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Influence of Growth Temperature on Morphological and Structural Properties of Sputtered- Zinc Oxide Nanorods

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ABSTRACT

Zinc oxide is highly sought after for several applications in biology, optoelectronics, electronics, and sensing. Zinc oxide nanorods exhibit a high exciton binding energy and a wide direct band gap, making them an attractive material for ultraviolet optoelectronic devices in the compound semiconductor field. This investigation focuses mainly on the influence of growing temperature on the crystal structure and surface morphology of ZnO nanorods, specifically for their application as UV photodetectors. Si (100) substrates were utilized for the growth of ZnO nanorods using radio frequency magnetron sputtering. The ZnO nanorods are grown at temperatures of 350 °C, 375 °C, and 400 °C, respectively. The crystal structure and surface morphology were examined using X-ray diffraction and scanning electron microscopy. The samples exhibited a same crystal orientation of the (002) diffraction peak at all growth temperatures. The growth temperatures show a direct influence on the density and length of nanorods, as evidenced by the scanning electron microscopy photographs. The results revealed the significant influence of substrate temperature on the regulation of nanorod length and crystal formation.

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1. Introduction

In recent decades, ZnO, a II-VI semiconducting compound, has attracted huge attention and effort thanks to its interesting characteristics. ZnO has a larger excitonic binding energy of 60 meV at ambient temperature than gallium nitride, which has a binding energy of 25 meV. Moreover, ZnO is an effective light emitter in the ultraviolet (UV) spectral region and useful for applications such as thin-film transistors (TFT) and transparent conducting oxides (TCO) due to its high conductivity and transparency [1], [2]. Therefore, ZnO has been used in different applications such as light-emitting diodes, ultraviolet detectors, piezoelectric transducers, solar cells, and chemical sensors [3]–[11]. In particular, ZnO nanorods provide remarkable crystalline quality, a high electron mobility, a wave guiding effect, a high surface-to-volume ratio, and the potential for quantum confinement. Thus, the development of vertically well-aligned ZnO nanorods has garnered a lot of interest due to their potential use in near-UV detectors, laser diodes, and light emitting diodes.

Zinc oxide (ZnO) nanorods have been synthesized using several growth methods, such as plasma-enhanced chemical vapor deposition (PECVD), vapor-liquid-solid (VLS), vapor-solid, chemical vapor deposition (CVD), sol-gel, and sputtering [12]-[17]. Chemical methods, such as hydrothermal and solvothermal approaches, appeared to be the most common in terms of the number of reports. Sputtering is currently the most common physical vapor deposition technique used to produce thin films of ZnO. Sputter deposition provides better control over rod density as well as growth direction. Despite the flexibility and scalability, the production of ZnO nanorods has not been extensively researched. Samples produced using this technique would exhibit increased crystallinity as a result of the elevated deposition temperature and significantly reduced impurities in comparison to chemical methods. This is particularly advantageous for specific optoelectronic devices that have a p-n junction, such as nanorod light emitting diodes and nanorod lasers [19]. ZnO is an intrinsically n-type semiconductor with a small concentration of electrons.

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In this report, ZnO nanorods were grown on Si (100) substrate at different temperatures (350ºC, 375ºC, and 400ºC) with the RF-magnetron sputtering method. The obtained results and discussion mainly focused on the relationship between the structure and morphology of ZnO nanorods and the growth temperature. Samples presented similar ZnO crystal orientation of (002) diffraction peak at all substrate temperatures. Microscopic images revealed the dependance of density and length of nanorods on substrates temperatures. Those results were fundamental steps towards the fabrication of the entire UV photodetector where ZnO nanorods worked as an efficient UV-absorbing component.

2. Materials and Methods

The method of RF magnetron sputtering was employed to deposit ZnO nanorods onto Si(100) substrates, utilizing a ZnO ceramic target. Initially, the Si(100) substrate had a series of rinses in deionized water, isopropyl alcohol, a 5% H_2SO_4 solution, and a 20% HF solution. Afterwards, the Si(100) substrate was heated in the vacuum chamber under high pressure conditions (7.5×10^{-6} Torr) to eliminate any remaining water vapor or contaminants adhering to the surface of the substrate. Ultimately, ZnO nanorods were applied onto a Si(100) substrate at different temperatures: 350 °C (Tg350), 375 °C (Tg375), and 400 °C (Tg400). The RF power was consistently maintained at a level of 100 W during all deposition processes. To ensure a fair comparison, the deposition time has been set to 30 minutes in all cases. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were used to analyze the crystal structure and surface morphology.

3. Results and Discussions

The influence of deposition temperature on the crystal structure of ZnO rods grown on Si(100) substrate was examined by X-ray diffraction (XRD). Figure 1 displays the X-ray diffraction (XRD) patterns of ZnO/Si(100) samples grown at three distinct temperatures: 350 °C (Tg350), 375 °C (Tg375), and 400 °C (Tg400). The XRD patterns exhibited both the diffraction effect of the ZnO seed layer and the nanorod. There were four different diffraction peaks observed: (001), (002), (103), and (104). These peaks are in agreement with the hexagonal structure of wurtzite ZnO, as indicated by the JCPDS NO. 36-1451. The ZnO (002) peak had the greatest intensity in comparison to the other three peaks, namely ZnO (001) and ZnO (103). The (002) crystal planes are associated with ZnO structures that are formed with a significant alignment along the c-axis [18]. The full width at half maximum (FWHM) values of the ZnO (002) peak were determined to be 0.338°, 0.235°, and 0.245° for the Tg350, Tg375, and Tg400 samples, respectively. This demonstrates that higher deposition temperature led to improved crystallinity of ZnO samples, as indicated by reduced FWHM values. Upon increasing the substrate temperature, the d-spacing values exhibited a reduction from 2.613 to 2.602 Å (Table 1). Therefore, the temperature at which the ZnO/Si(100) sample is grown has a significant impact on the size of the ZnO seed layer crystals [20]. Table 1 presents a summary of the results obtained from XRD measurements for ZnO nanorods grown at three distinct temperatures.

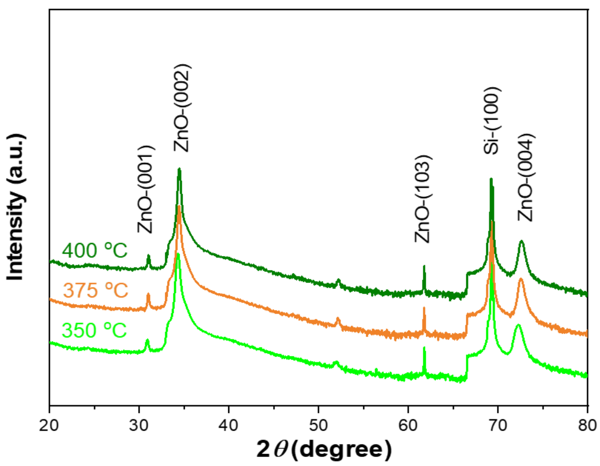

Figure 1. *XRD spectra of ZnO/Si(100) samples of Tg350; (b): Tg375 and (c): Tg400.*

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Table 1. *Information about structural properties obtained from the XRD spectra*.

Samples	(h k l)	2 theta (°)		FWHM (°)	*d*-spacing (Å)	*D* *(Crystal size)* (Å)
		Our data	Bulk			
Tg350	(0 0 2)	34.318	34.4	0.338	2.613	4.297
Tg375	(0 0 2)	34.440	34.4	0.234	2.604	6.209
Tg400	(0 0 2)	34.471	34.4	0.245	2.602	5.931

Figure 2 displays SEM images of ZnO nanorods deposited at three distinct temperatures: Tg350, Tg375, and Tg400. Figure 2a illustrates the absence of the nanorods. Figure 2b demonstrates the appearance of several ZnO nanorods in the Tg375 sample. The Tg375 sample consisted of large rods measuring 1082.1 ± 17.5 nm in length and 84.5 ± 7.8 nm in diameter. Figure 2c illustrates ZnO nanorods exhibiting a high degree of density. The Tg400 sample consisted of large rods measuring 1196.5 ± 13.8 nm in length and 141.8 ± 6.3 nm in diameter. Clearly, the ZnO nanorods of Tg400 exhibited a significantly greater length compared to those of Tg375.

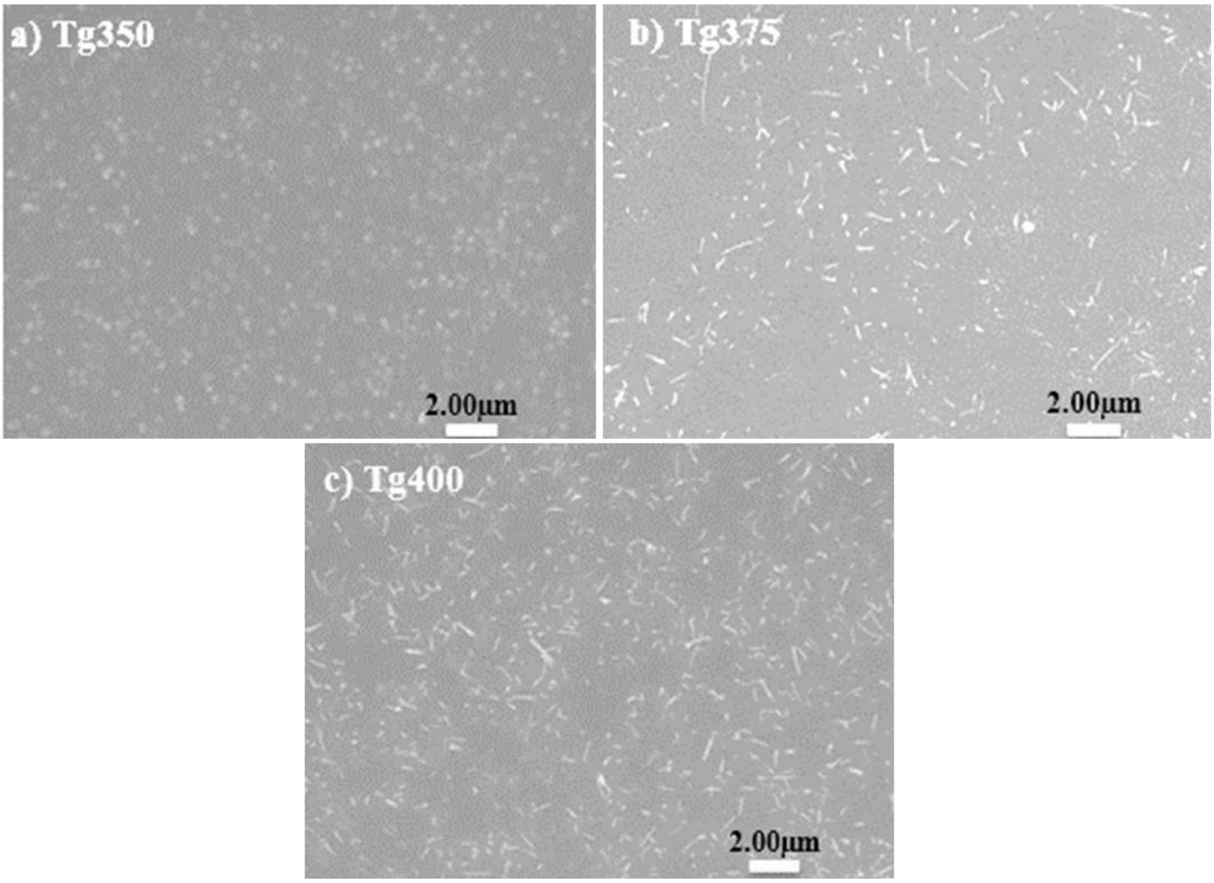

Figure 2. *The SEM images of ZnO nanorods grown at the different temperatures 350 ˚C, 375 ˚C, and 400 ˚C.*

Figure 3 displays the scanning electron microscope (SEM) images of three samples at a higher level of resolution. Following an increase in the growing temperature of ZnO nanorods, there was a corresponding increase in the density of the ZnO nanorods. The density values for Tg375 and Tg400 were approximately 1.84 (rod/µm^2) and 2.24 (rod/µm^2), respectively. The Tg350 image revealed the presence of large ZnO grains, which completely covered the whole surface of the sample. There were very few nanorods observed in this particular case. It has been suggested that what happens indicates the transition of ZnO from a thin film to

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nanorods when the temperature reaches 350°C. The ZnO grains in the Tg375, SEM imagine experienced a reduction in size and became sites for the formation of nanorods. However, the rod length and density dropped low of expectations. In the most recent instance of Tg400, the ZnO grains experienced a further decrease in size, leading to the formation of distinct nucleation sites, from which nanorods began to develop. Evidently, a decrease in the amount of ZnO substance deposited on the seeding layer results in a greater amount of matter on the rods, providing their growth in both size and length. Table 2 presents a summary of the data obtained from SEM images for ZnO nanorods grown at three different temperatures.

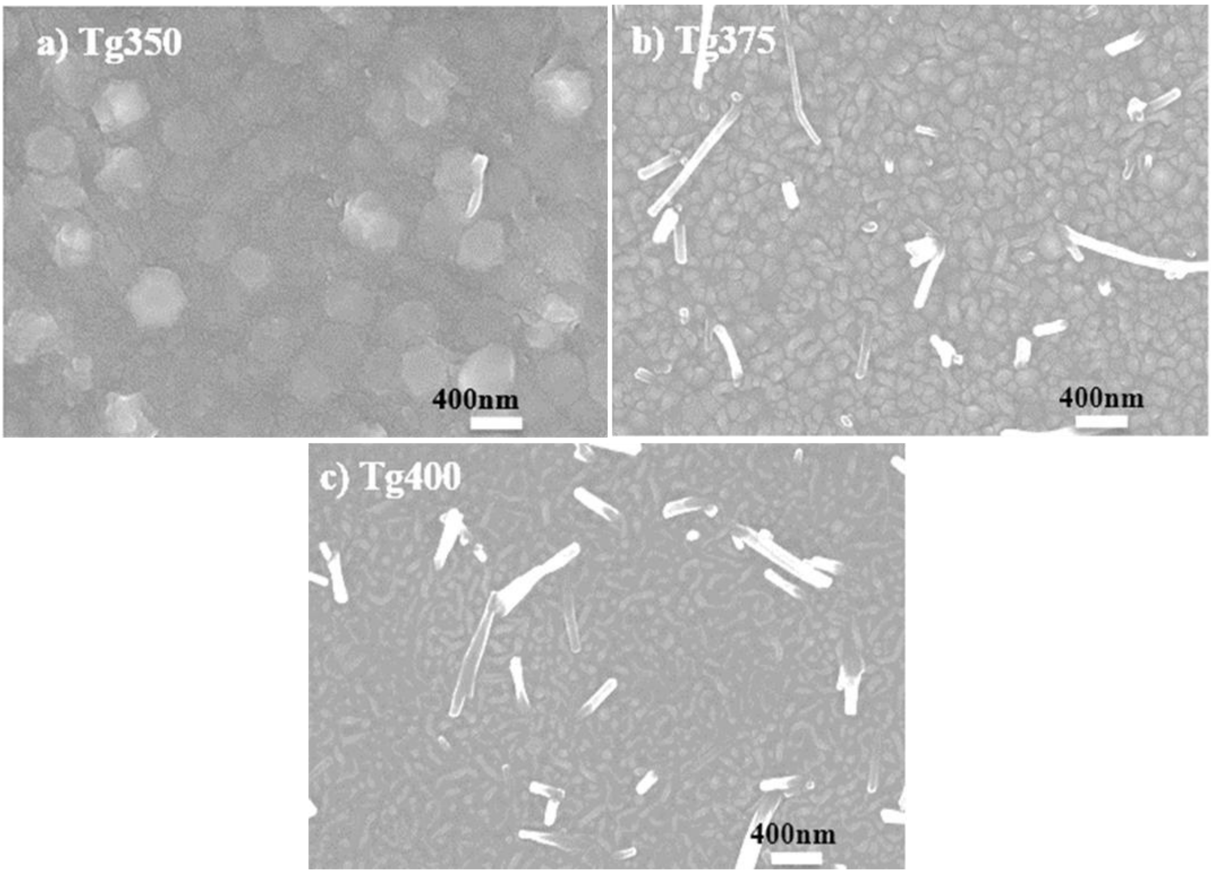

Figure 3. *The SEM images of three ZnO nanorod samples Tg350, Tg375, and Tg400 at higher resolution.*

Table 2. *Morphology analysis of the SEM scans for samples Tg350, Tg375 and Tg400.*

Samples	Growth temperature (°C)	Density (rod/µm^2)	Diameter of ZnO nanorods (nm)	Length of ZnO nanorods (nm)
Tg350	350	-	-	-
Tg375	375	1.84	84.5 ± 7.8	1082.1 ± 17.5
Tg400	400	2.24	141.8 ± 6.3	1196.5 ± 13.8

4. Conclusions

To summarize, ZnO nanorods were applied onto Si(100) substrates using RF-magnetron sputtering at varying substrate temperatures (350 °C, 375 °C, and 400 °C). Increasing the growth temperature led to an improvement in the crystallinity of ZnO nanorods, as indicated by the XRD data. Moreover, according to the scanning electron microscope (SEM) images, an increase in deposition temperature resulted in a corresponding increase in rod density. The future development of UV photodetectors is dependent on achieving these important results, as ZnO nanorods are an essential element for efficient light absorption.

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Conflict of Interest

The authors declare no conflict of interest.

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