TEMPERATURE DEPENDENT SEEDING EFFECTS ON HYDROTHERMALLY GROWN ZINC OXIDE NANORODS: TOWARDS LOW TEMPERATURES AND HIGH SCALABILITY

EFECTOS DE LA TEMPERATURA DE SEDIMENTACIÓN EN NANORODS DE ÓXIDO DE ZINC CRECIDOS POR CBD

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Zinc oxide has been widely recognized for its extensive functionality and versatility in electronic and opto-electronic applications [1,2,3]. Recently nanostructured metal oxides have gained increasing interest for use in novel photovoltaic devices, such as dye sensitized (DSSC), organic (OSC) and hybrid solar cells (HSC) [4,5,6]. ZnO, a wide band gap semiconductor, does not contribute to the absorption of light in the solar cell active layer but can be combined with other thin film absorber materials, to form active heterojunctions. In contrast to more conventional homojunction photovoltaic devices, carriers are photogenerated in the absorber and subsequently separated at the extended hybrid interface and finally transported out of the device via the separate material phases. The most commonly investigated form of nanostructure for hybrid solar cells are vertically aligned nanorods [5] which form an ordered, penetrating network with the absorber material, extending from the active layer to the electrode for efficient charge transport and collection. In this study we apply a two-step process to produce ZnO nanorods by chemical bath deposition technique (CBD). The first step, called seeding, refers to the creation, generally by spin coating, of a seed layer for promoting the nucleation on the substrate. We examine the influence of thermal annealing on seeding and in nanorods morphology by varying the seeding temperature from room temperature (RT) to 500ºC. We also investigate the effects of changing deposition cycles [1 – 10], thereby varying seed layer coverage on the substrate.

For the fabrication of ZnO seeds, a 2.5 mM solution of zinc acetate (Merck) in ethanol was prepared following the approach used in [7]. Fig. 1 shows AFM pictures of seed layers formed by spin coating the zinc acetate solution 5 times on top of glass substrates and thermally treating the samples from 250ºC to 500ºC.

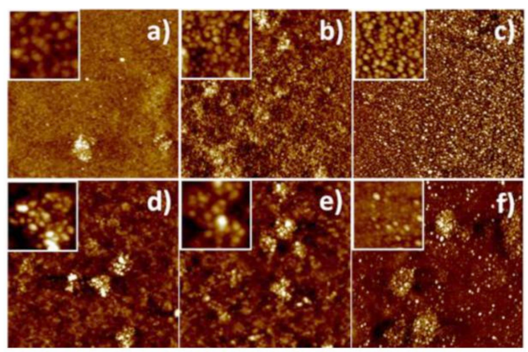

Figure 1. AFM images of seed layers annealed at a) 250°C, b) 300°C, c) 350°C, d) 400°C, e) 450°C and f) 500°C on top of glass substrates. The large images have scan dimensions of 1 µm and the insets have scan dimensions of 125 nm.

Features can be observed on the samples which evolve from homogeneous distributions to large clusters as temperature increases. This demonstrate the coalescence of particles into islands suggesting a thermally activated diffusion and nucleation process. The sample treated at 350ºC shows the most uniform particle size distribution. At higher temperatures the formation of agglomerates can be seen, which may induce disorder for nanorod growth.

SEM images of nanorods grown on prepared seed layers can be observed in Fig. 2.

The nanorods were obtained by placing the seeded substrates in a solution prepared as reported in [8] using a 1:1 ratio of zinc nitrate and hexamethilenetetramine (HMT) as precursors at a temperature of 80°C for 60 min. The nanorods were grown under the same CBD conditions to ensure that only the seeding process influences the morphology. As can be seen in figure 2, varying the annealing temperature of the seed layer does not appear to strongly influence the dimensions of the nanorods, which are roughly 500 nm long and 60 – 90 nm wide, indicating that these are primarily influenced by the CBD parameters. The distribution and relative orientation of the nanorods, however, are observed to depend on the annealing temperature used to prepare the seed layer. The distribution of nanorods on the substrate is found to be most homogenous for seed annealing temperatures between 300°C and 400°C. This correlates with the increased homogeneity of the seed size distribution observed from the AFM measurements at these temperatures (fig. 1). At temperatures above 400 °C we observe clustering of ZnO nanorods surrounded by bare substrate corresponding to the seed agglomerates occurring at higher annealing temperatures.

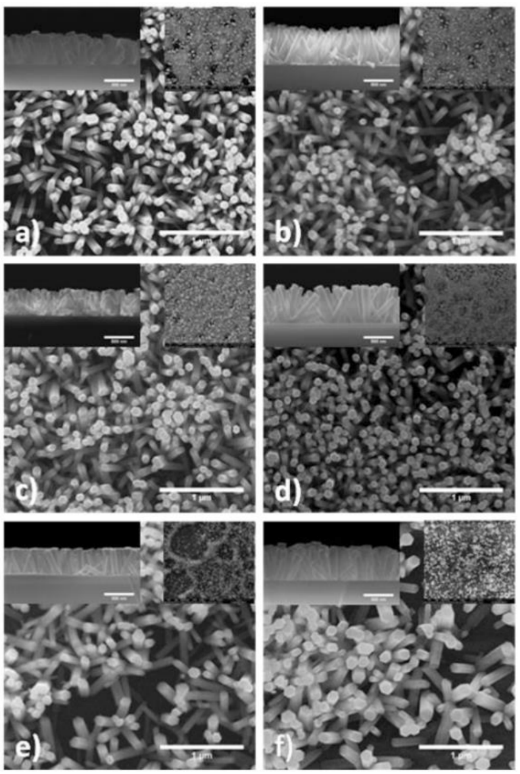

Figure 2: SEM images of ZnO nanorods grown on seed layers on glass annealed at a) 250°C, b) 300 °C, c) 350°C, d) 400°C, e) 450°C and f) 500°C. On the insets transversal and magnified view.

To verify the influence of the seeds on nanorod orientation, we took XRD spectra of the samples. The 002 peak is most prominent for all the samples, and together with the 003 peak is consistent with ZnO nanorods which grow perpendicularly from the substrate along the c-axis. The relative intensity of the 002 peak to other peaks associated with crystal growth along other axes (100, 101) can be used as an indicator for nanorod orientation. These values are summarized in table 1 for nanorods grown on the different seed layers showing that the most highly oriented nanorods are found for seed layers annealed at temperatures around 350°C.

Table I
Relative intensities of the 100 and 101 peaks with respect to 002 peaks for ZnO nanorods grown on seed layers prepared with annealing temperatures between 250°C and 500°C.

Annealing temperature °C	100/002	101/002
250	0.098	0.169
300	0.048	0.136
350	0.039	0.051
400	0.056	0.044
450	0.295	0.074
500	0.077	0.55

From the SEM images of samples grown using multiple deposition cycles of 1x, 5x and 10x (not shown here), it is clear that ZnO nanorods grown on seed layers deposited with a single cycle demonstrate poorer alignment than nanorods produced on seed layers deposited at 5x and 10x. No differences in the dimensions of the nanorods are observed between samples produced on seed layers which were deposited with 5x and 10x cycles.

We investigated the influence of temperature and deposition cycles on the seeding process for producing CBD grown ZnO nanorod arrays. We correlate seed sizes and distribution with the morphology of the resulting ZnO nanorod arrays. We varied the annealing temperature of the seed layer between 250°C and 500°C and found that annealing temperatures around 350°C result in the most highly oriented nanorods on glass substrates.

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