide (AAO) formed by pulse anodization. The AAO structure with alternating mild anodized (MA) and hard anodized (HA) layers having different porosities and thereby different refractive indices was fabricated in 0.3 M H₂SO₄ using potential pulses of 25 and 35 V. The effective refractive index of the HA layers can be tailored by changing the porosity of the HA layers. The porosity of the HA layers can be significantly increased by selective chemical etching of HA segments in 0.52 M H₃PO₄. Before etching, the porous AAO structure was supported by a polymer nanorod frame. On the selected surface area pores were infiltrated with polymers (polystyrene and PMMA). The designed AAO structure consists of alternating high and low refractive index layers and behaves as a distributed Bragg mirror reflecting light in two different ranges of wavelength. This behavior is extremely important in optical communication lines where two separate spectral bands of high reflectivity in the infrared region are desired.

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, porous anodic aluminum oxide (AAO) with self-organized arrays of hexagonally arranged nanopores, produced by electrochemical anodization, has been widely used as a flexible template for fabrication of various onedimensional nanostructured materials including nanowires, nanotubes, and nanodot arrays [1–8] as well as nanoparticles and nanopeapods [9–11]. The wide range of AAO applications also covers fields of research like sensing, catalysis, separation, design of modern devices and tissue engineering [12–15]. Among the various methods used for fabrication of one-dimensional nanomaterials, AAO template-assisted synthesis has proved to be a low cost, well-developed and high yield technique.

The structure of AAO layers formed by a self-organized two-step anodization of aluminum consists of a close-packed array of columnar hexagonal cells with nanopores at their centers [16]. Porous AAO with unidirectional channels provides an excellent architecture with a narrow pore diameter distribution, uniform pore depth and pore density conveniently controlled by changing the anodizing conditions. By adjusting the applied voltage in a constant voltage regime or current density under constant current anodizing, the pore dimensions and interpore spacing can be strictly controlled [16]. The most commonly used electrolytes for the preparation of porous AAO layers are sulfuric acid, oxalic acid, and phosphoric acid [16–22].

In general, the fabrication of AAO membranes is usually based on a conventional mild anodization (MA) [17–22] and hard anodization (HA), known also as high-field anodization [23–29], conducted under a constant voltage or constant current mode. In the mild anodizing process, the window of applicable voltages is narrow and strictly correlated with the type of electrolyte used. For the constant voltage mode, a hexagonal close-packed arrangement of cells in AAO layers is observed only for self-ordering regimes that equal 25 V, 40 V and 195 V for sulfuric acid, oxalic acid and phosphoric acid, respectively. Moreover, the rate of oxide growth in typical MA processes is low and does not exceed a few μ m h⁻¹. In the HA process, the ranges of applicable voltages and self-ordering regimes are different from those established for MA processes. The current density passing during hard anodization is much higher than in the MA process and the rate of oxide growth increases by about 25-35 times [25]. In order to avoid breakdown of the oxide film during hard anodization, aluminum is usually pre-anodized under MA conditions using the constant current density or constant potential mode. For both anodizing techniques (MA and HA), linear dependences between applied voltages and pore diameter (D_p) or interpore distance (D_c) are observed. Although the MA and HA processes are extremely flexible in the design of porous alumina structure, the diameter of the parallel channels cannot be engineered easily without changing the anodizing voltages. A modulation of the AAO pore diameter can be achieved in the MA process by changing the anodizing electrolyte to one having a different pH [30] or by subsequent combination of MA and HA processes [25, 31].

In recent years, a new technique, known as pulse anodization, has been developed for the formation of wellordered porous AAO with a periodically modulated diameter of channels in typical anodizing electrolytes [31-34]. The pulse anodizing process combines both mild and hard anodization conditions. A pulse sequential voltage technique, with a pulse frequency of 100 Hz, has been proposed for the strict control of pore diameter in the range of low anodizing voltages (below 3 V) where a linear dependence between pore diameter and forming voltage does not exist [14, 35]. A galvanostatic cyclic anodization, employing a periodic oscillatory signal during the anodization process, was used for advanced creation of modulated pore structures with different geometries [36, 37]. The main advantage of the cyclic anodizing method is the strict control of not only the pore diameter but also the geometry of the pore structure.

One-dimensional photonic structures based on a stack of thin layers of transparent dielectric with alternating high and low refractive index have found applications as distributed Bragg reflectors that offer a high reflectance similar to metallic mirrors [38]. The reflectivity of the Bragg mirror is characterized by a high reflectivity stop band and a stop band that enlarges and sharpens when the number of alternating layers in the Bragg mirror increases. It is widely recognized that the spectral width of the reflected wavelength ($d\lambda_{\text{Bragg}}$) at full width at half maximum (FWHM) is proportional to the reflected wavelength (λ_{Bragg}) [39] and decreases when the number of dielectrics stacked (*N*) is increased as

$$d\lambda_{\rm Bragg} = \frac{2\lambda_{\rm Bragg}}{N}.$$
 (1)

On the other hand, the intensity of the reflected light depends on the number of dielectrics stacked (*N*), and the low (n_L) and high (n_H) refractive indices of the alternating layers [40]. When absorption is neglected, the reflectivity at normal incidence of a multilayered structure with N+1 layers is given as follows:

$$R = \left(\frac{n_{\rm o} - (n_{\rm H}/n_{\rm L})^N n_{\rm H}^2/n_{\rm o}}{n_{\rm o} + (n_{\rm H}/n_{\rm L})^N n_{\rm H}^2/n_{\rm o}}\right)^2$$
(2)

where n_0 is the refractive index of the ambient medium.

Recent studies have demonstrated distributed Bragg reflectors based on various materials and fabricated using different methods, e.g., porous silicon layers by electrochemical etching [38, 41-45], PbTe/EuTe [46] and AlN/GaN [47] multilayers grown by molecular beam epitaxy and TiO2 nanoparticle multilayers by spin coating [48]. So far, there have only been a few reports on fabricating distributed Bragg reflectors on the basis of porous anodic alumina layers [49–51]. These Bragg reflectors for the visible range were fabricated using a sinusoidal modulation of anodizing potential resulting in periodically branched channel structures of the AAO. By fabricating a porous anodic alumina structure that consists of a sufficient number of alternating low and high porosity layers (with different refractive indices), Bragg reflectors can be designed to operate throughout the infrared region. The porosity in the AAO layers is varied in depth by changing the regimes of anodic alumina growth (MA and HA processes). This allows the production of a stack of porous anodic alumina layers with modulated refractive indices.

Herein, we report for the first time an investigation on the pulse anodic oxidation of aluminum as a method of fabricating a distributed Bragg reflector. A pulse anodization technique combining mild and hard anodizations was employed in order to build a stack of layers with different porosities and thereby different refractive indices. The selective etching of an HA layer allows its effective refractive index to be reduced.

2. Experimental details

2.1. Anodization of aluminum

A high-purity aluminum foil (99.999%) supplied by Goodfellow was used as the substrate material. After degreasing in ethanol, the electrochemical polishing of Al substrates was carried out in a stirred mixture of HClO₄ and C₂H₅OH (1:4 vol) under a constant voltage of 20 V for 3 min at 10 °C. The anodic porous alumina films were formed by a two-step procedure in 0.3 M H₂SO₄ at a temperature of 1 ± 0.02 °C. The first anodizing step was performed at a constant cell voltage of 25 V for 16 h. The resulting porous alumina layer was removed by chemical etching in a mixture of 6 wt% H_3PO_4 and 1.8 wt% $H_2Cr_2O_4$ at 45 °C for 12 h. Subsequently, a pulse anodization was performed by applying a series of 50 potential pulses comprising a mild anodizing (MA) pulse (25 V for 3 min) and a hard anodizing (HA) pulse (35 V typically for 1.5 s). In order to avoid breakdown of the anodized film during the first HA pulse, the duration of the first MA pulse (MA-0) was extended to 1 h. The applied voltage signal for pulse anodization of aluminum and the structure of the AAO layer grown are schematically shown in figure 1.



Figure 1. Pulse anodization of aluminum for pore diameter modulations. (A) A typical voltage signal applied during the pulse anodization of aluminum, where U_{MA} and U_{HA} are the anodizing potentials used to achieve mild anodizing (MA) and hard anodizing (HA) conditions, respectively. (B) The AAO structure grown after a few HA and MA pulses.

All the anodizations were performed in a 0.1 dm³ Teflon cell cooled by a powerful circulating system (Thermo Fisher, Haake Phoenix II) with vigorous stirring. The working surface area of the samples was 0.95 cm². A Pt grid was used as a cathode, and the distance between the two electrodes was about 2 cm. The electrochemical cell was connected with a Keithley 2430 power supply.

2.2. Fabrication of distributed Bragg reflectors

The general processes employed for fabricating distributed Bragg reflectors on the basis of AAO are schematically shown in figure 2.

Firstly, a few TEM grids (400 mesh, Plano W Planet GmbH) were placed on the AAO surface and a thin layer of Au was sputtered through the TEM grids on the top side of the AAO using a Cressington Sputter Coater 108 auto. After TEM grid removal, the accessible parts of the AAO pores were impregnated with polymers in order to form polymer nanopillars supporting the porous AAO structure. Solid polystyrene beads (PS, $MW = 100\ 000$, Alfa Aesar) were placed directly on the AAO layer and the sample was heated up to 250 °C. A pressure injection technique [52] was used for impregnation of the pores with melted PS. For impregnation of the pores with PMMA, a commercially available methyl methacrylate monomer (MMA, Alfa Aesar) stabilized with hydroquinone was passed through a short column of activated neutral gamma alumina (60 mesh, Alfa Aesar, Cat. No. 11502) to remove the inhibitor. Then, a mixture of purified methyl methacrylate (MMA) monomer with 2 wt% benzoyl peroxide (wetted with 25% H₂O, Alfa Aesar) as an initiator for polymerization was spin coated uniformly on the AAO substrates. The polymerization of PMMA was carried out in a glove box under an inert atmosphere of nitrogen at 50 °C for 12 h. After successful impregnation of the pores with

polymers (PS or PMMA), the excess top layer of polymer was removed by a chemo-mechanical cleaning in chloroform. Subsequently, the remaining Au layer was removed by chemical etching in a solution containing 0.6 M KI and 0.2 M I₂. Then, a selective removal of HA layers in the AAO structure filled partially with polymer nanopillars was performed through the unblocked pores. The HA segments of the AAO layer were removed by chemical etching in 0.52 M H₃PO₄ for 30 min at 45 °C. Finally, the remaining aluminum substrate was removed by chemical etching in a solution containing 0.1 M CuCl₂·2H₂O and 6.1 M HCl.

2.3. Characterization

The morphology of the fabricated nanoporous AAO templates was observed by field emission scanning electron microscopes (FE-SEMs: JSM-6701F, Joel and S-4700, Hitachi) after successive gold evaporation. The reflectivity data were collected using the ATR technique, with a Bio Rad Excalibur Series FT-IR spectrometer with a UMA 500 microscope and a silicon carbide rod (Globar) as a thermal light source. The reflectivity spectrum, normalized to the reflectance of the silver mirror, was measured for a 45° angle of incidence using unpolarized light. The Ag mirror's average reflection values were >97.5% and >96% for the ranges 450 nm–2 μ m and 2–20 μ m, respectively. A liquid nitrogen cooled mercury cadmium telluride (MCT) detector with a spectral range of 7500–650 cm^{-1} was used. The epitaxy supporting software (EPITAXYproject[®]) was used for reflectance spectrum simulation [53].

3. Results and discussion

Pulse anodization under a potentiostatic regime is a combination of mild anodization (MA) and hard anodization



Figure 2. Schematic illustration of the fabrication of distributed Bragg reflectors from AAO membranes: (A) AAO layer with alternating MA and HA layers fabricated by pulse anodization, (B) one of the TEM grid crosses on the AAO surface, (C) AAO with a Au layer sputtered through the TEM grids, (D) AAO with partially blocked pores (Au layer) after grid removal, (E) accessible pores in AAO impregnated with polystyrene (PS) by pressure injection of melt or by polymerization of PMMA inside the pores, (F) AAO after removal of excess PS and PMMA by chemo-mechanical cleaning or oxygen plasma etching, (G) AAO with unblocked pores after a chemical removal of the Au layer, (H) AAO with a polymer (PS or PMMA) nanowire skeleton after chemical etching of the HA layers, (I) a free-standing distributed Bragg reflector after the removal of the remaining Al.

(HA) conditions. In a pulse anodization process performed in sulfuric acid, the AAO structure is formed using alternating low potential (MA, 25 V) and high potential (HA, 35 V) pulses as shown in figure 1. The AAO structure consists of alternating MA and HA layers that exhibit different pore diameters, different contents of incorporated electrolyte species and fracture behavior [3]. The thicknesses of the anodized MA segments are strictly determined by the durations of the MA pulses. A uniform thickness of HA layers can be achieved by applying relatively long HA pulses [3]. As a consequence of the layered structure of the porous alumina (periodic MA and HA segments), the pore diameters of the AAO are periodically modulated along the pore axis (figure 3).

Figure 3 shows a cross-sectional SEM image of AAO with modulated pore diameters formed by pulse anodization in 0.3 M H_2SO_4 at 1 °C. The alternating potential pulses with step heights of 25 V and 35 V were applied for mild and hard anodizations, respectively. The durations of the MA and HA pulses were 180 and 0.5 s, respectively. The estimated pore diameters in the MA and HA segments were about 16 and 35 nm, respectively. The thicknesses of the HA layers in the formed AAO are not the same due to a relatively short HA pulse duration [3]. As was previously shown, uniform



Figure 3. SEM cross-sectional view of AAO with modulated pore diameters by pulse anodization in 0.3 M H₂SO₄ at 1 °C. Each cycle consisted of an MA pulse ($U_{\text{MA}} = 25$ V, $t_{\text{MA}} = 180$ s) and an HA pulse ($U_{\text{HA}} = 35$ V, $t_{\text{HA}} = 0.5$ s).

thickness of the HA segments can be achieved by extension of the HA pulse duration to at least 1.2 s [3]. Consequently, for the given durations of MA and HA pulses ($t_{MA} = 180$ s and $t_{HA} = 1.5$ s) the thicknesses of the alternating MA and HA layers can be relatively uniform (figure 4).

Figure 4 shows cross-sectional and side views of an AAO layer formed at 1 °C in 0.3 M H₂SO₄ by pulse anodization

with a potential waveform varied between 25 and 35 V. For pulse anodization, a sequence of 50 cycles was applied. Each cycle consisted of an MA pulse of 25 V (t_{MA} = 180 s) and an HA pulse of 35 V ($t_{\text{HA}} = 1.5$ s). It is well known that HA layers with a higher content of electrolyte impurities incorporated in cell walls are less chemically stable against phosphoric acid [3, 32]. Therefore, the AAO sample presented in figure 4 was pre-etched in 0.52 M H₃PO₄ at 45 °C for 20 min for better visualization of the HA segments. After significant etching of the HA layers, the top layers of the structure push down on the bottom layers and, the bottom HA segments are partially squeezed. Consequently, slightly different thicknesses of the HA layers (at the top and the bottom) are observed in figure 4(A). In order to avoid complete collapse of the layered structure after etching, the structure presented in figure 4(A) was supported by polymer nanopillars (bright part). The thicknesses of the MA and HA layers were estimated to be 750 and 800 nm, respectively.

Notice, importantly, that the layered AAO structure formed by pulse anodization has HA segments with a higher pore diameter. Since the porosity of hexagonally arranged nanoporous AAO depends on the square of the ratio of the pore diameter to the interpore distance, the HA layers possess a higher porosity than the MA layers. On the other hand, the refractive index of each layer is directly related to the porosity of that layer by an effective medium model. The refractive indices of the porous alumina layers can be calculated using effective medium approximations given by Bruggeman [54]:

$$(1-P)\frac{\varepsilon_{\text{Al}_2\text{O}_3} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{Al}_2\text{O}_3} + 2\varepsilon_{\text{eff}}} + P\frac{\varepsilon_{\text{void}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{void}} + 2\varepsilon_{\text{eff}}} = 0, \qquad (3)$$

Maxwell-Garnett [55]:

$$\varepsilon_{\rm eff} = \varepsilon_{\rm Al_2O_3} \frac{2\varepsilon_{\rm Al_2O_3} + \varepsilon_{\rm void} + 2P(\varepsilon_{\rm void} - \varepsilon_{\rm Al_2O_3})}{2\varepsilon_{\rm Al_2O_3} + \varepsilon_{\rm void} - P(\varepsilon_{\rm void} - \varepsilon_{\rm Al_2O_3})}, \quad (4)$$

Monecke [56]:

$$\varepsilon_{\rm eff} = \frac{2 \left[P \varepsilon_{\rm void} + (1 - P) \varepsilon_{Al_2 O_3} \right]^2 + \varepsilon_{\rm void} \varepsilon_{Al_2 O_3}}{(1 + P) \varepsilon_{\rm void} + (2 - P) \varepsilon_{Al_2 O_3}}, \quad (5)$$

Looyenga [57]:

$$\varepsilon_{\text{eff}}^{1-2A} = (1-P)\varepsilon_{\text{Al}_2\text{O}_3}^{1-2A} + P\varepsilon_{\text{void}}^{1-2A},\tag{6}$$

and Lorentz–Lorentz [58]:

$$\frac{\varepsilon_{\rm eff} - 1}{\varepsilon_{\rm eff} + 2} = P \frac{\varepsilon_{\rm void} - 1}{\varepsilon_{\rm void} + 2} + (1 - P) \frac{\varepsilon_{\rm Al_2O_3} - 1}{\varepsilon_{\rm Al_2O_3} + 2},\tag{7}$$

where *P* is porosity, $\varepsilon_{Al_2O_3}$ is the dielectric constant of Al₂O₃, ε_{eff} is the effective dielectric constant of porous alumina, ε_{void} is the dielectric constant of the medium inside the pores (for air $\varepsilon_{void} = 1$), and *A* is the depolarization factor which depends on the shape of the inclusions (for sphere inclusions A = 1/3). Assuming that the dielectric constant of air (ε_{void}) is unity, the dielectric constant of bulk aluminum oxide ($\varepsilon_{Al_2O_3}$) for a wavelength of 1550 nm is 1.746 [59], $n_{eff}^2 = \varepsilon_{eff}$ and the absorption coefficient of porous alumina is negligible, the effective refractive indices for various AAO porosities were calculated from equations (3)–(7) and are plotted in figure 5.



Figure 4. Cross-sectional ((A) and (B)) and side (C) views of an AAO structure with alternating MA and HA layers formed by pulse anodization of aluminum in 0.3 M H₂SO₄ at 1 °C. Each cycle of pulses consisted of an MA pulse ($U_{MA} = 25 \text{ V}$, $t_{MA} = 180 \text{ s}$) and an HA pulse ($U_{HA} = 35 \text{ V}$, $t_{HA} = 1.5 \text{ s}$). For better visualization of the periodically aligned MA and HA layers, the HA layers were chemically etched in 0.52 M H₃PO₄ at 45 °C for 20 min.

With increasing porosity of AAO its refractive index decreases independently of the effective medium model used. The different methods used for the approximation of the effective refractive index gave relatively similar results. In the middle of the bunch of plotted curves there is one describing the Bruggeman symmetric approximation. Therefore, we decided to use the Bruggeman's effective medium theory in further calculations.

The AAO structure with alternating MA and HA layers having different porosities and thereby different refractive indices is indeed a stack of layers acting as a distributed Bragg reflector (DBR). The porosity of the HA layers can even be



Figure 5. The relationship between porosity and refractive index of porous AAO as given by various effective medium approximations.

increased by selective etching of the HA segments performed in H₃PO₄. A significant extension of etching time leads to selective and nearly complete removal of the HA layers from the layered AAO structure [32]. As a result of selective etching of AAO, a multilayered dielectric structure consisting of alternating high and low refractive index layers (n_{MA} and $n_{\rm HA}$) is obtained. There are three main parameters that influence the reflectivity spectrum: periodicity, thicknesses of the layers and porosities (i.e. refractive index contrast, $n_{\rm MA}/n_{\rm HA}$). Pulse anodization allows control of the thickness of the HA layers only within a limited range. For short pulse durations, shorter than or equal to 1.2 s, nonuniform thicknesses of HA layers in the AAO structure are typically formed. On the other hand, for longer pulse durations, longer than a few seconds, a serious risk of dielectric breakdown phenomena appears. Therefore, the accessible thicknesses of the HA layers are limited. The refractive index contrast increases with increasing duration of chemical etching of AAO. Notwithstanding, wet etching of HA layers cannot be carried out too extensively in order to avoid collapse of the layered AAO structure. Our new approach, shown schematically in figure 2, allows for extended etching of the HA layers. The chemical etching of the HA layers is preceeded by impregnation of the layered AAO structure with polymers (polystyrene or PMMA). The polymer infiltration is carried out on the selected surface area in places previously occupied by grid bars. After etching of the HA layers, the polymer nanopillars inside the AAO structure serve as a frame which supports the whole construction of the porous structure. Figure 6 shows a cross-sectional SEM image of a typical DBR based on porous AAO impregnated with PMMA according to the procedure presented in figure 2. The designed DBR consists of 50 pairs of alternating MA and HA layers.

The thicknesses of the MA and HA layers (d_{MA} and d_{HA}) were estimated to be about 750 and 800 nm, respectively (see figure 4). The etching of the HA layers was carried out in



Figure 6. SEM image of a free-standing porous AAO stack of 50 alternating HA and MA layers infiltrated with PMMA according to the procedure presented in figure 2. Inset: a schematic diagram of the AAO surface after Au sputtering through the grid and grid removal (see figure 2(D)).

0.52 M H₃PO₄ for 30 min at 45 °C. After the etching process, the pore diameter in the MA layers increased to 28 nm and its porosity to 26.5% ($n_{MA} = 1.541$). An estimation of the porosity of the HA layers was not possible. The polymer light pillars in the etched AAO structure are clearly visible in the part where the grid bar was located. Some remains of the HA layers are visible in the right-hand side of the image similarly to what was observed in figures 2(B) and (C).

A schematic diagram of the designed periodic Bragg reflector based on a porous alumina multilayered stack together with its measured and simulated reflectance spectra are shown in figure 7.

For simulation of the reflectance spectrum, the following experimental data were used: $d_{MA} = 750 \text{ nm}, d_{HA} = 800 \text{ nm},$ $d_{MA-0} = 7500$ nm, $n_{MA} = 1.541$, and the number of pairs of HA and MA layers in the stack was 50. The effective refractive index of the HA layers, $n_{\rm HA}$, calculated from simulation, was 1.22. The reflectance spectrum collected from the bottom side of the AAO revealed wide Bragg peaks in the near infrared range. The simulated spectrum exhibits two peaks in a similar wavelength range to the measured reflectance spectrum. The measured reflectance spectrum is not as perfect as simulated one due to the presence of irregular remains in the HA layers of the Bragg mirror based on porous AAO. Additionally, a possible variation in the thicknesses of the alternating MA and HA layers also influences the quality of the designed DBR structure. The problem of further development and optimization of the fabrication procedures, assuring sufficient mechanical stability of the proposed device after the extended etching of HA layers, will require considerable research effort in future studies. Nevertheless, the fabricated AAO behaves as a double mirror reflecting two different wavelength ranges. It is especially important in optical communication lines where two separate spectral bands of high reflectivity in the infrared region are desired.



Figure 7. A schematic diagram of the Bragg reflector with 50 pairs of alternating HA and MA layers together with the measured and calculated reflectance spectra of the designed mirror. The alternating high (MA) and low (HA) index layers have thicknesses of 750 and 800 nm, respectively. The thickness of the initial MA layer (MA-0 layer) was 7500 nm.

4. Conclusions

In summary, a distributed Bragg reflector based on porous AAO was presented. Using pulse anodization of aluminum with periodic pulses of 25 and 35 V, a stack of alternating MA and HA layers with different porosities and different reflection indices was fabricated. The porosity of the HA layers can be tuned by selective wet chemical etching of the HA segments carried out in a H_3PO_4 solution. A considerable increase in the porosity of the HA layers on the selected surface area. The formed polymer nanopillars support the porous AAO and after etching of the HA layers as a double mirror reflecting light in the near infrared range.

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