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Size-controlled growth of well-aligned ZnO nanorod arrays with two-step chemical bath deposition method

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Abstract

Well-aligned ZnO nanorod arrays (ZNAs) with different sizes in diameter were fabricated on Si substrates by two-step chemical bath deposition method (CBD), i.e. substrate pretreatment with spin coating to form ZnO nanoparticles layer and CBD growth. The effects of substrate pretreatments, pH, angel (θ) between substrate and beaker bottom and growth time (t) on the structure of ZNAs were investigated in detail by X-ray diffraction (XRD), field emission scan electronic microscope (SEM) and photoluminescence (PL). The results show that substrate pretreatment, pH, θ and t indeed have great influence on the growth of ZNAs, and their influence mechanisms have been respectively explained in detail. The introduction of a ZnO nanoparticle layer on the substrate not only helps to decrease the diameter but also has a strong impact on the orientation of ZNAs. Under the growth condition of pH=6, $\theta=70^\circ$ and $t=2\text{h}$, the well-aligned ZnO nanorod arrays with 50nm diameter was obtained on the pretreated Si substrates. And only a strong UV peak at 385 nm appears in room temperature PL spectrum for this sample, which indicates that as-synthesized ZnO nanorods have a perfect crystallization and low density of deep level defects.

Keywords: A. Semiconductors; C. Crystal structure; D. Optical spectroscopy

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1. Introduction

Zinc oxide (ZnO) has generated great interests due to its direct wide band gap of 3.37eV, large exciton binding energy of 60meV, and stable physical and chemical properties[1,2]. Particularly, the device application of one-dimensional (1-D) ZnO nanostructure becomes one of the major focuses in recent nanoscience researches [3-5]. In order to utilize the applications of nanostructure materials, it usually requires that the crystalline morphology, orientation and surface architecture of nanostructures can be well controlled during the preparation processes. As concerned as ZnO nanorods arrays (ZNAs), although different fabrication methods, such as vapor-phase transport [6-8], pulsed laser deposition [9], chemical vapor deposition [10,11] and electrochemical deposition [12], have been widely used to prepare well-aligned ZNAs, the complex processes, sophisticated equipment and high temperatures make them very hard to large-scale produce for commercial application. On the contrary, chemical bath deposition (CBD) method shows its great advantages due to much easier operation and very low temperature (95°C) [13, 14], in addition to low cost. However, the ZNAs grown by this method show a poor reproducibility, difficulty to control size and bad orientation, particularly on substrates (such as Si) with large lattice mismatch and different crystalline structures in comparison with ZnO. Hence, it is still a significant challenge to obtain controllable growth with well-aligned ZNAs. Until now, the most successful approach for the CBD is growing ZnO nanorods on pretreated substrate, i.e. two-step CBD method [15-18]. Among those pretreated methods, thermal deposition [16], radio frequency magnetron-sputtering [17] and spin coating [18] techniques were usually applied to prepare ZnO seed layer on substrates. Clearly, the latter is much more easily carried out

and the process is more economical. Therefore, we select spin coating technique to introduce seeding layer on substrates and use CBD method to grow ZnO nanorods.

In this paper, well-aligned ZnO nanorod arrays with different diameter were uniformly fabricated on Si (100) substrates with two-step CBD method at mild condition and normal atmospheric pressure. The process shows a high reproducibility, the diameter of well-orientated ZnO nanorods can be controlled between 40 nm and 200 nm. The substrates were pretreated by spin-coating method in order to form ZnO nanoparticles layer. The effects of substrate pretreatment, pH, angel (θ) between substrate and beaker bottom and growth time (t) on the structure of ZNAs were investigated in detail. The influence mechanism of different conditions and optical properties of the ZNAs have been discussed.

2. Experiments

In our experiments, the synthesis process of ZnO nanorods contains substrate pre-treatment and CBD growth. All chemicals were of analytical reagent grade and used without further purification. All the aqueous solutions were prepared using distilled water. Si (100) substrates were ultrasonic cleaned for 15min in ethanol before spin coating. Four sets of samples under different growth conditions were prepared. The details were described as follows.

2.1 Substrates pretreatment (spin coating)

Zinc acetate dihydrate ($\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$) was dissolved in the pure ethanol with concentration of 5mM. This solution was coated onto Si (100) substrates by a spin coater (Laurell WS-400-8TFW-Full) at the rate of 2000 rpm for 30s. The thickness of the zinc acetate layer can be controlled by numbers of the spin coating and it shows a good

reproducibility. In our experiment, substrates were spin coated for four times. The coated substrates were dried in room temperature and then annealed in air at 250°C for 30min. The annealed temperature of 250°C is a little above the decomposition temperature of zinc acetate particles. In the following, all substrates were pretreated twice for the above processes before final growth of ZnO nanorods.

2.2 CBD growth process

In this process, the aqueous solutions of zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9% purity] and methenamine ($\text{C}_6\text{H}_{12}\text{N}_4$, 99.9% purity) were first prepared respectively and mixed together. The concentrations of both were fixed at 0.1M. The pre-treated Si substrates were immersed into the aqueous solution and tilted against the wall of beaker. The angel between substrate and beaker bottom is θ . Then the beaker was put into the oven and kept in it for different time under 93°C. After growth, the substrate was removed from the solution, rinsed with deionized water and then dried at room temperature. Ammonia water was added to adjust the pH of the growth solution. The amount of the added ammonia water was 2~4 mL which was depending on the zinc salt concentration and target pH.

2.3 Characterization

Scanning electron microscopy (SEM) pictures were recorded by using a JEOL JSM-6301F. An atomic force microscope (AFM, Dimension 3100) was use to detect the morphology of pretreated substrates. The powder diffraction curves were measured by using Philips PW1729 x-ray generator. Photoluminescence (PL) measurements were carried out at room temperature. A CCD detector (Spectrum One) and monochromator HR460 from Jobin Yvon-Spex were used to disperse and detect the ZnO emission. Laser

line with a wavelength of 266 nm from a diode laser (Coherent Verdi) pumped resonant frequency doubling unit (MBD 266) was used as excitation source.

3. Results and discussions

3.1 Effect of substrate pretreatment on the structure of ZANs

Figure 1 shows the SEM images with low and high magnification of the samples grown on the bare and pre-treated Si substrates under the condition of pH~6, $\theta=70^\circ$ and $t=5\text{h}$. On one hand, according to figure 1(a)-(b), all the top surfaces of the nanorods were hexagonal shape, and the average diameter of ZANs grown on the bare Si substrates is about 600nm. The diameter of ZnO nanorods is difficult to pre-control, in addition to poor reproducibility and very inhomogeneous over the surface. According to figure 1(c)-(d), the average diameter of ZANs grown on the pretreated Si substrates is about 125nm. And the nanorods uniformly cover entire surface with high density and all the top surfaces of the nanorods were also hexagonal shape. The latter shows an excellent reproducibility also. These big differences in diameter and density between two samples can be explained by the formation mechanism of CBD as follows: The CBD method consists of two steps, nucleation and growth, which is based on the formation of solid phase from the solution. The formation of nuclei is very critical to the size and orientation of the samples. Usually, nucleation generally occurs with much more difficulty in the interior of a uniform substance, by a process called homogeneous nucleation. Therefore, the diameter and dispersion of nuclei formed in the solution is random, which decided the diameter of ZnO nanorods is much larger, the distribution is non-uniform. However, for pretreated substrates, the ZnO nanoparticles layer was formed first on the substrates to act as nuclei. So the property of ZnO nanoparticles layer on the substrates will directly

influence the formation of ZANs. Figure 2 shows the $1\mu\text{m}\times 1\mu\text{m}$ AFM image of the pretreated substrates. From this image, it can be seen that the dispersion of ZnO nanoparticles is relatively uniform in the comparison with the nuclei formed on the bare substrates, and the average diameter and height of ZnO nanoparticles on the substrates is about 20nm and 3.5nm respectively, which is very beneficial to get uniform and small size ZANs just like that showed in figure 1(d).

Figure 1. SEM images of ZNAs grown on bare and pre-treated Si substrates. Inset is magnified top image of a single ZnO nanorod. Figure shows two different magnified SEM images of ZNAs grown on (a) and (b) bare Si substrates; (c) and (d) pre-treated Si substrates.

On the other hand, as also can be seen from figure 1, after substrate was pre-treated, the alignment of as-prepared ZNAs becomes better. Figure 3 is the XRD patterns of ZNAs grown on the bare and pretreated Si substrates. In comparison with the standard XRD pattern, only (002) diffraction peak appearing in figure 3(b) provides further evidence that the nanorods are preferentially oriented in the c-axis direction, which

Figure2. $1\mu\text{m} \times 1\mu\text{m}$ AFM image of pretreated substrate

Figure3. XRD patterns of ZnO nanorods grown on the bare (a) and pretreated (b) substrates.

indicates that the ZnO nanorods trend to grow perpendicular to the substrate surface. The relative intensity ratio between (002) and (101) diffraction peak is usually used to characterize the orientation of ZnO nanorods. From figure 3, it is obviously seen that there is only (002) diffraction peak in the XRD spectrum from ZNAs grown on pretreated Si substrate, which also testified that the c-axis orientation is much better than one grown on the bare substrates. There are mainly two reasons to explain the orientation difference.

(1) The orientation of the ZNAs is determined in a great extent by the orientation of ZnO nanoparticles on the pre-treated substrate. When the zinc acetate film spin-coated on the Si substrates was annealed, vast ZnO seeds formed and most of (0001) planes of these particles preferred to be parallel to the substrate under the higher temperature (250 oC)[19]. The nanorods grown from these ZnO seeds with the (0001) planes parallel to the substrate will be perpendicular to the substrate. However, for the bare Si substrates, the surface is too smooth at the nanoscale, in addition to the nucleation at relative low temperature (93°C), so the (0001) planes of the nuclei particles are likely randomly formed relative to the substrate surface, resulting in that the orientation of ZNAs on the bare substrate was poor.

(2) The ZnO seeds formed on the Si substrates usually offer an excess of nucleation positions. So the interactive and competitive effects among ZnO nanorods are inevitable during their growth process. As mentioned above, the nanorods grown from the ZnO seeds with (0001) planes parallel to the substrate will be perpendicular to the substrate. But not all the ZnO seeds have (0001) planes parallel to the substrate. When the nanorods grew from the ZnO seeds with (0001) planes deviating from the parallel plane of substrate, the nanorods will grow along a direction deviating from c-axis, which will easily meet other nanorods and be obstructed by them.

For single nanorod, the more deviation away from c-axis, the more obstructions might be met, which implies that the nanorods departing from c-axis direction of substrate are difficult to grow. Therefore, the nanorods are apt to grow along the c-axis on the basis of competition and optimization rules.

From these results, it can be conclude that a pre-coating ZnO nanoparticles layer on substrates can not only obviously decrease the average diameter of ZANs, but also improve the density and orientation of ZANs. Therefore, the following sets of samples were all grown on pretreated Si substrates.

3.2 Effect of pH value on the structure of ZANs

For chemical method, pH value usually has a great influence on the growth. A set of samples were grown on the pretreated Si substrates under the condition of $\theta=70^\circ$ and $t=2\text{h}$, in order to study the pH effect on the structures of ZANs. The pH of growth solution was adjusted to 6, 8 and 10 respectively. The different pH values were achieved by adding different amount of ammonia water, in our case typically 2~4 mL depending on the target pH value. For the original growth solution, the solution is transparent and there are some white dispensed precipitations of Zn(OH)_2 in it. The pH value is ~ 6 . The reactions in solution can be described as the following formulae [20-22] :

$\text{C}_6\text{H}_{12}\text{N}_4$, which is extensively used in the fabrication of ZnO nanostructures, provides the hydroxide ions (OH^-) and the ammonia molecules (NH_3) to the solution. As a common knowledge, four coordinated Zn cation largely occurs as tetrahedral complexes [23]. Therefore, two complexes, $\text{Zn(NH}_3)_4^{2+}$ and Zn(OH)_4^{2-} , were generated in the solution and became the precursors of ZnO. When the pH value was increase to ~ 8 through adding ammonia water, the amount of ammonia cannot form the $\text{Zn(NH}_3)_4^{2+}$ but instead form the Zn(OH)_2 , which can be validated by the white turbidity of the initial system. The reaction can be expressed as follows [24]:

With further adding ammonia water, the pH value of solution was increased to ~ 10 . The solution became a little transparent again because $\text{Zn(NH}_3)_4^{2+}$ was turn into the mainly precursors of ZnO. The reaction formulae were just as follows [24]:

Figure 4 showed the SEM images of ZANs grown on pretreated Si substrate under different pH situation. Although the chemical reaction was different, it can be seen from lower magnification images that the density, orientation and diameter of ZANs almost has no big difference, since the substrates coated with a similar density of ZnO nanoparticles were used. But the shape of ZANs changed from hexagon to tapered shape

Figure 4. SEM images of ZnAs grown on pretreated Si substrate under different pH (a)(b) pH~6; (c)(d) pH~8; (e)(f) pH~10

gradually as pH value increasing from 6 to 10, which can be seen from the high magnification images. For pH~8, both hexagon and tapered shapes existed in the sample. This shape transformation might be due to the competition between growth and erosion. As well as we known, the hexagonal wurtzite ZnO crystal is typical polar crystal with a dipole moment in the direction of c-axis. So (0001) crystal plane represents the polarity and is metastable, but the side planes are non-polar and relatively more stable. The polar

top planes are apt to attract OH^- , which could erode the planes in the solution according to the following equation:

For original growth solution, the OH^- in the solution is only enough for growing nanorods. After ammonia water was added, more and more OH^- were formed when the solution was heated so that the amount of OH^- can not totally be used for growth. Then the rest OH^- in the solution also took a part in the reaction of erosion at the same time. The relative erosion process will become more and more intensive as pH increasing. However, during the CBD growth process, the growth speed will be faster than that of erosion. As a result of the competition between growth and erosion, the top of ZANs becomes tapered shape as PH~10. Therefore, we can conclude that the pH value of 6 in the original solution is the optimized value to form ZANs with the top surface of hexagonal shape.

3.3 Effect of θ on the structure of ZANs

The effect of θ on the ZANs structure was also investigated. In our experiments, the samples were all grown in the solution without any holder, because it was very hard to say whether the materials of holder influence samples or not. The pretreated substrates just leaned against the beaker wall naturally so that the substrate is easier to fall down during the growth if θ is smaller than 60° due to the formation of NH_3 gas. Therefore, we only choose 60° and 70° to grow samples on pretreated Si substrates under the condition of pH~6 and $t=2\text{h}$. Figure 5 shows the low and high magnification SEM images of this set of ZANs. From these images, it can be seen that the ZANs at $\theta=60^\circ$ did not uniformly cover the whole substrate and the average diameter was also obviously larger

than that of $\theta=70^\circ$. That is maybe due to the different position of substrate center in the solution. For $\theta=70^\circ$, the position of substrate center is higher than that of $\theta=60^\circ$. Usually, there are concentration grads in the solution. For lower place of the solution, the concentration is a little higher. The formation of ZnO precursors will accelerate, which prompts ZnO precursors to accumulate together. As a result, the diameter of ZANs grown at lower position in the solution will increase.

Figure 5. SEM images of ZANs grown with different θ . (a)(b) $\theta=60^\circ$; (c)(d) $\theta=70^\circ$

3.3 Effect of growth time on the size of ZANs

A set of samples were grown on pretreated Si substrates under the condition of pH~6, $\theta=70^\circ$. Only growth time changed at here, i.e. 2h, 3h and 5h. The SEM images of this set of samples were shown in Figure 6. Figure 7 illustrated the cross sectional SEM image of the sample grown with 2h. It indicates that the lengths of ZnO nanorods are about 400 nm, which can be controlled by changing the duration of growth time. For three samples, the nanorods uniformly covered the entire surface, and the density and orientation were

Figure6. SEM images of ZnO nanorods grown on Si substrate with different growth time.
(a) (b) 2h; (c) (d) 3h; (e) (f) 5h

almost same. However, the average diameters of ZANs are significantly increased with the growth time. For 2h, 3h and 5h, the average diameter was about 50nm, 80nm and 120nm respectively. Therefore, the diameter of ZANs on pretreated Si substrate can be controlled through changing growth time when pH and θ are fixed at ~ 6 and $\sim 70^\circ$.

Figure 8 showed the room temperature PL spectrum of ZANs grown on the pretreated Si substrates under the condition of pH ~ 6 , $\theta=70^\circ$ and t=2h. The spectrum only consisted of a strong UV peak at 385 nm in wavelength, which was related to a near

band-edge transition of ZnO, namely, the recombination of the free excitons. Only UV peak in the spectrum indicated that as-synthesized sample has low density of the deep level defects such as Zn and O vacancies that often result the so-called green emission band with center wavelength around 510 nm.

Figure7. Cross sectional SEM image of the sample grown with 2h.

Figure8. Room temperature PL spectrum of ZNAs grown on the pretreated Si substrates under the condition of pH~6, $\theta=70^\circ$ and $t=2h$

4. Conclusion

The effects of substrates pretreatment, pH, angel (θ) between substrate and beaker bottom and growth time (t) on the structure of ZNAs were investigated in detail. Under the growth condition of pH=6, $\theta=70^\circ$ and $t=2\text{h}$, the well-aligned ZANs with 50nm diameter was obtained on the pretreated Si substrates. And only UV peak in PL spectrum indicated that as-synthesized sample has low density of the deep level defects such as Zn and O vacancies that often result the so-called green emission band with center wavelength around 520 nm. Such a low-temperature growth may provide a possibility to fabricate nanodevices onto many low-temperature-enduring substrates. The growth process requires no expensive and precise vacuum equipment, therefore permitting large-scale fabrication with a relatively low cost.

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