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Short communication

Self-organization and zinc doping of Ga_2O_3 nanoporous architecture: A potential nano-photogenerator for hydrogen

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ABSTRACT

The present work introduces the formation of a highly organized one dimensional Ga_2O_3 nanoporous architecture by anodization of Ga metal at −10 °C in a mixture of phosphoric acid and ethylene glycol. In addition to pure Ga_2O_3, we perform in situ Zn doping by alloying Ga with 1 at.% Zn. After zinc doping, the Ga_2O_3 nanoporous layers demonstrate promising properties for photo-induced hydrogen generation from water.

1. Introduction

Since the pioneering works of Masuda and Fukuda on highly organized porous Al_2O_3 and Assefpour-Dezfuly et al. and Zwilling et al. on anodic TiO_2 nanotubes [1], great attention has been paid to the electrochemical self-organization of one dimensional nanotubular or nanoporous structures of metal oxides, especially TiO_2 with its impressive photocatalytic properties [2–4]. Nevertheless, for probably the most important photocatalytic application, that is the direct splitting of H_2O into H_2 and O_2, TiO_2 under open-circuit conditions shows only a very sluggish H_2 evolution kinetics. This may partially be attributed to the fact that the thermodynamic driving force, that is the surface band edge position of the conduction band (−4.21 eV vs. vacuum) relative to the H_2O/H_2 redox couple, is not very high. An oxide that provides a much higher driving force is Ga_2O_3 which is a wide band gap (~4.8 eV) n-type semiconducting material with a valence band located at −2.95 eV and a conduction band located at −7.75 eV vs. vacuum [5]; i.e., the electrons at the conduction band of Ga_2O_3 have a high reduction potential suitable to reduce water into H_2, and the holes on valence band have an oxidation potential capable of oxidizing water and a large variety of organic molecules [5–9]. Despite the wide application of Ga_2O_3, the formation of self-organized oxide structures has been investigated very rarely [10]. In the present communication, we report on the formation of a highly ordered one dimensional Ga_2O_3 nanoporous structure in a H_3PO_4/ethylene glycol mixed electrolyte, and we also demonstrate that zinc can be doped to gallium, which leads after anodization to the formation of a highly ordered one dimensional nanoporous structure of zinc doped Ga_2O_3 which shows a considerable performance for the photocatalytic reduction of water.

2. Experimental

For Ga-anodization, Ga-metal disks (99.9999%, 1 cm diameter, 0.6 cm thickness, Chempur, Germany) were polished very gently using # 4000 grade SiC abrasive paper in a 1:1 ethanol:glycerol mixture followed by sonicating in ethanol for 5 min. For Zn-doping, 1 at.% of zinc dust (particle size: <10 μm, Sigma-Aldrich) was mixed with gallium melted at 45 °C using a stainless steel spatula and the mixture was heated under a constantly flowing argon stream at 600 °C for 20 h. After cooling to room temperature in an argon atmosphere, the alloy was stored in a refrigerator. As expected, EDX analysis showed a composition of about 1 at.% zinc in the alloy. For anodization, a thin film of GaZn alloy was coated on a clean titanium sheet (0.3 mm thick) by rubbing the GaZn alloy melts (heated at about 45 °C) continuously all over the surface and the film was frozen in a refrigerator before its use for anodization. A two-electrode cell with a Pt cathode was used for the anodization and the applied voltage was ramped initially at the rate of 500 mV s^{-1} up to the targeted anodization voltage. Details on the anodization set-up can be found elsewhere [2a]. As gallium has a low melting point (29.77 °C), all electrolytes were cooled in a refrigerator. During anodization, the substrate temperature was maintained using a Peltier element (quick cool, Conrad Electronics) and pumping out the heat using a thermostat (Huber Badthermostat-K6-NR, Germany)

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maintained at 0 °C. The anodized nanostructures were characterized using a field emission scanning electron microscope (FE-SEM, S4800, Hitachi), energy dispersed X-ray analyser (EDX, EDAX Genesis), X-ray diffractometer (XRD, X'pert Philip MPD with a Panalytical X'celerator detector and graphite monochromized CuKα radiation, λ = 1.54056 Å), X-ray photoelectron microscope (XPS, PHI 5600, US), transmission electron microscope (TEM) and selected area electron diffractometry (SAED, Philips CM30T/STEM).

For water splitting, the annealed and Pt decorated nanostructures, immersed in a degassed deionized water in air sealed quartz cell, were illuminated using a 266 nm laser (50 mW, FQCW266-50, CryLas, GmBH). For H_2 determination, 200 μL of the gas from the cell was withdrawn periodically and injected into a GC (GCMS-QP2010SE, Shimadzu, Japan).

3. Results and discussion

After investigating anodization of solid Ga at reduced temperatures in various electrolytes, an electrolyte containing 50 wt.% H_3PO_4 and 40 vol.% ethylene glycol was found ideal to grow self-organized oxide structures. Fig. 1a shows typical current transients during anodization of Ga and zinc doped Ga at various substrate temperatures. When the substrate temperature was maintained above −10 °C, the current transients at 30 V and 70 V show a sharp peak in the early stage of anodization indicating rapid dissolution of metal surface and subsequent formation of a passive oxide layer. For these conditions, SEM image shows the formation of oxide with some randomly oriented big holes and local breakdown of the oxide layer on the anodized surface (Fig. 1b). In contrast, when the substrate temperature was maintained at −10 °C or lower, decrease in current from early stage of anodization indicating passivation due to a formation of compact oxide film can be observed in Fig. 1a. After a certain lapse of time, the current rises slowly and decreases again forming a small hump, indicating an increase in surface area due to the formation of porous structures on the anodized surface. This trend of the current transients is in line with the trend for the formation of nanoporous Al_2O_3 and nanotubular TiO_2 structures [2a]. When the substrate temperature was held at −15 °C, a highly ordered self-organized nanoporous layer was formed. After anodization for 5 h at 70 V, the layer is ≈4.5 μm thick and contains regular pores of ≈160 nm diameter as shown in Fig. 1c and d. A similar result is obtained when the anodization is performed at a substrate temperature of −10 °C. This is the critical temperature above which no formation of self-organized nanostructures was observed. In order to ensure a sufficiently low temperature for the formation of self-organized porous

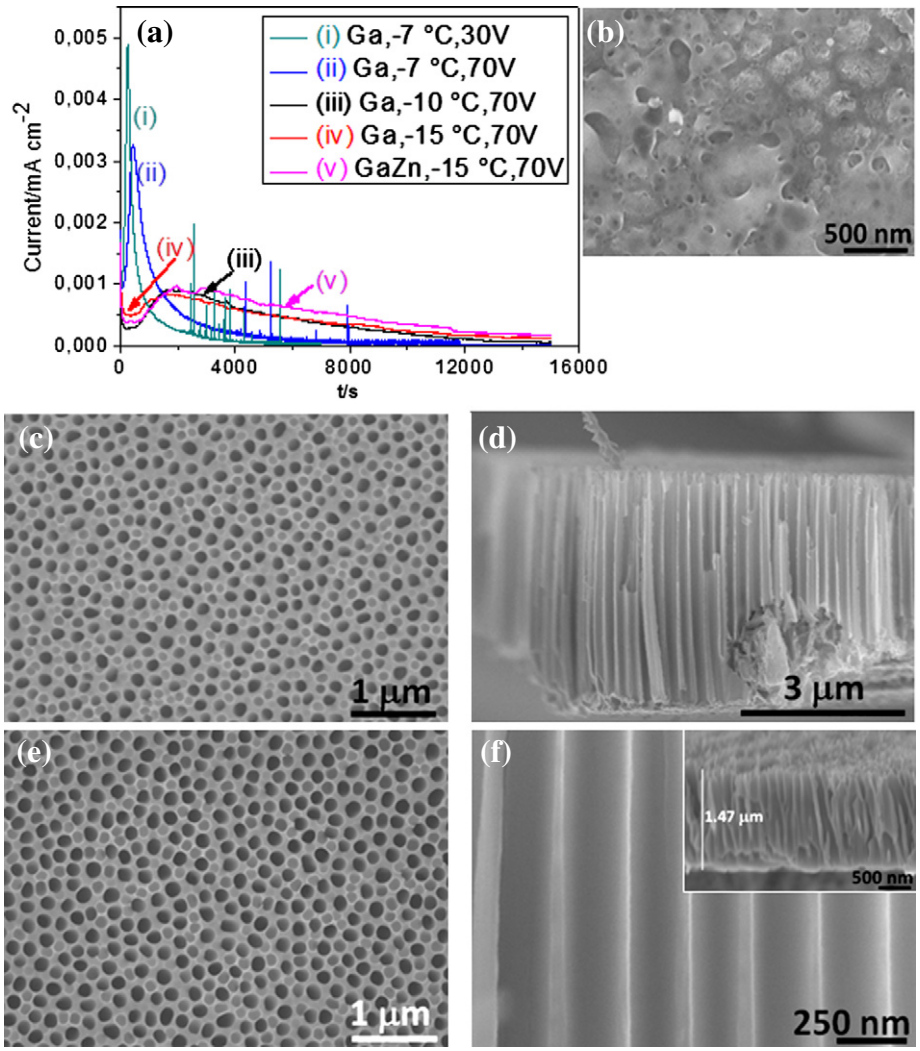

Fig. 1. (a) Current transients measured during anodization of Ga and GaZn at various voltages and substrate temperatures in electrolyte containing 50% H_3PO_4 in 40 vol.% ethylene glycol. SEM views of Ga anodized at 70 V, 3 h (b) top surface, −7 °C, (c) top surface, −15 °C and (d) fractured cross section, −15 °C. (e) Top surface and (f) fractured cross-sectional SEM views of anodized GaZn thin film coated on a Ti-sheet at −15 °C and 70 V for 5 h in electrolyte containing 50% H_3PO_4 in 40 vol.% ethylene glycol. Inset shows the total thickness of the anodized film.