Post-Annealing Effects on Properties of ZnO Nanorods Grown on Au Seed Layers

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Received November 25, 2010, Accepted January 6, 2011

ZnO nanorods were grown by hydrothermal method. Two kinds of seed layers, Au film and island seed layers were prepared to investigate the effect of seed layer on ZnO nanorods. The ZnO nanorod on Au island seed layer has more uniform diameter and higher density compared to that of ZnO nanorod on Au film seed layer. The ZnO nanorods on Au island seed layer were annealed at various temperatures ranging from 300 to 850 °C. The pinholes at the surface of the ZnO nanorods is formed as the annealing temperature is increased. It is noted that the pyramid structure on the surface of ZnO nanorod is observed at 850 °C. The intensity of ZnO (002) diffraction peak in X-ray diffraction pattern and intensity of near band edge emission (NBE) peak in photoluminescence (PL) are increased as the ZnO nanorods were annealed at the temperature of 300 °C.

Key Words : Zinc oxide, Nanorod, Pyramid, Au seed layer, Hydrothermal method

Introduction

ZnO is an n-type semiconductor with a hexagonal wurtzite structure and a large exciton binding energy of 60 meV, which is 2.4 times that of GaN.¹ ZnO has been studied extensively for its potential use in various applications, such as gas sensors,² solar cells,³ photo-detectors,⁴ and light emitting diodes.⁵ Especially ZnO nanorods also have the advantages of large surface area, radiation hardness,⁶ thermal and mechanical stability.⁷ The physical properties of the nano-ZnO materials depend on the microstructure including morphology, crystal size, orientation, aspect ratio and crystalline density.⁸ For many of these applications, it is important to investigate the device characteristics using small size and long and highly oriented nanorods, and to see if the length control can improve the device performance and design. To date, various synthetic approaches have been developed to fabricate ZnO nanorod arrays such as thermal evaporation,⁹ metal-organic chemical vapor deposition (MOCVD),¹⁰ chemical or physical vapor deposition,¹¹ hydrothermal method,¹² etc. The hydrothermal method showed some advantages compared with others, such as use of simple equipment, low-temperature deposition, low cost, less hazardous. The growth condition such as morphology of a zinc metal seed layer, pH, growth temperature, and concentration of zinc salt in aqueous solution determine growth characteristics of ZnO nanostructures.^{13,14} It is important to study their growth parameters to control growth of ZnO nanostructures. Especially, the seed material is important for the growth of high-quality ZnO nanostructures. Nevertheless, it is not well understood how the seed layer affects the growth of ZnO nanostructures.

In this study, two types of seed layers, Au film seed layer and Au island seed layer, were prepared. The ZnO nanorods were grown on Au seed layers by hydrothermal method and the ZnO nanorods grown on Au island seed layer were

annealed at various temperatures ranging from 300 to 850 °C. Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and photoluminescence (PL) were employed to investigate the structural and optical properties of the ZnO nanorods.

Experimental

ZnO nanorods were grown on p-type Si(100) substrates by hydrothermal method. The Si substrates were cleaned in a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 8:1$) at 110 °C for 15 min and then hydrofluoric acid ($\text{HF } 50\%:\text{H}_2\text{O} = 1:9$) for 5 min. Two kinds of seed layers which are Au film and Au island seed layer were used. The 5 nm of Au film seed layer was deposited by ion-sputter. The Au island seed layer was prepared by annealing process of the Au film at the temperature of 1000 °C. ZnO nanorods on the Au seed layers were grown by hydrothermal method. The aqueous solution of zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and hexamethylenetetramine (HMT) [$\text{C}_6\text{H}_{12}\text{N}_4$] were prepared for hydrothermal growth and mixed together. The concentrations of both were fixed at 0.3 M. The aqueous solution was stirred and then transferred into a Teflon-lined stainless steel autoclave. Then the substrate was immersed into the aqueous solution. The growth temperature was kept at 130 °C for 7 h. Subsequently, the autoclave was cooled down naturally. the substrate were thoroughly rinsed with de-ionized water and blown dry with nitrogen gas (6 N). The ZnO nanorods were annealed using thermal annealing system at 300, 500, and 850 °C for 5 min under argon atmosphere.

Results and Discussion

Figure 1 shows the AFM $1 \times 1 \mu\text{m}$ images of the surface of (a) Au film seed layer and (b) Au island seed layer. The root-mean-square (RMS) roughness of the Au film and

Figure 1. AFM images of (a) Au film and (b) Au island seed layer.

island are 5.15 and 7.69 nm, respectively. The Au film seed layer exhibits dense and uniform morphology. After the annealing process, the surface morphology of the Au seed layer changes from film to island. There are two possible reasons to demonstrate the changes in surface morphology of the Au seed layers. One is that the Au is pulled together from the nearest surface to form the island after the annealing because gold has a rather high surface tension. Other is formation of the Au-Si alloy ball on the Si substrate surface because Au nanoparticle reacted with the Si substrate.¹⁵ In general, the melting point of Au is 1064 °C, however, when a metal forms an alloy with Si at a certain atomic percentage, the melting temperature, called eutectic temperature, of the alloy can be much lower than that of both the metal and Si. The eutectic temperature for Au-Si alloys is 360 °C.¹⁶ In our case, the temperature of the 1000 °C is much higher than the eutectic temperature, so, Au-Si alloys were formed at the interface between the Si substrate and the Au film and then the Au film were gradually melted to Au island.

Figure 2 shows the SEM images of the ZnO nanorods on Au film seed layer and Au island seed layer. In the

growth process, Zn^{2+} and OH^- are provided by hydration of $\text{Zn}(\text{NO}_3)_2$ and HMT. The following reactions are pivotal in the formation of ZnO:

Here, Zn^{2+} are known to react readily with OH^- to form more soluble $\text{Zn}(\text{OH})_2$ complexes, which act as the growth unit of ZnO nanostructures. Finally, ZnO is obtained by decomposition of $\text{Zn}(\text{OH})_2$. Therefore, the key chemical reactions involved in hydrothermal synthesis can be formulated as follows:

When the concentration of Zn^{2+} and OH^- exceed supersaturation, ZnO nuclei are formed on the substrate surface. With increasing temperature, these complexes become dehydrated and heterogeneous nucleation of ZnO crystals takes place at the interface between substrate and solution. In the initial growth stage of the ZnO nanorods, the Au film and island, which was deposited onto a Si wafer, mainly act like nucleation sites. The SEM images show that the morphology and size of ZnO nanorods is obviously different. When the Au island seed layers are introduced, the dense-arrayed, regular oriented ZnO nanorods can be obtained as shown in Figure 2(a) and (b). As shown in top view of ZnO nanorods, the diameter of ZnO nanorods on Au film is much bigger than that of ZnO nanorods on Au island. The length of ZnO nanorods on Au film is also much higher than that of ZnO nanorods on Au island as shown in the cross section SEM images. The roughness and thickness of the seed layers affect the ZnO nanorods. In general, the seed layers with more rough surface and higher length can provide conditions to form nuclei easily. For the ZnO nanorods grown on Au island, the nuclei were formed with higher density due to rougher surface of the Au island seed layer compared to that of the Au film seed layer. So, the density and uniformity of the ZnO nanorods is improved. On the other hand, the density and uniformity is inversely proportional to length. The similar results were reported by

Figure 2. Top view SEM images of ZnO nanorods on (a) Au film and (b) Au island seed layer and cross section SEM images of ZnO nanorods on (c) Au film and (d) Au island seed layer.

Figure 3. XRD patterns of ZnO nanorods on (a) Au film and (b) Au island seed layer.

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Figure 3 shows the XRD spectra of the ZnO nanorods. All the ZnO nanorods exhibit a diffraction peak around 34°, which is the ZnO (002). The tiny ZnO (100), (101), (102), and (110) orientation XRD peak is also observed, indicating that small amounts of other domain structures exist in ZnO nanorods. To describe the preferred orientation, the texture coefficient (*TC*) was used. The *TC* represents the texture of the particular plane, deviation of which from unity implies the preferred growth. The *TC* has been calculated from XRD data, using the following expression¹⁸:

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{n} \sum_{i=1}^n (I_{(hkl)}/I_{0(hkl)})} \quad (5)$$

Where $TC_{(hkl)}$ is the texture coefficient for the reflection (*hkl*), $I_{(hkl)}$ is the relative diffraction intensity of (*hkl*) diffraction peak from experimental data, and $I_{0(hkl)}$ is the standard peak intensity for the reflection (*hkl*) according to JCPDS reference file. Since the data on JCPDS card are measured from pure single-phase powder samples, the effects of preferred orientation, solid solution and other impurities disturbance can be neglected. That is to say, the sample of JCPDS is in a random state. For randomly oriented crystals, $TC_{0(hkl)} = 1$ because $I_{hkl} = I_{0(hkl)}$. As $TC_{(hkl)}$ approach to 1, the less likely the (*hkl*) crystal planes possess preferred orientation. Deviation from 1 implies preferred orientation is likely. High $TC_{(hkl)}$ value means reflections than in a material with a random microstructure. Table 1 shows the calculated *TC* for ZnO nanorods on Au films seed layer and Au island seed layer. Both ZnO nanorods grown on Au film seed layer and

Table 1. The texture coefficients of the different planes for the ZnO nanorods grown on Au films seed layer and Au island seed layer

Seed layer	Texture coefficient (TC)				
	(100)	(002)	(101)	(102)	(110)
Au film	0.75	2.66	0.70	0.56	0.34
Au island	0.17	3.09	0.20	0.53	–

Au island seed layer have high $TC_{(002)}$ value. The high value of $TC_{(002)}$ indicates the maximum preferred orientation of the films along the (002). ZnO are well known to be usually grown with a c-axis preferred orientation because of the low surface energy of the basal plane in ZnO, leading to a preferred growth in the (002) direction.¹⁹ As seed layer changed from Au film to Au island, $TC_{(002)}$ is increased while other *TC* value which are $TC_{(100)}$, $TC_{(101)}$, $TC_{(102)}$, $TC_{(110)}$ are decreased. The annealed seed layers help form well-aligned ZnO nanorods in the hydrothermal process as nanorods are grown along the normal orientation of the ZnO thin films. It is also shown in SEM images in Figure 2, the ZnO nanorods on Au film seed layers were grown randomly, while the ZnO nanorods on Au island seed layers were well aligned.

The ZnO nanorod grown on the Au seed layers were annealed at the temperature of 300, 500, and 850 °C to investigate the post-annealing effects on properties of the ZnO nanorod and its morphology as shown in Figure 4. The surface of the ZnO nanorod annealed at 300 °C is almost same compared to that of the as-grown ZnO nanorod. However, the pinholes have been observed to appear on the surface of ZnO nanorods after annealing at above 500 °C as shown in Figure 4(c) and (d). The formation of the pinholes on the ZnO nanorods as functions of the annealing temperature was studied in our previous study.²⁰ In the previous work, two possible reasons for the formation of pores were discussed. One is desorption of zinc and oxygen at the defect sites and the other is decomposition of volatile gas and unreacted material. The release of volatile gas and surface reconstruction or evaporation of unreacted material such as zinc nitride during the annealing process is also discussed in the other studies.^{21,22} The surface of ZnO nanorods grown by hydrothermal method was prone to absorb various kinds of functional groups. According to the chemical reaction in the solution, these functional groups

Figure 4. SEM images of (a) as-grown ZnO nanorod on Au island seed layer and ZnO nanorods on Au island seed layer annealed at (b) 300 °C, (c) 500 °C, and (d) 850 °C.

Figure 5. XRD spectra of (a) as-grown ZnO nanorod on Au island seed layer and ZnO nanorods on Au island seed layer annealed at (b) 300 °C, (c) 500 °C, and (d) 850 °C.

should be related to the elements such as carbon, nitrogen, and hydrogen. Note that the ZnO nanopyramid is formed on the surface of the ZnO nanorods annealed at 850 °C. It is assumed that reaction between the residual, functional group, and unreacted material occurs at the relatively high annealing temperature which leads to form the ZnO nanopyramid. It is noted that, in the previous works, the ZnO nanopyramid was not observed. The reason of this is that more volatile gas was released and unreacted materials are evaporated as the annealing temperature is increased up to 850 °C. Thus the possibility to form ZnO nanostructure by evaporated material is increased. However, the detail mechanisms are not fully understood yet. Further studies are needed to demonstrate it.

Figure 5 shows the XRD spectra of the post-annealed ZnO nanorods at the various temperatures. The entire ZnO nanorods exhibit ZnO (002), (100), (101), (102). Table 2 shows the calculated TC for ZnO nanorods with various annealing temperature. $TC_{(002)}$ is increased as the ZnO nanorods in annealed at 300 °C, while $TC_{(100)}$, $TC_{(101)}$, and $TC_{(102)}$ are decreased. It is assumed that surface reconstruction and evaporation of unreacted material reduce the $TC_{(100)}$, $TC_{(101)}$, and $TC_{(102)}$. As the annealing temperature further increased, $TC_{(002)}$ decreased again, while $TC_{(101)}$ and $TC_{(102)}$ increased. It is assumed that the structural defects such as the pinholes appearing after annealing above 500 °C which is result of a degassing process.

Table 2. The texture coefficients of the different planes for the ZnO nanorods annealed at various temperature

Annealing temperature (°C)	Texture coefficient (TC)			
	(100)	(002)	(101)	(102)
As-grown	0.17	3.09	0.20	0.53
300	0.14	3.24	0.14	0.47
500	0.06	3.04	0.27	0.63
850	0.09	3.10	0.24	0.58

Figure 6. PL spectra of (a) as-grown ZnO nanorod on Au island seed layer and ZnO nanorods on Au island seed layer annealed at (b) 300 °C, (c) 500 °C, and (d) 850 °C.

In order to investigate the optical properties of the ZnO nanorods, we carried out PL measurement at room temperature by using a He-Cd laser with an excitation power of 30 mW and a 1-m single-grating monochromator with a photomultiplier tube. The PL spectra of the post-annealed ZnO nanorods at the various temperatures are shown in Figure 6. The PL spectra show a sharp near-band-edge (NBE) emission, which is generated by the free-exciton recombination at 380 nm. A broad deep-level emission (DLE), which is caused by impurities and structural defects, as observed from 578 nm (yellow emission) to 598 nm (orange emission). The yellow emission which are common in hydrothermally grown ZnO can be attributed to defects of O_i and the presence of $Zn(OH)_2$ on the surface.²³ The yellow-orange emission in ZnO has been also attributed to O_i .²⁴ After the ZnO nanorod annealed at 300 °C, a remarkable strong enhancement in PL intensity ratio appeared by almost a factor of 7 compared to the as-grown ZnO nanorod. However, after the ZnO nanorods were annealed under 500 and 850 °C, the NBE intensity apparently decreased step by step again in comparison with the PL spectrum of the ZnO nanorod annealed at 300 °C. The enhancement obtained for PL intensity ratio after annealing at 300 °C is probably related to desorption of hydroxyl groups, since the desorption rate of the hydroxyl groups peaks at ~150 °C, while hydrogen predominantly desorbs at ~420 °C.²⁵ Since hydrogen can passivate the defects and consequently enhance the NBE to DLE ratio,²⁵ the worsening of the NBE to DLE ratio for further annealing temperature is likely related to the release of residual hydrogen.

Conclusion

The surface morphology of the Au seed layer changes from film to island after the annealing process. The ZnO nanorod on Au island has higher density and uniform diameter compared to the ZnO nanorod on Au film. The pin-

holes were formed by annealing process with the temperature up to 700 °C. The ZnO nanopyramid was grown on the surface of the ZnO nanorod annealed at the temperature of 850 °C. The value of $TC_{(002)}$ is increased as ZnO nanorods annealed at 300 °C. The luminescent efficiency of NBE peak is also improved at ZnO nanorods annealed at 300 °C. It is suggested that the uniformity of the ZnO nanorods can be improved by annealing of Au seed layer. And also, the temperature of 300 °C is suitable to obtain the highly (002)-oriented ZnO nanorods with good luminescence performance.

Acknowledgments. This research was supported by Basic Science Research Program Through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2010-0016147).

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