

# Growth of Aligned ZnO Nanorod on $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$ Thin Film Template by Immersion Method

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## 1. Introduction

Zinc oxide (ZnO) is a wide-bandgap semiconductor of the II-VI semiconductor group. Having a several favourable properties like high transparency, high electron mobility, wide bandgap and high exciton binding energy bring ZnO to the bright future especially in electronics field [1-2].

One dimensional (1D) ZnO nanostructures has been extensively studied due to their attractive characteristics for various applications. These type of nanostructures can overcome the electron trapping phenomenon within grain boundaries occurred in nanoparticles thin film due to its large surface areas, exhibit quantum confinement effect and high electron mobility. The most attractive 1D nanostructures among all is aligned nanorods or nanowires which can be produced from various techniques including plasma enhanced chemical vapour deposition (PECVD) [3], hydrothermal deposition [4], thermal evaporation [5], and metal organic chemical vapour deposition (MOCVD) [6]. Another method that being less reported is immersion or chemical bath deposition where it can also deposit a very high quality of aligned ZnO nanorods with the advantage of low cost and temperature, and simplicity in the experimental setup. Applying this method, catalyst plays a big role in controlling and assisting the growth of aligned ZnO nanorods. Besides that, the position of substrate in the solution also contributes to the formation of ZnO nanorods. Hence, in this paper, for the first time, we report the growth of aligned ZnO nanorods on  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film template with the substrate that floating and facing down, allowing the nanorods to grow in extra long. The aligned ZnO nanorods can be widely used for nanodevice applications.

## 2. Experimental Setup

A glass coated ITO (indium tin oxide) as a substrate was prepared with  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film as a seed catalyst, which has been discussed earlier in [7]. For the preparation of 0.5-M ZnO solutions, zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98%, System) and hexamethylenetetramine (HMT,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ , 99%, Aldrich) were added into de-ionized water. These solutions being sonicated using an ultrasonic water bath (Hwasin Technology Power-sonic 405, 40kHz) at 50°C for half an hour before being left at room temperature and continuously stirred for 24 h. The substrate being immersed in a water bath for 4.5 h at 95°C. Field emission scanning electron microscope (FESEM, ZEISS Supra 40VP) and X-ray diffraction (XRD, Rigaku Ultima V) have been employed to study the surface mor-

phology of aligned ZnO nanorods and the crystallinity of the thin film, respectively. The material composition of the sample has been verified using an Energy Dispersive X-ray Spectrometer (EDS) that was attached to a Zeiss Supra 40 VP FESEM. Subsequently, the photoluminescence (PL) properties of the synthesized nanorods and the template were investigated using PL spectrophotometer (Horiba Jobin Yvon-79 DU420A-OE-325). All measurements were carried out at room temperature.

## 3. Results and Discussion

Nanoparticles of  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film template that was used as a catalyst is shown in Fig. 1(a), with the average diameter of 55 nm, revealing the uniformity of the thin film, while Fig. 1(b) shows the XRD analysis of the thin film. From the XRD pattern, the peak is so closed to ZnO peak, showing that it retains the hexagonal wurtzite structure of ZnO, parallel with the result found by Meher *et al.* in their study [8]. This is due to the ionic radius of  $\text{Mg}^{2+}$  (0.78 Å) that comparable to  $\text{Zn}^{2+}$  (0.83 Å), so that the dimension of their crystal cells is very close to each other. The oxygen and zinc vacancy in this thin film were deduced from the PL peak measured, which showing a wide and strong visible emission peak that widely attributed to defect states [9], which also contributes to the existing of a dangling bond state.

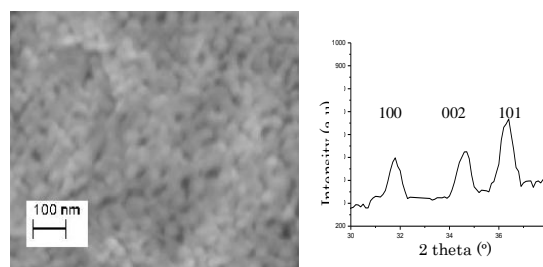


Fig. 1. (a) FESEM images of  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film template; (b) XRD spectra of  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film template

The FESEM images in Fig. 2 revealed plane and cross-sectional views of the prepared aligned ZnO nanorods on  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film template. By observing the plane view as shown in Fig. 2(a), a well oriented and high density ZnO nanorods have been uniformly deposited on an  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film which has successfully acted as cata-

lyst. In addition, a hexagonal shape of ZnO nanorods can be clearly seen in Fig. 2(b) at a higher magnification of the FESEM, where the mean diameters were observed to be less than 100 nm. Some studies reported that the diameter of their nanorods were in the range of 100 nm [3, 10], slightly larger than our nanorods. This was probably due to the fact that different catalysts used in the two studies, which were Al-doped ZnO thin film and ZnO nanocrystals, respectively. Furthermore, the cross-sectional view of the sample, as in Fig. 2(c), has been examined, which evidently showing an aligned ZnO nanorods were grown on the template used. It was observed that the length of the nanorods is in the average of 3  $\mu\text{m}$ , quite long compared to others [3, 10]. Contemplating the phenomenon, we speculated that the position of the substrate during the deposition process plays a big role, as well as the catalyst used. By positioning the substrate floating, facing downward, the growth of ZnO was influenced by the flow of precursor in the solution. During the deposition, the water bath is heated at 95  $^{\circ}\text{C}$ , so do the ZnO solutions. This will generate two obvious pressure area in ZnO solutions; high pressure at the bottom and low pressure at the top. This situation will caused the liquid with high pressure to flow to the low pressure area to reduce pressure differences and reach equilibrium, which is moving towards the surface area. This will increased the volume of  $\text{Zn}^{2+}$  ion and  $\text{OH}^{-}$  at the surface of the ZnO solutions. Because of the substrate that was positioning downward and floating at the solution's surface,  $\text{Zn}^{2+}$  ion and  $\text{OH}^{-}$  will easily attracted to the  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film that exhibits a dangling bond, an unsatisfied valence on an immobilized atom, where it will attract another atom to fill the valence shells. The continuous attraction of  $\text{Zn}^{2+}$  ion and  $\text{OH}^{-}$  simultaneously to the  $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}$  thin film template for 4.5 hours amazingly resulted in a 3  $\mu\text{m}$  long of aligned ZnO nanorods. Finally, the EDS spectrum as in Fig. 2(d) reveals the material composition of the sample, in which Zn and O were detected in large quantities.

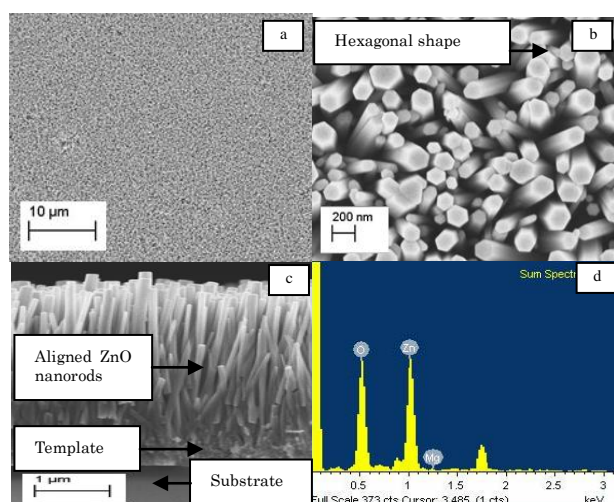


Fig. 2. (a) Overall plane view; (b) higher magnification; (c) cross-sectional view; (d) EDS spectrum of aligned ZnO nanorods .

The XRD measurements were carried out as shown in Fig. 3 where it reveals that ZnO nanorods have a very intense (002) peak centered at 34.6 $^{\circ}$  and preferential growth along  $c$ -axis, indicating that the prepared sample was in a highly-crystalline, purely hexagonal phase of ZnO nanorods, which is in a good agreement with the EDS result.

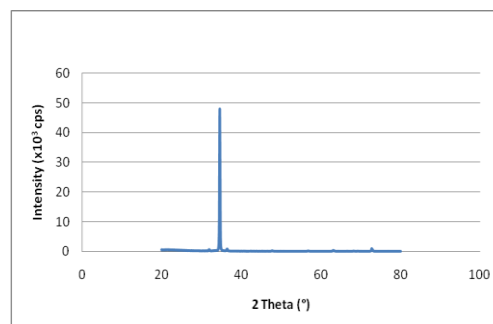


Figure 3. XRD spectra of aligned ZnO nanorods.

#### 4. Conclusion

The synthesis of aligned ZnO nanorods can be achieved using immersion method with the used of  $\text{Mg}_{0.3}\text{Zn}_{0.7}$  thin film template as a catalyst. We also demonstrated the novel technique to deposit an extra long ZnO nanorods of at least 3  $\mu\text{m}$  in length has been measured. It is observed that the diameter of the nanorods is in the range of 70-80 nm. The XRD result shows that the synthesized nanorods have preferential growth along the (002) plane, which is vertical to the substrate. With all those mentioned fabulous characteristics, it could be concluded that our synthesized aligned ZnO nanorods is suitable to be used in many nanoelectronics devices.

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