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Optical properties of thin nanoporous aluminium oxide films formed by anodization

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The anodic porous alumina templates are used for fabrication of nanomaterials such as nanowires, nanorods and nanotubes. In the present work the aluminum oxide thin films were fabricated by anodization of Al layer obtained by dc magnetron sputtering. The anodic alumina layer was formed in a two-step procedure under a constant cell voltage of 20 or 30V in a 2 or 4 wt % H_2SO_4 at temperature of 25°C. It is found that the reflectance of the film decreases and the transmittance increases with the increasing of the time of anodization. The optical constants and thickness of the aluminum oxide thin films after anodization were determined from normal incidence reflectance data.

Keywords: thin aluminum films, anodization, porous films, refractive index

INTRODUCTION

The surface of metals such as Al, Ta, Nb and Ti is instantaneously covered with a native oxide film when exposed to oxygen containing environment and can be used for fabrication of ordered pore arrays. Fabrication of nanoporous metal oxide templates has been attracting considerable interest because of their application in many areas such as fabrication of porous electrodes in gas sensors, nanoporous membranes for separation, template membranes used for skin tissue engineering, nanostructured materials with a periodicity lower than 100 nm and templates for growing of metal nanowires for metamaterials [1, 2].

The conditions of anodization influence strongly the processes occurring on the surface of the aluminum. Depending on the applied electrical voltage and the density of the current, processes of oxidation, self-organization and formation of periodic structures, electro-polishing and surface etching can be observed [3].

The anodic porous alumina templates used for fabrication of nanomaterials can be commercially purchased or laboratory made. Crucial faults of the commercially available templates are the lack of order in the nanopore arrangement and higher than the declared pore diameter. That's why the searching of conditions for fabrication of alumina templates with periodic structures is an appealing research task [4].

Porous anodic aluminum oxide templates are generally fabricated by anodization of aluminum foils. The anodized aluminum foils are not suitable for many applications in micro- and nano-devices. In these cases it is necessary to perform the anodization process on thin metal films [5].

The aim of the present work is to present our initial results for the anodization of thin aluminum films deposited on glass substrate by dc magnetron sputtering. The thickness and the refractive index of the created Al_2O_3 overlayer are determined applying the double layered model.

EXPERIMENTAL DETAILS

Thin aluminum films were deposited by dc magnetron sputtering technique in argon atmosphere with pressure $2.5.10^{-1}$ Pa in thin film deposition system Leybold Heraeus Z700 P2. The thickness of the thin films measured by profilometer was determined to be d = 107 nm. Anodization process was performed in the following steps:

1. The aluminum films were annealed at 380°C for 30 min to remove mechanical stresses and enablingre-crystallization.
2. Anodization was conducted under constant cell potential in 2wt % and 4 wt% water solutions of H_2SO_4 (sulfuric acid). The temperature in both cases was kept constantat25°C. The DC voltages were 20 and 30V. The current density was 1 and 5 A/cm^2.

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The surface of the thin films was observed by a scanning electron microscope Joel Superprobe 733 (Japan). The transmittance (T) and reflectance (R) were measured by a UV–VIS–NIR spectrophotometer Cary 5E (Australia) in the range 350–2000 nm to an accuracy of $\Delta T = \pm 0,1\%$ and $\Delta R = \pm 0,5\%$.

RESULTS

SEM images of thin aluminum films treated in 2 or 4 wt % water solutions of H_2SO_4 are presented in figure 1. Lines and indications for crystallization were observed on the surface of the films.

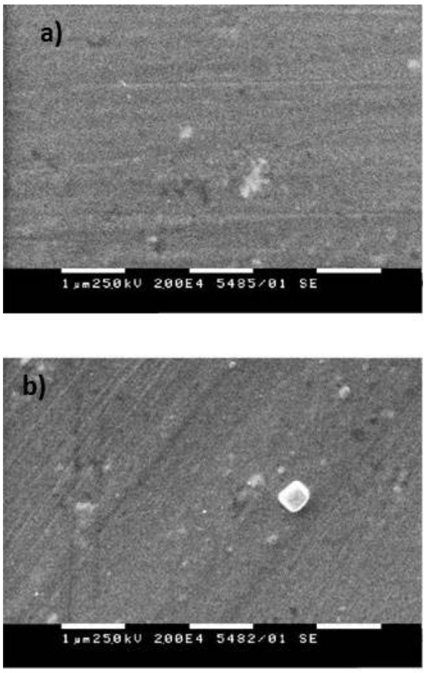

Fig. 1. SEM image of thin aluminum film after anodization in 2wt. % water solutions of H_2SO_4 for 60 min (a) and 90 min (b).

We suggest that the lines observed in the SEM images are due of the mechanical tensions in the films. In [6] it was observed that mechanical tensions lead to similar lines on the surface of the aluminum foil after anodization.

In Figure 2a the reflectance spectra of thin aluminum films before and after anodization process in 2 or 4 wt % water solutions H_2SO_4 at 25°C are presented. It is seen that the reflectance of treated in H_2SO_4 samples decreases and it depends on the time of the treatment. To understand the origin of these changes in the spectra we calculated the theoretical reflectance of a double-layered system consisting from Al_2O_3/Al on a glass substrate. It is seen on the Fig. 2b that the oxide overlayer affects the reflectance spectra in the visible spectral range.

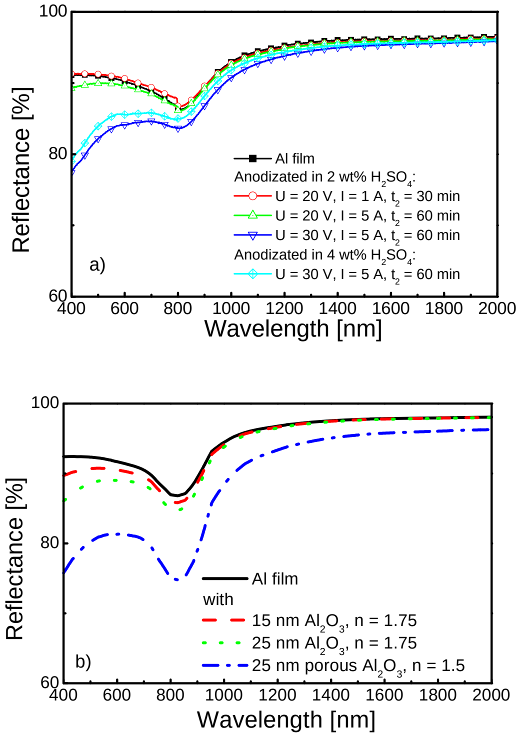

Fig. 2. Reflectance spectra of Al thin films before and after anodization at different times (a); theoretical simulation of the spectrum of Al film with thin Al_2O_3 overlayer with different thicknesses and refractive index (b).

In next step we have calculated the optical constants of non-treated Al film. The procedure of the calculation of the refractive index, *n* and extinction coefficient, *k* from transmittance and reflectance spectra is described in [7, 8].

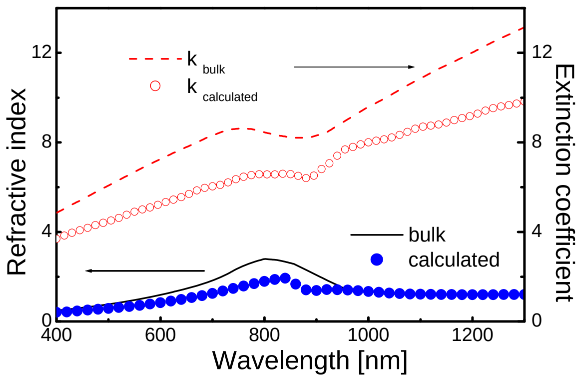

Fig. 3. Dispersion of the refractive index, *n* and extinction coefficient, *k* for thin films.For comparison the data for bulk aluminum taken from [9] are given.

The results for the dispersion of *n* and k of the thin films are presented in Figure 3. The data for the dispersion of the optical constants of the bulk aluminum taken from [9] are given in the same figure. It is seen that the thin aluminum film possesses lower values of the extinction coefficient *k* at all wavelengths in the spectral range of 400-1300 nm. Deviation of the refractive index, *n* of the thin films from that of the bulk metal is observed in range of 700-900 nm where the resonant peak of Al centered at 800 nm is situated.

Once the refractive index and extinction coefficient of the aluminum thin films are determined, they can be used in the further calculations of the refractive index and thickness of aluminum oxide layer created during the process of anodization. In these calculations we applied the double layered model, described in [8]. For description of the dispersion of the refractive index of thin Al_2O_3 films we used the Sellmeier's equation:

$$n^2(\lambda) = 1 + \frac{A_1 \lambda^2}{\lambda^2 - A_2{}^2} \tag{1}$$

where A_1 and A_2 are Sellmeier's coefficients. We varied the thickness, *d* of Al_2O_3 layer and parameters A_1 and A_2 until the discrepancy between the experimental and calculated reflectance spectra

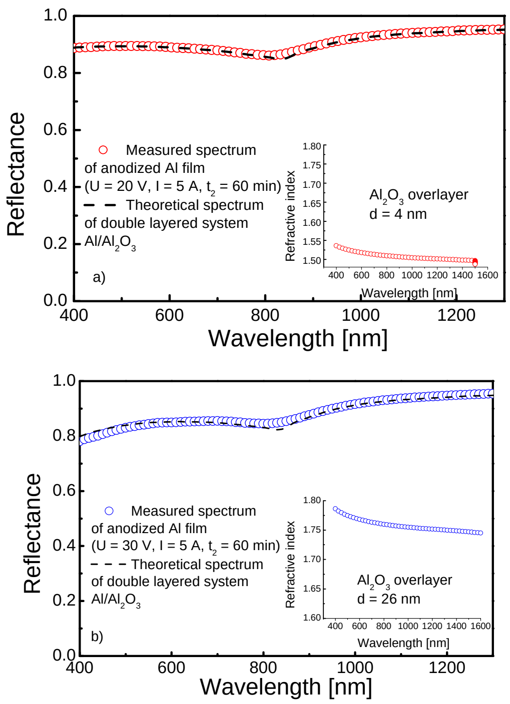

Fig. 4. Measured and theoretically calculated reflectance spectrum of a double layered Al/Al_2O_3 coating after anodization at U = 20 V (a) and U = 30 V (b). The dispersion of the refractive index of Al_2O_3 overlayers is given in the inset.

becomes lower than the accuracy of the measurements.

The results for the refractive index and thickness of the Al_2O_3 overlayer created after anodization in 2 % water solutions of H_2SO_4 for 60 min at 20 and 30 V are shown in Fig. 4. The calculated refractive index dispersion of the overlayer obtained at electrical potential U = 20 V and determined to be with thickness *d* = 4 nm, is presented in Fig. 4a. In this case the Sellmeier's coefficients were determined as follows - A_1 = 1.24 and A_2 = 123.51 nm. The refractive index for this layer varies between 1.51-1.55 in the spectral range 400-1300 nm. The obtained values of *n* are lower than the ones reported for Al_2O_3 [9] and show that the oxide over layer is still a discontinuous film. The thickness of Al_2O_3 film was found to be 26 nm, when the applied potential was increased up to 30 V (Fig. 4b). The calculated Sellmeier's coefficients are A_1 = 2.04 and A_2 = 114.31 nm. In this case the values of the refractive index are close to hose of the bulk materials [9].

CONCLUSION

In the present work results are reported from the experiments on anodization of thin aluminum films deposited by dc magnetron sputtering. We made an experimental characterization of the impact of the applied potential and the time of treatment on the anodization of thin films from aluminum. Double layered model was used for the description of the optical properties of the anodized aluminum films. It was established that the thickness of the alumina layer depends on the applied electrical potential. The thickness of the Al_2O_3 overlayer was found to be in the range of 4-26 nm.

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ОПТИЧНИ СВОЙСТВА НА ТЪНКИ НАНОПОРОЗНИ ФИЛМИ ОТ АЛУМИНИЕВ ОКСИД, ПОЛУЧЕНИ ПОСРЕДСТВОМ АНОДИЗАЦИЯ

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(Резюме)

Порестите алуминиеви темплейти получени чрез анодизиране на алуминиево фолио намират приложение за производство на различни наноматериали, като наножици, нанопръчици и нанотръбчки. В настоящата работа тънки филми от алуминиев оксид са получени чрез анодизация на Al слоеве. Металните покрития са отложени чрез постояннотоково магнетронно разпрашване. Алуминиевият оксид се получава чрез двуетапна анодизация при постоянно напрежение от 30V и в 2 или 4 тегловни % водни разтвори на H_2SO_4 при температура от 25°C. Установено е, че коефициента на отражение на слоевете намалява и пропускането нараства с увеличаването на времето за анодизация. Оптичните константи и дебелината на тънкия слой от алуминиев оксид образувал се след анодизация беше определен от спектрите отражение измерен при нормално падане на светлината.