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Formation and field emission property of single-crystalline Zn microtip arrays by anodization

C.Y. Kuan [a], J.M. Chou [b], I.C. Leu [c,*], M.H. Hon [a]

[a] Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC
[b] Department of Materials Science and Engineering, I-Shou University, Kaohsiung Hsien 840, Taiwan, ROC
[c] Department of Materials Science and Engineering, National United University, Miao-Li 360, Taiwan, ROC

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Abstract

A highly ordered array of single-crystalline Zn microtips is obtained after anodizing of Zn foil in NH_4Cl/H_2O_2 solution, and the formation mechanism and field emission property of such Zn microtips have been described. Sixfold single-crystalline Zn microtips are obtained by selective anisotropic etching of crystallographic planes with different dissolution rates. From the results of TEM analysis, the single-crystalline Zn microtips, formed on the Zn foil after anodic dissolution treatment, are enclosed by $\{1\bar{1}00\}$ and are preferentially oriented along the *c*-axis. Besides, the improvement of turn-on field from 33.9 to 20.0 V/μm is achieved with thin surface ZnO after annealing treatment.

Keywords: Anisotropic etching; Microtip; Field emission

1. Introduction

One-dimensional (1D) systems take a significant share of research activity regarding the whisker, tips, tubes, wires, rods, belts, brushes, and so on. Anodization technique has been employed in many materials, such as, aluminum, and silicon [1,2] for forming 1D nanostructures. However, the application of anodic technique for zinc in NaOH, KOH, and in a mixture of HF-containing ethanol solution have been reported for the synthesis of conversion layers for corrosion protection, porous structures, and other kinds of passive films [3–5]. But there has been no previous study on the preparation and characterization of single-crystalline Zn microtips by anodic dissolution method for field emitter application. Herein, new methodologies and strategies to guide the design and solution syntheses of microtip structures have been successfully carried out. The mechanism for Zn microtip formation proposed in this study is expected to be applicable to other metals, and the method used to fabricate field emitters can be an alternative to the reported Spindt method [6].

2. Experimental procedure

A polycrystalline Zn foil (99.9%, Alfa Aesar) was first mechanically polished to 1 μm finish, and was electropolished with 2:1 mixture of ethanol and 85% phosphoric acid at a current density of 69 mA/cm^2 for 10 min. The anodization experiments were carried out by using a standard two-electrode cell under stirring at room temperature. A zinc foil (12 × 12 mm) and a platinum foil (radius 6 mm) were used as anode and cathode, respectively. The distance between anode and cathode was 50 mm. Anodic etching was conducted in NH_4Cl/H_2O_2 solution at a molar ratio of 32 with different current densities (14, 28, and 55 mA/cm^2) for different times (5, 15, 30, and 60 s).

* Corresponding author. Tel./fax: +886 6 2380208.
E-mail address: icleu@mail.mse.ncku.edu.tw (I.C. Leu).

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3. Results and discussion

The morphologies of Zn foil obtained by anodic dissolution with increasing current density from 14 to 55 mA/cm^2 (raising the applied voltage from 0.2 to 0.8 V) for 1 min are shown in Fig. 1. It is interesting to find that the degree of uniformity in shape depends on the level of the current density. It has been reported that self-ordering occurs at a critical voltage which is strongly dependent on the dissolution ability, i.e., proper current density is the key controlling factor [7]. Then, the relationship between current density and the density of Zn microtips is illustrated in Fig. 1(d) in which the density of Zn microtips varies from 4.5 to 1.8 tips/μm^2 with increasing current density, corresponding well to the result of SEM observation.

To realize the mechanism of the formation of microtips arrays, the different treatment time (5, 15, 30, and 60 s) is applied with current density 55 mA/cm^2. With increasing reaction time, the morphology evolves from ridge patterns, to micro-horn, and microtips shown in Fig. 2. After anodization treatment for 5 s, the ridge patterns are obtained, as shown in Fig. 2(a), the process is analogous to forming porous microstructure in anodized aluminum and silicon induced by electric-field effect [8,9]. The formation of these ridges is most likely to be attributed to the progress of localized pits accumulation during the electrochemical process. A micro-horn morphology is formed from the broken ridges, as shown in Fig. 2(b). When a voltage passes through a ridge pattern, the distribution of current density is non-uniform, which in turn results in morphology variation [10]. The appearance of micro-horns and their development during anodization can be explained from the viewpoint of a competence between oxide growth with metal dissolution when the latter prevails [11]. With increasing the thickness of oxide film, the internal stresses result in the initiation of cracks on the interface, therefore, the formation of micro-horn microstructures can be described as crack-induced localized dissolution assisted by electrical field. By prolonging the anodic etching treatment for 30 and 60 s, the microtip morphologies of Zn are formed, as shown in Fig. 2(c) and (d). In general, different crystallographic faces of crystals have different surface energies, those facets of crystals dissolve in solutions at different rates, and an anisotropic dissolution behavior is observed [12–14]. The main consequence of the formation of the pyramid microtip morphology of Zn is believed to be caused by the variation of etch rate with orientation, which will be discussed in more detail later.

Generally, the dissolution of water-insoluble materials is always accompanied by the formation of some reaction products, involving a change in the oxidation state, and then followed by the dissolution of such products. The anodic etching process in this research can be described by the two main steps: (i) formation of surface oxide films

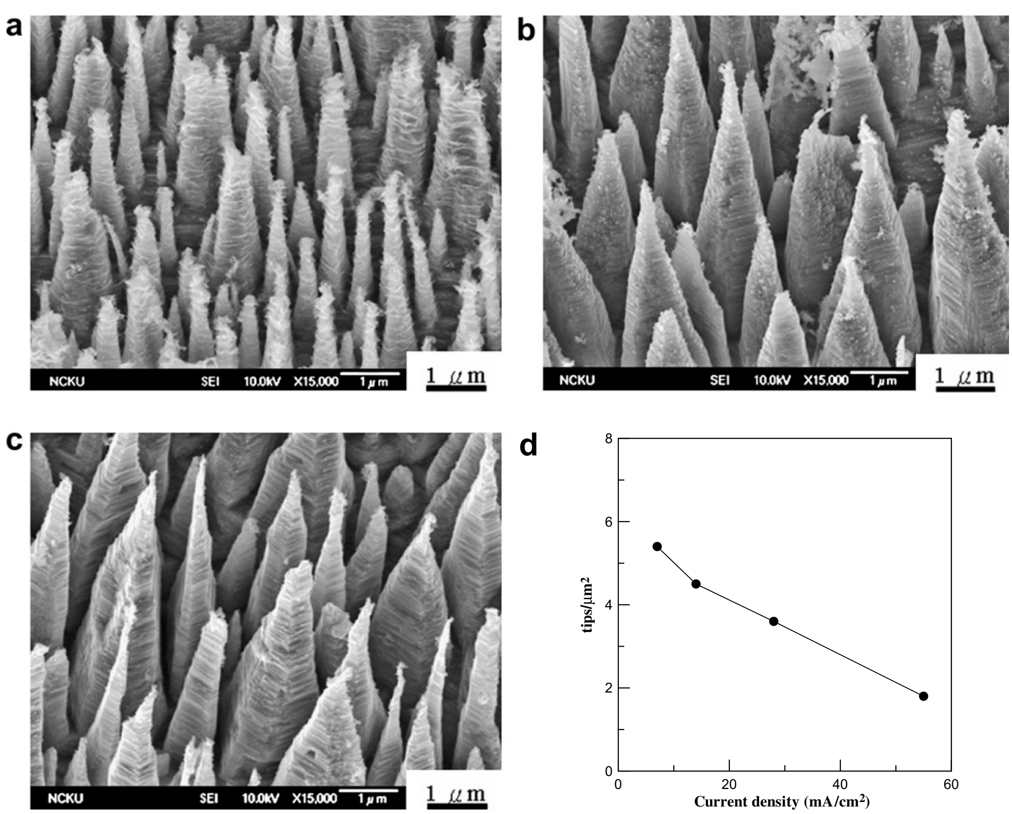

Fig. 1. The microscopy for arrays of Zn microtips on polycrystalline Zn foil on different current density: (a) 14, (b) 28, (c) 55 mA/cm^2, and (d) illustrates the relationship between current density and density of Zn microtips.