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Research Article

Annealing Heat Treatment of ZnO Nanoparticles Grown on Porous Si Substrate Using Spin-Coating Method

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ZnO nanoparticles were successfully deposited on porous silicon (PSi) substrate using spin-coating method. In order to prepare PSi, electrochemical etching was employed to modify the Si surface. Zinc acetate dihydrate was used as a starting material in ZnO sol-gel solution preparation. The postannealing treatments were investigated on morphologies and photoluminescence (PL) properties of the ZnO thin films. Field emission scanning electron microscopy (FESEM) results indicate that the thin films composed by ZnO nanoparticles were distributed uniformly on PSi. The average sizes of ZnO nanoparticle increase with increasing annealing temperature. Atomic force microscopic (AFM) analysis reveals that ZnO thin films annealed at 500°C had the smoothest surface. PL spectra show two peaks that completely correspond to nanostructured ZnO and PSi. These findings indicate that the ZnO nanostructures grown on PSi are promising for application as light emitting devices.

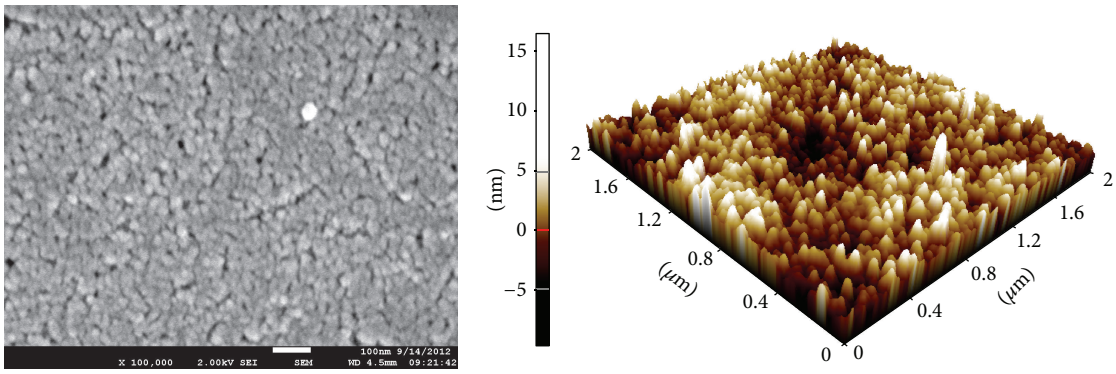
1. Introduction

In the past decade, developing high-quality semiconductor nanostructures has attracted increasing attention due to promising applications in electronic and optoelectronic devices arising from their physical properties. ZnO is a wide band gap semiconductor with excellent chemical stability and high exciton binding energy [1]. These properties make it widely used in optoelectronic devices such as solar cells, gas sensor, UV sensor, LED applications, and so on [2–6]. In order to synthesis ZnO, various methods were applied such as laser deposition [4], RF magnetron sputtering [3, 5], mist-atomization [7], and sol-gel deposition [2, 6, 8, 9].

High quality ZnO nanostructures were obtained by very expensive and complicated equipment [10]. However, expensive and complicated equipments for ZnO synthesization are not applicable in large scale productions. In this work, ZnO thin film was deposited by sol-gel spin coating. This simple method is using less expensive equipment and easy to handle compared to other technique. So, this low-cost technique becomes more promising in bulk productions.

Other than that, substrate selection is very important to ZnO thin film properties. Physical, optical, and electrical properties of ZnO will be different using different substrates. Suresh Kumar et al. have studied the deposition of ZnO nanostructure on indium-tin oxide (ITO), glass and polyethylene terephthalate polymer (PET) substrates [11]. They found that different substrates will produce different type of ZnO nanostructures. Besides, substrate selections are also based on its device application. Mamat et al. have fabricated UV photoconductive sensors on glass substrate [12] and Gao et al. have deposited ZnO films on silicon wafer in order to study the optical properties for solar cells applications. Besides, Yang et al. suggested that white light emitting diode can be produced by depositing ZnO films on PSi substrate [5].

In this work, PSi substrate was prepared by modifying the silicon wafer surface using electrochemical anodization method. Kim et al. suggested that modification of silicon



(a) (b)

Figure 1: (a) FESEM image and (b) three-dimensional AFM image of PSi.

surface can reduce the effect of large lattice mismatch between single crystalline silicon wafer and ZnO [13, 14].

Investigation on various parameters such as heat treatment, molarity of precursor and stabilizer, and aging time was being conducted. The results show that the growth of ZnO thin films is influenced by these parameters, including its optical and electrical properties [15–18]. In order to study the postheat treatment, annealing temperatures were varied in a range of 300°C to 700°C while other parameters are maintained.

2. Experimental

Zinc acetate dehydrates were used as a starting material, while diethanolamine and isopropyl are used as a stabilizer and solvent, respectively. P-type silicon wafer was used in PSi preparation. Firstly, silicon wafer was cleaned by acetone, followed by methanol and diluted hydrofluoric 40% acid in ultrasonic bath. Then, the silicon was dried by nitrogen gas before being etched by electrochemical etching. Hydrofluoric acid 48% was mixed with absolute ethanol (HF48%: absolute ethanol = ratio of 1 : 1) was used as an electrolyte. Current densities and time were maintained at 20 mA/cm^2 and 20 minutes during etching process. ZnO precursor was prepared by dissolving 0.15 M of znic acetate into isopropyl and stirred. Then, diethanolamine was added slowly into the solution and heated at 60°C for an hour to yield a clear and homogenous solution. After that, the solution was continued stirred and aged at room temperature for 24 hours. The ratio of zinc acetate to diethanolamine was fixed at 1.0.

Spin coating method was used to deposit ZnO thin films on PSi surface. Rotation per minute was maintained at 3000 within 60 seconds. Then, 10 drops of ZnO precursor were dropped on surface of rotated PSi. After that, ZnO thin film was dried at 150°C for 10 minutes to remove any volatile components. These processes were repeated 10 times to increase the thicknesses of ZnO thin film. Finally, ZnO thin films were annealed in various temperatures in a range of 300°C to 700°C for an hour.

ZnO thin films were studied by FESEM, model JEOL JSM-J600F. AFM (model XE-100 of Park Systems) was employed to study the roughness of ZnO thin films. PL spectra were studied at room temperature by HORIBA Jobin Yvon's LabRAM 800HR with 325 nm He-Cd laser as a source.

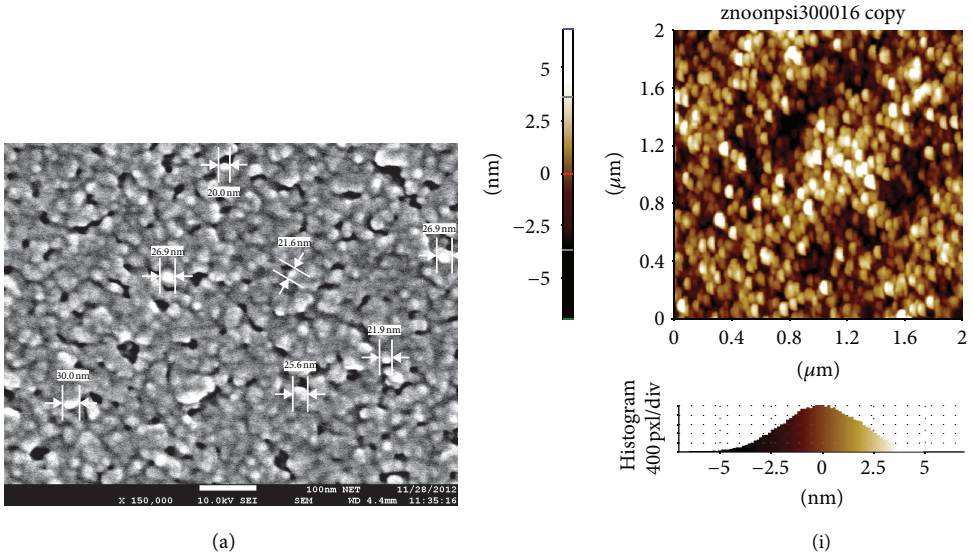
3. Result and Discussions

The p-type silicon wafer surface was successfully modified to porous after being etched at current densities 20 mA/cm^2 for 20 minutes. Figure 1 shows the FESEM and AFM images of PSi. As seen in Figure 1, irregular pores with sizes in range of ~11.9 nm to ~30.6 nm were distributed over the PSi surface. The surface roughness average of porous is 1.953 nm while silicon wafer is 0.314 nm. This shows that PSi was successfully prepared in this work. The interreaction between silicon wafer and hydrofluoric acid is suggested in (1) [19]:

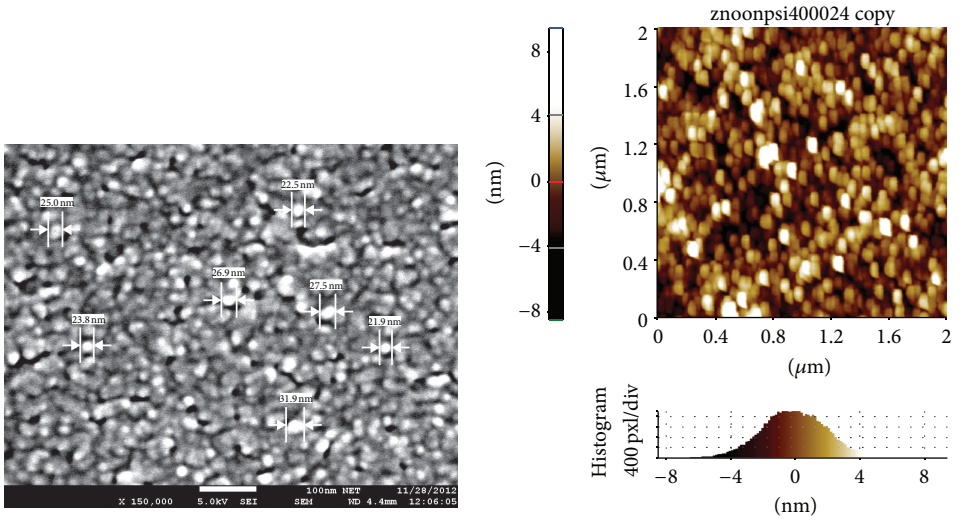
$$\mathrm{Si} + 6\mathrm{F}^- + 2\mathrm{H}^+ \longrightarrow \mathrm{SiF}_6^{2-} + \mathrm{H}_2 \quad (1)$$

ZnO thin film deposited on PSi was shown in Figure 2. The left hand side is FESEM images while three-dimensional AFM image is on the right hand side. Based on FESEM images, the thin film are composed by ZnO nanoparticles. Besides, the pores can also be seen on the surface.

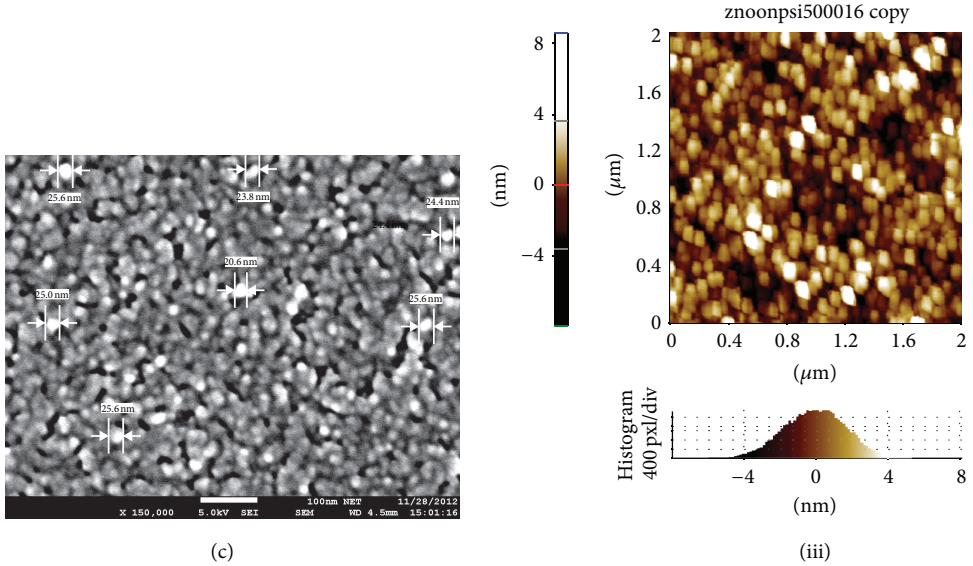
The pores are clearly seen when the thin films were annealed at 500°C. The averages of particle size depend on postannealing temperatures. Figure 3 shows the average particle sizes of ZnO nanoparticle in different annealing temperatures. The particle size of 24.7 nm increases 25.64286 nm when annealing temperature increased from 300°C to 400°C. This can be explained by thermal expansion where the kinetic energy of atom increases due to increases of annealing temperatures. However, the average particles sizes were decreased to 24.37143 nm at annealing temperature of 500°C and 21.32857 nm at 600°C. It is attributed by the atom which got sufficient thermal energy and move to any space within the particle or crystalline rearrangement. So, the size of particle decreased due to full filled space within the crystalline. It is believed that the crystalline quality also increased because the atom will move to the favorable position [20]. The atom will move to the adjacent particle at 700°C. So, it will merge into adjacent particle and form larger particle.



(a) (i)



(b) (ii)



(c) (iii)

Figure 2: Continued.

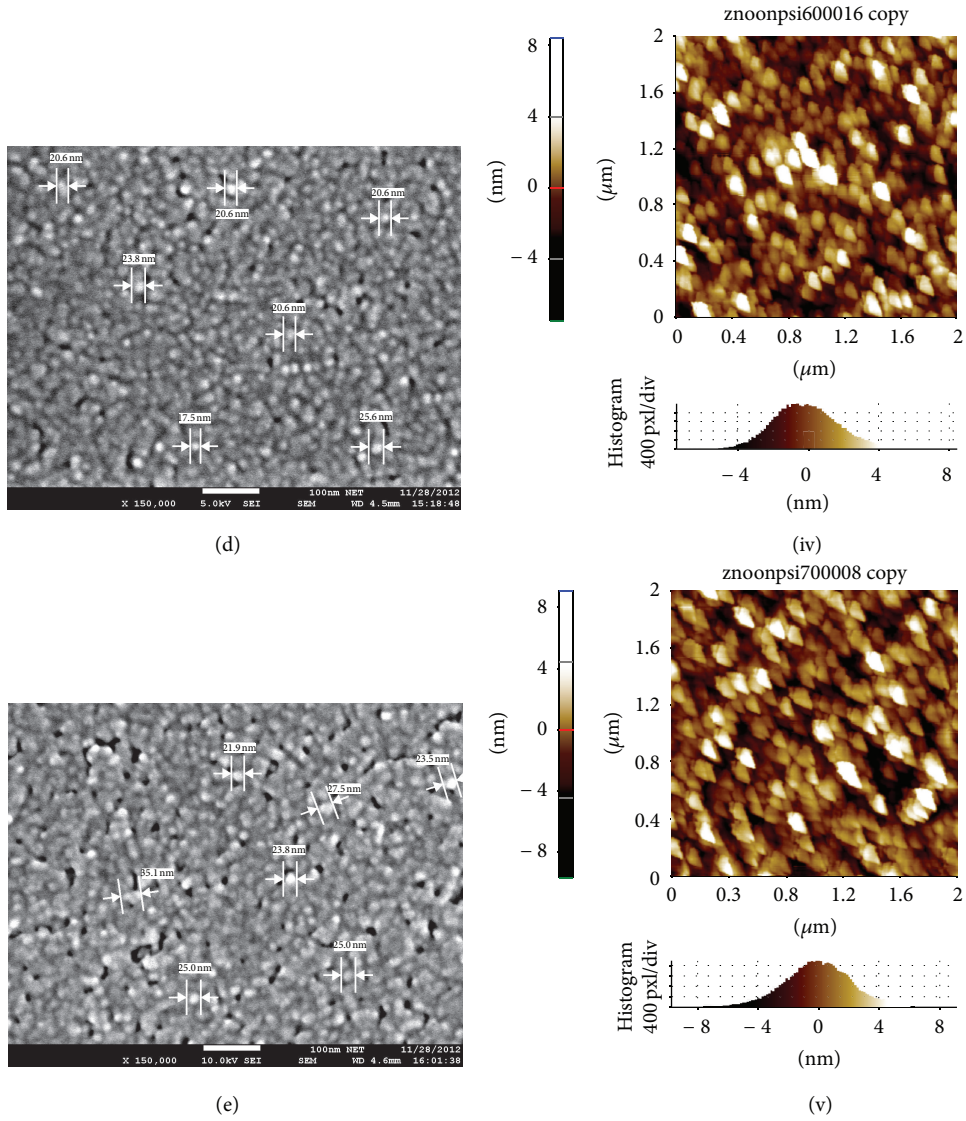


Figure 2: FESEM and AFM images of ZnO thin films on PSi annealed at (a) and (i) 300°C, (b) and (ii) 400°C, (c) and (iii) 500°C, (d) and (iv) 600°C, and (e) and (v) 700°C.

The average surface roughness of ZnO thin film surface is 1.501 nm at annealing temperature of 300°C and increases to 1.643 nm at 400°C. However, the average surface roughness decreases to 1.455 nm at 500°C. Then it becomes rougher after increasing the annealing temperatures. The average surface roughness of thin film is increased at 400°C due to increases of particle size.

After being annealed at 500°C, the crystalline quality increases due to that atom arrangements that are in favorable position make the average surface roughness decreases. However, the average surface roughness increases after that due to increases of particle size.

Figure 4 shows the PL spectra of ZnO thin film composed nanoparticles on porous in a range of 350 nm to 900 nm. There are three main peaks within the range of 400 nm to 420 nm, 550 nm to 600 nm, and 625 nm to 725 nm belongs to ZnO, defects of ZnO thin film and PSi, respectively [21, 22]. The peak within the range of 400 nm to 420 nm is free-exciton recombination of ZnO thin film [20].

The deep-level emissions (550 nm to 600 nm) from the ZnO nanostructures were possibly caused by intrinsic and structural defects in ZnO that form deep energy levels in the ZnO band gap. These defects represent oxygen and zinc interstitials, as well as oxygen and zinc vacancies [21]. Kim et al. reported that the peak within the red region is generated by radiative recombination of excitons on the surface of PSi [20]. The peaks which contributed free-exciton recombination are less affected by postannealing temperature in this work. However, the intensities of the peak in the range 550 nm to 600 nm gradually decrease due to increases of postannealing temperatures. This is attributed by the crystalline of the ZnO thin film. By increasing the temperature, the atom moves to a favorable position. So, the defects such oxygen vacancies and zinc interstitial will reduce.

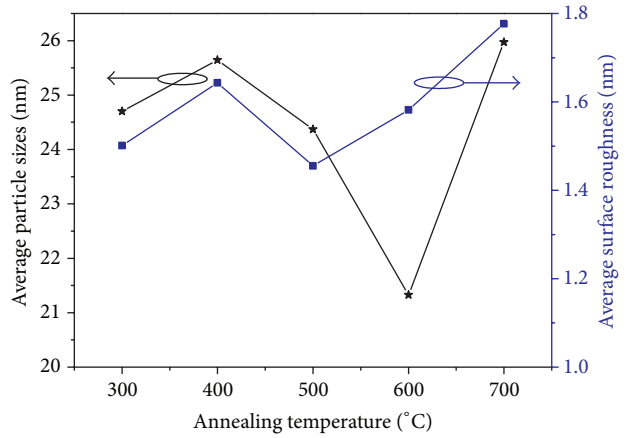


Figure 3: Average particle size of ZnO nanoparticles and surface roughness in different annealing temperatures.

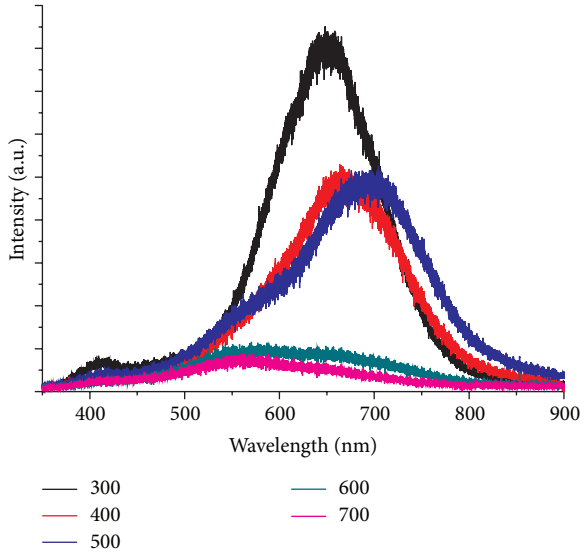


Figure 4: PL spectra of ZnO thin film composed nanoparticles on PSi in range of 350 nm to 900 nm.

The peaks in range of 625 nm to 725 nm are highly affected by postannealing temperatures. The peak at postannealing of 300°C was attributed by the combination of defects of ZnO and radiative recombination of excitons on the surface of PSi. The increases of crystal-line quality of ZnO reduced the intensities of the peaks and red-shifted attributed by only PSi surfaces. The intensities tend to diminish after being annealed at 600°C and 700°C. We suggested the pores on silicon surfaces were full-filled by ZnO nanoparticles.

4. Conclusions

In summary, the ZnO thin film was successfully deposited on PSi. FESEM and AFM images revealed that the thin films are composed by ZnO nanoparticles. The average ZnO particles sizes depend on postannealing temperatures. Besides, the PL spectra are also affected by the annealing temperature attributed by the physical changes of ZnO nanoparticles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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