The effects of substrate on enhancement of UV emission of ZnO nanorods

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Abstract. We have synthesized ZnO nanorods by hydrothermal at 95 °C for two hours on different substrates i.e. glass, ZnO, and ITO. Morphologically, the average diameter of ZnO nanorods on glass, ZnO, ITO are 117.6 µm, 133 µm, 98.4 µm, respectively. According to the international center for diffraction data (ICDD) number #01-079-0207, the ZnO nanorods on all substrates possess a polycrystalline wurtzite structure. By full width at half maximum (FWHM) of ZnO NRs in (002) plane, we have determined crystallite size and micro-strain using Scherer’s equation and Stokes-Wilson equation, respectively. The crystallite size and micro-strain of ZnO NRs vary with different kind of substrates. Optically, ZnO nanorods on a glass substrate have the strongest excitonic-related ultraviolet (UV) emission. Further observation, we have determined the UV/GB ratio to confirm the crystalline quality of ZnO NRs on glass, ZnO, and ITO substrates. These UV/GB ratios are 101.35, 68.14, and 22.74. It is indicating the ZnO NRs on glass has a better crystalline quality which indicates fewer native defects concentration compared to the others.

1. Introduction
ZnO as metal oxide semiconductor has potential applications in electronic, optoelectronic, and electrochemical devices. It’s due to ZnO has a wide band gap energy of 3.4 eV and large exciton binding energy of 60 meV at room temperature [1,2]. Therefore, ZnO was claimed as competitor material for GaN [3].

Since the last decade, one dimension (1D) ZnO nanostructure has a great interest in the fabrication of nano-devices such as light emitting diodes (LED), transparent conductor, nanogenerator, etc. [4,5]. It’s because of their unique advantages of low growth temperature and high mechanical stability. Even though, to realize devices based homojunction 1D ZnO nanostructure still becomes a bottleneck. It’s due to the presence of native defects such as oxygen vacancy (Vo), zinc vacancy (Vzn), interstitial zinc (Zni), interstitial oxygen (Oi), antisite oxygen (Ozn) which responsible to n-type properties of ZnO [6]. These defects also exhibit the strong visible emission which observed under photoluminescence investigation [7]. Nevertheless, 1D ZnO nanostructures such as nanorods, nanowires, and nanotubes generally have shallow native defects, hence, optically and electrically still need some improvements [8].
In order to improve optical and electrical properties of ZnO nanorods, some efforts such as optimization compositions of precursor [1], heat treatment [2,9], and doping of specific elements [8] have introduced by various techniques [4]. Compared to the various techniques, hydrothermal offer desirable advantages such as low-cost, easy control precursor and doping compositions, and low growth temperature [10,11].

In our previous report, well-aligned ZnO nanorods with improvement in the ultraviolet (UV) and orange-yellow intensity can be obtained by proper precursor concentration [1]. Moreover, S. Baek et al report the Fe doping can improve the optical properties of ZnO nanorods [5]. Meanwhile, ZnO nanorods which growth on different substrate i.e. silicon and Cu substrates have different morphology and optical properties [12].

In this paper, we growth ZnO nanorods (NRs) by hydrothermal at 95 °C for two hours. We used three substrates i.e. glass, ZnO, and indium tin oxide (ITO). The effects different substrates on morphology, structure and photoluminescence properties of ZnO nanorods will be discussed.

2. Experimental details
ZnO seed layer was deposited on three different substrates i.e. glass, ZnO, ITO by ultrasonic spray pyrolysis with a frequency of 1.7 MHz at the temperature of 450 °C. The growth solutions were then prepared by dissolving zinc nitrate tetrahydrate (Zn (NO$_3$)$_2$.4H$_2$O, 99.99%, Merck) and hexamethylenetetramine (C$_6$H$_{12}$N$_4$, 99.99%, Merck) in de-ionized (DI) water with the equimolar concentration of 0.1 M. The seed layer immerses into the sealed bottles contain growth solution. Then, the sealed bottles placed in the oven at 95 °C in the normal atmosphere for 2 hours. After the growth process, samples were rinsed ultrasonically in distilled water and dried out on a hot plate set at 60 °C for 10 minutes.

The morphology, structure, photoluminescence (PL) of the samples have performed using JOEL JSM-6510LA Analytical scanning electron microscope (SEM), X-ray diffraction (XRD) PANalytical EMPYREAN, spectrometer laser pico, respectively.

3. Results and discussion
Figure 1 shows SEM images of ZnO NRs on three different substrates (a) glass, (b) ZnO, (c) ITO.

![Figure 1. SEM images of ZnO NRs on different substrates (a) glass, (b) ZnO, (c) ITO.](image-url)
As can be seen from the figure 1 (a)-(c), the ZnO NRs on different substrates have random growth orientations with different average diameter. The average diameter of ZnO NRs on glass, ZnO, ITO substrates are 117.6 nm, 133 nm, 98.4 nm, respectively. As well known, the ZnO seed layer can be used to reduce the energy barrier between nanorods and the substrates [12]. Hence, the nucleation density of ZnO NRs will improve by ZnO seed which deposited on each substrate. Further investigation, we observed that the ZnO NRs on ITO have higher density with fine nanotip.

Figure 2 shows the XRD pattern of ZnO NRs on three different substrates. We observed seven (hkl) plane i.e. (100), (002), (101), (102), (110), (103), and (112). According to the international center for diffraction data (ICDD) number #01-079-0207, all samples possess ZnO NRs polycrystalline hexagonal wurtzite structure with no other phase.

![Figure 2. XRD pattern of ZnO nanorods on different substrates.](image)

By comparing the XRD pattern, the ZnO NRs on ITO has better polycrystalline quality. It’s indicated by the strong intensity for all (hkl) planes compared to ZnO NRs on another substrate. Moreover, the coefficient of texture (TC) was used to determine preferred orientation.

| Substrates | $2\theta$ | $a = b$ (Å) | $c$ (Å) | FWHM | Crystallite Size (nm) | Micro-strain (%) |
|------------|-----------|-------------|---------|------|----------------------|-----------------|
| Glass      | 34.349    | 3.249       | 5.204   | 0.127| 69.77                | 0.184           |
| ZnO        | 34.359    | 3.245       | 5.203   | 0.221| 44.97                | 0.291           |
| ITO        | 34.462    | 3.250       | 5.207   | 0.119| 58.32                | 0.223           |

According to our previous results [10], we consider (002) plane as the preferred orientation of ZnO NRs on ITO. Furthermore, by the full width at half maximum (FWHM) of ZnO NRs in (002) plane, we have determined crystallite size and micro-strain using Scherer’s equation and Stokes-Wilson equation, respectively. Table 1 is the listed of FWHM, crystallite size, and micro-strain of ZnO NRs in (002)
plane. The crystallite size of ZnO NRs is highest on a glass substrate, meanwhile, the micro-strain is highest on ZnO substrate. These results indicate the ZnO NRs growth on three kinds of substrates has different lattice mismatch. The smallest crystallite size confirms the ZnO NRs on the ZnO substrate has better nucleation.

Figure 3 shows room temperature PL spectra of ZnO NRs on glass, ZnO, and ITO substrates. It can be seen from the figure there are two typical emissions i.e. excitonic-related ultraviolet (UV) and defect-related visible (green band, GB) emissions. These two emissions have center peaks at ~377 nm and ~580 nm, respectively. As well known, the intensity peak ratio of UV and GB can be used to evaluate the concentration of native defects which correspond to crystalline quality [13,14]. As reported by X.M. Fan et al, the native defects which naturally exist on ZnO structure responsible to the deep level emission (DLE) [6]. Even though, according to X.M. Fan reports, there are different explanation to explain the origin of green emission i.e. (i) ionized vacancies, (ii) electron transition from the level of the ionized oxygen vacancies to the valence band, (iii) electron transition from the bottom of conduction band to the antisite defect Ozn level [6].

Our results confirm the ZnO NRs on glass, ZnO, and ITO is 101.35, 68.14, and 22.74, respectively. However, the XRD pattern of ZnO NRs on ITO has better polycrystalline quality. In this case, we predict more (hkl) plane has more site for the defects exist on the structure. It’s can be understood that the stacking fault occurs on the lattice plane. Therefore, the ZnO NRs on glass has a better crystalline quality which indicates fewer native defects concentration compared to the others. We conclude the UV/GB ratio can be used to confirm crystalline quality relative to a single crystalline structure.

4. Conclusions
In conclusion, we have synthesized ZnO NRs on different substrates i.e. glass, ZnO, ITO by hydrothermal at 95 °C for two hours. Morphologically, the ZnO NRs growth on different substrates has a different average diameter and randomly oriented relative to the substrate. According to the
international center for diffraction data (ICDD) number #01-079-0207, the ZnO nanorods on all substrates possess a polycrystalline wurtzite structure. By full width at half maximum (FWHM) of ZnO NRs in (002) plane, the crystallite size and micro-strain of ZnO NRs vary with different kind of substrates. Further investigation, the PL spectra of ZnO NRs on a glass substrate have the strongest excitonic-related ultraviolet (UV) emission. Further observation, in order to confirm the crystalline quality of ZnO NRs on glass, ZnO, and ITO substrates, we have determined UV/GB ratios. We believed the UV/GB ratio can be used to confirm crystalline quality relative to single crystalline structure. These UV/GB ratios are 101.35, 68.14, and 22.74.

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