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# Buffer layer effect on ZnO nanorods growth alignment

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#### Abstract

Vertical aligned ZnO nanorods array was fabricated on Si with introducing a ZnO thin film as a buffer layer. Two different nucleation mechanisms were found in growth process. With using Au catalyst, Zn vapor could diffuse into Au nanoclusters with forming a solid solution. Then the ZnO nucleation site is mainly on the catalyst by oxidation of Au/Zn alloy. Without catalyst, nucleation could occur directly on the surface of buffer layer by homoepitaxy. The density and the size of ZnO nanorods could be governed by morphological character of catalyst and buffer layer. The nanorods growth is followed by vapor–solid mechanism. © 2005 Elsevier B.V. All rights reserved.

#### 1. Introduction

One-dimensional (1D) wide band-gap nanowhiskers have attracted much interest because their remarkable physical and chemical properties [1,2]. Fabrication of nanowires of SiC, GaN, ZnSe and ZnO has been reported [3–6]. Among them 1D ZnO nanostructures attract special attention due to the large excitonic binding energy of 60 meV and high mechanical and thermal stabilities [6]. Recently, 1D nanostructures of ZnO, including nanowires, nanobelts, and nanotubes, have been fabricated by various methods [6–8]. Electronic and optical devices based on 1D ZnO nanostructures, such as lasers, sensors, light-emitting diodes, and field emission devices, were studied [6–9].

Sapphire substrate coated with a thin layer of Au is often used to grow well-aligned array of ZnO nanorods [6]. Aligned growth of ZnO nanorods has also been realized on Si substrate with or without catalyst [10,11]. In this Letter, a thin film of ZnO is employed as a buffer layer to obtain aligned growth of ZnO nanorods on Si substrate. Buffer layers are usually introduced in the heteroepitaxial growth process of high quality semiconductor thin films [12]. This buffer layer could provide a clean and smooth surface to further fabricate quantum well and superlattices devices with small lattice mismatch. Our results suggest that a buffer layer of ZnO could guide an oriented growth of ZnO nanorods. Moreover, the density and the size of nanorods could be changed by the use or not of catalyst.

## 2. Experimental detail

The ZnO nanorods were fabricated via a simple vapor-phase transport process in a conventional furnace with a horizontal quartz tube (the inner tube diameter is 4 cm). A mixture of commercial ZnO and graphite powders in a certain ratio (1:1) was placed in an alumina boat as the source material. Si substrates were used with in addition ZnO buffer layer and/or Au nanoclusters deposited on polished side. The ZnO buffer layers were deposited on Si surface by electron beam evaporation

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method. The Au nanoclusters were obtained by sputtering method. The thickness of ZnO and Au thin films was 200 and 6 nm, respectively. The polished side of Si substrate was faced downward on the alumina boat just over the source material with a separation of about 5 mm. Synthesis was carried out at 950 °C under a constant flow of Ar (99.99%) of 50 sccm for 30 min. A thermal couple was used just close the substrate to measure the temperature. After the reaction a light or dark grey layer was found on substrate surface. Crystallographic and morphological properties of the as-grown samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM, HIT-ACHI S4200), transmission electron microscopy (TEM, Philips CM20, operated at 200 kV), and selected-area electron diffraction (SAED). In XRD measurement a symmetric configuration was used, in which integral breadth of each diffracted intensity peak has been corrected to instrumental (geometrical element of set up) and spectral (K $\alpha$  X-ray lines width) contribution in order to deduce the material intrinsic characteristics (microstrain and diffraction domain sizes).

## 3. Results and discussion

XRD is an ideal probe to characterize structure and orientation of thin film with respect to the substrate. The XRD pattern of as-grown ZnO buffer layer is shown in Fig. 1a. Except diffractive peak from Si substrate, only one diffractive peak is found in the spectra, which is corresponding to the [002] direction of ZnO wurtzite structure. The intensity of this peak is 10 times less than other samples. The integral breadth of 002 direction diffractive peak is 1.33°. This large value corre-



Fig. 1. XRD spectra of ZnO thin film (a) and ZnO nanorods grown on different substrates (b) Au/Si, (c) ZnO/Si and (d) Au/ZnO/Si.

sponds to a high level of microstrain and to small domains (smaller than ZnO film thickness)

Fig. 1b-d show the XRD spectra of ZnO nanorods deposited on different substrates. For the ZnO nanorods grown on Au/Si surface the growth is not oriented (Fig. 1b). The diffractive peaks of both [002] and [101] directions are strong in the spectra. The diffractive peaks attributed to metal Au and Zn are clearly seen located at 38.2° and 38.8°, respectively, without preferential orientation (deduced from other peaks not presented here). With introducing a thin film of ZnO buffer layer, the diffractive peak of [002] direction becomes very strong in the spectra with an integral breadth as narrow as 0.19°. This means the product is highly oriented with c-axis perpendicular to the substrate surface with extended domains in [002] direction. When using Au as a catalyst on buffer layer, beside ZnO wurtzite structure only diffractive peaks from cubic Au are detected in the spectra. Moreover, the intensity of [111] Au peak is 20 time higher than the signal from Au directly grown on Si substrate (for similar gold deposited quantity), from which we can deduce at high temperature, [002] oriented ZnO buffer layer induces a preferential [111] orientation of Au clusters.

The SEM images of ZnO nanorods directly grown on Au/Si substrate are shown in Fig. 2a, in which the nanorods diameter is between 60 and 140 nm with the length of  $1-3 \mu m$ . The density of ZnO nanorods is  $10 \mu m^2$ . The nanorods grow randomly on the substrate surface.

Fig. 2b shows the SEM top view image of ZnO nanorods grown on ZnO thin film. The diameter of ZnO nanorods grown on ZnO/Si substrate ranges from 120 to 180 nm with the length of 1  $\mu$ m. The density of nanorods decreases to 5  $\mu$ m<sup>2</sup>. The hexagonal shaped top of nanorods is clearly observed in the image. When using a thin layer of Au as a catalyst on ZnO thin film the density of ZnO nanorods increases to 20  $\mu$ m<sup>2</sup> (Fig. 2c). The diameter decreases to the range of 50–100 nm with the equal length of 1  $\mu$ m as shown in Fig. 2c. The 45° tilted images shown in Fig. 2d and e (respectively, for ZnO/Si and Au/ZnO/Si substrates) indicates that the ZnO nanorods grow vertically to the substrate in both cases, which is in good agreement with the XRD results.

TEM image Fig. 3a shows a group of nanorods presenting a narrow diameter distribution around 70 nm. Each nanorod is faceted as indicated in Fig. 3b. The ZnO nanorods are single-crystalline as shown in the electron diffraction pattern and in HR-TEM image (Fig. 3c, d), where the lattice spacing of 0.26 nm between adjacent lattice planes is observed. This confirms the preferential growth of ZnO nanorods along *c*-axis orientation. Among high resolution and electron diffraction observation, we can deduce the growth morphology of ZnO nanorods. This is illustrated in Fig. 3b and is in accordance with low index crystallographic faces growth.



Fig. 2. SEM images of ZnO nanorods grown on different substrates (a) Au/Si; (b), (d) ZnO/Si; (c), (e) Au/ZnO/Si. (a)–(c) are top view; (d) and (e) are 45° tilted view.



Fig. 3. (a) TEM image of a group of ZnO nanorods, (b) a facetted ZnO nanorod with a schematic representation of the crystallographic facets, (c) HR-TEM image of ZnO nanorod and the corresponding electron diffraction pattern (d).

Based on the above results we can deduce that a buffer layer can guide the growth orientation of nanorods in both cases, with and without catalyst. This effect mainly takes place on the nucleation process. For the samples grown with and without catalyst the nucleation mechanism is quite different. If without catalyst, some unsaturated bonds on the surfaces of ZnO thin film could act as nucleation sites. Because in our experiment Zn and CO vapors were only generated by the reaction of ZnO and graphite, no additional oxygen source was used, this low oxygen concentration results in threedimensional growth mode of ZnO nanocluster. It is the case of a homoepitaxy growth, in consequence the preferential [002] orientation of the buffer layer induces a vertically [002] nanorods orientation, which is illustrated in Fig. 4a. When using Au as a catalyst, in our previous work, we have deduced the zinc vapor could be dissolved in Au nanoclusters by forming Zn/Au solid solution. With further oxidation, the ZnO nucleation site is formed on these Zn/Au clusters, the nucleation of ZnO nanorods begins with a thin shell covering



Fig. 4. A sketch map for the ZnO nanorods growth mechanism on different substrates: (a) with a ZnO buffer layer, (b) with both ZnO buffer layer and Au catalyst, (c) with only Au catalyst.

Zn/Au clusters [13]. At the growth temperature of 950 °C, Zn and Zn sub-oxides (the melt points of Zn and  $ZnO_x$  is approximately at 419 °C, x < 1) should be in vapor phase [14]. No liquid phase is present in the growth process. Therefore, the nanorods growth should follow VS mechanism. So, when we use the Au/ZnO/Si substrate the nucleation sites of ZnO have the same orientation as ZnO thin film by the effect of the buffer layer. We have observed the [111] lattice plane of cubic Au was aligned with the [002] direction of ZnO. And the interface between them was extremely sharp, which means the Au catalyst could transfer the orientation from buffer layer to nanorods leading to a vertically growth (Fig. 4b) [13]. Finally, if no buffer layer is present, the nucleation of ZnO on Au nanoclusters is in random direction, which indicates the nanorods grown on Au/Si substrate lose the orientation (Fig. 4c).

Another point is the influence of the use of gold catalyst on the rod density. With considering ZnO buffer layer surface compared to the Si one, we could say that the density of defects, in terms of roughness and unsaturated bonds, is higher on ZnO buffer layer surface. This induces, for the same Au deposited quantity, a higher Au clusters density on ZnO surface and consequently a higher density of ZnO nanorods. Therefore, the nanorods diameter, which is tuned by catalyst clusters diameter, is lower in the case of ZnO buffer layer.

## 4. Conclusion

In a word, vertically aligned ZnO nanorods have been obtained on Si substrates with using a thin film of ZnO as a buffer layer. The size distribution of rods is relatively narrower compared with samples only used catalyst but without using buffer layer. We provide a new method to fabricate the vertical aligned nanorods, in which the growth process, the density and size of nanorods are simply controlled by catalyst and buffer layer on low cost substrate.

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