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Incorporation of copper chelate ions into anodic alumina walls



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ABSTRACT

Anodic aluminum oxide (AAO) is typically applied as a template for nanofabrication. It was found that during anodization the anions of electrolytes are being incorporated into the nanopore walls giving rise to an emission in the UV/VIS range. In this paper, incorporation of copper-EDTA chelate ions was studied. The anodization of all studied samples was carried out in 0.02 M CuSO₄+0.02 M EDTA in 2 wt% sulfuric acid, which has provided suitable conditions for self-organized two-step process of AAO growth. Nanoporous alumina was formed and studied with Scanning Electron Microscopy. Chemical composition analysis of the anodic alumina revealed that the greater the oxide growth rate, the more copper is being incorporated. The photoluminescence studies confirmed the presence of copper in the AAO pore walls.

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1. Introduction

Anodic aluminum oxide is a well-known nanoporous template material commonly applied in nanofabrication of nanodots, nanowires and nanotubes. Typically, to form self-organized, hexagonally-arranged array of nanopores, aluminum is being anodized in acidic electrolytes like sulfuric acid [1,2], oxalic acid [1,3–6] or phosphoric acid [1,6,7]. It was found that, during anodization, positively polarized anode attracts electrolyte's anions [7,8]. These anions are being incorporated into the walls of anodic aluminum oxide [7–9]. Hence, presence of incorporated anions and F-centers in anodic aluminum oxide are sources of photoluminescence [10–13]. It was also found that incorporation of d-electronic anions resulted in photoluminescence owing to the electronic transitions between splitted d orbitals [13–15]. Experiments with incorporation of chromate anions showed that the greater the temperature of the electrolyte and the greater anodizing voltage, the more chromate ions are being incorporated into the anodic aluminum oxide [14]. Of course, high temperature of the electrolyte and high voltage during anodization translate into high current density. According to Diggle et al. the greater current density, the greater ions incorporation into the anodic alumina [16].

The main concept of the presented research is the incorporation of copper in the form of chelate anions. Typically, d-electronic

elements were being incorporated into alumina walls in anionic forms at high oxidation states (acidic anions like chromates). Hence, incorporation of transition metals at lower oxidation states may be advantageous in terms of photoluminescent properties, especially when the element is being chelated. Anionic chelate ligand provides also negative charge into the chelate complex anion with transition metal and enables its attraction by the anode. Thus, ionic species like [Cu(EDTA)]²⁻ have a chance to be incorporated and provide emission originating from d orbitals in accordance to the ligand field theory.

2. Materials and methods

High-purity aluminum foil (99.9995%, Alfa-Aesar) was cut into coupons (0.5 × 2.5 cm), degreased in acetone and ethanol and subsequently electropolished (HClO₄:C₂H₅OH 1:4 vol. ratio, 10 °C, 0.5 mA/cm², 60 s, platinum grid as a cathode). After electropolishing the samples were insulated with acid-resistant dye at its back and edges, to prevent anode from “burning”. Anodizations were performed in 2 wt% H₂SO₄ with addition of 0.02 M CuSO₄ and 0.02 M EDTA (Ethylenediaminetetraacetic acid) to form Cu-EDTA chelate ions in the electrolyte. Aluminum was being anodized at 0 and 15 °C and four various voltages: 15, 17, 19 and 21 V. After 20 h of first step of anodization formed oxide was chemically removed in mixture of 6 wt% H₃PO₄ and 1.8 wt% H₂CrO₄ at 60 °C for 1 h. Next, samples were re-anodized at the same experimental conditions.

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Absorption spectra of the aqueous solutions were taken with UV–vis Cary spectrophotometer (Varian Company) at wavelength range from 190 to 1050 nm.

Top-view and cross-sectional micrographs and chemical composition of the anodic aluminum oxide was measured by use of the FE-SEM (FEI, Quanta 3D FEG) equipped with energy dispersive X-ray spectrometer (EDS). The EDS were performed for micro-areas of $3.4 \cdot 10^5 \mu\text{m}^2$ (magnification of 1.500x) at 30 kV. Oxide growth rates were estimated from the thickness of the AAO cross sections and divided by the duration of the second step of anodization.

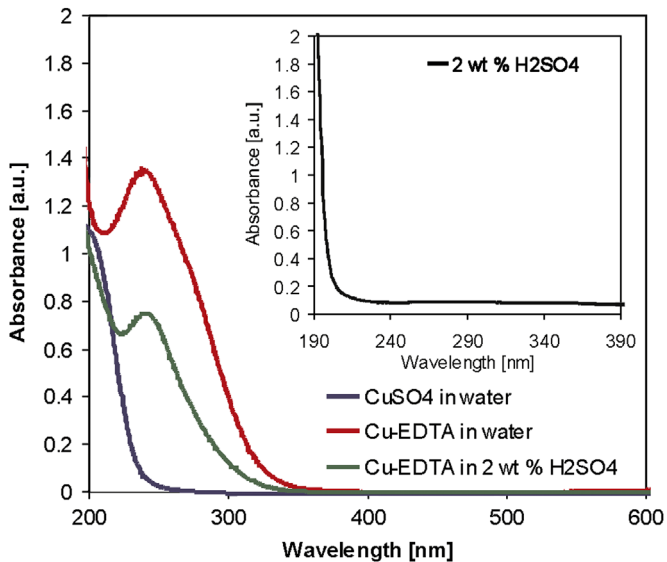


Fig. 1. UV–vis spectra of 0.02 M CuSO_4 (a), 0.02 M CuSO_4 +0.02 M EDTA in water (b) and 0.02 M CuSO_4 +0.02 M EDTA in 2 wt% H_2SO_4 .

The photoluminescence spectra were taken with FL 900 spectrofluorimeter (Edinburgh Instruments) with Xe lamp, using front-surface measurement mode. The excitation spectra were taken from 250 to 400 nm and emission spectra from 250 to 550 nm which allowed us to evaluate photoluminescence excitation-emission maps.

3. Results and discussion

At first, stability of chelate Cu–EDTA species in sulfuric acid was investigated. UV–vis spectra revealed that this anion is quite stable in 2 wt% sulfuric acid (Fig. 1). Sulfuric acid provides suitable conditions for anodization and the presence of negatively charged ion like $[\text{Cu}(\text{EDTA})]^{2-}$ may provide incorporation of chelated copper into the nanoporous anodic aluminum oxide walls. Absorption band originating from electronic excitation in aqueous complex is centered at around 200 nm and absorption band from Cu–EDTA chelate ionic species is at 250 nm, what makes them distinguishable and enables direct observation of d–d electronic transitions (Fig. 1). In 2 wt% sulfuric acid and lower values of pH, EDTA can attach protons and form H_3EDTA^- , $\text{H}_2\text{EDTA}^{2-}$ and HEDTA^{3-} anions [17] resulting in formation of different species of chelate ions with Cu^{2+} cation. Nevertheless, Cu^{2+} chelate ions with $\text{H}_2\text{EDTA}^{2-}$ and HEDTA^{3-} anions can also be incorporated into the anode because of their charge and hydrodynamic radius (size). This fact, however, decreases the absorbance intensity for Cu–EDTA solution in 2 wt% sulfuric acid (Fig. 1).

Two-step self-organized anodization resulted in nanoporous alumina (Fig. 2). Pore diameter of so formed AAO was ranging from 14 ± 5 nm (15 V, 0°C) to 35 ± 4 nm (21 V, 15°C) and interpore distance was ranging from 42 ± 1 nm (15 V, 15°C) to 55 ± 6 nm (21 V, 0°C). Chemical composition analysis of the nanoporous alumina revealed the presence of copper in the nanopores' walls (Table 1). According to Le Coz et al., anions are being successfully

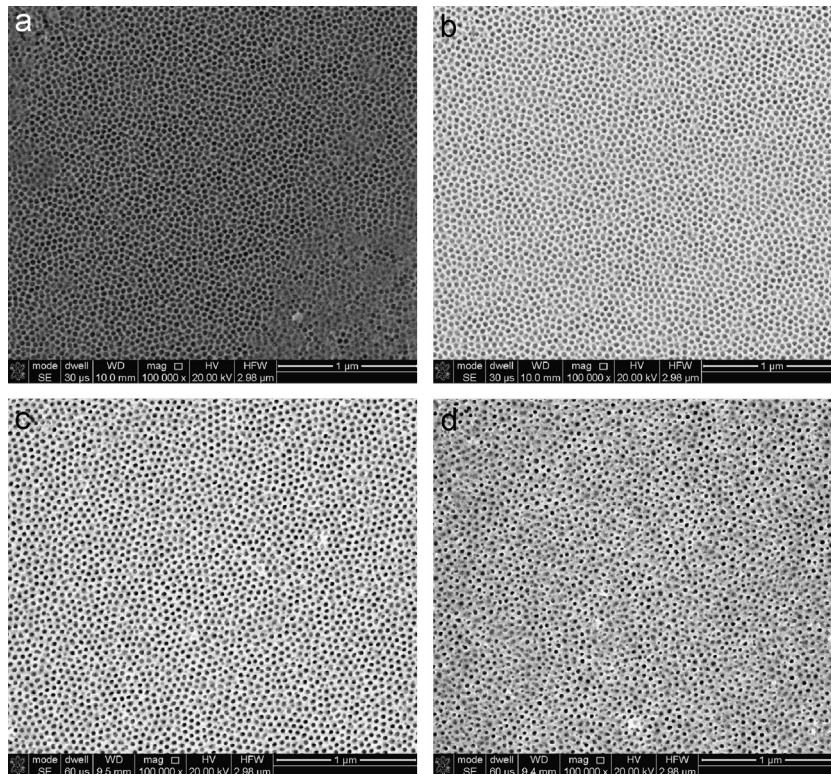


Fig. 2. FE-SEM micrographs of anodic aluminum oxide formed in 0.02 M CuSO_4 +0.02 M EDTA in 2 wt% H_2SO_4 at 15°C at 15 (a), 17 (b), 19 (c) and 21 (d).

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