



# Origin of the surface recombination centers in ZnO nanorods arrays by X-ray photoelectron spectroscopy

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## ABSTRACT

The surface composition of as-grown and annealed ZnO nanorods arrays (ZNAs) grown by a two-step chemical bath deposition method has been investigated by X-ray photoelectron spectroscopy (XPS). XPS confirms the presence of OH bonds and specific chemisorbed oxygen on the surface of ZNAs, as well as H bonds on (10 $\bar{1}$ 0) surfaces which has been first time observed in the XPS spectra. The experimental results indicated that the OH and H bonds play the dominant role in facilitating surface recombination but specific chemisorbed oxygen also likely affect the surface recombination. Annealing can largely remove the OH and H bonds and transform the composition of the other chemisorbed oxygen at the surface to more closely resemble that of high temperature grown ZNAs, all of which suppresses surface recombination according to time-resolved photoluminescence measurements.

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## 1. Introduction

Zinc oxide (ZnO) as one of the most important semiconductors has attracted significant attention in recent years. Especially, quasi-one-dimensional ZnO nanostructures (e.g. nanorods, nanowires, nanotubes and nanobelts) have been considered highly potential for sensor application such as gas sensor [1,2] and biosensor [3–5], and nanophotonic applications such as nanolasers [6–8], optical waveguides [9–11], and light emitting diodes [12]. However, one of the significant differences between nanostructures and an epilayer is the larger surface-to-volume ratio of the former. This large surface-to-volume ratio can be an advantage for some applications, for example sensor devices [1–5]. However, it can also be a problem in other applications, for example, optoelectronic devices such as light emitting diodes [12] and solar-cell [13,14] devices, since surface states are created within the band gap region either because of surface inhomogeneities like nonstoichiometry or because of the selective adsorption of foreign species in addition to the abrupt termination of lattice periodicity. Such surface states will strongly influence the electronic and optical properties at the semiconductor surfaces and interfaces since the surface recombination rate may become dominating, resulting in a short carrier life time [15–18]. The potential implications of these effects are

especially noticeable in the case of nanostructured materials. Therefore, to optimize devices based on ZnO nanostructures, it is necessary to understand the surface recombination mechanisms and explore effective way to control surface states. Furthermore, knowing surface chemical origins in ZnO nanostructures are also essential for their applications in sensor devices based on surface properties. For example, Bai et al. have reported that the coverage of hydroxyl (OH) groups on the surface of tetrapod-shaped ZnO can inhibit the ethanol adsorption [19,20], i.e. the high ratio of the coverage of OH group can depress the high surface activity of the tetrapod-shaped ZnO sensor and block the adsorption or reaction sites for the ethanol molecules, which lead to a smaller consumption and sensing signal. Besides, as well known, the attraction or repulsion action between chemical groups on the ZnO surface and detective molecule also influence the sensitivity of ZnO sensor. Therefore, the investigation on the surface recombination and chemical origins of surface recombination centers are significant for the applications of ZnO nanostructures.

As we known, ZnO nanorods are a suitable material for the research on surface recombination due to their large surface-to-volume ratio. Recently, we successfully controlled the size of well-aligned ZnO nanorod arrays (ZNAs) from 40 nm to 150 nm with the two-step chemical bath deposition (CBD) method [21,22], i.e. by first spin coating the substrate with a seed layer of ZnO nanoparticles and then using the CBD growth. And we also investigated in detail the surface recombination of ZNAs with different diameters by time-resolved photoluminescence measurement and revealed that the surface recombination can be

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strongly suppressed by annealing at 500 °C at ambient conditions [23,24]. We pointed out that the surface recombination may originate from the functional groups absorbed by ZNAs surface during the chemical reaction in the solution, which should be related to the elements such as carbon, nitrogen and hydrogen, but we could not identify the origin of the surface recombination due to the limitation of the used characterization techniques [24]. Although some groups have reported the possible functional groups attached in the surface of the ZnO [25–35], so far, there are no investigations which try to build the relationship between the chemical origin and surface recombination centers. On the basis of the discussion in the first paragraph, we believe that the investigation on identifying the chemical origin of surface recombination center is rather important than just revealing the existence of surface recombination in the emission process, because it will open to an effective way to control the surface recombination, utilize the surface states for sensor application and efficiently enhance the properties of optoelectronic devices based on ZnO nanostructures.

Therefore, in this paper, we utilized X-ray photoelectron spectroscopy (XPS) to investigate the surface composition of as-grown ZNAs and ZNAs annealed in 500 °C for 1 h in air atmosphere. The results clearly revealed the correlation between the chemical origin and the surface recombination centers of ZNAs grown by CBD method for the first time as far as we know.

## 2. Experimental

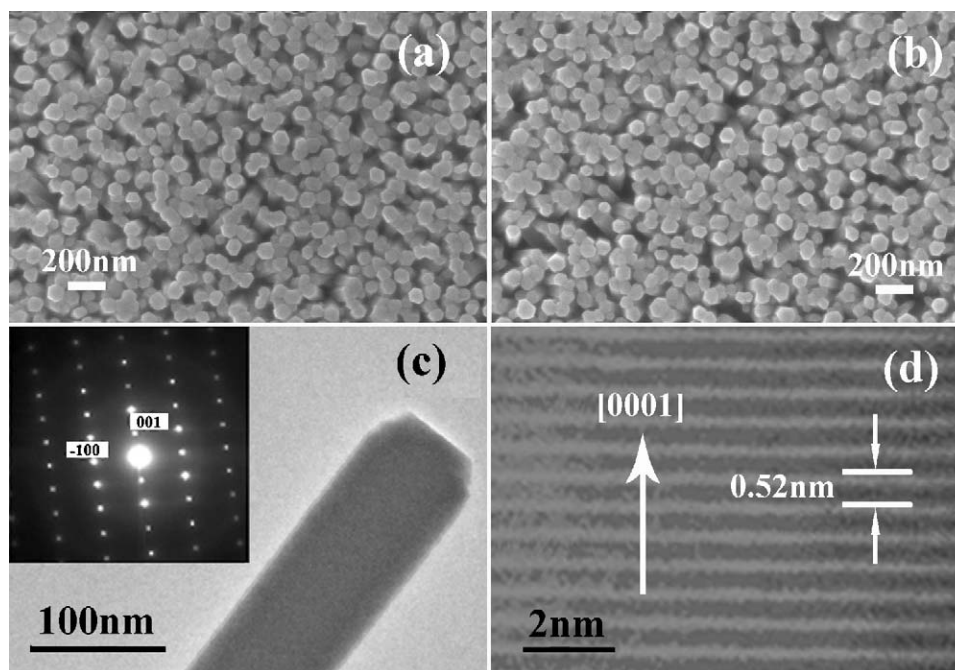
The ZNAs used in this investigation were grown on Si substrates by the CBD method, which includes a two-step process, i.e. a substrate treatment prior to the CBD growth. The pre-treatment of the substrates, by coating the substrate with a solution of zinc acetate dihydrate ( $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ ) dissolved in pure ethanol with concentration of 5 mM, was used to control the diameter of ZnO nanorods. In the CBD growth, 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 and mixed together. The concentrations of both were fixed at 0.1 M. The pre-

treated Si substrates were immersed into the aqueous solution and ZnO was grown at an elevated temperature of 93 °C. The more details of controllable preparation process of ZNAs and some other controllable growth conditions can be found elsewhere [21–24]. To guarantee the comparability, a big piece of sample was cut into two parts. One was used as as-grown sample, the other was post-growth thermal treated at 500 °C for 1 h in air atmosphere and then quenched to room temperature by removal from the oven.

Scanning electron microscopy (SEM) pictures were recorded by using a JEOL JSM-6301F. Transmission electron microscope (TEM) (200 keV, JEM-2100HR, Japan) was used to get the high resolution TEM (HRTEM) image and the selected-area electron diffraction (SAED) pattern of samples. Time-resolved photoluminescence (TRPL) was performed by using an excitation laser line from a frequency tripled sapphire:Ti laser emitting at 266 nm with a 200 fs pulse width and an 80 MHz repetition rate. The luminescence signal is dispersed by a 0.3 m monochromator and time resolved by a streak camera. The spectral resolution is about 1 meV and the time resolution is 7 ps. The measurements were done under weak excitation conditions ( $0.5 \text{ W/cm}^2$ ) at 1.8 K. XPS measurements were performed using a Scienta<sup>®</sup> ESCA200 spectrometer in ultra-high vacuum (UHV) with a base pressure of  $10^{-10}$  mbar. The measurement chamber is equipped with a monochromatic Al ( $K\alpha$ ) X-ray source providing photon with  $h\nu = 1486.6$  eV. The XPS experimental condition was set so that the full width at half maximum (FWHM) of the clean Au  $4f_{7/2}$  line was 0.65 eV. All spectra were measured at a photoelectron take-off angle of  $0^\circ$  (normal emission) and room temperature. The binding energies were obtained referenced to the Fermi level with an error of  $\pm 0.1$  eV.

## 3. Results and discussions

The SEM images of the as-grown and 500 °C annealed ZNAs with 90 nm diameters are shown in Fig. 1(a) and (b). In order to show the homogeneity of both samples, only top-view SEM images are shown here. The length of nanorod is about  $1 \mu\text{m}$ . From Fig. 1(a), it can be seen that the as-grown ZNAs are vertically



**Fig. 1.** (a) and (b) SEM images for as-grown and 500 °C annealed ZNAs; (c) TEM image of single as-grown ZnO nanorod, the inset is the corresponding SAED pattern; (d) HRTEM of as-grown ZnO nanorod.

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