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# Co-Synthesis and Characterization of $In_2O_3$ and ZnO Nanowires

(Sintesis Bersama dan Pencirian bagi Nanowayar $In_2O_3$ dan ZnO)

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ABSTRACT

*Co-synthesis of $In_2O_3$ and ZnO nanowires (NWs) were grown on silicon and alumina substrates using vapour transport deposition method. Their morphological structures showed that the NWs were rather aligned on silicon substrate and randomly oriented on alumina substrate. The formation of NWs on silicon substrate was found to be dominated by the growth of ZnO NWs while that on alumina substrate was dominated by the growth of $In_2O_3$ NWs. The $In_2O_3$ and ZnO NWs were highly crystalline and have wurtzite structure.*

*Keywords: Co-synthesis; $In_2O_3$; nanowires; ZnO*

ABSTRAK

*Sintesis bersama bagi nanowayar $In_2O_3$ dan ZnO telah ditumbuhkan ke atas substrat silikon dan alumina menggunakan kaedah pemendapan wap. Struktur morfologi menunjukkan bahawa nanowayar tumbuh dengan agak teratur di atas substrat silikon manakala secara rawak pada substrat alumina. Penumbuhan nanowayar di atas substrat silikon didominasi oleh nanowayar ZnO, manakala di atas substrat alumina didominasi oleh nanowayar $In_2O_3$. Nanowayar $In_2O_3$ dan ZnO mempunyai kualiti kristal yang agak tinggi dan berstruktur wursit.*

*Kata kunci: $In_2O_{3,,}$ nanowayar; sintesis bersama; ZnO*

## INTRODUCTION

Semiconductor nanowires (NWs) have been regarded as one of the most promising building blocks for semiconductor electronic and optoelectronic circuits for future integrated circuit. Zinc oxide has been extensively studied due to its unique properties of wide bandgap (3.37 eV) and large exciton energy (60 meV) at room temperature. Nowadays many researchers study the material properties and the way to enhance their electrical (Li et al. 2007; Mashkoor et al. 2009) and optical properties (Xu et al. 2004; Zhou et al. 2005).

ZnO has been doped with various kinds of metals or elements to enhance their mechanical, optical and electronic properties. Various group III metals (such as Al and Ga) have been successfully used as dopants to optimize the electrical property of ZnO NWs (Bai et al. 2007; Kim et al. 2009; Pala et al. 2009). Doping with group III metal would increase the number of majority carrier and enhance the n-type behaviour of ZnO NWs. On the other hand, doping with group V metals (P, Ni and Sb) would change the NWs to p-type material (Cao et al. 2007; Mandalapu et al. 2006; Marzouki et al. 2010). Reports on the indium (In) doped ZnO NWs have just started recently (Li et al. 2007; Mashkoor et al. 2009). Because In is one of the important elements in group III, it may have novel properties which will eventually provide a lot of opportunities for future electronic devices and systems.

In this work, we have co-synthesized $In_2O_3$ and ZnO NWs on both silicon (Si) and alumina substrates. Their morphologies and properties were characterized to provide more information about the mixture of $In_2O_3$ and ZnO NWs for both fundamental research and technological applications.

## EXPERIMENTAL DETAILS

Co-synthesis of $In_2O_3$ and ZnO NWs were achieved by vapour transport deposition (VTD) method in a quartz tube furnace system. Pure ZnO and $In_2O_3$ powders, with a weight ratio of 1:1, were mixed and milled together to achieve micro scale dimensions. The powder was again mixed with micron-sized graphite powder to reduce the eutectic melting temperature. The ratio of the mixture for (ZnO+$In_2O_3$):graphite was 1:1. Si and alumina were used as substrates. They were cleaned by sonication in methanol, acetone and finally rinsed with deionized water. As catalyst, 10 nm Au layer was then deposited on the substrates using sputter coater machine.

The mixed powder was then placed in the middle of quartz tube and heated up to 1000°C for 2h. Both Si and alumina substrates were placed about 10–15 cm at the downstream of the source with temperature of 300-350°C. Nitrogen gas was used as carrier gas which has no chemical reaction with ZnO. After 2h the furnace was

cooled down to room temperature. A layer of white colored product was formed on the substrates. For comparison, pristine ZnO NWs were grown on the Si substrate under the same condition without the use of $In_2O_3$ powder. Both of the samples were characterised by field emission scanning electron microscope (FESEM) for morphological structure, energy dispersive X-ray spectroscopy (EDX) for composition study, X-ray diffraction (XRD) for crystallinity structure, and photoluminescence for optical characteristic.

## Results and Discussion

Figure 1 shows the FESEM image for the pristine ZnO NWs grown on the Si substrate. The NWs were found to be rather aligned on Si substrate. FESEM images of the nanostructures on Si substrate grown from the mixed source of $In_2O_3$ and ZnO are shown in Figure 2(a) and (b) with low and higher magnification, respectively. The nanostructures were uniformly distributed on the Si substrate. The diameter of NWs was around 20-60 nm while the length was in the order of few hundred nanometers to a few microns. The NWs formed on the alumina substrate as shown in Figure 2(c) and (d) were randomly oriented. The morphologies on these two samples can be distinguished easily. It could be seen that majority of the NWs grown on the Si substrate were ZnO NWs but those on the alumina substrate were dominated by $In_2O_3$ NWs. Both $In_2O_3$ and ZnO NWs were formed separately. It was observed that the ZnO NWs were long and smooth while the $In_2O_3$ NWs consisted of non-uniform layered stacking structures. Nevertheless, some $In_2O_3$ were expected to be incorporated into ZnO NWs to form stacking and tapering In doped ZnO NWs as shown in red box in Figure 2(d). The same morphology for the In doped ZnO NWs have been confirmed by Yousefi et al. (2010).

Figure 2(d) shows that some of the ZnO NWs were bent with large angle up to 90°, indicated by the red arrows. Basically, gradual bending of the NWs could be

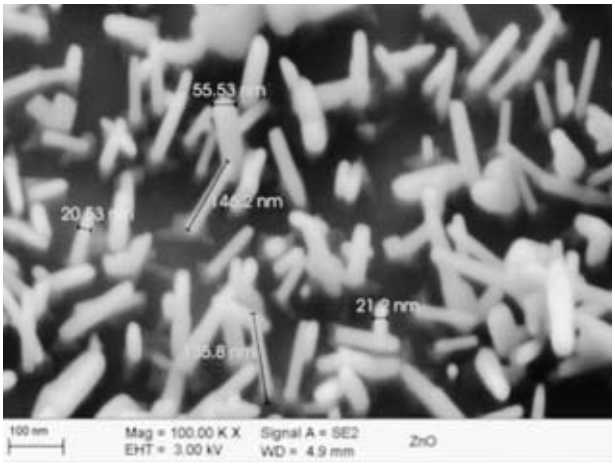


FIGURE 1. Morphological structure of ZnO NWs grown on Si substrate.

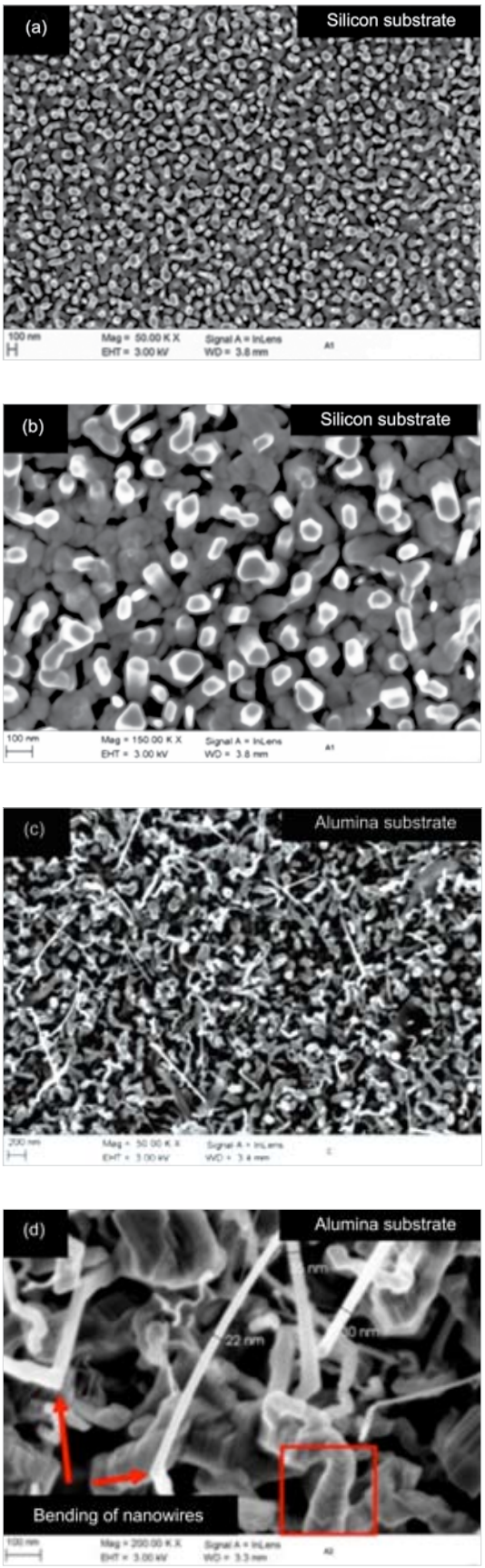


FIGURE 2. Morphological structure of mixture of $In_2O$ and ZnO NWs with (a) low magnification and (b) higher magnification on Si substrate, and on the alumina substrate with (c) low magnification and (d) high magnification

observed when the strength of the NWs failed to support their own weight during the growth process when the NWs were elongating. It would cause a smooth change in the direction to form curve-like NWs. One of the reasons why a sudden change in the direction during the growth of ZnO NWs occurred is when the composition of In in ZnO NWs has increased (Huang et al. 2009; Liu et al. 2008; Kar et al. 2011). At the same time bending structures for ZnO NWs have not been observed in the sample grown on Si substrate. All ZnO NWs on top of Si substrate were straight.

Formation of NWs in random directions on alumina substrate might be due to the substrate's crystal lattice and its orientation (Park et al. 2006). Because alumina are amorphous in nature, the NWs may not be well aligned on it. Compared to Si substrate, where it has uniform crystal orientation, in which the NWs could grow in a more aligned manner on top of it. Figure 3(a) and (b) shows the cross section of the NWs on Si and alumina substrate, respectively.

The growth mechanism for the process followed the vapor liquid solid (VLS) mechanism with Au used as catalyst (Kar et al. 2011). The VLS process consists of liquid alloy droplet formation, crystal nucleation upon gas adsorption and axial growth from the crystalline catalyst seed to form NWs. In this process, Au nanoparticles become liquid droplet under reaction temperature. As expected before, we assume that the NWs would grow by the assistance of catalyst seed layer.

The elemental composition of nanostructures on Si and alumina substrates can be observed in the EDX spectra as shown in Figure 4(a) and (b), respectively. Both spectra showed the presence of a trace amount of In. XRD spectra in Figure 5(a) and (b) show highly crystalline structure in the samples for both Si and alumina substrates. The main peaks in both spectra, at around 21.50° and 35.47° were due to $In_2O_3$ NWs. ZnO peaks at around 30.52° and 34.39°, while gold catalyst formed peaks at around 38.27° and 44.39°. Generally, XRD spectra for the co-synthesis of $In_2O_3$ NWs and ZnO NWs grown on alumina shows a higher peak

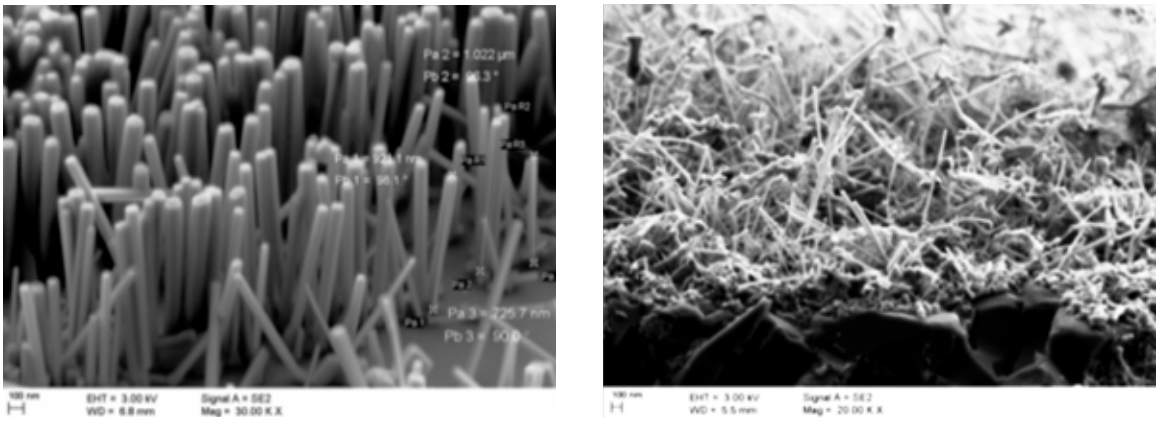

FIGURE 3. Cross section images of mixture of $In_2O_3$ and ZnO NWs on (a) silicon and (b) alumina substrat

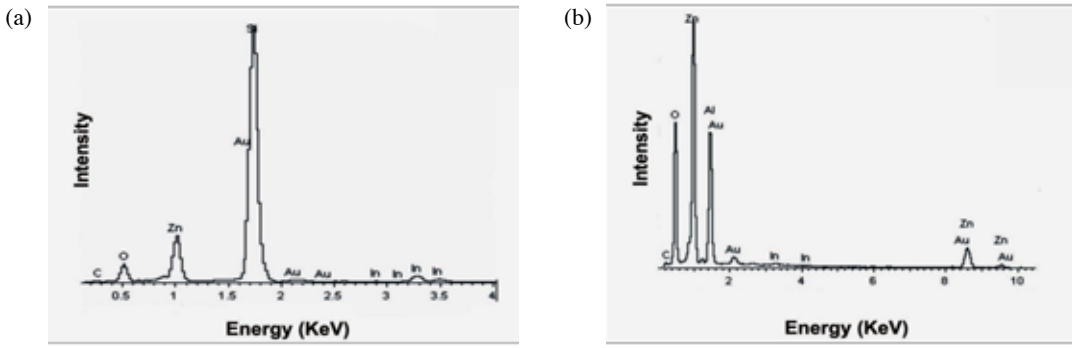


FIGURE 4. EDX result for elemental composition of mixture of $In_2O_3$ and ZnO NWs with Au catalyst on (a) Si and (b) alumina substrat

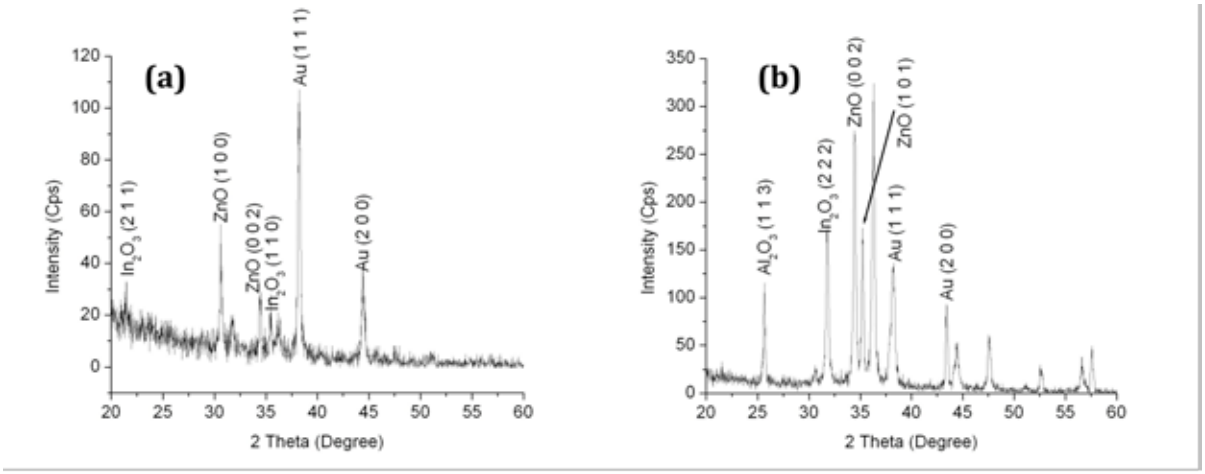


FIGURE 5. XRD spectra of mixture of $In_2O_3$ and ZnO NWs on (a) Si substrate and (b) alumina substrate with Au catalyst

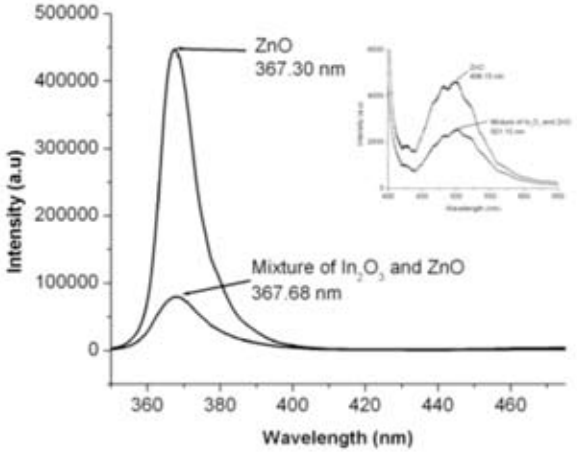


FIGURE 6. Photoluminescent spectra of pristine and mixture of $In_2O_3$ and ZnO NWs

for $In_2O_3$ compared to NWs grown on Si substrate. This result is in agreement with to the morphology observation through FESEM.

The room temperature photoluminescent (PL) spectra of mixture of $In_2O_3$ and ZnO NWs grown on Si substrate are shown in Figure 6. PL for pristine ZnO NWs is also shown for comparison. There are two distinguished peaks, one in the near ultra violet region and another in the visible range. Both of pristine ZnO and co-synthesis of $In_2O_3$/ZnO NWs have the same peak located at around 367 nm. This near band edge emission originated from the recombination of free excitons through an exciton-exciton collision process. Another broad peak of mixture of $In_2O_3$ and ZnO NWs in visible region has shifted to the green region (as shown in inset). The peaks were at 498.15 nm and 501.15 nm for pristine ZnO NWs and co-synthesis of $In_2O_3$/ZnO NWs, respectively. The deep level emission in green region was caused by the impurities (In) and structure defects in the crystal (oxygen vacancy and Zn interstitial) (Li et al. 2009).

## CONCLUSION

Co-synthesis of $In_2O_3$ NWs and ZnO NWs has been achieved using vapour transport deposition method on Si and alumina substrates. The morphological study showed that the mixture of $In_2O_3$ and ZnO NWs have better alignment on Si wafer compared to alumina substrate. The formation of NWs was dominated by ZnO if a Si substrate was used while $In_2O_3$ NWs would be the main product on an alumina substrate. XRD results showed the high crystalline and wurtzite structure for both pristine and $In_2O_3$ mixed ZnO NWs. PL spectra at visible region revealed that the peak for pure ZnO NWs has shifted to the green band region for $In_2O_3$ mixed ZnO.

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