The Effect of SiO₂ Thickness on the Nucleation and Growth of ZnO Nanostructures

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Zinc Oxide (ZnO) nanostructures were deposited on SiO₂ using the sol-gel method. The effects of SiO₂ thickness on the nucleation and growth of ZnO nanostructures were studied. The oxidation time was varied from 5 minutes to 20 minutes to vary the SiO₂ thickness. We observed different surface morphologies of ZnO nanostructures when deposited without SiO₂ and with different thickness of SiO₂ using scanning electron microscope (SEM). The structural property of nanostructured ZnO was investigated using an x-ray diffractometer (XRD), and showed different crystal growth orientations. We also measured the electrical current-voltage (IV) response and found that it is strongly dependent on the size of ZnO nanostructures. The optical property was measured using a photoluminescence (PL) spectrometer which indicates that the peak intensity is inversely proportional to the ZnO crystallite size. In this experiment, we found that SiO₂ which oxidized for 5 minutes has the optimum optical property and is suitable for optical device applications.

Keywords: Zinc Oxide, Silicon dioxide, Nucleation, Nanostructures, Sol-gel.

1. INTRODUCTION

ZnO nanostructures have been studied extensively due to their unique physical, optical and electrical properties compared to the bulk structures [1-3]. Its wide band gap energy of approximately 3.37 eV and large excitonic binding energy of approximately 60 meV make it a strong candidates for various applications such as new optical displays, MEMS related devices, light emission devices and solar cells [4-10].

There are several deposition methods used to prepare nanostructured ZnO such as molecular beam epitaxy (MBE), pulse laser deposition (PLD), r.f. magnetron sputtering and etc [8,9,10]. However, these methods require expensive equipments and setup. Therefore in this work, the sol-gel method was utilized due to its simple, rapid and low cost technique [6]. Using the sol-gel method, high crystallinity of nanostructured ZnO at room temperature and atmospheric ambient can be obtained.

2. EXPERIMENTAL PROCEDURES

SiO₂ layer with different oxidation time ranging from 5 to 20 minutes was produced in atmospheric ambient condition, resulting in different SiO₂ thickness grown on (100) silicon wafer.

An aqueous solution of the same molar ratio (0.01M) of zinc nitrate hexahydrate and hexamethylenetetramine was diluted in 200 mL de-ionized water. The solution was prepared at room temperature and stirred for 24 hours.

Samples with different SiO₂ thicknesses were immersed in the solution for 3 hours. After drying, the samples were annealed at 500°C for 1 hour. All samples were characterized using a scanning electron microscope (JOEL JSM6380LA) and an x-ray diffractometer (D8

Advance Bruker) to observe the morphological and structural properties, respectively. The optical property was measured using a Photoluminescence (PL) Spectrometer (Horiba Jobin Vyon FluoroMax-3). In order to measure the electrical property, samples were coated with platinum (Pt) electrode. This electrode provided an interface between the electrical measurement probe and the nanostructured ZnO. Then, the current-voltage (I-V) response was measured using a Keithley 2400 IV measurement system.

3. RESULT AND DISCUSSION

The SEM results shown in Fig. 1 indicate that different surface morphologies of ZnO nanostructures were obtained when different SiO₂ thicknesses were used in the deposition. Fig. 1(a) depicts the ZnO nanorods grown on silicon without SiO₂. There are lattice mismatch between Zn and Si due to their different atomic structures. Silicon is a diamond cubic structure while ZnO is hexagonal wurtzite structure [9,12]. Therefore, the adherence energy between the ZnO molecules with Si is not very strong.

Fig. 1(b) shows the nanorods becoming smaller and denser when deposited using SiO₂ oxidized for 5 minutes. Individual nanorods are observed and the size is less than 100 nm. SiO₂ has less lattice mismatch compare to silicon since SiO₂ has Cristobalite-high structure. SiO₂ with smaller thickness may provide high energy for the nucleation of individual nanosized rods as illustrated in the inset.

When the SiO₂ thickness increases by increasing the oxidation time to 10 minutes, nanostructured ZnO as shown in Fig. 1(c) was grown. The structure has changed as illustrated in the inset and the size has increased.

Fig. 1. SEM images of ZnO nanostructures on (a) Si; (b) SiO₂ oxidized at 5 minutes; (c) SiO₂ oxidized at 10 minutes; (d) SiO₂ oxidized at 15 minutes; (e) SiO₂ oxidized at 20 minutes (inset in Fig. (b)-(e) is the schematic diagram of ZnO nanorod growth).

Further increase on the SiO₂ thickness by oxidizing the Si for 15 minutes has resulted in the formation of nanostructured ZnO as shown in Fig. 1(d). Nanorods with branches were deposited as illustrated in the inset. Increasing the SiO₂ thickness may provide more nucleation sites on the nanorods, thus nanorods with branches were grown.

Fig. 1(e) shows the nanostructured ZnO when SiO₂ thickness was increased by increasing the oxidation time for 20 minutes. More branches were grown on the nanorod as illustrated in the inset. Once again, the SiO₂ has affects the nanorod growth by providing more nucleation sites leading to the addition of nanorod branches.

The growth orientation of ZnO crystals is characterized using an XRD as shown in Fig. 2. The XRD spectra indicate that hexagonal wurtzite structure with high crystallinity was obtained. When Si was used as a substrate without any existence of SiO₂, the ZnO crystal is preferentially grown at [100] direction only. However, when SiO₂ was introduced, more growth orientations with strong peak intensities have been observed. This may be due to the change of structural shape, from individual nanorod using only Si substrate, to nanorod with branches deposited using SiO₂ catalyst. The strongest [002] growth orientation for sample (b) indicates that the ZnO nanorods are preferentially grown at [0001] direction.

Fig. 2. The XRD pattern of ZnO nanostructures: (a) Si; (b) SiO₂ oxidized at 5 minutes; (c) SiO₂ oxidized at 10 minutes; (d) SiO₂ oxidized at 15 minutes; (e) SiO₂ oxidized at 20 minutes.

The electrical property of ZnO nanostructures grown on different SiO₂ thickness is shown in Fig. 3. The current-voltage (IV) response of ZnO nanostructures is strongly dependent on the shape of ZnO structures. Referring to Fig. 3, the IV characteristic for sample (a) has the lowest conductivity. This is due to poor attachment of the nanorods to each other. Therefore, the transfer of electrons amongst the nanorods is not efficient [13].

Fig. 3. The IV characteristics of nanostructured ZnO on: (a) Si; (b) SiO₂ oxidized at 5 minutes; (c) SiO₂ oxidized at 10 minutes; (d) SiO₂ oxidized at 15 minutes; (e) SiO₂ oxidized at 20 minutes.

The electrical contact using Platinum on ZnO nanorods will result Schottky IV response [14]. We observed that the current response increases for sample (b) due to the increasing in the nanorods density covering the substrate. The same phenomenon i.e. increase in current is also observed in sample (c) (compared to sample (a) and (b)) which is assumed to be due to larger nanorods. Sample (d) has the largest nanorods size compared to the other samples. The attachment between the neighbouring nanorods will be better and the electrons transfer between the nanorods should be higher. Therefore, the current

response increases sharply. Since the size of nanorods in sample (e) is nearly the same as (c), the current response is about the same.

Fig. 4 shows the room temperature PL spectra of ZnO nanostructures grown on different SiO₂ thicknesses. Overall, the PL spectra show sharp ultraviolet emission band at approximately 363 nm. It is called near band edge emission generated by free-exciton recombination [6]. Visible emission band is also observed between 400 nm to 570 nm, which is known as deep level emission mediated by oxygen vacancies and other defects [5]. Previous researches have shown that PL spectrum of ZnO is sensitive to its particle shape, size, and preparation conditions.

Fig. 4. Room temperature PL spectrum of nanostructured ZnO on: (a) Si; (b) SiO₂ oxidized at 5 minutes; (c) SiO₂ oxidized at 10 minutes; (d) SiO₂ oxidized at 15 minutes; (e) SiO₂ oxidized at 20 minutes.

Referring to Fig. 4, sample (a) has the highest UV peak compared to the other samples. This may be due to the smaller size and structure of the sample (a). Sample (c) and (d) have nearly the same PL emission, and are higher than sample (a). The lowest PL intensity is displayed by sample (e). This is possibly due to the flower-like nanostructured ZnO that exhibits low radiative annihilation of excitons [7]. Therefore, from the PL spectra, we can conclude that the ZnO PL emission at room temperature is strongly dependant on the size and shape of the material.

4. CONCLUSION

In summary, the effect of different SiO₂ thickness on nucleation, towards the growth of ZnO nanostructures has been studied. The Sol-gel method was utilized in the deposition of ZnO nanostructures on SiO₂ catalyst. Results from SEM indicated that the structure of ZnO will change when the SiO₂ thickness is changed. We observed that the surface morphology of an individual ZnO nanorods changed into nanorods with branches and finally to ZnO nanoflower by increasing the SiO₂ thickness. Different growth orientation with high crystallinity was also produced by using different SiO₂ thickness. The electrical properties of nanostructured ZnO is dependent upon the size of the nanorods. The larger the ZnO nanorods size, the better the IV response. The best annealing time for SiO₂ growth which result optimum electrical performance and high PL emission is

between 15-20 minutes. The result proves that SiO₂ thickness affects the nucleation and growth of nanostructured ZnO. As a result of the revolution of surface morphologies caused by different SiO₂ thickness, the electrical and optical properties of the ZnO nanostructures have also changed.

5. ACKNOWLEDGEMENT

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6. REFERENCES

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