Materials Letters 146 (2015) 55–58

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Luminescence from micro-/nano-scale anodic aluminum oxide containing electrochemical etching derived nanoporous silicon

Cao Xuan Thang, Vuong-Hung Pham *

Advanced Institute for Science and Technology (AIST), Hanoi University of Science and Technology (HUST), No. 01, Dai Co Viet road, Hanoi, Vietnam

ARTICLE INFO

Article history:
Received 22 December 2014
Accepted 31 January 2015
Available online 11 February 2015

Keywords:
Nano-silicon
Luminescence
AAO
Nanophosphors
Micro-/nano-scale
Nanopores

ABSTRACT

This paper reports a novel way of the fabrication of micro-/nano-anodic aluminum oxide containing electrochemical derived nanoporous Si (AAO–Si) to achieve strong co-emission of light with controllable intensities. The AAO–Si was fabricated by electrochemical anodizing of aluminum followed by spin coating of nanoporous Si particles onto AAO. The microstructure and its luminescence of micro-/nano-AAO were controlled by electrochemical anodizing times. The fabrication of micro-/nano-AAO containing nanoporous Si resulted in a light-emitting from both AAO and nanoporous Si emission under a single excitation source. These results suggest that the potential application of micro-/nano-AAO contains Si for potential application in optoelectronic and biocompatible substrates for tissue engineering.

1. Introduction

Development of environmental friendly materials with strong and stable luminescence as well as good biocompatibility is particular important for designed functional materials in the field of modern optoelectronic applications such as white light emission diode (white LED) and nanomedicine [1–3]. Fundamentally, the most common way to generate white LED is relied on utilizing Red/Green/Blue (RGB) tri-color materials [4,5]. However, the present commercially present blue light emission is nitride materials, which requires high temperature and well- equipped instruments synthesis set up [6,7]. Thus, the development of strong and stable blue light emission materials for potential application in white LED has received considerable attention in both industrials application and researches. Similarly, there is a demanding for development of biocompatible substrates for tissue engineering such as growth of cartilage cell and hepatocyte cell [8,9]. This encouraged scientists and engineers to explore new ways of tightly controlling and tailoring the physical and chemical surface characteristics of materials to address new functional materials, for example, by surface modification and embedding activator onto the host materials [10,11]. As a promising material, anodic aluminum oxide (AAO) has received considerable attention in designing the functional materials because AAO can emit blue light and incorporate a wide variety of inclusions based on the nanoporous structure [12,13]. Similarly, nanoporous silicon is a suitable material for embedding onto AAO for designing functional materials such as optoelectronic and nanomedicine applications because of its strong red light emission and excellent biocompatibility [14,15].

Nevertheless, there are only a few reports on the effect of embedding materials on the functional properties of AAO [16,17]. In particular, in our knowledge, there are no reports on the luminescence of AAO with micro-/nanostructure and micro-/nano-AAO containing Si for modern optoelectronic application in white LED and nanomedicine. Therefore, this study proposes a novel way of controlling the light emission from micro-/nano-AAO and micro-/nano-AAO containing Si, which can be achieved by applying an anodizing process and nanoporous Si layer coating. The microstructure and chemical composition of the AAO–Si were characterized by field emission scanning electron microscopy (FE-SEM) and a transmission electron microscope (TEM), respectively. The luminescence was also determined by photoluminescence spectrometer.

2. Experimental procedure

A pure aluminum (Al, 99.99%; Bukang Coalloy, Korea) of dimensions 30 mm × 10 mm × 0.25 nm was used as a substrate. Prior to the creation of AAO by electrochemical anodizing, the Al substrate was dipped into a diluted H_3PO_4 solution for 60 min to etch the surface and remove the native oxide layer on the Al. After which, the dipped Al substrate was then ultrasonic washed with ethanol and then distill water. The etched Al substrates were anodized in an electrolyte solution of 0.3 mol/L oxalic acid using a platinum grid as a counter-electrode. The electrochemical anodizing was operated under the fixed voltages of 50 V with a various

* Corresponding author. Tel.: +84 4 36230435; fax: +84 43 6230 293.
E-mail address: vuong.phamhung@hust.edu.vn (V.-H. Pham).

http://dx.doi.org/10.1016/j.matlet.2015.01.162
0167-577X/

anodizing times in order to control the microstructure of the nanoporous AAO. Nanoporous Si nanoparticles were fabricated by electrochemical etching of Si wafer as outlined in our previous work [18]. Prior to spin coating of nanoporous Si onto AAO, 1 mg of nanoporous Si particles were suspended into 5 ml of absolute ethanol using ultrasonic vibration for 30 min. The AAO–Si was fabricated by a spin coating method using spin coater (Laurell, USA) under the fixed rotate speed of 3000 rpm/min with a various repeated times (5, 7, 9 and 11), denoted as AAO–5Si, AAO–7Si, AAO–9Si and AAO–11Si, respectively in order to control the layer by layer of nanoporous Si onto AAO.

The microstructure of the micro-/nano-AAO and micro-/nano-AAO–Si was determined by field emission scanning electron microscopy (JEOL, JSM-7600F, JEOL Techniques, Tokyo, Japan) and the transition electron microscope (JEOL, JEM 1010, JEOL Techniques, Tokyo, Japan). Room temperature photoluminescence (PL) tests were performed under excitation wavelength of 276 nm. A NANO LOG spectrofluorometer (Horiba, USA) equipped with 450 W Xe arc lamp and double excitation monochromators was used. The PL spectra were recorded automatically during the measurements.

3. Results and discussion

The microstructures variation in micro-/nano-AAO anodized with different times was examined by SEM as shown in Fig. 1(A)–(E). The nanoporous AAO anodized with a time of 5 min showed an initial pore formation with a relatively smooth pore surface (Fig. 1(A)). On the other hand, interestingly, the formation of nanoporous structure became clearer evidence with a diameter of ~5 nm as increasing the anodizing time to 10 min (Fig. 1(B)). A longer anodized time of 20 min allowed for the creation of opened pore structure with a diameter of ~10 nm (Fig. 1(C)). The formation of nanopores became more vigorous with increasing anodizing time to 30 min (Fig. 1(D)) and 45 min (Fig. 1(E)), while the pore size increased to ~20 nm and ~30 nm, respectively. It should be note that chemical etched Al substrates allowed for the creation microstructure within distinctly different grains. This finding suggests that the Al grains with different crystallographic orientations would be etched independently by means of the erosion generated during a etching process, which would leave the original grain boundaries, as is often the case with metals etched with etchants [19,20]. In addition, the surface became smoother with increasing anodizing time. This suggests the potential use of a combination of chemical etching and anodizing of Al substrates for creation of a unique micro-/nano-structure of AAO surface.

The photoluminescence of the nanoporous AAO was evaluated by photoluminescence spectroscopy (PL), which is very useful for analyzing the refractive index, thickness, porosity, efficiency of trapping, migration and transfer of charge carriers and understanding the fate of electron–hole pairs in the semiconductor [21,22]. The typical photoluminescence spectra of the nanoporous AAO monitoring at 254 nm

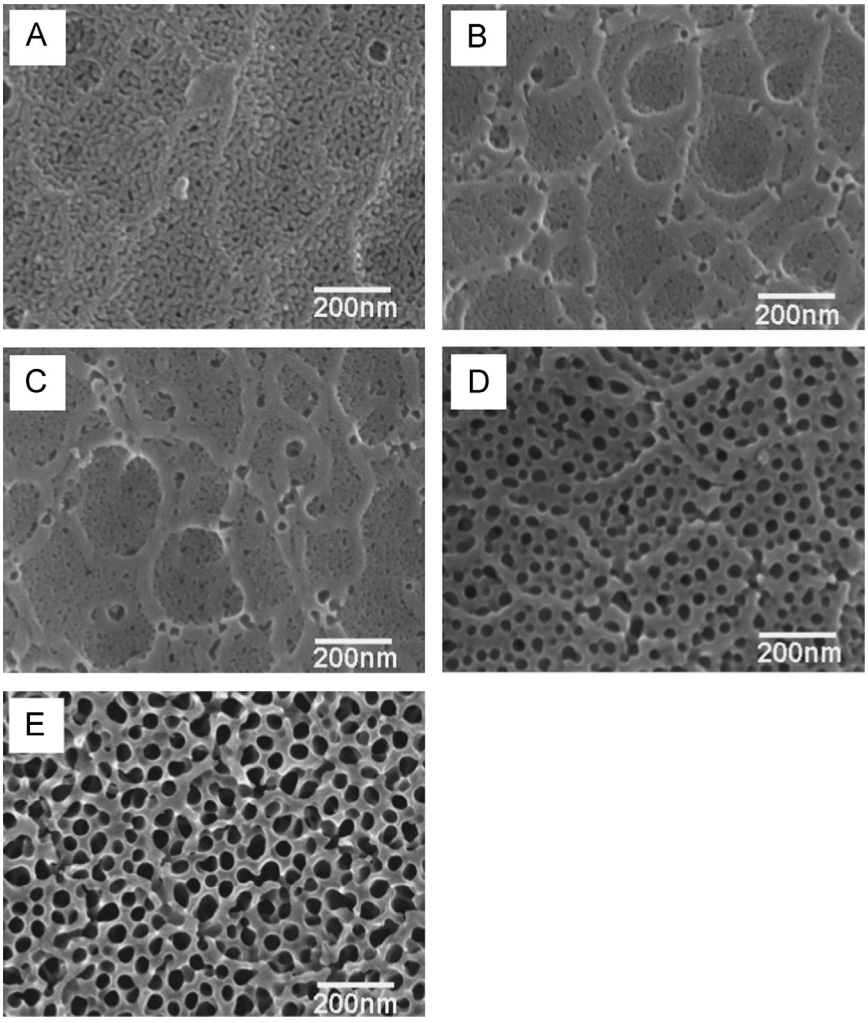

Fig. 1. Microstructures of the micro-/nano-AAO by electrochemical anodizing (A) 5 min, (B) 10 min, (C) 20 min, (D) 30 min, and (E) 45 min.