EFFECT OF HEAT TREATMENT ON THE PROPERTIES OF SOL-GEL DEPOSITED ZnO SEED LAYERS

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Abstract

Zinc oxide nanorods as a potential material for nanoscale devices are prepared by chemical bath deposition (CBD). The effect of the quality of the sol-gel deposited seed layer on the vertical alignment of the nanorods to a silicon substrate is discussed. Emphasis is put on the investigation of the impact of the heat treatment on the properties of the seed layer deposited by dip-coating. The sol-gel method is a multi-stage process consisting of three principal steps: (i) preparation of a solution with suitable precursors, (ii) deposition of the precursor solution, and (iii) the heat treatment. The preheating needs to be performed to thermally decompose the zinc acetate precursor into zinc oxide seeds. Three different temperatures of preheating are compared (300 °C, 350 °C, 400 °C) followed by annealing in argon at 800 °C and the influence on the quality of the seed layers and vertical alignment of nanorods are discussed. When the preheating temperature is higher than 350 °C, the seed layer comprises smaller and denser crystallites with a preferential orientation along the *c*-axis. CBD growth of ZnO nanorods on these seed layers results in their good vertical alignment.

Keywords: ZnO nanorods, sol-gel, seed layer, heat-treatment, chemical bath deposition

1. INTRODUCTION

ZnO is an abundant non-toxic material with a high exciton binding energy (60 meV), a wide band-gap energy (3.37 eV at room temperature) and high electron mobility [1]. Zinc oxide nanorods (NRs) are an attractive material for many potential applications in nanoscale-engineering devices, such as piezoelectric and optoelectronic devices and photovoltaic cells [2-7].

ZnO NRs can be grown either from the vapor phase by chemical or physical vapor deposition or in solution by chemical bath deposition (CBD) [8, 9]. The synthesis in the liquid phase has been studied over the past decade, since it is a low-cost, low-temperature, surface scalable, and easily implemented process [10]. However, the CBD growth of ZnO NRs strongly depends on (i) the morphology of the zinc oxide seed layer, namely on its crystal orientation, polarity, porosity, roughness and characteristic dimensions [11-13] as well as on (ii) the preparation conditions, such as temperature, time, pH, nature of chemical precursors and related concentrations [14-18].

It is well known that on commercially relevant substrates, such as glass or silicon, the presence of a thin seed layer is necessary for the nucleation and formation of ZnO NRs [8,11,17]. The seed layer usually consists of ZnO nanocrystals and can be prepared by vapor phase methods or by sol-gel process, where the precursor solution is deposited by dip-coating or spin-coating followed by a heat treatment. The properties of the seed layer, especially the morphology and crystallite orientation, have a crucial impact on the growth of ZnO NRs. The relationship between the seed layer quality and the vertical alignment of the NRs to a substrate is still not completely understood and it has been an objective of many recent studies [8,11,14,19-24].

The sol-gel synthesis in combination with dip-coating process includes several steps, of which most important are an immersion of the substrate into a precursor solution and subsequent heat treatment of the deposited layer. The key parameters that influence the sol-gel process are: (i) preparation of the precursor solution, especially the nature and concentration of chemicals (precursors, solvents, additives), aging time of the solution, pH, air humidity; (ii) withdrawal speed by dip-coating and the substrate; and (iii) the heat treatment involving both the preheating and annealing, which both depend on temperature, time and surrounding atmosphere [13]. In this work we focused on the heat-treatment; we varied the preheating temperature in the range of 300 °C to 400 °C. This change influences the crystallinity and morphology of the seed layer and thereby affects the vertical alignment of ZnO nanorods grown by CBD.

2. EXPERIMENTAL SECTION

Zinc oxide seed layers were obtained by sol-gel synthesis. The chemical precursor solution was prepared by dissolving equimolar amount (0.375 M) of zinc acetate (ZAD, $Zn(CH_3COO)_2 \cdot 2 H_2O$) from Sigma-Aldrich and monoethanolamine (MEA, C_2H_7NO) in 2-methoxyethanol from Carl Roth. The solution was heated and stirred to dissolve ZAD and to initialize the hydrolysis of the sol. Then the polymerization continued for another 24 hours. The seed layers were deposited either by one, three, or five times repeated dip-coating process and, after each cycle of dip-coating, the silicon substrate was preheated at a temperature of 300 °C, 350 °C, or 400 °C for 10 min in a laboratory muffle furnace to evaporate solvent and to decompose and remove the organic compounds. Finally, the prepared seed layers were annealed at 800 °C in argon atmosphere for 1 h in a tube annealing furnace to obtain well crystallized seed layers and to ensure the final decomposition of the organic compounds.

ZnO nanorods were grown on the seeded substrates by chemical bath deposition in solution of equal amount of 0.05 M of zinc nitrate ($Zn(NO_3)_2 \cdot 6 H_2O$) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) from Sigma-Aldrich dissolved in deionized water. The growth took place in a common batch reactor for all combinations of the dip-coating steps and the preheating temperatures and in a μ-flow reactor on three times dip-coated substrates. The temperature and time were set to 95 °C and 2 h, respectively in both reactors, the flow rate in the μ-reactor was 2 μl / min. The volume of the μ-reactor made from aluminum was 130 μl and the depth of the reactor was 1 mm. The great advantage of the μ-reactor is the possibility to achieve a temperature and concentration gradient while keeping constant concentration in separated parts of the sample during the whole growth. The growth solution is continuously exchanged and there is no concentration reduction due to the growth material consumption (as it is in a batch reactor). On the other hand, there is a decrease in the concentration along the μ-reactor length (**Figure 1**), which allow us to observe the concentration gradient.

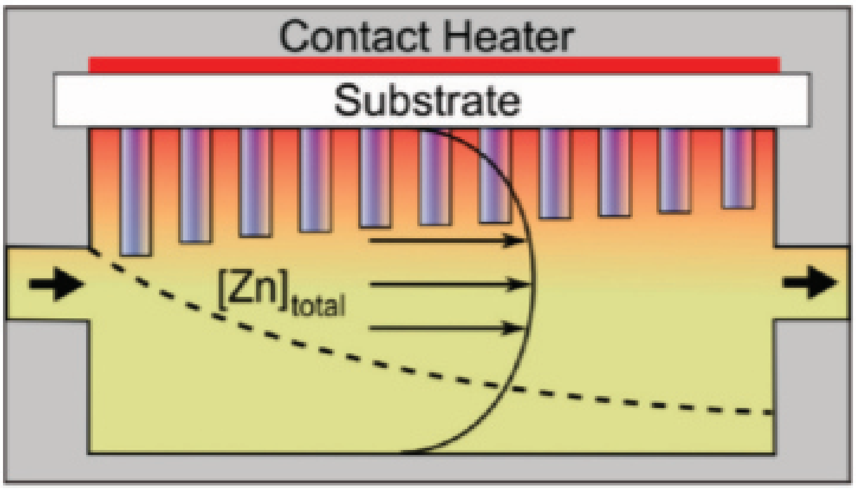

Figure 1 Schematic picture of Zn concentration gradient in the μ-flow reactor decreasing along the reactor length (dashed line) [25]

Morphological properties of ZnO seed layers as well as of the NRs were characterized by scanning electron microscopy (SEM) and by X-Ray diffraction (XRD). SEM images were collected with Tescan Lyra3 GM using the In-beam SE detector. The XRD diffractograms were collected by **XRD - diffractometer PANanalytical X´Pert PRO using the CuKα_1 radiation in range of 30 ° to 80 °.**

3. RESULTS AND DISCUSSION

The changes in morphological properties of the seed layers depend both on the number of dip-coating steps and on the temperature of preheating. **Figures 2a-i** shows representative SEM images of the seed layers with 1, 3, and 5 dip coating steps and preheating temperatures of 300 °C, 350 °C, and 400 °C. The orientation of ZnO NRs depends strongly on the morphology and texture of the seed layers. The nucleation starts preferentially on the polar *c*-axis oriented ZnO nanocrystallites, and thus governs the basis for vertical growth of the ZnO NRs (**Figures 3a-i**). It should be noted that the ZnO NRs are better aligned when the nanocrystallites of the seed layer are smaller, denser, and the porosity of the seed layer is reduced. The diameter of crystallites decreases with increasing temperature of preheating. We assume that higher temperature facilitates the nucleation and leads to higher surface density of smaller nanocrystallites. Greene et al. used thermogravimetry (TG) and differential thermal analysis (DTA) to show that the temperature of approximately 335 °C is necessary for complete evaporation of liquid ZAD [8]. Furthermore, the appearance of exothermic effects at approximately 350 °C could be explained by combustion of residual organics and/or by crystallization of amorphous zinc oxide. Increase of the preheating temperature to 400 °C already leads to appearance of first nanoplatelets as can be observed in **Figure 2**. However, the presence of these nanoplatelets usually disturbs the vertical alignment of subsequently grown ZnO NRs (**Figure 3**).

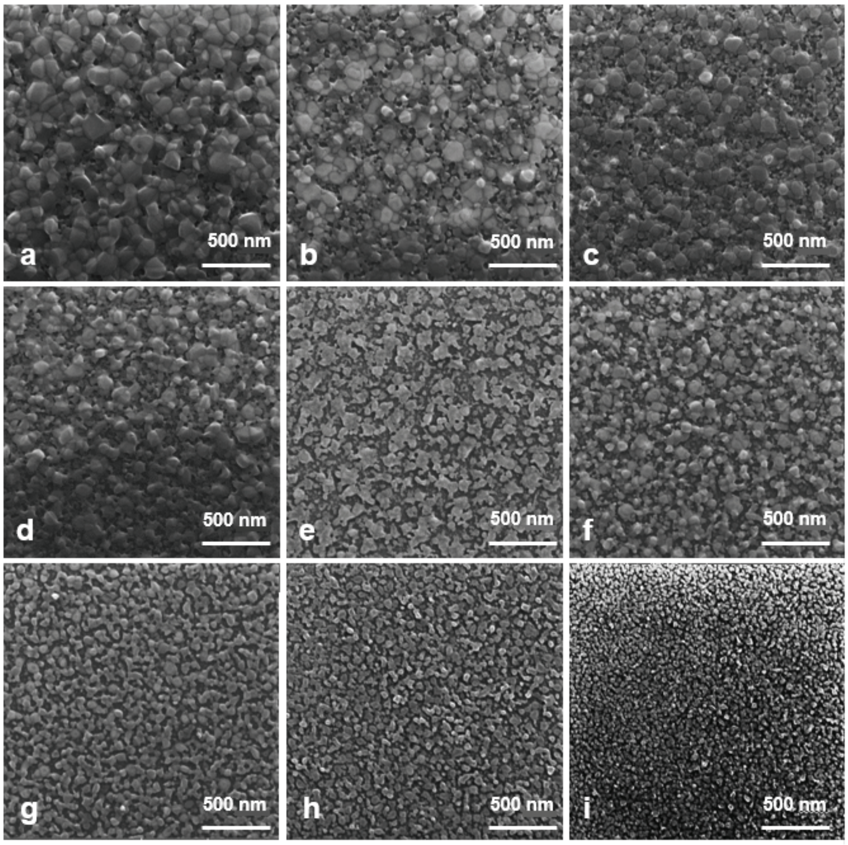

Figure 2 SEM images of the seed layers obtained by applying different preheating temperatures and numbers of dip-coating (DC) cycles: a - 300 °C, 5 DC; b - 350 °C, 5 DC; c - 400 °C, 5 DC; d - 300 °C, 3 DC; e - 350 °C, 3 DC; f - 400 °C, 3 DC; g - 300 °C, 1 DC; h - 350 °C, 1 DC; i - 400 °C, 1 DC.

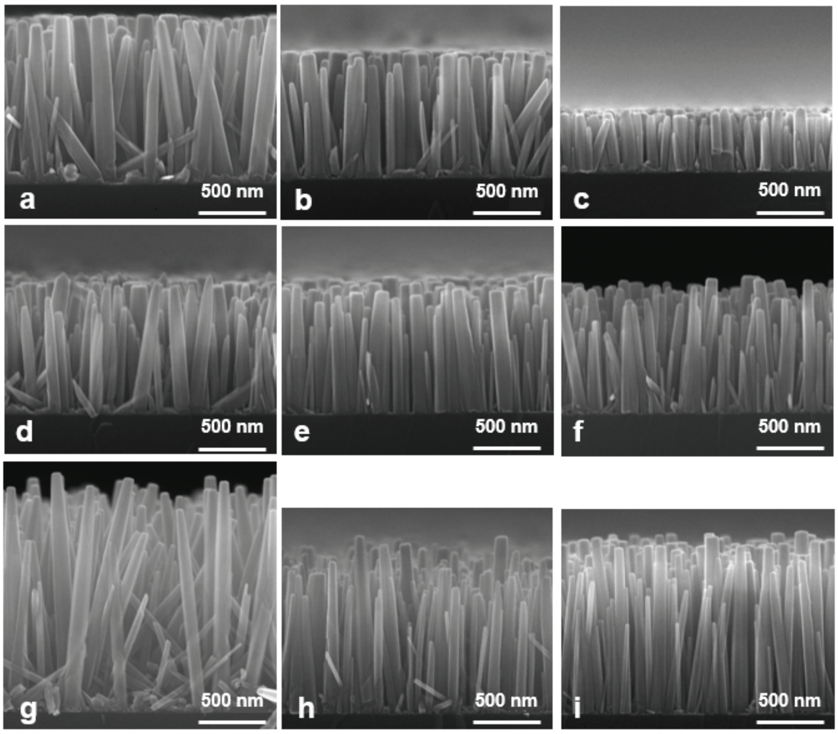

Figure 3 SEM images of CBD grown ZnO NRs on the seed layers from Figure 2. Parameters of seed layers: a - 300 °C, 5 DC; b - 350 °C, 5 DC; c - 400 °C, 5 DC; d - 300 °C, 3 DC; e - 350 °C, 3 DC; f - 400 °C, 3 DC; g - 300 °C, 1 DC; h - 350 °C, 1 DC; i - 400 °C, 1 DC

Zinc oxide NRs grown by CBD deposition in μ-flow reactor under the same conditions as in the batch reactor with the flow speed of 2 μl / min, provided similar results. The concentration in this reactor decreases continuously along its length, which results in different sizes and shapes of the grown NRs. Nevertheless, the tendency for *c*-axis growth remains the same. The best vertical alignment was achieved by the growth on the seed layer preheated to 350 °C (**Figure 4**).

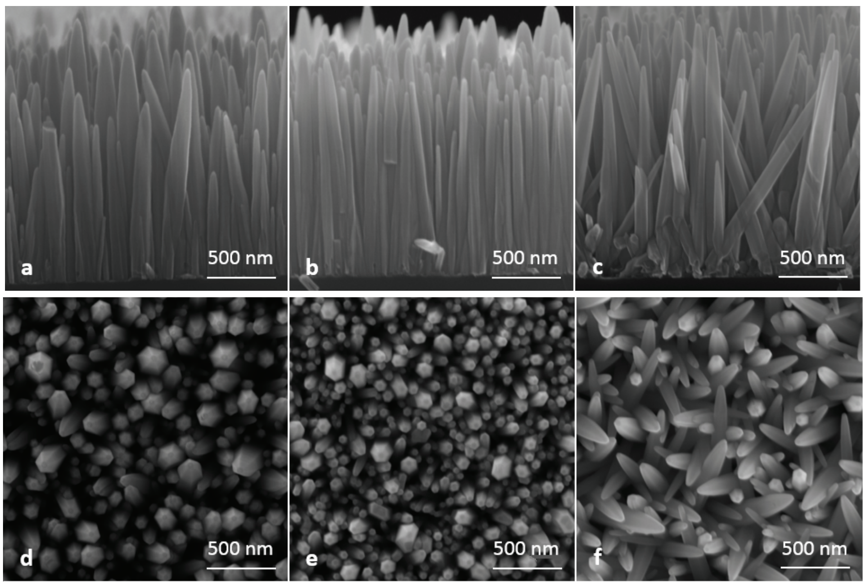

Figure 4 Cross-sectional and top view SEM images of ZnO NRs grown in μ-flow reactor by CBD method on three times dip-coated seed layers with increasing temperature of preheating: a, d - 300 °C; b, e - 350 °C; c, f - 400 °C

The *c*-axis orientation of ZnO nanorods was approved and quantified by the XRD analysis, which gives us detailed view on morphological properties throughout the sample. It was confirmed by the increase of intensity on (002) peak that the orientation in *c*-axis increases with the preheating temperature from 300 °C to 350 °C and 400 °C, respectively (**Figure 5**). The highest value of the intensity and the best alignment in *c*-axis have the samples with the preheating temperature set to 350 °C.

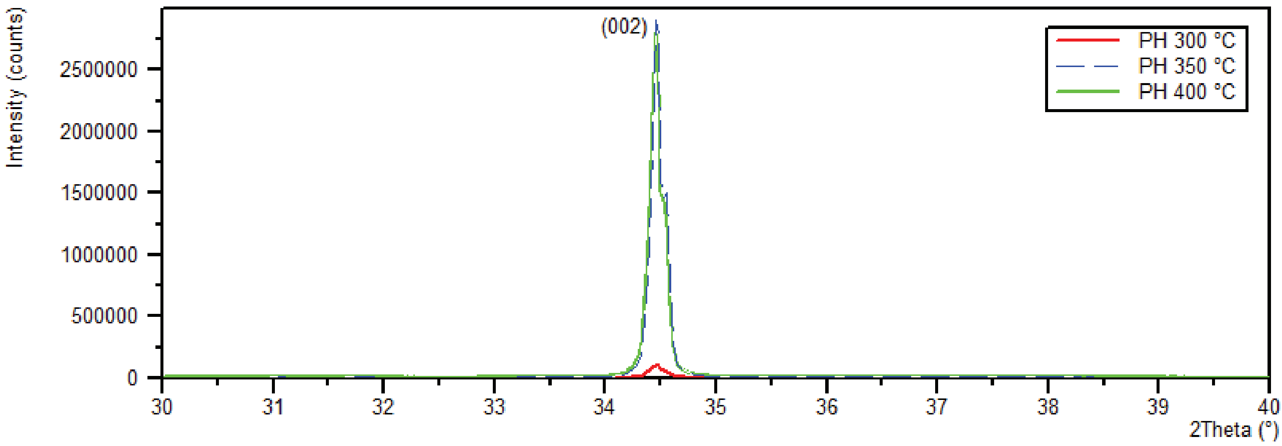

Figure 5 XRD patterns obtained for the samples preheated at 300 °C (red line), at 350 °C (blue dashed line) and at 400 °C (green line). Comparing the intensities of the characteristic peak for ZnO orientation in (002)

4. CONCLUSION

We presented the impact of preheating temperature applied subsequently after dip-coating on the properties of the seed layers and on the growth of ZnO NRs. Three different temperatures of the heat treatment were employed (300 °C, 350 °C, 400 °C) in combination with varying number of dip-coating steps (1, 3, 5 cycles). The results were validated by CBD growth in two reactors, in the batch reactor and in the µ-flow reactor. A conventional temperature of preheating is 300 °C; however, we have realized that the appropriate temperature of preheating is 350 °C. The density of crystallites increases while the surface porosity and the size of crystallites decrease with increasing preheating temperature. When the preheating temperature is too high (above 350 °C), some of the crystallites develop into platelets during annealing in argon at 800 °C and disturb vertical orientation of the ZnO NRs. Our results correspond with the thermal analyses that proved the necessity to increase the preheating temperature above 335 °C [8]. Although, this fact has been known for several years, many procedures of preparation of the seed layer use lower temperatures of preheating. The preheating temperature is a crucial parameter in obtaining well crystallized seed layers and perfectly aligned ZnO nanorods.

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