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ScienceDirect

Physics Procedia 84 (2016) 415 – 420

Physics Procedia

International Conference "Synchrotron and Free electron laser Radiation: generation and application", SFR-2016, 4-8 July 2016, Novosibirsk, Russia

Structure and optical properties of thin porous anodic alumina films synthesized on a glass surface

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Abstract

The structure and luminescent properties of thin nanoporous aluminum oxide films obtained by anodization of aluminum films thermally deposited on glass have been investigated. The pore size and the interpore distance depend on the anodization voltage. For all studied samples the highest emission intensity obtained at the excitation wavelength equal to 330 nm. This behavior of luminescence curves caused by defect F^+ luminescent centers (O^- oxygen vacancies). The presence of porous alumina films on the glass surface increases the optical absorption in the visible light region. The oscillations on the spectra are caused by Fabry-Perot interference on the anodic alumina oxide film/glass interface. The suggested technique can be used for obtaining porous aluminum oxide films on other substrates, including Indium-Tin-Oxide, and can be applied in the technology of light-emitting devices and infrared-visible-ultraviolet detectors.

Peer-review under responsibility of the organizing committee of SFR-2016.

Keywords: microporous materials; chemical synthesis; luminescence; microstructure; optical properties

1. Introduction

Porous anodic aluminum oxide (AAO) has become widespread in nanotechnology applications [1] due possibility of its utilization as a template for preparation different nanostructured materials and as a dielectric matrix with pores filled with metals or semiconductors [1-5]. Furthermore, anodic alumina have been utilized in different optical

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Peer-review under responsibility of the organizing committee of SFR-2016.
doi:10.1016/j.phpro.2016.11.070

applications, such as photonic crystals [6,7], optical sensors [8], carrier for surface-enhanced Raman scattering active particles [9,10] and different luminescent materials [11,12]. Therefore, studying optical properties of anodic alumina is important for practical applications. In recent years, most of investigators have focused their attention on the optical properties of free-standing anodic alumina films obtained from the thick aluminum foil [13-18]. Nevertheless, some applications require nanostructure arrays to be obtained on different surfaces including glass, silicon wafers, and ITO films on glass [19-22]. AAO synthesis on different smooth surfaces is basically similar to obtaining them on aluminum plates or foils. The main difference is the request of deposition aluminum film on the substrate prior to anodization. Traditional methods of aluminum deposition are radio-frequency (RF) or DC magnetron sputtering [23], electron-beam evaporation [24] and thermal evaporation [25]. All of these techniques have their advantages and drawbacks. Aluminum films obtained by RF-sputtering have high purity, but low adhesion to the substrate due to a low-temperature of deposition process, which leads to exfoliation of the deposited film from the substrate. The most reliable and adhesive Al films are obtained by the electron-beam evaporation technique, but this method requires expensive equipment. The method of aluminum thermal evaporation is technologically the most efficient method. Films deposited using this technique are chemically clear and have good adhesion to substrates.

In this work aluminum films with thickness of 500 nm were deposited on the glass substrate via thermal evaporation technique. Anodic alumina films were fabricated by anodization of sputtered layer in 0.3 M solution of $H_2C_2O_4$ and anodization voltages 30, 40 and 50V. The influence of anodization voltage on the structural and optical properties of synthesized microporous material was studied.

2. Materials and methods

High pure aluminum films (99.99%, 0.5 μm) were deposited on soda lime glass substrates by a thermal evaporation method. Before the deposition process, the substrates were thoroughly cleaned by the standard procedure: washing in alcohol and acetone, ultrasonic alcohol rinsing for 10 minutes and drying with compressed air. The substrates temperature during deposition process was 25 ºC.

Anodization was carried out in a two-electrode cell using a stainless steel wire as a cathode. During the anodization the electrolyte temperature was kept at about 2-3 °C. Chemical synthesis was performed in 0.3M aqueous solution of oxalic acid $H_2C_2O_4$ at anodization voltages 30, 40, and 50 V.

XRD investigations were carried out using Rugaku Miniflex 600 difractometer with Co-*K*α wavelength. SEM micrographs were obtained using scanning electron microscope (Leo Supra 50VP). Optical transmission and absorption spectra were recorded by a UV/VIS spectrometer PerkinElmer Lambda 950 in the full reflection mode, and calculations were performed using the Kubelka-Munk equation [26]. Luminescence analysis was carried out at room temperature using a PerkinElmer LS 55 spectrometer.

3. Results and discussion

Micrograph of sputtered aluminium layer is shown on the Fig.1. The obtained aluminum films are quite smooth and formed from small grains. Thickness measured by interferometry method was 500 nm.

The anodization of thermally deposited aluminum films was carried out in a solution of oxalic acid $(COOH)_2$ with a molar concentration of 0.3 M and at anodic voltages of 30, 40 and 50 V. As a result, samples whose typical form is shown in Fig.2 were synthesized.

During the anodization process the current density *vs.* time graphs were recorded for all samples. It had been shown earlier in [27-29] that, regardless of electrolyte concentration and anodization voltage, the passing charge density about 2 Q/cm^2 leads to the formation of a anodic alumina film with a thickness of 1 μm. The area of our samples was 3.14 cm^2, and passing 3 Coulomb charges led to the formation of 0.57 μm thick films. Figure 3 shows chronoamperometric curves recorded during oxidation at different voltages. On the first stage we observe the nucleation of porous structure, the uniform growth of oxide film on the second stage with following drop of current density to zero due to dissolving all aluminum. Increasing of anodization voltage leads to rising current density which indicates to an accelerated oxidation rate. This leads to decreasing anodization duration.