EFFECT OF TEMPERATURE ON SINUSOIDAL PULSE ANODIZATION OF ALUMINUM AND THE OPTICAL PROPERTIES OF THE RESULTED POROUS GRADIENT-INDEX FILTERS

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Abstract

Pulse anodization of aluminum is a promising method to produce porous photonic crystals (PCs) with tunable photonic stopbands (PSBs) by a fully programmable change of electrochemical conditions. The spectral position of the PSBs is mainly determined by thickness and porosity of alternate layers forming the periodic structure. Temperature is one of the most important factors influencing the growth of porous anodic alumina (PAA). It alters the rate of PAA formation and the porosity of PAA layers. In this work, the effect of the anodizing temperature on the characteristic PSBs of graded-index PCs produced by sinusoidal pulse anodization (SPA) is analyzed. Two different anodization periods (t_p) of the sinusoidal function were used whereas the amplitude and the number of cycles were kept constant. It was revealed that upon increasing the temperature from 5 to 30 °C the ion transport from electrolyte reservoir to the pore base becomes progressively hindered by increasing total PAA thickness which was manifested in the delayed current recovery to the initial values. As an effect, the periodic structures with inhomogeneous layers' thickness were formed providing broad and irregular PSBs in optical spectra. The quality of PSBs can be, however, significantly improved by post-processing pore broadening. Well-resolved and intensive peaks, which shift towards red part of the spectrum with increasing temperature and t_p, could be then obtained. After a proper modification of the pulse sequence (e.g. application of the current density-controlled mode) the PCs can be used in optical sensing platforms operating from UV to NIR spectral range.

Keywords: Anodization, porous anodic alumina, anodizing temperature, gradient-index filters, optical properties

1. INTRODUCTION

Porous anodic alumina (PAA) is a well-known template used in various fields of nanotechnology owing to fully controllable geometrical parameters, such as pore diameter or interpore distance, achieved by a simple change of anodization conditions (e.g. applied voltage, type of electrolyte, anodizing temperature) [1,2]. Upon application of pulse anodization the porosity of the material can be periodically modulated forming thus 1D photonic structure that prohibits light of a certain wavelength to propagate through the material. As a consequence of constructive interference of the light reflected from each boundary between low and high porosity layers, photonic stop band (PSB) is created which is manifested as a peak in a reflectance spectrum or a dip in a transmittance spectrum [3, 4]. Various pulse anodization modalities were used to precisely modulate pore geometry in PAA in order to obtain high quality optical filters with PSBs in a given part of the spectrum [5-8]. A sinusoidal pulse anodization (SPA) was performed previously in sulfuric acid solution [9,10]. The effect of anodization amplitude, offset, period, time, and the acid concentration of a sinusoidal

function on the quality of characteristic PSBs was systematically studied. It was shown that all parameters are statistically important in PSBs engineering, however, the anodization time appeared to be the most significant in defining the quality of photonic resonances. The influence of anodizing temperature was also analyzed in these works, however, the range of temperature variation was very narrow: from -2 to 6 °C. Here, we study the system behavior subjected to the SPA in oxalic acid solution in a broad temperature range: 5 - 30 °C. We demonstrate that both quality and the spectral position of PSBs are strongly affected by anodization temperature. By using this approach graded-index filters with photonic properties extended from UV up to NIR can be engineered.

2. MATERIALS AND METHODS

High-purity aluminium foil (99.9995% Al, Puratronic, Alfa-Aesar, Haverhill, MA, USA) was used to produce the PAA-based PCs. The aluminium substrate was electropolished in a mixture of ethanol and perchloric acid 4:1 at 25 V for 2.5 min at 0 °C. After the electropolishing, the samples were rinsed several times in distilled water and then in ethanol. Subsequently, the dried Al specimens were protected with acid-resistant paint at its the back and the edges. Next, the first anodization step was performed in a 0.3 M oxalic acid at 40 V for 20 h. After the first anodization alumina was selectively dissolved in a mixture of phosphoric acid and chromic acid at 65 °C for three hours. Then, PAA-based PCs were fabricated by sinusoidal pulse anodization with 150 cycles, amplitude (A) of 6 V (U_{max} = 52 V, U_{min} = 40 V), and two different anodization periods (t_p): 100 and 200 s (**Figure 1a**). The current density response was measured during the potentiostatic anodization performed under the time-controlled mode. A platinum grid served as a cathode. The distance between electrodes was kept constant (ca. 5 cm). A 1 L electrochemical cell was used with a powerful constant-temperature bath (with temperature stability ±0.01 °C) and vigorous stirring (250 rpm). The anodization temperature was varied between 5 °C, and 30 °C. A programmable DC power supply, model 62012P-600-8 Chroma, was employed to control the electrochemical parameters. Morphology of the samples was studied by a field-emission scanning electron microscope FE-SEM FEI Quanta 3D FEG. The transmission measurement were obtained using the Agilent CARY 7000 UV-Vis-NIR.

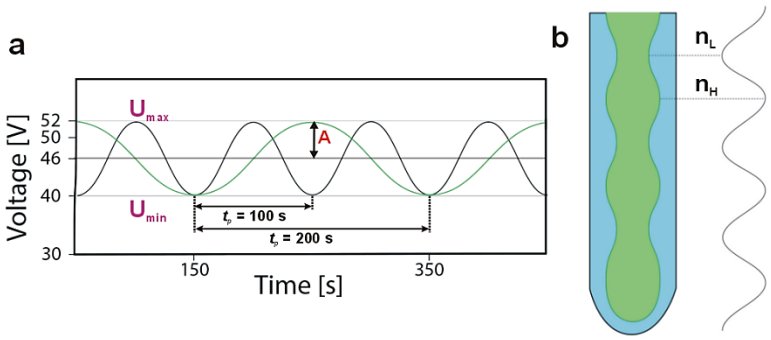

Figure 1 The parameters of the voltage sinusoidal function used in the pulse anodization (**a**) and a scheme of pore profiling resulted from the sinusoidal pulse anodization (SPA) (**b**)

3. RESULTS AND DISCUSSION

The application of the sinusoidal pulse anodization allows for pore shape profiling and thus obtaining periodically changing porosity with a gradual variation of refractive index from maximal (n_L) to minimal (n_H) values (**Figure 1b**). In **Figure 2**, voltage and current density vs. time transients recorded during sinusoidal pulse anodization of aluminum at temperatures of 5 -30 °C for the two different anodization periods (t_p = 100 and 200 s) are shown. Current density (red lines) tends to increase with increasing anodizing temperature for

both t_p. Moreover, current recovery process becomes increasingly difficult when the samples are anodized above 25 °C for t_p = 100 s and above 15 °C for t_p = 200 s. This observation indicates the appearance of diffusional-related problems with ion transport from the electrolyte bulk to the pore base [11,12]. In this situation, the growth rate of porous anodic alumina occurs faster than the delivery of fresh ions to the reaction center. As an effect, the overall current does not reach the same value for the succeeding U_{max} in the following anodization cycles as the process proceeds. This, in turn, results in a progressive reduction of thickness of the subsequent low and high porosity segments [13]. Furthermore, the current oscillation during the sinusoidal pulse anodization with t_p = 200 s occurs within a much smaller j values than that during the anodization with t_p = 100 s. This is due to a milder voltage change when increasing to U_{max} and when decreasing to U_{min} (**Figure 1a**). At 30 °C, the amplitude of current oscillation decreases of more than two times at the end of the anodization as compared to the beginning of the process for both t_p. For t_p = 200 s, the irregular current behavior is observable already at temperature > 15 °C.

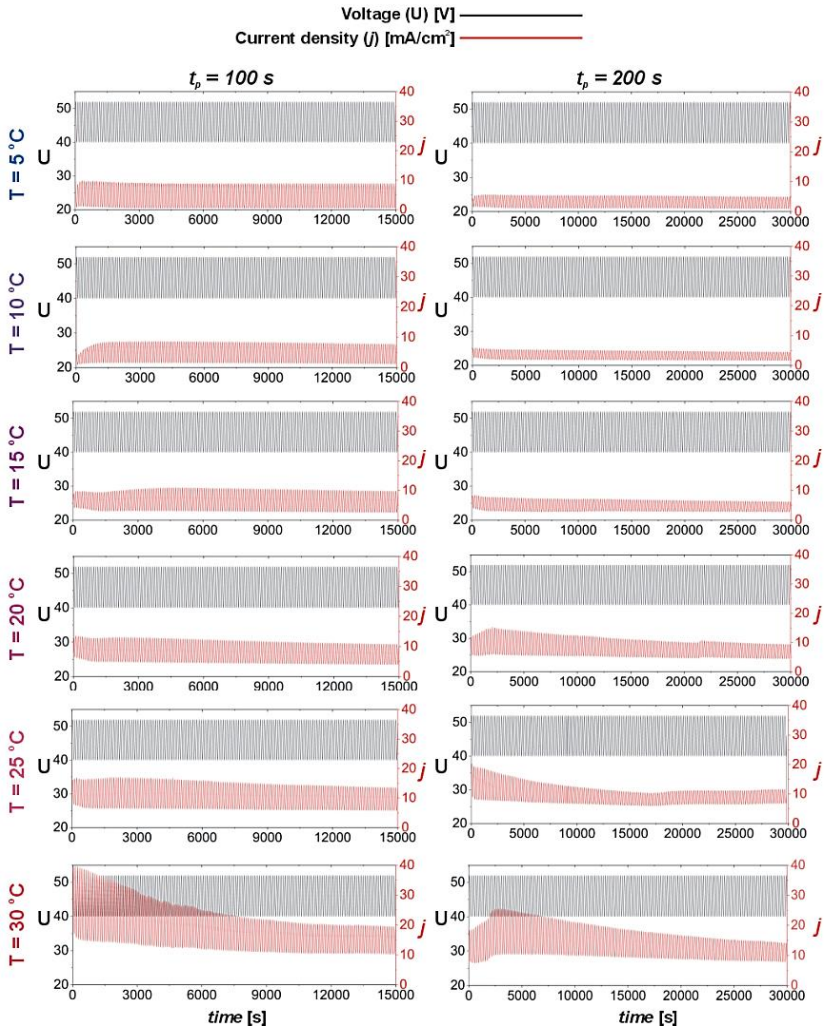

Figure 2 Voltage and current density vs. time transients recorded during sinusoidal pulse of aluminum at temperatures 5 -30 °C for two different anodization periods (t_p = 100 and 200 s)

In **Figure 3**, exemplary SEM images of porous gradient-index filters synthesized at 20 °C, are demonstrated. Periodic variation of applied voltage from U_{max} to U_{min} allows to distinguish separate segments of the thickness that depends on t_p. The thickness of separate segments as well as the total thickness of PAA prepared with t_p = 200 s (**Figure 3b**) is double the relevant thicknesses of PAA produced with t_p = 100s (**Figure 3a**).

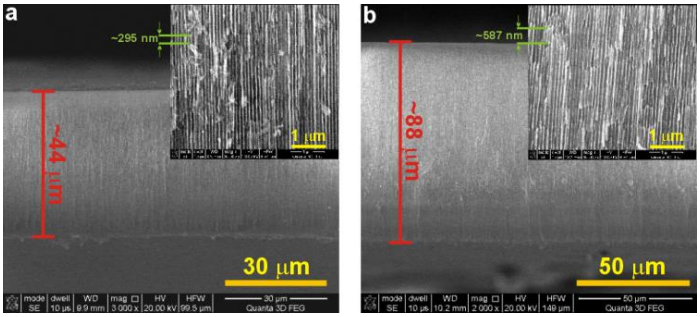

Figure 3 Exemplary SEM images of the porous gradient-index filters prepared at 20 °C for t_p = 100 s (**a**) and t_p = 200 s (**b**) (the insets: larger magnifications of the relevant images)

Optical spectra of the samples directly after the synthesis are shown in **Figure 4**. It can be seen that the quality of PSBs is rather low. Moreover, with temperature the peaks become progressively broadened and shift towards red part of the spectrum. This trend is opposite to that observed by Law et al. [10]. It should be, however, noticed that in the work [10] temperature was changing by 1 °C in the range -1 - 6 °C, which caused only a slight increase in the porosity (and thus the decrease of effective refractive index). This, in turn, according to the Bragg-Snell law [14], made the PSB to shift towards shorter wavelengths. In this experiment, owing to the much larger temperature variation, the increase of segment thickness was more significant than the increase in porosity and, therefore, the PSBs moved towards longer wavelengths.

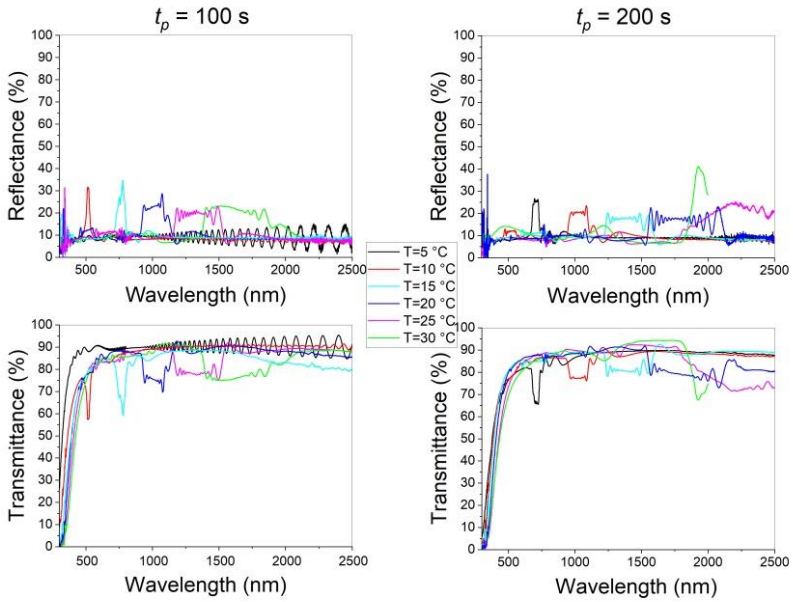

Figure 4 Reflectance and transmittance spectra of the gradient index optical filters produced at various temperatures (5-30 °C) directly after anodization (before pore broadening)

It was shown before that pore widening has a substantial effect on position and shape PSBs [15]. In **Figure 5**, the optical spectra of the same samples but after pore broadening (the samples were immersed in 5 wt% H_3PO_4 acid solution for 30 min at 30 °C) process are shown. As can be seen, the quality of PSBs was considerably improved. Well-resolved and symmetric first order PSB (λ_{PSB1}) can be distinguished that widen with increasing temperature. The spectral position of the λ_{PSB1} shifts to the red part of the spectrum with increasing both anodizing temperature and t_p (**Figure 6**). The shift of λ_{PSB1} is about 65 nm/°C and 52 nm/°C for t_p = 200 s and 100 s, respectively.

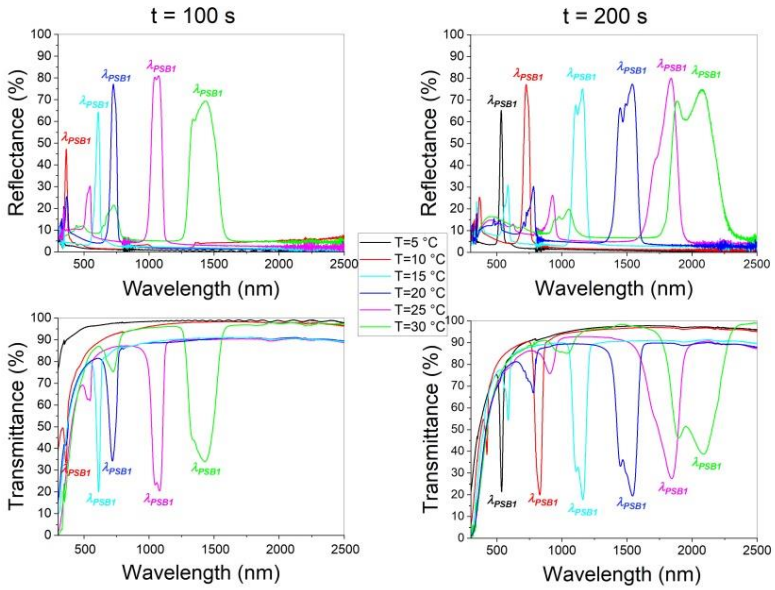

Figure 5 Reflectance and transmittance spectra of the gradient index optical filters produced at various temperatures (5-30 °C) and after pore broadening in 5 wt% H_3PO_4 acid solution

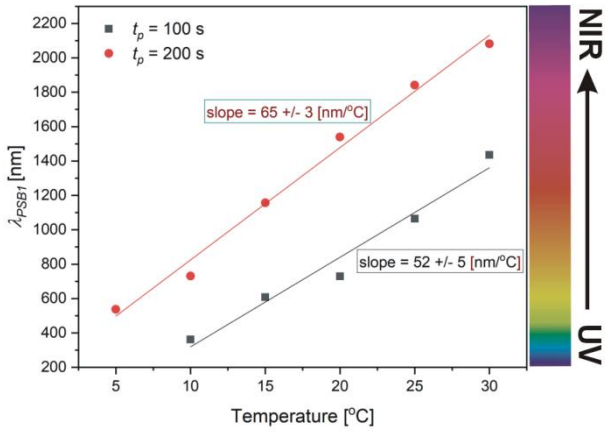

Figure 6 Spectral position of the PSBs as a function of anodizing temperature for the samples anodized with t_p = 100 s and 200 s

4. CONCLUSION

Gradient-index filters were synthesized by sinusoidal pulse anodization of aluminum. The effect of anodizing temperature in the range between 5 and 30 °C on electrochemical performance and optical properties of the optical filters was studied for two anodization periods (t_p): 100 and 200 s. It was show that with increasing the temperature the current recovery to the initial values recorded during the first anodization cycles becomes hindered by diffusion-related problems. The irregular current flow starts to be significant at temperature > 25 °C for anodization with t_p = 100 s and at temperature > 15 °C for the anodization with t_p = 200 s. This behavior is reflected in the optical characteristics of the samples. Directly after the synthesis the filters demonstrate very wide, irregular photonic stopbands (PSBs) of low intensity. Post-process pore widening improves considerably the quality of PSBs. Well-resolved and symmetric first order PSBs (λ_{PSB1}) can be distinguished that shift towards longer wavelengths with both increasing anodizing temperature and t_p with proportionality constant of about 65 nm/°C and 52 nm/°C for t_p = 200 s and 100 s, respectively. The λ_{PSB1}

become, however, broadened as the anodization temperature increases. The approach shown in this work can be used for engineering porous optical filters for a broad spectral range spreading from VIS to NIR.

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