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Self-assembled ZnO nanostripes prepared by acidified ethanolic anodization

S. W. NG, F. K. YAM, L. L. LOW, K. P. BEH*, M. F. MUSTAPHA, E. N. SOTA, S. S. TNEH, Z. HASSAN
Nano-Optoelectronics Research Laboratory, School of Physics, Universiti Sains Malaysia, Minden, 11800 Penang, Malaysia

ZnO nanostripes have been fabricated via anodization method. Two sets of samples with different acid to ethanol volume-to-volume ratio have been introduced in the electrolyte and the results were studied. Based on the electron micrographs, current transient profile, chemical reactions within the electrochemical cell, also energy dispersive x-ray spectroscopy, a formation mechanism of the nanostripes has been proposed. Also the nanostripes anodized under less amount of acid added were smaller than its counterpart, with greater amount of precipitate present. In addition, x-ray diffractogram of the pre-anodized samples were obtained. Both samples having similar pattern, which corresponded to hexagonal zinc.

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1. Introduction

Zinc oxide (ZnO) is a versatile, non-toxic material that has paved its way to various fields such as gas sensing and optoelectronics. This is due to its unique electronic properties i.e. wide bandgap (~3.3 eV) and high exciton binding energy (~60 meV) at room temperature.

ZnO can be obtained in many ways. Typical methods such as sputtering, thermal evaporation, direct oxidation, and anodization can be found in the literature [1-11]. Among these methods, anodization of zinc (Zn) metal provides a flexible route to obtain ZnO. This is largely due to the various parameters present in the anodizing environment, such as applied potential, anodizing duration, type of electrolyte, pH of the electrolyte, also temperature, which can be manipulated. This leads to the ease of producing nanostructured ZnO compared to the aforementioned methods.

One of the anodizing parameters received intensive attention from various research groups is the type of electrolytes used. Common chemicals such as HF, H_2SO_4, H_2O_2, NaOH and NH_4Cl have been used to obtain different nanostructured ZnO such as nanopores, nanowires, and nanobelts [3-8]. Due to the reactivity of Zn metal towards such chemicals, often organic additives such as ethanol has been added as a retardant in order to slow down the chemical reaction thus having the anodizing environment under control. *Kim et. al.* have investigated the effects of grown ZnO nanostructure by varying the concentration of H_2SO_4 in ethanolic medium.

In this work, we have investigated the surface morphology of nanostructured ZnO by manipulating the volume-to-volume (v/v) ratio of H_2SO_4 and ethanol. In addition, the structural analysis was done on the as-anodized samples. This investigation will provide a new insight towards the growth of nanostructured ZnO under such media.

2. Experimental details

In this work, galvanized steel (zinc coated on a steel plate, here forth denoted as Zn) plates were anodized in a conventional two-electrode configuration (shown in Fig. 1) with nickel (Ni) wire serving as a counter electrode. Prior to anodization process, the Zn plates were sonically degreased in acetone and ethanol for 5 minutes respectively. After that, the resulting Zn plates were dried in nitrogen stream.

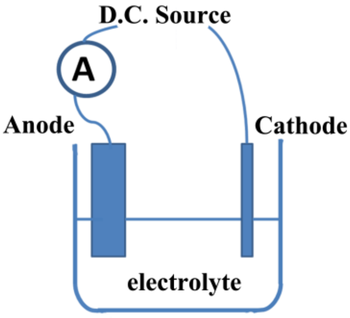


Fig. 1. Experiment setup.

In order to examine the effect of electrolyte towards the formation of ZnO, only the volume-to-volume (v/v) ratio of H_2SO_4 to ethanol (acid:ethanol) was varied, while other parameters remained at constant. The potential difference between two electrodes was held at 10V, while the anodizing duration lasted for 1 hour. There were two v/v ratio used in this experiment, namely 1:20 and 1:10 (sample A and sample B respectively). The initial concentration of H_2SO_4 is 0.5M. All experiments were done under normal room temperature condition. During the anodizing process, the change in electrical current was measured.

After anodization process, the sample was removed from the electrolyte and rinsed with DI water; then dried in nitrogen stream prior for characterization. The structural characteristics of the galvanized steel (prior to anodization) were characterized using high resolution x-ray diffraction (HR-XRD, model PANalytical X'Pert PRO MRD PW3040) with CuKα1 source of 0.154 nm; operating at 40 kV and 30 mA. The surface morphology of the samples was characterized using scanning electron microscopy (SEM, model JSM 6460 LV) and energy dispersive x-ray spectroscopy (EDX).

3. Results and discussions

Fig. 2 displays the XRD pattern of the galvanized steel. The detected peaks (marked by a black dot) corresponded to hexagonal zinc. The peaks marked with "*" indicated unknown peaks. The four zinc peaks situated at 36.3° (002), 39° (100), 43.2° (101), and 54.4° (102).

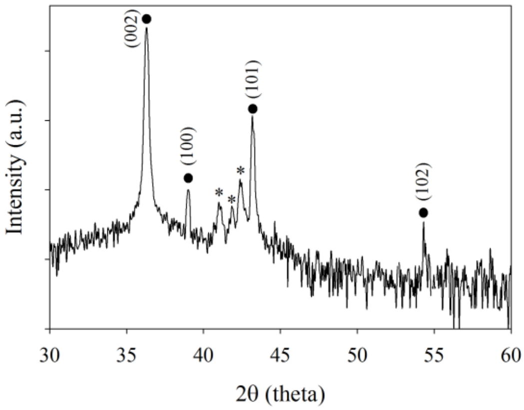


Fig. 2. XRD pattern of galvanized steel plate. The vertical axis is a logarithm of the original.

Fig. 3 shows the electron micrographs of both sample A and B. Nanostripes of ZnO were present in both samples. An average value for the width and length of the nanostripes was obtained statistically. From sample A, the width of the nanostripes was about $81.3nm$, while the length was $1.23\mu m$. The nanostripes in sample B were found to be bigger than that of sample A, namely $87.5nm$ and $1.6\mu m$ for width and length respectively. We believed that the increase of the nanostripes size might be due to the additional amount of H_2SO_4. The dimensions of the nanostripes were governed by the chemical reactions in the electrochemical cell. In order to decipher these discrepancies, other supporting data were presented.

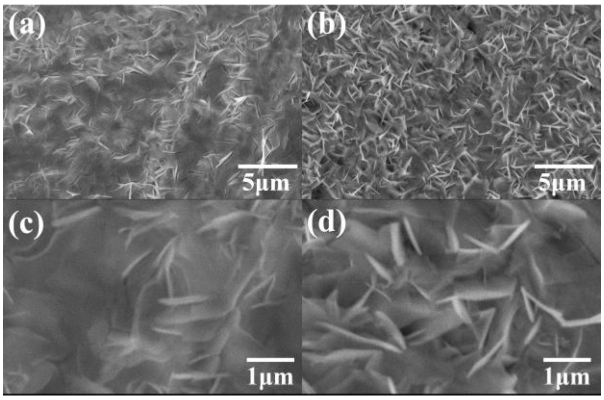


Fig. 3. 5k magnification of nanostripes anodized under v/v ratio (a) 1:20 and (b) 1:10 and 20 k magnification v/v ratio (c) 1:20 and (d)1:10.

One of the supporting data will be the current – transient profile of both samples, which is exhibited in Fig. 4. In Fig. 4, both profiles shared similar trends, in which there is a decrease in current at *region b*. One discernable difference was the time taken in the current reducing region (*region b*) at sample A was shorter than sample B. The chemical reactions presented in the electrochemical cells were shown [4]:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \qquad (1)$$

$$H_2SO_4(aq) \rightarrow 2H^{+}(aq) + (SO_4)^{2-}(aq) \qquad (2)$$

$$H_2O(l) \rightleftharpoons H^{+}(aq) + (OH)^{-}(aq) \qquad (3)$$

$$Zn^{2+}(aq) + 2(OH)^{-}(aq) \rightarrow Zn(OH)_2(s \rightarrow aq) \qquad (4)$$

$$Zn(OH)_2(aq) \rightarrow ZnO(s) + H_2O(l) \qquad (5)$$

$$ZnO(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2O(l) \qquad (6)$$

$$Zn^{2+}(aq) + (SO_4)^{2-}(aq) \rightarrow ZnSO_4(s/aq) \qquad (7)$$

$$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g) \qquad (8)$$

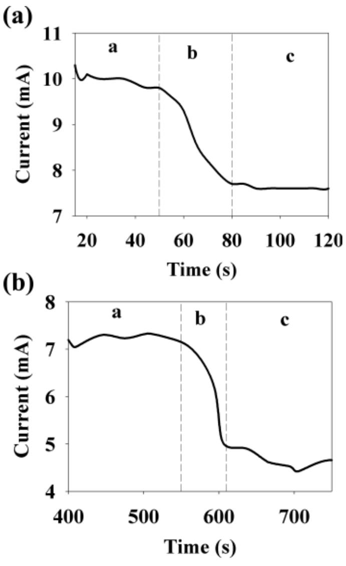
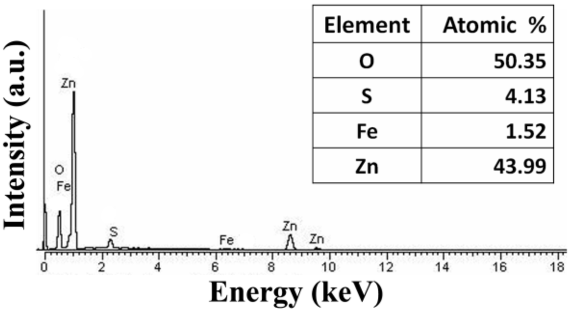


Fig. 4. Current-transient profile of v/v ratio (a) 1:20 and (b) 1:10.

The chemical reactions were believed to occur simultaneously throughout the experiment. However, certain reactions exhibited a higher degree of occurring at designated region. At *region a*, it was likely that reaction (1) to (3) being the dominant ones, as there was no decrease in electrical current. It is highly possible that the nanostripes began to form between *region a* and *b* (the vertical dotted line). $Zn(OH)_2$ was formed as an intermediate state to allow the formation of ZnO. Under aqueous condition, $Zn(OH)_2$ was likely to be dissolved in the electrolyte. Reaction (5) and (6) defined the formation-dissoultion of ZnO, thus forming ZnO nanostripes. Reaction (7), however, explained the precipitation present in both samples, as $ZnSO_4$ is insoluble in ethanol [12]. Since sample B having more aqueous than A, $ZnSO_4$ was more likely to be dissolved into the electrolyte. Hence, the amount of precipitations obtained in both samples was different. This leads to the sudden drop of electrical current displayed at *region b*. As sample A having less acid added, the drop was significantly faster than that of sample B. The time taken in the drop for sample A was 10 s, while that of sample B was 6 times of sample A. In addition, this indicates that sample B having more time for formation-dissolution of ZnO, thus the resultant nanostripes were bigger than that of sample A.



Element	Atomic %
O	50.35
S	4.13
Fe	1.52
Zn	43.99

Fig. 5. EDX spectrum of sample A (v/v ratio 1:20).

After the drop in electrical current for both samples, the increase in current was not observed for in both samples (hence shown in *region c* of Fig. 4). One plausible reason is that the H^+ ions were reduced (shown in reaction (8)), thus halting the formation and dissolution process.

The presence of $ZnSO_4$ was further reinforced by taking into account of EDX measurement. From EDX measurement, the amount of sulfur element present in both samples was different, namely 4.13 and 2.28 at% for sample A and B respectively. Fig. 5 shows the EDX spectrum of sample A.

4. Conclusion

ZnO nanostripes have been synthesized by anodic oxidation process of galvanized steel. From XRD analysis, Zn peaks were detected, indicating that the starting material consist of Zn. Both chemical and mechanical mechanism for the formation of ZnO nanostripes were elucidated by proposed chemical equations and current-transient profiles. It is discernable that dense ZnO nanostripes could be observed when more acid is added.

Acknowledgement

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[*] Corresponding author: kpbeh@hotmail.com