Selective area growth behaviour of ZnO nanorod arrays in hydrothermal synthesis

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Abstract. ZnO nanorod arrays have become to attract much attention because the uniform and symmetry of ZnO nanorods can provide great optical and electrical potential in many nanodevices. Here, we have controlled nucleation sites using electron beam lithography technique and grown ZnO nanorods via hydrothermal synthesis to observe growth behaviors. We have measured nanorods’s diameter and density of each aperture area. The results are presented strongly effect of aperture size and distance between adjacent apertures for growth ZnO nanorods. The both of aperture size and distance affect not only nanorod’s density and diameter but also nucleation growth and growth rate. There is no nanorod growth through aperture area when aperture size is large and distance between apertures is small. In the same growth condition, there are several nanorods growth through large aperture size with large distance between apertures. These phenomena show behavior of ZnO nanorods growth with difference aperture size and distance which are useful to enhance great properties ZnO nanorods and also achieve high performance of nanodevices.

1. Introduction

ZnO nanostructures have been interesting for nanoscale devices during the past decades. Due to their unique electrical and optical properties, ZnO nanomaterial is a stable wurtzite structure, a wide band gap energy of 3.4 eV and a large exciton binding energy at 60 meV. They were adopted for electronic, optoelectronic and photovoltaic devices [1-2]. More recently, the periodic of ZnO nanorods has attracted attention because adjustable nanorods, uniform separation and high symmetry lead to enhance the electrical and optical properties.

The fabrication of ZnO nanorod growth has been accomplished with numerous techniques [3] for example chemical vapor deposition (CVD), vapor liquid solid phase (VLS) and hydrothermal technique. Especially, hydrothermal technique has been widely used due to low cost effective, low growth temperature and large scale synthesis. To growth ZnO nanorod as periodic structure, there are various techniques to control nucleation sites for growing ZnO nanorods such as photolithography, electron beam lithography (EBL), UV-nanoinprint lithography and nanosphere lithography.
In this work, the position, arrangement and size of ZnO nanorod arrays were controlled via aperture of polymethyl methacrylate (PMMA) pattern on ZnO seed layer/silicon substrate. The combination of two techniques between electron beam lithography (EBL) to obtain the precise control and hydrothermal method were used to provide the ZnO nanorod arrays. Subsequently, the behavior of ZnO nanorod arrays was observed when the PMMA template was changed. Finally, the samples were characterized by scanning electron microscope (SEM). The results showed the aperture sizes and distances between individual nanorod strongly affect to the morphology of ZnO nanorods.

2. Experimental

2.1. Fabrication of template for ZnO nucleation sites
To grow the single crystal of ZnO nanorod arrays, the ZnO seed layer was served by DC magnetron sputtering with a thickness about 140 nm on silicon substrate. The PMMA resist was then coated onto seed layer by the spin-coating technique with spin speed of 4000 rpm for 60 sec and baked on a hotplate at 180°C for 90 sec to obtain resist thickness of 250 nm. In order to control nucleation sites for ZnO nanorods, the periodic structures were firstly written on the resist by EBL with 55 µC/cm² dose. In developing process, the written samples were drowned in the developer solution for 45 sec to remove exposed PMMA, dipped into isopropanol for 60 sec to clean the developer and finally dried in nitrogen flow.

2.2. Growth of ZnO nanorods by hydrothermal processes
This section has presented the growth of ZnO nanorods at low temperature by a hydrothermal technique. For mixing a chemical solution of precursors, zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] and hexamethylenetetramine [(CH₂)₆N₄·HMTA] were put together, dissolved in DI water and stirred for 1 hour. The sample with EBL designed nucleation site was immersed in the mixture solution with concentration of 10 and 20 mM from 1:1 molar ratio of Zn(NO₃)₂·6H₂O : HMTA. The sample surface was faced down to avoid the precipitates of precursors and heated in an oven at 90 °C for 3 hours. The ZnO nanorods were grown into the apertures of the PMMA templates.

3. Results and discussion

3.1. The effect of concentration
ZnO nanorod arrays were grown into PMMA template with 1000 nm spacing and 100 nm aperture sizes by the hydrothermal method in different concentrations at 90 °C for 3 hours as seen in figure 1. Figure 1(a) and (b) represented the grown nanorods in the same aperture size of 100 nm from at concentration of 20 and 10 mM, respectively. The average diameter of ZnO nanorods was around 134 nm (figure1(a)) and 64 nm (figure1 (b)) in the holes. It was obviously that the diameter of ZnO nanorods at 20 mM is larger than the aperture size with several nanorods in each hole. When the ZnO nanorods were grown in 10 mM, the diameter of nanorods was reduced and smaller than aperture size. Moreover, the number of nanorods was stable.

![Figure 1](image-url)

Figure 1. SEM images of periodic ZnO nanorod arrays grown in 20 mM on PMMA template with 1000 nm spacing and aperture size of (a) 100 and (c) 150 nm and in 10 mM on the template with the same spacing and aperture size of (b) 100 (d) 150 nm
From the SEM image, figure 1 (c) and (d) showed ZnO nanorods with diameter of 112 and 68 nm with 5 nanorods in each hole at 20 and 10 mM, respectively. It was concluded that a higher concentration more provided a number of Zn ions that affected the formation of nanorods. ZnO nanorods tend to grow in lateral growth direction as revealed in figure 1 (a) and (c). It was clearly that the concentration was not determined the density of nanorod in aperture but it enhanced crystal growth in the lateral side.

3.2. The effect of aperture size
To explore the influence of aperture size on ZnO nanorod morphology, the ZnO nanorods in 10 mM concentration were grown into the PMMA template with a range of aperture size from 100 nm to 350 nm at 1000 nm spacing as seen in figure 2. The graph in figure 3 (a) showed that diameter of nanorod became smaller while aperture size was increased. In contrast, the number of nanorods in aperture was growing up.

![Figure 2: SEM images of periodic ZnO nanorod arrays grown through PMMA template with 1000 nm spacing and different aperture sizes of (a) 100 nm, (b) 150 nm, (c) 200 nm, (d) 250 nm, (e) 300 nm and (f) 350 nm at 10 mM concentration.](image)

This has been confirmed by reducing the spacing to be 500 nm with the same range of aperture sizes and growth condition. As presented in figure 3 (b), the diameter of nanorod was slightly decreased while the density of nanorods in one aperture was increased. The similar results on both 500 nm and 1000 nm spacing of PMMA template indicated that the density and diameter of nanorods correlated each other in the opposite manners when the periodic aperture sizes were increased.

![Figure 3: Aperture size dependence on the nanorod diameter and density on PMMA template with (a) 1000 nm and (b) 500 nm spacing.](image)

This has been explained that the small aperture area consumed a number of Zn ions for crystal growth more than nucleation growth. Thus, the diameter of nanorods are large but there are a few of nanorods. On the other hand, the large aperture area made more consumption of Zn ions for nucleation growth, therefore, the Zn ions for lateral crystal growth were pulled, and this led to the decrease of the nanorod diameter and the increase of the number of nanorods in one aperture area.
3.3. The effect of spacing distance

To investigate the effect of spacing distance, this section compares the diameter and density of nanorods with the same aperture size but different spacing. The aperture sizes of 150 nm and 300 nm were varied in spacing from 200 to 1000 nm. From the figure 4 (a), the graph showed the lateral growth when distance between each aperture was increased and the number of nanorods was changed in opposite direction. The reason is mainly due to the consumed Zn ion competition of neighboring nanorods at the narrow spacing while there is no competition for the large spacing. Consequently, the larger nanorods were appeared.

Figure 4. Variation of diameter and density of nanorods when varying spacing distance and aperture sizes at (a) 150 nm and (b) 300 nm

In the figure 4 (b), it shows an interesting phenomenon, when the aperture size is around 300 nm with narrow spacing, ZnO nanorods was not exist in the aperture as shown in figure 4 (b) inset. However, there are existing of nanorod at larger spacing. Because of the large nucleation site with narrow spacing distance, the nanorod was grown with competition effect. Therefore, it used a number of Zn ions for nucleation growth which was used more than 150 nm aperture size, the Zn ions is not enough to grow crystal structure in 3 hours.

4. Conclusions

In summary, ZnO nanorod arrays were fabricated via combination of the EBL and hydrothermal method to observe behaviour of ZnO nanorod growth with various nucleation sites. The concentration of chemical solution of precursors obviously affected the crystal growth of nanorod in lateral direction. The results clearly observed that the number of nanorods in one aperture relied on the aperture area and also presented competition effect of neighbouring nanorods at narrow spacing. More interesting, the correlation between aperture size and spacing showed the non-existing of nanorod at the optimized condition. Considering of behaviour of ZnO nanorod growth with controlled nucleation sites would impact not only the properties of ZnO nanostructure but also the properties of nanodevices in further applications.

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