Synthesis and Temperature Dependence of I-V Characteristic of Spin-Coated Nanostructured ZnO on P-Type Silicon

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Abstract. P-type silicon was used as a substrate of deposition of nanostructured ZnO by sol-gel spin coating technique, while zinc acetate, diethanolamine, and isopropyl were used as starting material, stabilizer and solvent respectively. Surface morphology was studied by Field Emission Scanning Electron Microscopy (FESEM). It was found that nanostructured ZnO was distributed uniformly over the P-type Silicon substrate. This was supported by atomic force microscopy (AFM) image which shows the all the surfaces are covered by nanoparticle of ZnO. X-ray diffraction (XRD) was employed to analyse the structural and crystalline of nanostructured ZnO. Three peak (100), (002), and (101) correspond to nanostructed ZnO are appear. Temperature dependence I-V characteristic was investigated in range of 25 K to 300 K by using Close Cycle Cryostat and using Helium as cooler agent. It is found that the resistance were decrease toward the higher temperature. The result shows that resistivity gradually decrease due to increases of temperature.

1. Introduction

ZnO semiconductor is very interesting due to its electrical and optical properties. Its direct wide band gap energy of \(\approx 3.37\) eV large binding energy of \(\approx 60\) meV makes it very interesting. These properties make it potentially in optoelectronic device such as ultraviolet photoconductive sensors \([1-3]\), gas sensors \([4, 5]\), UV laser \([6]\), and thin film transistor \([7]\). Besides, it is also important in bio-medical application \([8]\). There are several method have been used to deposits ZnO on various substrate includes pulsed laser deposition (PLD) \([9]\), DC reactive magnetron \([10]\), activated reactive evaporation \([11]\), RF magnetron sputtering \([12]\) and sol-gel method\([6, 7, 13-15]\). Among them, sol-gel deposition method is very interesting due to low-cost, simple and highly controlled way \([16]\). Structural of znO in different thickness by sol-gel deposition method were studied by Shariffudin et al \([17]\). They found that 42.7 nm of thickness gave the lowest resistivity. Electrical properties of ZnO on glass prepared by dip-coating in room temperature have been studied and the result shows that the withdraw speed influence the resistivity of ZnO thin film and the result shows high withdraw speed produce more resistivity \([13]\). Besides, structural and electrical properties ZnO thin film on silicon and quartz also studied by Zhao et al \([9]\) based on substrate temperature and oxygen pressure. They found that resistivity increases substrate temperature and oxygen pressure. In this study, the nanostructured ZnO were deposited on silicon substrate by sol-gel spin coating method. Atomic force microscopy
(AFM), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) were used to study the structural and surface morphologies of nanostructured ZnO. Current versus voltage were investigated using close cycle cryostat.

2. Experimental

Zinc acetate as a starting material, diethanolamine (DEA) as stabilizer, and isopropyl as a solvent were used in this work, while P-type silicon (Si) with orientation (100) was used as a substrate. In order to prepare P-type silicon substrate, cleaning process was started by using acetone and methanol to remove any residual on the substrate surface. Then, dilute HF, mixed of HF40% and di-water with ratio 1:10 was used for etching the surface of Si. After that, the etched Si was washed by di-water before dried by nitrogen gas. All cleaning process was done in ultrasonic bath.

ZnO Sol-gel of 0.5 M concentration was prepared by dissolving zinc acetate dihydrate into isopropyl. Then, diethanolamine was added slowly to produce clear solution. Furthermore, the solution was heated for an hour at 60°C followed by aged for 24 hour at room temperature. Nanostructured ZnO was deposited on P-type Si substrate by spin coating method. Rotations of spin coater were kept at 300 rpm within 60 s while 10 drops of precursor were dropped on substrate to produce thin film. Then, nanostructured ZnO thin film was dried at 150°C within 10 minutes. The process of deposition by spin coating and drying were repeated to enhance the thickness of thin film before annealed at 500°C for an hour.

X-ray diffraction (XRD) characterization with Cu Kα radiation was employed to analyze the crystalline and diameter size of nanostructured ZnO. Field Emission Scanning Electron Microscopy (FESEM), JOEL JSM-J600F was used in order to investigate the surface morphology of nanostructured ZnO. I-V temperature dependence was studied by close-cycle cryostat and Helium as a cooling agent. Temperature ranges of 25 K to 300 K were used in this work. Gold metal contact was deposited on nanostructured ZnO by sputter coater before connected to the circuit.

3. Result and Discussion

3.1. Structural and morphological properties

Figure 1 shows the FESEM image of nanostructured ZnO deposited on silicon by spin coating. Based on figure 1, it is found that ZnO thin films are composed by nanoparticle of ZnO. Nanoparticles of ZnO were distributed uniformly over the silicon surface. Average sizes of nanoparticles of ZnO are found about ~ 61.92 nm obtained by direct measurement from FESEM Images. It is believed that the ZnO nanoparticles are product of reaction between zinc acetate and isopropyl which is stabilized by diethanolamine [14]. Minrui et al [14] were studied the reaction of zinc acetate in isopropyl and stabilized by diethanolamine. In sol-gel synthesis, hydrolysis and condensation are reactions that involved in sample preparation [16]. They proposed that [CH₃COOZn]⁺ ion, [CH₃COO]⁻ ion, H⁺ ion, and (OH)⁻ ion are produced from hydrolysis of zinc acetate as shown in (1). Then, when DEA added to the solution, the reaction is described in (2). We are suggest that ZnO is resulted from decomposition of Zn(C₂H₄O)₂NH after heat treatment.

\[
\text{Zn(CH₃COO)₂.2(H₂O) → [CH₃COOZn]⁺ + [CH₃COO]⁻ + 2H⁺ + 2(OH)⁻} \quad (1)
\]

\[
[CH₃COOZn]⁺ + \text{HN(C₂H₄OH)₂ → CH₃COOH + Zn(C₂H₄O)₂NH + H⁺} \quad (2)
\]
Two-dimensional and three-dimensional AFM image of nanostructured ZnO thin film are shown in figure 2. In order to analyze the surface morphology and grain size, XEI imaging software was used that covered 2µmx2µm area. The result of roughness averages of 4.977 nm shows nanostructured ZnO thin film has a smooth and dense surface morphology [14]. The particle size of ~62.4 nm was found by direct measurement using the XEI imaging software. So, the particle sizes measured are almost same to particle size obtained from FESEM image.

Figure 2: AFM images in two-dimensional and three-dimensional of nanostructured ZnO on silicon.

X-ray diffraction spectra of nanostructured ZnO was shown in figure 3. By referring to JCPDS No. 36-1451, three peaks of 32.044°, 34.662°, and 36.447° are corresponding to (100), (002), and (101) plane [17-19]. The low intensity of these three peaks might be the thicknesses of nanostructured ZnO
films are very thin and it shows that crystalline randomly oriented [17] due to the peak are almost same in term of intensity. Besides, silicon peaks appears in high intensity prove that the silicon substrate more detected compared to nanostructured ZnO.

![XRD spectra of nanostructured ZnO on P-type silicon.](image)

**Figure 3**: XRD spectra of nanostructured ZnO on P-type silicon.

3.2. Temperature dependence of I-V characteristic

In order to study the temperature dependence of I-V characteristic of nanostructured ZnO, gold metal contact, copper wire and silver paste was used to complete the circuit. Then, forward bias was applied to the circuit while close cycle cryostat systems were used as temperature controller. Figure 4 shows the I-V curve in different temperatures ranging of 25 K to 300 K. Generally, current induced were increase due to increases of temperature. Tangents represent reciprocal of resistance or conductances of each peak were listed in table 1. Based on table 1, resistivity were obtained by using equation (3) and (4), and then displayed in figure 5. Symbol V, I, and R are represents voltage, current and resistance respectively. The result shows the magnitude of current is increasing significantly at a given voltage as increases of temperature.

\[ V = IR \]  
\[ \frac{I}{V} = \frac{1}{R} \]
By increasing the temperature, penetration barrier will be decreased due to increases of thermal energy [20]. So, the carrier concentration becomes higher and increasing the conductance. It also attributed by the change of current transport process from generation recombination at low and intermediate temperature to thermionic emission at higher temperature as suggested by Mtangi et al [21]. So, obviously temperature influences the I-V characteristic of nanostructured ZnO.

### Table 1: Conductance (G) obtained from tangent of I-V curve

| Temperature (K) | Conductance (mΩ⁻¹ or mS) |
|-----------------|--------------------------|
| 25              | 2.52E-03                 |
| 50              | 2.63E-03                 |
| 75              | 3.01E-03                 |
| 100             | 3.53E-03                 |
| 125             | 3.91E-03                 |
| 150             | 4.34E-03                 |
| 175             | 4.76E-03                 |
| 200             | 5.52E-03                 |
| 225             | 6.45E-03                 |
| 250             | 6.50E-03                 |
| 275             | 7.87E-03                 |
| 300             | 9.35E-03                 |

**Figure 4:** I-V curve in different temperatures.

**Figure 5:** Resistance of nanostructured ZnO in different temperatures.
4. Conclusions

Nanostructured ZnO was successfully synthesized on P-type silicon by very simple and low-cost method. Based on FESEM and AFM images, it is found nanostructured ZnO thin film were composed by nanoparticles. The decomposition of zinc acetate in solvent and condensation during heat treatment were produced an averages of ~ 62 nm nanoparticle. Temperature I-V characteristic shows that conductance increase when the temperature increases as found in Table 1.

5. References

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