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Low-temperature solution selective growth of zinc oxide nanorods on different substrates

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In this paper, regular ZnO nanorods with excellent reproducibility were grown by a simple solution method at low temperature. The growth parameters, which can affect the ZnO nanostructures were studied, including the substrate types, the growth temperature, the growth time and the concentration of the solution. Among these conditions, the influence of different substrates on the resulting nanostructures was investicated carefully. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the morphology and microstructure of the as-grown ZnO nanorods. It is concluded that the substrates can affect the ZnO growth remarkably and the selective growth of ZnO is possible through the choice of the substrates.

Key words: low-temperature, substrate, selective growth, zinc oxide nanorods, solution-based.

Introduction

Zinc oxide (ZnO), which is an important electronic and photonic material with a wide band gap energy of 3.37 eV and large excitation binding energy (60 meV) at room temperature, has been extensively studied for its potential applications in manufacturing electronic and optoelectronic devices in recent years. Various ZnO nanostructures, such as nanowires [1], nanorods [2], nanoflowers [3] and nanocombs [4], etc, have been reported. Among them, nanorods are one of the potential building blocks for future nanoelectronics and nanosensors. Both physical and chemical methods have been developed for the preparation of ZnO nanorods, including vapor-liquid-solid (VLS) [5, 6], metal-organic vaporphase epitaxial growth [7], electrochemical Deposition (ECD) [8], and so on. Compared with the methods mentioned above, approaches based on solution exhibited obvious advan- tages in terms of cost, facilities, complexity, energy consumption, and high production yield. Thus, the solutionbased methods are receiving more and more attention recently [9, 10].

In previous papers, studies were mainly concentrated on the preparation of ZnO nanostructures and the influence of solution parameters (such as solution con- centration, pH value, temperature, etc.) on the morphology and microstructure of ZnO nanorods. Undoubtedly, substrates can also affect the growth of ZnO. Unfortunately, few papers studying the influence of different substrates on nanostructured ZnO growth can be found. The investigation of a substrate effect can help us to probe growth mechanisms. In addition, an understanding of the substrate effect has the potential to realize the selective growth of nanomaterials, which are very useful for future nanoelectronics, nanodevices and nanosensors [11].

In this paper, three types of substrates including PZT, glass, quartz, silicon, copper-, gold- and platinum- covered silicon substrates were used and the growth bebavior of nanostructured ZnO on these substrates were investigated. The experimental results showed that the quantity of ZnO products on these substrates were very different.

Experiment

Raw materials

Analytical-grade zinc acetate dehydrate[$Zn(CH_3COO)_2$ · 2H₂O] and hexamethylenetetramine (HMT; C₆H₁₂N₄) were purchased from the Shanghai Chemical Regent Co. Ltd. All of the reagents were used without further purification.

Preparation of substrates

In this paper, three types of substrates were used to study the growth of ZnO, including: I. Metal (Au, Pt, Cu) -covered silicon wafers; II. Single-crystalline substrates, silicon and quartz; III. Mixed substrates: Ceramic (PZT) covered silicon wafers and glass. In this paper, they are denoted as Type I, Type II, and Type III, respectively.

For Type I substrates, silicon wafers with a thickness of \sim 500 µm were cleaned by an organic solvent and etched in dilute hydrofluoric acid to remove contaminations and surface oxides. Then, the silicon wafers were cleaned by a hot Paraha solution (H₂SO₄ : H₂O₂ = 3 : 1 in volume) for 10 minutes, followed by rinsing with DI water. Then, these silicon wafers were coated with a Cu, Au or Pt layer

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by thermal evaporation with a quartz crystal thickness monitor for thickness control. The thicknesses of the metal thin films were controlled to be around 200 nm.

For Type II substrates, Quartz substrates, with a thickness of $\sim 100 \ \mu\text{m}$, and dimensions of 1 cm \times 1 cm were also cleaned as for type I.

A glass substrate was also used for comparison purposes. For Type III substrates, PZT thin films were deposited on silicon substrates by a sol-gel technique. Details of this sol-gel [12, 13] process can be found elsewhere. The resulting PZT thin films were about 1 mm in thickness. Glass substrates were also used for the deposition.

All wafers were cut into small chips with dimensions of 1 cm \times 1 cm. Prior to an experiment, all the substrates were rinsed again with distilled water in an ultrasonic bath for use in future. The glass substrate was also used for comparison purposes.

Solution-based growth of ZnO

Equimolar zinc acetate dehydrate $(Zn(CH_3COO)_2 \cdot 2H_2O)$ and methenamine $(C_6H_{12}N_4)$ was dissolved in distilled water as the precursor solution with a concentration of 0.01 M. The prepared solution was distributed into different glass beakers with a volume of 300 ml. Before growth, all the substrates were cleaned, then, the three types of substrates (PZT, glass, quartz, silicon, copper-, gold- and platinumcovered silicon substrates) were put into the corresponding glass beakers.

Finally, the glass beakers were sealed and placed into an oven at a constant temperature of 95 °C. After growth, all substrates were taken out of the solution, thoroughly washed with deionized water, treated in an ultrasonic water bath for 3-10 minutes, and dried in air at room temperature. Finally, all samples were annealed at 500 °C for 10-30 minutes. The ZnO nanorods grown on different substrates were then characterized by different instruments.

Characterization tools

The crystalline phase of the ZnO products was examined by a Bruker D8 ADVANCE X-ray diffraction (XRD) with Cu Ka radiation ($\lambda = 0.15405$ nm) with the instrument resolutional ~0.02° steps in 2 θ . The morphologies of the assynthesized ZnO products were observed by scanning electron microscopy (SEM, Philips XL-30)

Results and Discussion

The as-prepared substrates were characterized by the different instruments and the results are given below:

Influence of different substrates

Three types of substrates were studied under the same growth parameters, and the properties of the resultant ZnO nanostructures were characterized by SEM and XRD.

The crystalline microstructure of the as-grown ZnO was first characterized by X-ray diffraction (XRD). Fig. 1 shows the XRD curve of the synthesized ZnO nanorods in the range of 2 θ between 30°-80° on a silicon substrate. The diffraction data are in agreement with JCPDS card of ZnO (JCPDS 36-1451). Four pronounced ZnO diffraction peaks appearing at 2 θ = 31.798, 34.430, 36.303 and 56.511 in Fig. 1, are related to (100), (002), (101) and (110) diffraction, respectively. All diffraction peaks can be indexed from the hexagonal wurtzite structure of ZnO. ZnO grown on different substrates has a similar microstructure.

Fig. 2 gives scanning electron microscope (SEM) images of as-prepared ZnO nanorods grown on three metal coated substrates.

SEM micrographs of ZnO grown on Type I substrates are shown in Fig. 2. After ultrasonic agitation, we found



Fig. 1. X-Ray diffraction (XRD) pattern of as-prepared ZnO nanorods on a silicon substrate.



Fig. 2. SEM micrographs of ZnO nanorods grown on Type ²: Metal substrates Cu (a), Au (b) and Pt (c).

only rarely ZnO nanorods can be grown on the Au, Cu and Pt coated substrates.

SEM micrographs of ZnO grown on Type II substrates are shown in Fig. 3. It was found that the ZnO nanorods had a well-defined hexagonal column configuration, with a diameter of ~1 μ m and a length of ~10 μ m. From the SEM images, we can find that some nanorods were broken due to the ultrasonic agitation. If we count the number of nanorods, it is found that the growth density of ZnO on silicon and glass was very similar. This is because the silicon surface is covered with a native oxide layer, with a thickness of ~1 nm. The nature of the silicon and the glass are similar. Both of them are composed of SiO₂.

The ZnO nanorods, grown on the Type I substrates, had a similar configuration to the Type II in Fig. 3(b) and Fig. 4. But the density decreased greatly.

SEM micrographs of ZnO nanorods grown on Type III substrates are shown in Fig. 5. It was found that the configuration of ZnO nanorods were similar to those on Type I and Type II substrates. But the grown nanorod density is higher than for Type I. Roughly, the ratio of the ZnO grown density on Type I and Type III are $\sim 1 : 30$.

Among the three types of substrate, the crystalline quartz substrate had the highest nanorod density. The density ratio between quartz crystal and metallic surface substrates can reach $\sim 100:1$.



Fig. 3. SEM micrographs of ZnO nanorods grown on Type II: Single-crystalline substrates Si (a) and Quartz (b).

In our experiments, in the growth process, all types of substrates had the same growth parameters, such as temperature, growth time and agitation condition. The asreceived ZnO nanorods had a similar configuration. So it is concluded that the substrates do not change the structure of the nanorods.

Through our experiments, we found that nanorods could be grown on PZT, glass, silicon and quartz substrates easily. But it was difficult to grow the nanorods on Cu, Au and Pt substrates. According to the degrees of difficulty



Fig. 4. SEM micrograph of ZnO nanorods grown on a quartz substrate.



Fig. 5. SEM micrographs of ZnO nanorods grown on Type III: Mixed substrates including PZT (a) and glass (b).

of the growth of the ZnO nanorods, the sequence of substrates is as follows: quartz > glass, silicon > PZT > Cu > Au > Pt.

In principle, the different growth density could be attributed to two aspects: 1. ZnO nanorods have different growth rates on the different substrates; 2. ZnO nanorods have the same growth rate but have different adhesion capability with the substrates. However, in our experiments, we found the asreceived ZnO nanorods on different substrates had almost the same configuration, but their dimensions had a small difference. we thought the same configuration indicated the growth rate in the solution was identical, but the small difference in dimensions was due to the nanorods deposited on substrates continuing to grow with increasing time, but for the difference of physisorption between different substrates and nanorods, the dimensions of the final nanorods was slightly different. From this viewpoint, our experiments demonstrated that the ZnO nanorods had poor adhesion capability with metal substrates and had good adhesion capability with single crystalline quartz. Our study indicated that the process was a self-generating process in solution and that the substrate almost had no influence on the configuration of ZnO nanorods.

Influence of the other growth conditions

In order to further illustrate that the process of ZnO nanorods growth in solution was decided by the solution itself, we performed experiments with other growth conditions such as growth time, growth temperature, the value of PH and the concentration of the solution. The configuration and the morphology of ZnO products were studied by SEM.

Influence of the concentration of solution

ZnO nanorods with solution concentrations of 0.1 M, 0.01 M and 0.0001 M were grown on a silicon substrate under the same experimental conditions, and the results are shown in Fig. 6. It can be seen that the concentration had a big influence on the resultant ZnO. As the concentration was lowered, the diameter and the length of ZnO nanorods got narrower and shorter and the quantity of ZnO nanorods decreased. This seems an effective method to obtain the required ZnO nanorods by changing the solution concentration.

Glass substrates were also used for the same ZnO growth process, and similar results obtained. Our results showed that the precursor concentration had a crucial influence on ZnO products.

Influence of growth time, temperature and the value of the PH

ZnO nanorods with aging times of 24 h and 48h were prepared when the other growth conditions were kept unchanged, and the results are shown in Fig. 7. As Fig. 7 shows, ZnO nanorods were obtained when the time was 24 h [Fig. 7(a)]. When the time was 48 h, the morphology of ZnO products was utterly changed [Fig. 7(b)]. No nanorods were grown but the thin film structure.

The pH value of the solution concentration also had an influence on the resultant ZnO. When the value of PH is too high, the substrates are etched too severely to grow ZnO products. When the pH value is too low, ZnO products also do not grow. The influence of growth temperature is similar to the value of the PH.

The seletive growth of ZnO nanorods on different substrates

The selective growth refers to the growth of ZnO nanostructures on patterned substrates. The selective growth of nanostructures is quite important for future nanoelectronics and nanodevices. Fig. 8 shows a SEM image of ZnO nanorods grown on a Au-patterned quartz substrate. As shown in Fig. 8, many ZnO nanorods are grown in the quartz region while few ZnO nanorods are grown in the Au region. It is also found that there exists a transition region between the quartz and the Au regions. Almost no nanorods can be grown in this region. In two regions, ZnO nanorods have well-defined hexagonal facets.

In order to study the influence of selective growth of ZnO nanorods, the substrate with three types of region including PZT, Au and Pt were also used. Fig. 9 is a SEM image of as-grown ZnO nanorods on this form of substrate. From Fig. 9 we can conclude that there were the least ZnO nanorods on the Pt substrate, fewer was on the Au substrate, and the most were on PZT regions (the white parts on the right of Fig. 9 and the interval gray parts are Pt substrates).

This result illustrated that we could achieve the selective growth of ZnO nanoproducts.

Discussion

The above supposed growth mechanism of ZnO nanorods



Fig. 6. SEM micrographs of ZnO nanorods grown on a silicon substrate with the concentrations of 0.1 M (a), 0.01 M (b) and 0.0001 M (c).



Fig. 7. SEM micrographs of ZnO nanorods grown on a silicon substrate with growth times of 24 h (a) and 48 h (b).



Fig. 8. SEM micrograph of ZnO nanorods on the same substrate patterned with both Quartz and Au.

suggested above was illuminated in detail in ref [3, 14].

$$(CH_2)_6N_4 + 10H_2O = 6HCHO + 4NH_3 \cdot H_2O$$

 $NH_3 \cdot H_2O = NH_4^+ + OH$
 $Zn^{2+} + 2OH = Zn(OH)_2$
 $Zn(OH)_2 (s) = ZnO(s) + H_2O$

It is known that Au and Pt are good catalysts. According to the vapor-liquid-solid (VLS) [5, 6] growth mechanism,



Fig. 9. SEM micrograph of ZnO nanorods on the same substrate patterned with PZT, Pt and Au.

the ZnO nanorods prefer to grow on the Au or Pt covered sites at high temperature. In other words, with high temperature growth, the solid-liquid interface will play an important role in the growth of ZnO. However, in our solution-based growth, the catalytic properties of them are not novel. The growth of ZnO naorods is a pure chemical solution process, and the solid-liquid interface had little influence on the whole growth process of the ZnO nanorods. So in our growth process, the combination between the ZnO nanorods and the substrates is the physisorption such as was governed by the free surface energy, etc. By choosing the substrate type, it is possible to realize the selective growth of ZnO.

Conclusions

In this paper, the growth of ZnO nanorods on different substrates were studied carefully. It is concluded that the ZnO nanorods were grown easily on silicon, quartz, PZT substrates and were difficult to grow on the metal substrates such as Au, Pt, Cu. The same morphology on different substrates illustrated that the growth process of ZnO nanorods in solution was a chemical process of the solution itself and the selective growth on different substrates was due to the physisorption between the substrate and nanorods.

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References

- Y.S. Zhang, K. Yu, S.X. Ouyang and Z.Q. Zhu, Materials Letters, 60[4] (2006) 522-5262.
- D.L. Tao, W.Z. Qian, Y. Huang and F. Wei, Crystal Growth, 271[3-4] (2004) 353-357.

- 3. X.D. Gao, X.M. Li and W.D. Yu, Solid State Chemistry, 178[4] (2005) 1139-1144.
- W. Bai, K. Yu, Q.X. Zhang, F. Xu, D.Y. Peng and Z.Q. Zhu, Applied Surface Science, 253[16] (2007) 6835-6839.
- Y.W. Wang, L.D. Zhang, G.Z. Wang, X.S. Peng, Z.Q. Chu and C.H. Liang, Journal of Crystal Growth, 234[1] (2002) 171-175.
- Xianghua Kong, Xiaoming Sun, Xiaolin Li and Yadong Li, Materials Chemistry and Physics, 82[3] (2003) 997-1001.
- A. Dadgar, N. Oleynik, D. Forster, S. Deiter, H. Witek, J. Bläsing, F. Bertram, A. Krtschil and A. Diez, J. Christen, et al., Crystal Growth, 267[1-2] (2004) 140-144.
- 8. Y.J. Zhang, Y. Zhang, J.H. Yang and L.L. Yang, Superlattices and Microstructures, 41[1] (2007) 1-6.
- 9. Y.Z. Lv, Y.H. Zhang, C.P. Li, L.R. Ren, L. Guo, H.B. Xu,

L. Ding, C.L. Yang, W.K. Ge and S.H. Yang, Luminescence, 122-123 (2007) 816-818.

- X.D. Gao, X.M. Li, W.D. Yu, L. Li, J.J. Qiu and F. Peng, Solar Energy Materials and Solar Cells, 91[6, 23] (2007) 467-473.
- X.H. Wang, J. Zhang and Z.Q. Zhu, Applied Surface Science, 252[6] (2006) 2404-2411.
- J. Zhang, K.H. Au, Z.Q. Zhu and S. O'Shea, Optical Materials, 26[1] (2004) 47-55.
- Chen Shaoqiang, Zhang Jian, Feng Xiao, Wang Xiaohua, Luo laiqiang, Shi Yanling, Xue Qingsong, Wang Chang, Zhu Jianzhong and Zhu Ziqiang, Applied Surface Science, 241[3-4] (2005) 384-391.
- 14. Z.T. Chen and L. Gao, Crystal Growth, 293[2] (2006) 522-527.