PREPARATION AND CHARACTERIZATION OF ZINC OXIDE ON AU-COATED NANOSTRUCTURED POROUS SILICON SUBSTRATE
BY THERMAL-CVD

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ABSTRACT

Zinc oxide (ZnO) samples have been prepared on nanostructured porous silicon (NPSi) substrate by vapor phase Thermal-CVD method. The NPSi have been prepared by electrochemical etching method in the mixture of hydrofluoric acid and ethanol electrolyte using an optimized parameter. Then the as-prepared NPSi sample was sputtered by Au-sputter coater to form a catalyst on top of the NPSi substrate. Vapor process by Thermal-CVD was employed at low deposition temperature ranging from 400 -600 °C. The samples were characterized using scanning electron microscopy (SEM), X-ray diffractometer (XRD) and photoluminescence spectroscopy (PL). SEM micrograph and XRD spectra confirm the growth of ZnO structure and indicates the sample formed a wurtzite structure of ZnO while PL spectra showed that the PL intensities increases as the deposition temperature increases. An estimated bandgap energy from PL observation of the ZnO samples are in the range of 3.118- 3.133 eV.

INTRODUCTION

There is a rising interest in nanostructured porous silicon (NPSi) over the last few years due to its efficient optical emission with respect to the bulk silicon (Si). The demonstration and observation by Canham on the observation of efficient photoluminescence (PL) at room temperature make NPSi become one of the important Si based luminescence materials \cite{1}. NPSi that have strong PL properties produces direct bandgap semiconductor typically exist in the range of 600-800 nm (1.5-2.0 eV) compared to bulk crystalline Si which has indirect bandgap at 1.1 eV at room temperature \cite{2-4}. Hence this unique properties results in a very efficient radiative recombination producing light in the visible region \cite{4}.

In recent years, due to the remarkable combination of great optical and physical properties; ZnO is being one of the promising semiconductor materials in low-voltage

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and short-wavelength opto-electronic applications such as light emitting diodes and laser diodes [5]. This is due to its direct bandgap (~3.37 eV at room temperature) and high exciton binding energy (60 meV) that is much higher than Zinc selenide (22 meV) and Gallium nitride (25 meV) [6, 7]. Besides, since it is thermally stable and has high sensitivity to the chemical environment; make ZnO has a big potential in gas sensor applications [8, 9].

Various methods have been attempted to grow ZnO nanostructure, such as: metal-organic chemical vapor deposition (MOCVD) [10], thermal evaporation [11], chemical vapor deposition (CVD) [12], pulsed laser deposition (PLD) [13] and hydrothermal method [14] which results in diverse group of growth morphologies such as nanowires, nanorods, nanocombs, nanoflowers and etc [15, 16]. These revealed that different method of preparation and parameter such as deposition temperature, type of substrate and catalyst influenced the morphology of ZnO.

In this paper, we concentrate on the structural and photoluminescence properties of the ZnO nanostructure on NPSi substrates prepared by double furnace system of Thermal-CVD method on Au-coated NPSi substrate. The effect of using Au-coated NPSi substrate and various deposition temperatures also studied.

EXPERIMENTAL METHOD

NPSi was prepared using electrochemical etching method on p-type boron doped (100)-oriented Si substrate with 4-8 ohm.cm⁻¹. The etching process was employed under fixed current density of 20 mA.cm⁻² in ethanoic hydrofluoric acid at 1:1 volume ratio for 20 minutes of etching time. Ethanol is added to improve the penetration of the solution into the pores and facilitate evacuation of hydrogen bubbles, which develop during the process. After etching process finished, the NPSi was immediately dried at room temperature then used it as a substrate for the ZnO nanostructures preparation.

The ZnO nanostructures were grown on Au-coated NPSi substrate using double furnace system of Thermal-CVD method. The Thermal-CVD system that consists of two furnaces was purged with Argon gas throughout the experiment. Commercially available zinc acetate dihydrate; Zn(CH₃COO)₂·2H₂O (MERCK) as a starting material was placed in a ceramic boat in the first furnace and was vaporized at 300 ºC. The prepared NPSi substrate covered with Au coating obtained by Au sputter coater served as catalyst and was placed in another ceramic boat was inserted into the center of a quartz tube in the second furnace and heated to the desired deposition temperature ranging from 400 ºC to 600 ºC. Argon gas was used as carrier gas and was introduced into the quartz tube at a flow rate of 0.5 L/min. When the temperature had reached the setting temperature (i.e. 400-600 ºC), the system was allowed to stabilize for 30 minutes before the deposition of ZnO took place. The deposition time was fixed for 30 minutes. Upon completion, the system was cooled down to room temperature. After the reaction, a light grey layer was found on the substrate surface. The morphology of ZnO nanostructures were characterized by scanning electron microscope (SEM), the
crystallinity of the as-grown structures were determined from the X-ray diffraction (XRD) measured by Rigaku D-Max while the luminescence properties was measured by PL spectrometer (Jobin Yvon, FluroMax-3) where Xe lamp has been used as illumination source.

RESULTS AND DISCUSSION

Figure 1 (a) shows the top-view FESEM image of NPSi sample prepared at 20 minutes etching time while (b) the cross-sectional view of the sample. Observed that a uniform distribution of pores has been observed for NPSi sample prepared at optimized condition. Besides, from the cross-sectional analysis of the surface shows the columnar structure on the NPSi. The columnar structures are also very flat with pores interconnected each other.

![Figure 1: FESEM image of NPSi sample prepared at 20 minutes etching time (a) top-view and (b) cross-sectional view](image)

Figure 2 (a) demonstrates the PL spectrum of the prepared NPSi sample which represents a broad PL band centered at 660 nm while Figure 2(b) shows the band gap obtained for that NPSi sample is 1.889 eV.

![Figure 2: (a) PL spectrum and (b) bandgap energy of NPSi sample prepared at 20 minutes etching time.](image)

Figure 3 below shows the morphologies obtained from ZnO deposited on Au-coated

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NPSi substrate at various deposition temperatures from 400 ºC to 600 ºC. As we can see, the structure of ZnO changes when different deposition temperature was employed. A non-aligned rod-like structure with sharp nano-tip was formed at temperatures 400 and 450 ºC. The ZnO structure starts to decompose when high temperature (i.e. 500 ºC) was employed. A bulky cluster of spherical ZnO was found. We observed that when increasing the temperature from 550 to 600 ºC, the ZnO tend to form an abundant of nano-spherical structures with higher density.

We observed that, morphologies of the ZnO were strongly influenced by deposition temperature. When concerning with the vapor growth mechanism, temperature is the critical parameter need to be concern and the other importantly matter is the relation between the diffusion and growth temperature. Higher temperature lead to faster diffusion as the diffusion coefficient increases with temperature [17].

Figure 3: SEM images of (a) ZnO rod-like nanostructure at deposition temperature 400 ºC, (b) ZnO rod-like nanostructure at deposition temperature 450 ºC, (c) bulky cluster of ZnO spherical at deposition temperature 500 ºC, (d) nano-spherical ZnO at deposition temperature 550 ºC and (e) nano-spherical ZnO at deposition temperature 600 ºC.

Figure 4 shows the XRD pattern of ZnO nanostructures deposited on Au-coated NPSi substrate at temperature 400 ºC to 600 ºC. All the diffraction peaks obtained from the XRD pattern were indexed to pure hexagonal wurtzite ZnO phase (JCPDS card No. 079-2205). From the XRD analysis, the strongest XRD peak obtained from all samples (a-e) corresponds to the (101) plane of wurtzite ZnO at 2θ = 36.15º. The relative peak intensity of the lattice plane (100), (002), (102) and (110) at 2θ = 31.57º, 34.53º, 47.54º.
and 56.56º respectively. XRD spectra confirm the growth of ZnO structure and indicate the sample formed a wurtzite structure of ZnO.

![XRD spectra](image)

Figure 4: XRD spectra of ZnO nanostructures deposited on Au-coated NPSi substrate at deposition temperature (a) 400 ºC, (b) 450 ºC, (c) 500 ºC, (d) 550 ºC and (e) 600 ºC by TCVD method.

PL spectra of ZnO grown on Au-coated NPSi (Figure 5(a)) shows a similar pattern when the emission is attributed to the UV region and this emission generally corresponds to the direct recombination excitons through an exciton-exciton collision process, where one of the excitons radiatively recombines to generate photon [18,19]. Besides strong UV emission, all the ZnO samples exhibit the blue – green emissions at ~450 nm -460 nm and 500 nm. In addition, it can be observed that the PL intensity increases as the deposition temperature increased.

Estimation of bandgap energy is also obtained from PL measurements. In this study, bandgap energy of ZnO samples is focused at UV near band edge area. Figure 5 (b) shows the PL photon energy of ZnO rod-like structure and nano-spherical grown on Au-coated NPSi sample at deposition temperatures (a) 400 ºC, (b) 450 ºC, (c) 500 ºC, (d) 550 ºC and (e) 600 ºC by Thermal-CVD method. The estimated bandgap energy was calculated using $E = \frac{hc}{\lambda}$ equation. The bandgap energy of ZnO samples grown on Au-coated NPSi substrate does not show a big difference in value which is sample (a) is 3.118 eV which is similar to sample (c), sample (b) is about 3.133 eV while for sample (d) and (e) the photon energy value is 3.125 eV. These revealed that the deposition temperature does not give a big difference in photon energies since the values approximately equal to each other.
Figure 5: (a) PL spectra and (b) Bandgap energy of ZnO nanostructures deposited on Au-coated NPSi substrate at deposition temperature (a) 400 ºC, (b) 450 ºC, (c) 500 ºC, (d) 550 ºC and (e) 600 ºC by TCVD method.

CONCLUSION

It can be conclude that ZnO has been successfully grown on Au-coated NPSi substrates at various deposition temperatures ranging from 400 – 600 ºC. As revealed by SEM results, the deposition temperature and substrate itself gave a big influence to the formation and morphologies of ZnO nanostructure. This suggests that deposition temperature is a critical and important parameter in determining the amount of the reactive vapor generated and the surface diffusion length of the adsorbed vapor species [8, 9]. Varying the deposition temperature for the ZnO growth influenced the surface morphologies. A unique rod like structure is formed at deposition temperature of 400 ºC to 450 ºC. The rod formation is non-align on top of the substrate with greater density. Increasing the deposition temperature from 500 ºC to 600 ºC the ZnO start to decompose and formed a nanospherical structure. There is a unique and questionable issue in the growth formation of this ZnO structure correlating with the deposition temperature. In addition, from the XRD spectra we confirmed the growth of ZnO structure and which formed a wurtzite structure of ZnO while PL spectra showed that the PL intensities increases as the deposition temperature increases. An estimated bandgap energy from PL observation of the ZnO samples are in the range of 3.118-3.133 eV.

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