Hierarchical-oriented Si/ZnO heterostructure nanowires

Su Kong Chong¹, Eng Liang Lim², Chi Chin Yap², Wee Siong Chiu¹, Chang Fu Dee³ and Saadah Abdul Rahman¹*

¹Low Dimensional Materials Research Centre, Department of Physics, University of Malaya, 50603 Kuala Lumpur, Malaysia.
²School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia (UKM), Bangi, Selangor, Malaysia.
³Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia (UKM), Bangi, Selangor, Malaysia.

*Email address: saadah@um.edu.my

Graphical Table of Content (TOC) Abstract

Figure caption: (a) Backscattered FESEM image of a ZnO seeded Si NW. FESEM images of the Si/ZnO hierarchical NWs prepared at ZnO growth time of (b) 60, and (c) 90 minutes. Insets in (b) are the EDX mapping images corresponding to Si, Zn and O elements. (d)
HRTEM micrograph of a ZnO seed formed on the Si NW surface. TEM micrographs of the laterally grown ZnO nanorods with a (e) regular, (f) and irregular diameters.

Nanosized ZnO seeds were spin-coated on the Si nanowires (NWs) surface to catalyze the growth of ZnO nanorods (NRs). The seeds generally showed a hexagonal facet with \(\{0\bar{1}0\}\) non-polar planes. ZnO NRs were laterally grown on the Si NWs’ backbone by supplying ZnO molecules via vapor transport and condensation process. Larger sized seeds (average size ≥ 24 nm) were favorable to induce the c-axis growth. We observed that the initial growth of the ZnO NRs possessing a regular diameter. Increase in ZnO deposition time led to the changing in NRs’ diameters due to the activation of the non-polar growth sites or the insufficient supplement of ZnO vapors.

Abstract

In this work, self-catalytic growth of zinc oxide (ZnO) nanostructures on silicon nanowires (Si NWs) was studied using a vapor transport and condensation (VTC) method. ZnO seeded Si NWs were used as a base for the growth of branches of the ZnO nanostructures. We investigated the changes in morphologies of the ZnO nanostructures by varying the average size of the ZnO seeds and ZnO evaporation time. Our observation showed that the larger ZnO seeds are energetically more stable in promoting the c-axis growth of ZnO nanorods (NRs) along the [0001] direction. Increase in ZnO evaporation time lengthens the ZnO NRs, however, results in non-uniform diameter along the NRs due to irregular supplement and precipitation of ZnO vapors on the non-polar surfaces of the NRs. The mechanisms of the seed size-dependent growth and time-dependent growth of ZnO nanostructures on Si NWs base were addressed in the text. The hierarchical oriented Si/ZnO heterostructure NWs reveal interesting optical properties, for instance the enhancement in near band edge emission and
suppression in optical reflection of the Si NWs.

**Keywords:** silicon, zinc oxide, hierarchical, nanowires, optical

### 1. Introduction

Zinc oxide (ZnO) is a wide direct band gap (3.37 eV at room temperature) semiconductor with a large exciton binding energy of 60 meV [1], which makes it an attractive material for optoelectronics and light-emitting diodes [2,3]. The morphological diversity and versatility of the ZnO nanostructures were reported in various related literatures [4]. Evidently, one-dimensional ZnO nanorods (NRs) are attracting most of the attention in research related to photocatalysis, sensors, light-emitting devices and excitonic solar cells [2,3,5]. The optical and electrical properties of the ZnO are strongly dependent on its dimensions and morphology. ZnO NRs with a large diameter (≥100 nm) are usually required for efficient excitonic emission of ZnO [6]. However, Chang et al. [7] showed that an intensive excitonic emission from 10 nm ZnO layer deposited on Si nanopillars is the result of the high surface to volume ratio from the Si nanopillars. Moreover, larger interfacial excitonic surface area in excitonic solar cells has led to the improvement in power-conversion efficiency by enhancing the electron mobility [8].

The recent advancement in materials synthesis has stimulated a tremendous number of complex nanowires (NWs) structures, such as dendritic, branching and hierarchical NWs [9-13]. Inspired by their novel morphologies, these structures have significantly increased device efficiency in water splitting [9,10], sensors [11], Li-ion battery [12] and photovoltaic devices [13]. Following this strategy, density of the ZnO NRs can be greatly increased by
implementing the high surface area of one-dimensional NWs as substrate to form a three-dimensional branching of nanostructures. In order to fabricate the hierarchical structure, vertically-aligned NWs arrays are generally required to form a base for the secondary growth of ZnO NRs.

Si wire/NWs have been widely used as building blocks to make hierarchical growth in a variety of nanostructures [9,10,13-17]. Deeper understanding of the growth and properties of Si NWs [18] has presented an advantage of the hierarchical heterostructure NWs and inclined to be used as in Si-based electronics. ZnO can naturally form a p-n junction with Si [19], which is suitable for junction photovoltaic devices. Baek et al. [13] demonstrated an improvement in solar cell efficiency by decorating the Si rods with ZnO NRs. In another study, hierarchical Si/ZnO nanoheterostructures fabricated by Sun et al. [15] showed a peak responsivity of 12.8 mA/W at around 900 nm, which makes it applicable as photo detectors. On the other hand, the natural conduction band alignment of Si/ZnO interface favors the electrons transfer from the Si conduction band to the ZnO conduction band [20]. As a result, electrons will accumulate at the ZnO surface and thus makes it easier to tunnel through a vacuum. This significantly improves the turn-on field and field enhancement factor when hierarchical Si/ZnO NWs are used as field emitters [16,17,20].

Understanding the secondary growth process is essential in order to produce homogeneous ZnO NRs on the Si NWs. Despite several previous efforts of study, it remains a challenge to control the hierarchical growth of ZnO NRs on a vertically-aligned NW. One of the main challenges is to avoid ZnO from forming an outer-shell layer on the Si NWs due to the more favored in planar growth rather than the c-axis growth on the Si NWs [21]. Metal catalyst [22], photo-resist layer [14] and ZnO seeds layer [13,15,17] were independently used by
researchers in order to direct the c-axis growth of ZnO NRs. ZnO seed layer is a better candidate as it avoids contamination due to the diffusion of catalyst or residual photo-resist compound. Moreover, controlled growth of ZnO NRs on Si NWs is more difficult than on micron-sized Si wires because of the smaller dimensions of the NWs (in some cases the dimension is equivalent to the dimension of ZnO NRs itself). Therefore, it is necessary to optimize the size of the ZnO seeds to maximize the yield of ZnO NRs on Si NWs.

Most studies utilized electroless metal etching Si NWs as bases for the secondary growth of ZnO nanostructures [15-17,20]. Nevertheless, the high density of Si bundles limits the space for the elongation of ZnO molecules [15]. In this work, we prepared Si NW arrays with micron sized interspacing between the NWs using indium (In) catalytic hot-wire chemical vapor deposition (HWCVD) [23]. ZnO seeds were overlaid on the surface of the NWs using a spin coater to direct the growth of ZnO NRs. The secondary growth of ZnO NRs on the ZnO seeded Si NWs were studied using a vapor transport and condensation (VTC) method. By varying the spinning speed, different sizes and densities of ZnO seeds were formed on the Si NWs. This allowed us to study the catalyst size effect on the growth of hierarchical ZnO NRs. Morphological, structural and optical properties of the as-grown hierarchical-oriented Si/ZnO heterostructure NWs were examined by using a variety of characterization techniques.

2. Experimental details

2.1 Synthesis of silicon nanowires

Si NWs were synthesized on p-type crystalline Si(111) and glass substrate using a home-built plasma-assisted HWCVD system [24]. The substrates were cleaned using a standard RCA method [25] prior to the deposition. The size of the In seeds formed onto the substrate by
evaporating the In wire (1.3±0.1 mg) in a H\textsubscript{2} plasma environment were ~70±12 nm. The In seeds acted as catalysts for the growth of Si NWs. Hydrogen (H\textsubscript{2}) diluted silane (SiH\textsubscript{4}) gas was used as the Si source. The flow rates of SiH\textsubscript{4} and H\textsubscript{2} were fixed at 5 and 100 sccm, respectively. A coiled tungsten filament placed 3 cm above the substrates was heated at a temperature of 1700-1800\textdegree{}C to decompose the SiH\textsubscript{4} and H\textsubscript{2} gases. The gas pressure for sample preparation was at 0.6 mbar. The deposition time was fixed at 10 minutes. The details of the deposition protocol have been previously described [23,26-28].

2.2 Spin coating of ZnO seed layer

ZnO seeds were deposited onto the surface of the Si NWs using a spin coater. 0.2 M zinc acetate dehydrate and 0.2 M diethanolamine dissolved in ethanol were stirred at 60\textdegree{}C for 30 min. The colloidal solution was spin coated onto the Si NWs samples at varying spinning speeds ranging from 1500 to 2500 rpms for 30 s. The samples were then heated at 100\textdegree{}C for 15 min to remove residual solvents. The same process was repeated 3 times. Dense ZnO seeds were eventually formed on the Si NWs by annealing the samples at 300\textdegree{}C for 1 hour in a furnace.

2.3 Vapor transport and condensation growth of ZnO nanorods

ZnO nanostructures were deposited onto the ZnO seeded planar (c-Si and glass) substrates, and Si NWs coated (c-Si and glass) substrates via a VTC process using a quartz tube furnace [29]. Mixture of ZnO and graphite powder (ratio of 1:1) with a total weight of ~0.2 g was placed inside the quartz tube at the center of its hot zone. One end of the quartz tube was
sealed and connected to N₂ gas inlet, while the other end remains open. The powder mixture was heated to ~1100°C for durations of 60 to 120 minutes. The samples were placed downstream of the quartz tube at a distance of about 12 cm from the evaporation source. This resulted in a gradient temperature change of 600 to 500°C from the center towards the opened end.

2.4 Characterization techniques

The morphology of the samples was studied using a Hitachi SU 8000 field emission scanning electron microscopy (FESEM). An X-MAX Oxford Instrument energy dispersive X-ray spectroscopy (EDX) spectroscopy attached to a JSM-7600F JEOL FESEM was utilized to obtain EDX spectra and mapping images for composition analysis of the samples. Structural properties of the samples were analyzed using a SIEMENS D5000 X-ray diffractometer. The X-ray diffraction (XRD) patterns of the samples were obtained at a grazing angle of 5°. A JEOL JEM 2100F High resolution transmission electron microscopy (HRTEM) was employed to generate HRTEM micrographs and fast Fourier transform (FFT) electron diffraction patterns to study crystallographic structures of the samples. Raman and photoluminescence (PL) measurements were performed using a Renishaw InVia PL/Raman spectrometer. Raman spectra were observed under both Ar+ and HeCd laser sources operating at excitation wavelengths of 514 and 325 nm, respectively. PL spectra were recorded under an excitation of only the He-Cd laser (325 nm). The optical properties of the samples were studied using a Perkin Elmer Lambda 750 ultraviolet-visible-near infrared (UV/VIS/NIR) spectrometer. The optical reflection (R) and transmission (T) measurements were performed.
in a spectral range from 250 to 800 nm and 250 to 1500 nm, respectively. For optical R measurement, samples were measured in a scanning area of 0.5 cm\(^2\) under an incident beam angle of 5\(^\circ\) of the arc. A Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer equipped with a 60 mm of integrating sphere compartment was utilized to study the total reflectance (R\(_T\)) properties of the samples.

3. Results and discussion

Tapered Si NWs with length (l) of ~2 \(\mu\)m and base diameter (d) of ~120 nm were used as a base for the ZnO deposition. The FEEM images of the Si NWs can be found in our previous reported works [22,28]. By assuming the NWs possess a cone-shape, lateral surface area of a NW can be estimated using the relation as: \(\frac{1}{2} \pi dl^2 + \frac{d^2}{4}\). Effective surface area of the Si NWs substrate can thus be calculated by adding up the total surface area for Si NWs and the effective planar area of the Si substrate after Si NWs coating. The effective surface area of the Si NWs substrate in an area of 1.0 \(\mu\)m\(^2\) was calculated as 2.47 \(\mu\)m\(^2\). In other words, the total surface area of the substrate was increased by a factor of 2.5 owing to the Si NWs layer which provided a larger area for the lateral growth of ZnO nanostructures.

Figure 1(a) shows a typical FESEM image of the Si NWs after deposition of the ZnO seed layer. The surface of the NWs was decorated by a high density of ZnO seeds. EDX spectrum taken on the ZnO seeded Si NWs [inset in Figure 1(a)] clearly illustrates the deposition of ZnO seeds on the NW base. The distribution of the ZnO seeds on the NWs was noticeably observed by backscattered electron FESEM image as shown in Figure 1(b). The bright spotty
ZnO seeds and Si NW are labeled in the figure. Inset in Figure 1(c) shows a typical TEM micrograph of the ZnO seeds (darker spots) decorating Si NWs. HRTEM micrograph [Figure 1(c)] shows that crystalline ZnO seeds are freely distributed on the Si NWs’ backbone. The ZnO crystals generally present a hexagonal facet although crystal defects such as rough edges were occasionally observed due to the incomplete nucleation during the annealing process to form the hexagonal facets. The FFT electron diffraction pattern taken on the ZnO seed [inset in Figure 1(c) upper right] reveals a common diffraction pattern for hexagonal ZnO crystal with \{2\bar{1}0\} and \{01\bar{1}0\} non-polar planes. Meanwhile, the electron diffraction pattern of Si NWs’ backbone [inset in Figure 1(c) lower right] reveals a feature of <110>–oriented Si NWs. In order to study the size dependent growth, different average sizes of the ZnO seeds were formed by controlling the spinning speed during the ZnO seed layer preparation. Figure 1(d) shows the varying densities and sizes of the ZnO seeds prepared at different spinning speeds. The density of the ZnO seeds on SiNWs increases from ~40 to ~140 \(\mu\text{m}^{-2}\) with the lowering of spinning speed. On the other hand, the ZnO seeds with different average sizes of 15, 24 and 32 nm were obtained for the spinning speeds of 2500, 2000 and 1500 rpms, respectively. By lowering the spinning speed, a thicker compound layer of ZnO could be retained, thus larger size of the ZnO seeds could be formed during the annealing process at 300°C [30].

The ZnO nanostructures were grown on the ZnO seeded Si NWs using a VTC method. Figures 2(a)-(c) show the FESEM images at low magnification of the Si/ZnO heterostructure NWs induced by different average sizes of the ZnO seeds varying from 15 to 32 nm. The
homogeneous features observed from the FESEM images indicate that the ZnO nanostructures were grown at high uniformity throughout the Si NWs base. Increase in the size and density of the ZnO seeds significantly enhances the growth of ZnO nanostructures. The morphologies of the ZnO nanostructures induced by different sizes of ZnO seeds are displayed by high magnification FESEM images as depicted in Figures 2(d)-(f). The ZnO seeds with average size of 15 nm [Figure 2(d)] only cause the growth of triangular-shaped ZnO nanostructures. The magnified image from the ZnO triangular feature [inset in Figure 2(d)] reveals a six sided cross-section with three short facets observed at the corners of the triangular cross-section. This may in some instance indicate that the triangular feature is evolved from the small ZnO seeds due to irregular expansion of three preferential facets. Short ZnO NRs (~250 nm in length) were grown on the Si NWs when seeding was done by the larger ZnO seeds with an average size of 24 nm [Figure 2(e)]. The NRs act to preserve the hexagonal shape of the ZnO seeds. In this case, the condensation of ZnO vapors tends to form ZnO NRs growing along the c-axis. This may indicate that the axial growth only took place when ZnO crystals of a certain size were used as a seeding point for growth. Under the same ZnO growth time, the length of the ZnO nanostructures was found to increase significantly to ~450 nm with the rise in average size of ZnO seeds up to 32 nm [Figure 2(f)]. The NRs mostly have uniform diameters and possess a hexagonal shape as displayed by the inset of Figure 2(f).

The elemental composition of the as-grown Si/ZnO hierarchical NWs were analyzed by using EDX spectroscopy. Typical EDX spectrum of the Si/ZnO hierarchical NWs is shown in
Figure 3. No traces of other elements were observed besides the Si, Zn and O signals within the detection limit (>0.1 wt%) of the EDX spectroscopy. This confirms high purity of the samples grown using the presented techniques. It is expected that the observed strong signal of Si element could have originated from the Si substrate in addition to the Si NWs. In order to confirm the formation of three-dimensional Si/ZnO heterostructure NWs, an EDX mapping on a single hierarchical NW was studied. The hierarchical NWs were extracted from the substrate (to eliminate the Si signal due to the substrate) by sonication and drop which was casted onto a lacy copper grid. Insets in Figure 3 shows the EDX mapping images corresponding to the Si, C and O elements of a Si/ZnO hierarchical NW illustrated by the FESEM image. The core NWs is thus confirmed as Si, while the NRs branches consist mainly of Zn and O elements.

The typical XRD patterns of Si NWs and Si/ZnO hierarchical NWs are presented in Figure 4(a). The diffraction peaks of the Si NWs are indexed to face-centered cubic Si structures [23,25]. The Si diffraction peaks were retained in XRD pattern of the Si/ZnO hierarchical NWs. The residual peaks are well-matched to wurtzite structure of ZnO (JCPDS card: 36-1451). The appearance of Si and ZnO diffraction peaks indicates the formation of a highly crystalline structure of the Si/ZnO hierarchical NWs composite. The full width at half maximum of the Si(111) and ZnO(101) diffraction peaks were obtained by fitting the peaks using Gaussian function. The crystallite sizes of Si and ZnO crystals calculated using Scherrer’s equation [31] are 28±2 nm and 40±2 nm, respectively. This is comparable to the diameters of the Si NWs (~30-50 nm) and hierarchical ZnO NRs (~50-80 nm) as observed
from TEM micrographs. In addition, the identified wurtzite ZnO structures correlate with the hexagonal shape of ZnO NRs. The Raman spectra of the Si NWs and the Si/ZnO hierarchical NWs were recorded at 514 nm and 325 nm laser excitations as shown in Figures 4(b) and (c), respectively. The Raman active $E_2$ mode ($439 \text{ cm}^{-1}$) as a characteristic of hexagonal ZnO [32] was observed in the 514 nm Raman spectra in addition to the transverse optical (TO) mode of crystalline Si ($\sim 520 \text{ cm}^{-1}$). Meanwhile, the peak position of the $E_2$ mode is similar to the bulk ZnO (437-439 cm$^{-1}$), which indicates an unstrained state of the hierarchical ZnO NRs [33]. By using the 325 nm laser excitation wavelength on the Si/ZnO hierarchical NWs, the longitudinal optical (LO) phonon modes of ZnO went up to three orders together with the TO mode of crystalline Si as shown in the Raman spectrum. The observed multiphonon LO modes were due to the wurtzite ZnO under resonant Raman condition [34].

The TEM analyses on the Si/ZnO heterostructure NWs are presented in Figure 5. Figure 5(a) displays the TEM micrograph of a ZnO nanostructures decorated Si NW prepared by ZnO seeds with average size of 15 nm. The HRTEM micrograph [Figure 5(b)] reveals crystalline ZnO facets, while FFT electron diffraction pattern [inset in Figure 5(b)] identifies both non-polar \{01\overline{1}0\} and polar \{0\overline{1}11\} crystal planes from the ZnO crystal. It can be observed that the evolution of the ZnO facets (from hexagonal to triangular) is due to the expansion of the non-polar and polar planes. The TEM micrograph of a hierarchically-grown ZnO NRs on Si NW using 24 nm ZnO seeds is presented in Figure 5(c). The HRTEM study [Figure 5(d)] indicates a single crystalline structure of the hierarchical ZnO NRs. Crystal lattices of 5.2 Å and 2.8 Å observed in the figure corresponded to (0001) and (1010) of ZnO crystallographic
planes, respectively. FFT electron diffraction pattern as illustrated in inset of Figure 5(d) shows the diffraction spots due to \{0001\}- and \{01\bar{1}0\}-orientation of the ZnO crystals. The axial growth orientation of the hierarchical ZnO NRs can thus be identified as [0001] direction, whereas the lateral planes of the NRs reveal \{01\bar{1}0\}-orientation.

The time dependent growth of the hierarchical ZnO NRs was studied by fixing the average size of the ZnO seeds at 32 nm and varying the ZnO growth time. Morphologies of the Si/ZnO hierarchical NWs prepared at 60, 90 and 120 minutes are illustrated by the cross-sectional FESEM images depicted in Figures 6(a), (b) and (c), respectively. It can be seen that the length of the NRs increased from ~450 nm to ~1 \(\mu\)m when the growth time was increased from 60 to 120 minutes, respectively. On top of the increasing in NRs’ length, longer exposure time to the ZnO vapors also tends to produce higher density of ZnO NRs cladding on the surface of the Si NWs. As the density of the ZnO seeds are conserved, the increase in density of the NRs could be due to multiple growths from single seeds [17]. Figures 6(d) and (e) show the planar and cross-sectional views, respectively, of the Si/ZnO hierarchical NWs prepared at 90 minutes ZnO growth time. Hyper-branches of ZnO NRs were grown on the free standing Si NWs as revealed in the figures. However, in contrast to the uniform diameter of the hierarchical ZnO NRs prepared at deposition time of 60 minutes [inset in Figure 6(a)], the diameter of the hierarchical ZnO NRs becomes uneven when the deposition time increases to 90 minutes and above [inset in Figure 6(c)]. The diameter of the stem along the NRs changed as the NRs were exposed longer to the ZnO vapors. TEM image of the hierarchical ZnO NRs cladding on a Si NW [Figure 6(e)] reveals a larger diameter at
the upper region of the NRs. This to some extent indicates a more complicated growth mechanism due to lateral expansion [35].

The growth mechanisms of the hierarchically grown ZnO nanostructures by ZnO seeds on vertical-aligned Si NWs using VTC method are suggested based on the above observation. Schematic diagrams of the different sizes of ZnO seeds coated on Si NWs are illustrated in Figures 7(a) and (b). Considering the hexagonal ZnO seeds possess a top surface of (0001) plane and side surface of (01\overline{1}0) plane, the cross-section of the hexagonal ZnO seeds nanostructures evolved from 6 facets to 3 major facets of {01\overline{1}0} due to irregular lateral growth of the ZnO molecules on the preferred growth sites. Therefore, the smaller sized ZnO seeds (average size ~21 nm) were unable to retain their hexagonal shape during the condensation of ZnO vapors [Figure 7(a)]. A reduction in primary facet number from hexagonal into triangular faceted cross-section due to evolution in lateral/radial growth process was also observed in hexagonal Si wire by Oehler et al. [36]. In our case, we believed that the facet evolution eventually transformed the ZnO seeds into the triangular pyramid structures with the top polar facets. From the surface energy viewpoint, the polar faces, for instance {0\overline{1}1\overline{1}} faces possess a lower surface energy compared to the non-polar side {01\overline{1}0} faces [37]. Thus, the growth velocity towards [0\overline{1}1\overline{1}] orientation is higher and this tends to shape the ZnO seeds into a triangular pyramid top. As a result, the growth of ZnO along the c-axis in [0001] direction is terminated by the expansion of the {0\overline{1}1\overline{1}} facets. The further condensation of the ZnO molecules could only expand the volume of the ZnO pyramid crystals. On the other hand, the condensation of ZnO vapors on the facet of the ZnO seeds is
more uniform for the larger sized ZnO seeds [Figure 7(b)]. The elongation of the ZnO structures towards the lowest energy of c-axis indicated a more stable growth of ZnO crystal in this condition. Therefore, the hexagonal structures with \{01\bar{1}0\} faces surface of the grown ZnO nanostructures were retained. Moreover, the result revealed a significant increase in the length and trace increment in the diameter of the ZnO NRs when the average size of the ZnO seeds increased from 24 to 32 nm. This might infer that a volume expansion for the ZnO seeds was actually taking place at the initial stage of the growth of NRs. The c-axis growth only accelerated once a certain size of the ZnO crystals was reached. For smaller sized ZnO seeds (average size ~24 nm), longer nucleation time is required to initiate the growth of ZnO NRs, thus the NRs are relatively short in this condition. The larger sized ZnO seeds (average size ~32 nm) however, create larger growth sites for the condensation of ZnO vapors. Hence, they can achieve higher axial growth rate compared to the smaller sized seeds.

In the initial growth stage, the ZnO NRs reveal a uniform diameter as the supplement of ZnO vapors prefer to condense onto the polar surface of ZnO; for instance positively charged (0001)-Zn or negatively charged (000\bar{1})-O planes. However, as the ZnO evaporation time increased, the ZnO vapors tend to condense on the non-polar \{01\bar{1}0\} or \{2\bar{1}0\} surfaces, thus creating a change in the diameter along the ZnO NRs. Figures 7(c) and (d) illustrate the schematics for the diameter evolution as observed on the hierarchical ZnO NRs when increasing the ZnO growth time. The exposure of the as-grown ZnO NRs in the high temperature region (~500-600°C) has made their non-polar surfaces an alternative growth sites for the ZnO vapors. In other words, the mobility of the ZnO vapors on the surfaces of the
NRs was increased due to the high temperature of the NRs surface [38]. This subsequently increases the tendency of the precipitation of ZnO vapors on the NRs’ surface, and resulting in the increment in diameter at the top of the hierarchical ZnO NRs [Figure 7(c)]. On the other hand, Shen et al. [39] observed that a diameter evolution of the ZnO NRs using a mixture of Zn, In and In$_2$S$_3$ powders are sources of evaporation. They attributed the changes in the morphology of the ZnO NRs to the effect of the In concentration. Nevertheless, in our case, the role of In element (catalyst for the growth of Si NWs) in the morphology evolution of ZnO NRs is revealed as the In element which are absent in EDX and XRD measurements. Figure 7(d) illustrates another diameter evolution process with an abrupt reduction in diameter of the NRs which occurred after the NRs were extended up to a certain length. This bottle-like ZnO NRs were observed in some regions of the sample. It is believed that the reduction in diameter is due to insufficient supplement of ZnO vapors, which decreased the vapor pressure of the particular regions and induced the growth polar {0\(\bar{1}1\)} faces on the edges of NRs. Thus, the coverage of the polar (0001)-plane was reduced up to a stage where the c-axis growth has an effect again.

The typical PL spectra of ZnO NRs on planar Si, Si NWs and Si/ZnO hierarchical NWs are shown in Figure 8. Both ZnO NRs on planar Si and on Si NWs were prepared under the same conditions. The FESEM image of the ZnO NRs grown on planar c-Si substrate is inserted in Figure 8. The Si NWs exhibit orange and red emissions peaking at 620 nm and 680 nm, respectively, due to the radiative recombination center of the incomplete oxidation of In catalyst and emissive nanocrystallites Si on the surface of the Si NWs [40]. ZnO NRs grown
on ZnO seeds coated Si substrate using VTC method revealed a broad range of green to red emission, centered at ~550 nm with a shoulder at a range of 650 to 720 nm, and minute UV emission (~380 nm). The green emission is normally assigned to the participation of oxygen vacancy defect [41,42] in ZnO NRs, while the orange and red emission could be due to the Zn vacancy [43] or Zn interstitials defects [44]. The weak UV emission is attributed to the near band edge emission of ZnO [45]. The PL spectrum of Si/ZnO hierarchical NWs conceals combined emissions of the Si NWs and ZnO NRs. The visible emission covers a wider visible spectral range from 450 to 730 nm due to the combination of green emission from ZnO NRs and orange to red emission from Si NWs. In addition, the intensity of the UV emission of Si/ZnO hierarchical NWs was enhanced by about an order of magnitude compared to the ZnO NRs grown on planar Si. The one-dimensional Si NWs provide larger surface area for the growth of hierarchical ZnO NRs with significant higher density, thus resulting in sufficient ZnO crystals for efficient UV emission [11].

The optical properties of the Si/ZnO hierarchical NWs were also studied in order to investigate the role of hierarchical ZnO NRs on the Si NW arrays. Figure 9(a) shows the optical R spectra of the ZnO NRs, Si NWs and Si/ZnO hierarchical NWs measured at an incident light angle of 45° from normal of the samples. It is important to point out again the ZnO NRs and Si NWs were prepared under the same deposition conditions as the Si/ZnO hierarchical NWs. The tapered Si NWs show a low R% of <10% compared to the ZnO NRs (<15%) within the spectral range of 250 to 800 nm. The average R% of the Si NWs is reduced from ~5.4% to 1.4% in the visible region (330 to 750 nm) by decorating the NWs with
hierarchical-oriented ZnO NRs. In order to investigate the light scattering effect from the hierarchical nanostructures’ surface, the $R_T$ spectra of the samples were measured by an integrating sphere as shown in Figure 9(b). The results show that the percentage of $R_T$ of the Si NWs was suppressed from an average of 9% to about 5% by decorating the NWs’ surface with hierarchical ZnO NRs. The suppression of the $R$ is attributed to the effect of nanostructured coating of ZnO NRs on the Si NWs which enhance the total internal reflection [28] during the interaction between photon and the samples. Meanwhile the $R$ spectra of the Si/ZnO hierarchical NWs preserved the characteristic of ZnO NRs with an $R$ peak at 380 nm in the absorption region of the ZnO. The low $R$ in the Si/ZnO hierarchical NWs indicates a signification reduction in the diffraction loss of incident excitation photon from the samples [46]. This might also explain the significant enhancement in the near band edge emission for the hierarchical ZnO NRs on Si NWs as discussed in the PL results.

The optical $T$ spectra of ZnO NRs, Si NWs and Si/ZnO hierarchical NWs are displayed in Figure 9(c). Transparency of the as-grown ZnO NRs sample ($T >88\%$) in the visible region is confirmed by its $T$ spectrum. The Si NWs show a high $T$ (~80%) in near infrared region. The $T\%$ is reduced in the visible region and the spectrum shows an absorption edge at $\lambda \sim 500$ nm. $T$ spectrum of the Si/ZnO hierarchical NWs exactly follows the trend of the $T$ spectrum Si NWs, with a shifting in the absorption edge to $\lambda \sim 440$ nm. Hence, our results show that the Si/ZnO hierarchical NWs exhibit good antireflection properties and retain the intrinsic transmission properties of the Si NWs. The blue-shifted in the absorption edge indicates an increase in the optical band gap ($E_g$) of the Si NWs due to the coating of ZnO NRs. The
optical indirect $E_g$ and direct $E_g$ of the Si/ZnO hierarchical NWs were evaluated from the T and R spectra using Tauc’s relation [47]. The Tauc plots for the indirect allowed transition $[(\alpha E)^{1/2} \text{ versus } E]$ of the Si NWs and the Si/ZnO hierarchical NWs, and direct allowed transition $[(\alpha E)^2 \text{ versus } E]$ of the ZnO NRs and the Si/ZnO hierarchical NWs are shown in Figure 9(d). The indirect $E_g$ of Si NWs (~1.4 eV) and direct $E_g$ of ZnO NRs (~3.3 eV) obtained in this work are close to the literatures [1,48]. The Si/ZnO hierarchical NWs exhibit an indirect $E_g$ and direct $E_g$ of ~1.8 and 2.8 eV, respectively, which lay in between the $E_g$ of Si NWs and ZnO NRs. The blue-shift in $E_g$ can be due to the incorporation of ZnO molecules into the Si NWs matrix or the formation of the SiO$_x$ layer on the Si NWs during the growth of ZnO NRs. However, the origin of the shifting in the $E_g$ remains unclear and needs further investigation.

4. Conclusion

The hierarchical growth of ZnO NRs on ZnO seeded Si NWs were studied using a VTC process. The c-axis growth of ZnO NRs is strongly dependent on the size of the ZnO seeds, where a larger size (~32 nm) of the ZnO seeds are more capable of forming nucleation sites for the precipitation of ZnO vapors and are energetically more stable to accelerate the c-axis growth. The competition between axial or c-axis growth with lateral growth results in the uneven diameter of ZnO NRs as observed when the condensation time of ZnO vapors were increased. The crystalline wurtzite structure of the hierarchical ZnO NRs was identified using XRD, micro-Raman and HRTEM measurements. The hierarchical-oriented Si/ZnO heterostructure NWs exhibit a combined photoluminescence spectrum from the ZnO NRs and
Si NWs. Additionally, the near band edge emission of ZnO is enhanced by an order of magnitude for the hierarchical ZnO NRs compared to planar ZnO NRs. The significant suppression in R is shown by the hierarchical-oriented ZnO NRs without reducing the T of the Si NWs, making them a promising candidate for NWs-based photovoltaic applications.

Acknowledgements

This work was supported by the UM/MOHE High Impact Research Grant Allocation of F000006-21001, the Fundamental Research Grant Scheme (FRGS) of KPT1058-2012 and the University Malaya Research Grant (UMRG) of RP007B-13AFR.

References


Figure 1 (a) Secondary electron, and (b) backscattered electron FESEM images of ZnO seeded Si NWs. Inset in (a) is the EDX spectrum of the ZnO seeded Si NWs. (c) HRTEM image of ZnO seeds coated on a Si NW. Insets in (c) are a TEM micrograph (upper left), and FFT electron diffraction patterns taken on ZnO seed (upper right) and Si NW’s backbone (lower right). (d) Variation of sizes and densities of the ZnO seeds on Si NWs prepared at different spinning speeds from 1500 to 2500 rpms.
Figure 2 FESEM images of the Si/ZnO heterostructure NWs formed using different average sizes of ZnO seeds of (a, d) 15 nm, (b, e) 24 nm, and (c, f) 32 nm. The ZnO growth time was fixed at 60 minutes for all samples. Insets in (d) and (f) are the magnified images from the open square areas in the respective images. (Scale bar = 100 nm)
Figure 3 typical EDX spectrum of the Si/ZnO hierarchical NWs. Insets are FESEM and EDX mapping images of a Si/ZnO hierarchical NW.
Figure 4 typical (a) XRD patterns and (b, c) Raman spectra of the Si/ZnO hierarchical NWs. The Raman spectra were obtained under laser excitation wavelengths of (b) 514 nm, and (c) 325 nm.
Figure 5 (a, c) TEM, and (b, d) HRTEM micrographs of the ZnO nanostructures formed on Si NWs base using ZnO seeds with average sizes of 15 and 32 nm, respectively. Insets in (b) and (d) are FFT electron diffraction patterns transformed from the respective HRTEM micrographs.
Figure 6 Cross-sectional FESEM images of the hierarchical ZnO NRs prepared on Si NWs using ZnO seeds with an average size of ~32 nm at different ZnO evaporation time of (a) 60, (b) 90, and (c) 120 minutes. Insets in (a) and (c) are the high magnification images of the hierarchical ZnO NRs magnified from the respective figures. (d) Planar, (e) cross-sectional views of FESEM, and (f) TEM images of a ZnO NRs cladding Si NW.
Figure 7 Growth mechanisms for hierarchical ZnO nanostructures on Si NWs base. Schematic diagrams of the growth of ZnO NRs on Si NWs base using (a) smaller sized, and (b) larger sized ZnO seeds. Schematic diagrams of the (c) nail-like, and (d) tapered hierarchical ZnO NRs grown by increasing the evaporation time of the ZnO powders to 90 minutes and above.
Figure 8 PL spectra of the Si NWs, ZnO NRs and Si/ZnO hierarchical NWs obtained at an excitation wavelength of 325 nm. Inset in the figure is the planar view FESEM image of the ZnO NRs grown on planar Si substrate.
Figure 9 Optical (a) R, (b) R_T, and (c) T spectra of the ZnO NRs, Si NWs, and Si/ZnO hierarchical NWs. (d) Tauc’s plots of the ZnO NRs, Si NWs and Si/ZnO hierarchical NWs based on their optical T and R data.