The Effect of a Sputtered Al-Doped ZnO Seed Layer on the Morphological, Structural and Optical Properties of Electrochemically Grown ZnO Nanorod Arrays

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The effect of both a RF sputtered Al-doped ZnO (AZO) thin film seed layer onto a FTO/glass substrate and its growth time onto the morphological, structural and optical properties of the resulting electrochemically grown ZnO nanorod arrays (NRAs) have been studied. ZnO NRAs grown onto the different AZO seed layers exhibit smaller mean diameter and length than those grown onto a bare FTO/glass substrate, but ZnO NR density presents an opposite behavior. By using an AZO seed layer ZnO nanorod density can be increased by a factor of six. ZnO nanorods are highly crystalline with a wurtzite hexagonal structure and with a preferential growth perpendicular to the substrate. The c-axis of most of the ZnO NRs grown onto an AZO seed layer is aligned within ±6° from the substrate surface normal. Both NRAs mean length and density increases light scattering, without greatly affecting the spectra shape. The diffuse reflectance intensity is more sensitive to NR density variations than to length or diameter variations. NR diameter affects directly the shape of these diffuse reflectance spectra: they red-shifts and broadens when NR mean diameter increases. A small influence in the UV edge due to size quantization may also be present.

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In recent years, ZnO, a wide bandgap semiconductor with a direct bandgap of about 3.37 eV and high exciton binding energy (60 meV) at room temperature, has attracted increasing interest due to its unique ability to form a variety of nanostructures such as nanowires, nanorods, nanobelts, nanocombs, nanospheres, nano-tetrapods. Among them, the most interesting are nanorods and nanorod arrays (NRAs) vertically aligned with respect to the substrate. These ZnO nanostructures present a pseudo-one dimensional (1D) structure with an enhanced surface-to-volume ratio and confinement effects. ZnO nanorods exhibit fewer defects than its thin-film structure, it is, therefore, a promising material for optoelectronic applications. In fact, recently, single crystal ZnO nanowire and nanorod arrays have emerged as promising building blocks for a new generation of devices in different hi-tech domains such as optoelectronics, gas sensing, field emission, piezoelectrics and solar cells.

In particular, ZnO one dimensional nanostructures are good candidates for photovoltaic applications for three straightforward reasons: i) they have a low reflectivity that enhances the light absorption; ii) relatively high surface to volume ratio that enables interfacial charge separation and iii) fast electron transport along the crystalline 1D nanostructures that improves the charge collection efficiency. In fact, ZnO arrays of 1D nanostructures, such as nanowires and nanotubes, have been widely utilized as they provide a direct conduction pathway for the rapid collection of the photogenerated electrons, reducing the non-radiative recombination and carrier scattering loss dramatically, and providing as well a high junction area. Moreover, electron transport in the crystalline nanorod is expected to be several orders of magnitude faster than percolation through a random polycrystalline network.

The incorporation of well-aligned ZnO NRAs of high quality is required in practical applications. Moreover, it is important to grow well-aligned ZnO NRAs onto transparent conducting oxides (TCOs, i.e.: ITO and FTO) electrodes for better light management in optoelectronic devices. On the other hand, the physical properties of ZnO NRAs are strongly affected by their morphology in terms of shape, surface density, size and vertical alignment. So, a synthetic process allowing the control of the rod shape, size, orientation, and density is of utmost importance for controlling their properties and performance.

In the last years, ZnO nanorod arrays (NRAs) have been prepared by different growth methods including chemical vapor and metal-organic chemical vapor deposition, vapor-liquid-solid deposition, electron beam evaporation, pulsed laser deposition, spray pyrolysis and electrochemical deposition. Among these methods, the electrochemical deposition (ED) method has many advantages such as low growth temperature, simple and low cost process without the need for vacuum systems for preparing ZnO nanorods with high crystalline quality, well suited for scale-up and good electrical contact between structures and substrate.

Several studies of electrodeposition of ZnO NRAs have been reported in the literature. These studies showed the influence of deposition parameters such as growth temperature, zinc precursor concentration, pH, electrodeposition potential and growth time on controlling nanowire morphology, in particular the nanowire diameter and length (i.e. aspect ratio), and surface density. However, on a bare TCOs surface, the controllable growth of well-aligned ZnO NRAs is somewhat hard and difficult. It is however of great importance to be able to precisely control the morphology and aspect ratio of the as-grown ZnO nanostructures. This is mandatory for the application of NRAs in solar cells and light-emitting devices where a good control of the morphology of the ZnO NRAs is needed in order to optimize light management in the sample. Then, in order to grow ZnO NRAs controllably and reproducibly, different works reported the electrochemical growth of ZnO nanorods onto a previously deposited ZnO seed layer. The reported studied and assayed ZnO seed layers have been grown by different techniques such as electrodeposition, sol-gel, spray-pyrolysis, atomic layer deposition and sputtering. However, in the sputtering case, the influence of the seed layer thickness on nanorod diameter and length, density of NRAs, structural and optical properties of the NRAs, has not been studied.

In the present work, different thicknesses of Al-doped ZnO (AZO) thin films have been prepared by a radio frequency (RF) sputter deposition method and used as seed layers for the growth of ZnO NRAs by an electrochemical method. The effect of the AZO thin film seed
layer onto the morphological, structural and optical properties of the resulting electrochemically grown ZnO NRAs have been studied.

Experimental

**Synthesis of Al-doped ZnO (AZO) thin film seed layer.**—The Al-doped ZnO (AZO) thin film seed layers were grown onto transparent substrates, consisting of glass plates with a conductive thin film of fluorine-doped tin oxide (SnO2:F, FTO) on one side (Nippon Sheets, layer has been grown onto the previously cleaned substrates by radio-frequency (RF) magnetron-sputtering, at 300 °C, for times of 5, 15, 30 and 45 min by using a Magnetron Sputtering System ORION-5-UHV (AJA International). A ZnO with Al2O3 content of 2 wt% (99.9%) ceramic target (AJA International, Inc.) with dimensions 2” diameter×0.125” thickness has been employed. During deposition, the chamber pressure and RF power have been kept at 1.4 Pa and 100 W, respectively.

**Synthesis of ZnO nanorod arrays.**—ZnO nanorod arrays were grown by the electrochemical deposition method from a 1 mM zinc acetate aqueous solution maintained at 70 °C. For supporting electrolyte, 0.1 M sodium acetate was employed to ensure a good electrical conductivity in the aqueous solution (Milli-Q quality water, 18 MΩ cm). The pH of the solution was initially adjusted to 6.76. The ZnO nanorods were grown onto the previously modified AZO seed layer/FTO/glass transparent electrode substrates. The electrodeposition was performed in a conventional three-electrode electrochemical cell with the substrate as the cathode, a zinc sheet as the counter electrode and a saturated calomel electrode (SCE) as the reference one. Electrodeposition was carried out potentiostatically at −1.0 V vs. SCE. The electrolyte was saturated with pure molecular oxygen by bubbling for 45 min prior to start the electrodeposition and continuously during of the growth process. The electrochemical deposition time was 3600 s. After electrodeposition, the ZnO NRAs/ AZO/FTO/glass substrate samples were thoroughly and carefully rinsed with DI water to remove un-reacted products from the surface and dried under a moderate air flux.

**Morphological and structural characterization.**—Field-emission scanning electron microscopy (FE-SEM) pictures of the AZO/FTO/glass substrate seed layers and ZnO NRAs were obtained on a Helios Nanolab 650 Dual Beam from FEI company equipment. These FE-SEM images have been taken under the following conditions: 2 kV and 100 pA, of the operating voltage and current, respectively; and in Mode II: Immersion through lens detector.

The surface morphology of the deposits was examined using an atomic force microscope (AFM). Topographic AFM examinations were performed by using a Nanoscope V tapping-mode AFM (Veeco Instruments) employing sharp silicon tips.

The film thicknesses of the AZO seed layers were measured using a Veeco Dektak 150 Profiler equipment. It is a thin and thick film step height measurement tool capable of measuring steps below 10 nm. The system provides a step-height repeatability of 0.6 nm. The average roughness (Ra) (i.e.: the arithmetic average deviation from the mean line within the assessment length), has also been provided by the same equipment.

**Structural characterization of the AZO seed layers.**—In previous research reports, it has been found that the characteristics of ZnO NRAs strongly depend on the surface roughness, thickness and crystallinity of the ZnO seed layer.38,39 So, in the present work a study of the different AZO seed layers has been carried out.

The thickness of the AZO seed layer was controlled with the RF sputter deposition time (tSL), and its value has been determined by using a stylus profilometer. Moreover, the average roughness of the AZO seed layers has been obtained from these profiles. The obtained values of thickness and average roughness for the different AZO seed layers are listed in Table I.

First, the morphological properties of the different AZO thin film seed layers grown onto the FTO/glass substrates have been characterized by both FE-SEM and AFM images. FE-SEM micrographs have been used to evaluate the deposition homogeneity on the substrate and to have a first estimation of the film roughness. Figure 1 shows plan view FE-SEM images of different AZO seed layers grown onto FTO/glass substrates as a function of the seed layer growth time (tSL). The surface morphology of the FTO (tSL = 0 min) is also shown for comparison. It can be seen that as the seed layer growth time is increased, the whole FTO substrate is gradually covered in a uniform way by the AZO seed layer. Furthermore, AFM analysis has been limited to smaller areas, randomly chosen on the substrates, for a better morphological characterization of the AZO seed layers and quantification of AZO thin film grain size. Figure 2 shows AFM

**Results and Discussion**

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| Table I. Typical morphological surface properties of the different AZO seed layers grown onto the FTO/glass substrates. |
|-----------------|-----------------|-----------------|
| Seed layer growth time (min) | Thickness of the AZO seed layer (nm) | Average Roughness (Ra) of the AZO seed layer (nm) |
| 0 | 0 | 6.1 ± 0.9 |
| 5 | 61 ± 5 | 6.1 ± 0.8 |
| 15 | 58 ± 5 | 6.5 ± 1.0 |
| 30 | 113 ± 4 | 5.6 ± 0.6 |
| 45 | 133 ± 6 | 5.8 ± 0.7 |

Grazing Incidence: 20 scan at fixed oo. Parabolic Mirror (W/Si multilayer) Parallel beam (equatorial divergence = 0.04°). Divergence Slit: 1/16” (equatorial) (determine beam cross section in X direction). Axial Mask: 10 mm (beam size on sample ~17 mm in Y direction). Soller Slit: 0.04 radians (axial divergence = 2.29°). Secondary Optics (diffracted beam): Parallel Plate Collimator (opening = 0.27”). Detector (Mode): PIXcel 0D Mode: Receiving Slit (punctual) Active Length = 14.025 mm. Grazing Incidence measurements: angle of incidence oo = 0.15, 0.30; 20 scans from 10 to 85°, step 0.05°, 3 seconds/step (1/minute). The surface structural characterization of the ZnO NRAs was carried through X-ray diffraction (XRD) measurements. Pole figures were obtained, with the same radiation wavelength, on a Philips X’Pert multiple-purpose diffraction (MRD) goniometer.

**Optical characterization.**—The optical properties of the ZnO NRAs were studied by visible Transmittance and Reflectance Spectroscopy. For Reflectance measurements an integrating sphere Ocean Optics (OO) ISP-REF was used, a tungsten lamp (attached to the sphere) was used as the source excitation. The Diffuse Reflectance (DR) Spectra was measured using its attached light trap to remove the specular reflected beam. A Spectralon Reflectance Standart (OO WS-1-SL) was used. For Total Transmittance (TT) measurements a second integrating sphere (OO FOIS-1) was used to couple both the direct and diffuse component of the transmitted light through the ZnO NRAs. Both signals were analyzed by a Spectrometer (OO S2000) coupled with the sphere by a 50 μm optical fiber. All the measurements were performed at room temperature.
Figure 1. FE-SEM plan-view micrograph images of: (a) naked FTO substrate; and AZO thin film seed layers grown onto an FTO substrate obtained at different growth times: (b) $t_{SL} = 15$ min, (c) $t_{SL} = 30$ min and (d) $t_{SL} = 45$ min.

images of the FTO and AZO thin film surfaces for four different seed layer growth times ($t_{SL} = 5, 15, 30$ and $45$ min). The bare FTO substrate exhibits a very rough surface which looks like wedges and with polyhedral pyramidal grains with very marked sharp edges. After $5$ min of deposition ($t_{SL} = 5$ min), the FTO grains have been covered in a conformal way by a very thin AZO seed layer. In fact, now the FTO grain edges have been rounded by the presence of the AZO thin layer. However, the AFM image shows that the surface roughness is still high (very similar to the bare FTO substrate, see Table I). As the seed layer growth time further increases, $t_{SL} = 15$ min, the thickness of the AZO thin film increased, but still the shapes of the FTO grains can be distinguished underneath the seed layer. Moreover, a granular structure can be distinguished, which can explain the increase of surface roughness (see Table I). For a $t_{SL} = 30$ min, the shape of the FTO nanocrystals disappear under the thicker AZO layer, and the granular structure is also evident. Finally, for long deposition times, $t_{SL} = 45$ min, the seed layer is polycrystalline and composed of ZnO nanoparticles with a spherical cap like shape, as shown in Fig. 2e. A mean ZnO nanoparticle size of 60–70 nm can be estimated.

It must be pointed out that for clearness, in some parts of the paper, discussion will be given as a function of the seed layer growth time ($t_{SL}$) instead of the AZO film thickness.

Morphological properties of the ZnO nanorod arrays and structural characterization of single ZnO nanorods.—Figure 3 shows FE-SEM micrograph images of the ZnO NRAs obtained by electrodeposition on a naked FTO/glass substrate, and onto different AZO thin film seed layers grown with different growth times ($t_{SL}$) onto an FTO/glass substrate as indicated. Figure 3a shows a typical FE-SEM micrograph of ZnO nanorod arrays electrochemically grown onto a bare FTO/glass substrate. It can be appreciated that all of them show hexagonal cross section and hexagonal faceted and smooth surfaces (which arises due to their wurtzite structure),\textsuperscript{24,40,41} and exhibit planar

Figure 2. AFM images of: (a) bare FTO substrate; and AZO seed layers grown onto an FTO/glass substrate obtained at different growth times: (b) $t_{SL} = 5$ min, (c) $t_{SL} = 15$ min, (d) $t_{SL} = 30$ min and (e) $t_{SL} = 45$ min.
In fact, the nanorods is evident from their faceted crystal habit and from XRD results (vide infra), and confirmed by HRTEM analysis. In fact, the nanorods is evident from their faceted crystal habit and from XRD correction with 0.26 nm (0002) lattice fringe parallel to the basal plane.42

Figure 3. (a) Tilted FE-SEM micrograph view with a tilt angle of 45° of ZnO nanorod arrays electrochemically grown onto a bare FTO/glass substrate. Inset shows a high magnification top view image of a ZnO NRAs revealing hexagonal prism shape of the nanorods with planar top ends. (b) HRTEM micrograph of a single ZnO nanorod grown under same conditions as in (a). Tilted FE-SEM micrograph view with a tilt angle of 45° of ZnO nanorod arrays electrochemically grown onto different AZO thin film seed layers grown onto an FTO substrate obtained at different growth times: (c) tSL = 5 min, (d) tSL = 15 min, (e) tSL = 30 min and (f) tSL = 45 min.

Moreover, Fig. 3 shows that the majority of the nanopillars are vertically oriented to the substrate plane and the axial direction is aligned with the c-axis of the hexagonal ZnO crystal structure. However, ZnO nanorods grown on different seed layers exhibit obvious differences in diameter (D), length (L) and then aspect ratio (AR). The corresponding results are plotted as a function of the AZO seed layer growth time in Fig. 4. The sample without a seed layer was comprised of ZnO nanorods of approximately D = 200 nm. On the other hand, the mean nanorod diameter varied from 50 to 90 nm for arrays deposited onto the different AZO thin film seed layers. Remarkably, and except for the AZO seed layer with a tSL = 5 min (with ZnO NRs exhibiting average length values of 424 nm), the NRs length was found to be almost constant among the AZO seed layers, varying in a range of ca. 540–550 nm. Then, and consequently, the aspect ratio (AR) of the ZnO nanorods varies as a function of the reported NRs diameter and length values. Figure 4 shows that the ZnO NRs aspect ratio exhibits a maximum for an AZO seed layer growth time tSL = 15 min.

In addition to ZnO NRs diameter and length values, the density (N) of ZnO nanorods is another important parameter of the samples. It is well known that N depends on the density of sites energetically favorable for the nucleation of ZnO and on the solution supersaturation before the nucleation process.45 From a statistical analysis, mean values of the nanorod density was estimated, and the obtained values are depicted in the inset of Fig. 5 as a function of the AZO seed layer growth time. An N value of ~5 × 109 cm−2 was obtained for nanorod arrays deposited directly on naked FTO/glass substrates. On the other hand, by using an AZO seed layer the ZnO nanorod density can be increased by a factor of six to ca. 2.5–3.0 × 109 cm−2. These ZnO NR density values are very similar to that reported in literature for electrochemically grown ZnO NRAs.45,46 As can be seen in the inset of Fig. 5 this ZnO NR density does not change significantly with the AZO seed layer growth time, and it remains roughly constant at about this 2.5–3.0 × 109 cm−2 value. Thus, the ZnO NR density increases for all AZO seed layers, in comparison to naked FTO/glass substrate, showing that ZnO nanocrystalline layers provide a higher density of nucleation sites for nanorod growth.45,46 Moreover, the densely packed ZnO nanocrystals of the AZO seed layer act as homoepitaxial nucleation sites.45,46 On the other hand, bare FTO/glass substrate has a high nucleation potential barrier resulting in lower density of nucleation sites.45,46

As in the case of ZnO NRAs fabricated by chemical bath deposition, the ZnO NRAs growth by electrodeposition should be limited...
by the mass transport of the chemical precursors in solution.46 In fact, as being the zinc ion in the electrolytic solution present at very low concentration values (1 mM), electrochemical growth process (at these ED potential values), will be mass transport limited. That is, it is expected that the average diameter and length of ZnO NRs are strongly related to their density (N).46,52 Recently, Boercker et al. have pointed out that these characteristic dimensions should be inversely proportional to their density.52 Figure 5 shows the experimentally determined nanorod diameter and height as a function of nanorod density. As shown, both nanorod diameter and height were found to be proportional to 1/N, in very good agreement with the theoretical modeling. Thus, we conclude that: i) the characteristic dimensions of ZnO NRs such as their average diameter and length are completely driven by their density,46 and ii) the ZnO NR growth process is indeed mass transport limited.52

**Structural characterization of the AZO seed layer and ZnO nanorod arrays.—**In growing one dimensional (1D) semiconductor nanostuctures two key steps that control the quality of the products can be remarked.49 These are: i) nucleation, which initiates the growth of the 1D nanostructures, and ii) the growth, which, in the case of 1D nanostructures it is important to achieve anisotropic growth with good control over size, shape and orientation.51 The different ZnO seed layers not only serve as nucleation sites but also provide a crystallographic growth direction to the resulting ZnO NRs.49 In fact, it is well known that the structural properties of ZnO seed layer have very significant influence on the structural properties of the ZnO NRAs grown onto it.49,53,54 Thus, in order to investigate the effect of seed layer crystallinity on nanorod growth, first a structural characterization of the RF sputtered AZO seed layer has been done. Figure 6 shows typical grazing angle X-ray diffraction (GARXD) patterns of the different AZO seed layers grown onto FTO/glass substrates as a function of the seed layer growth time. The solid line is a guide for the eye. The inset shows the average density of ZnO nanorod arrays as a function of the seed layer growth time. The solid line is a guide for the eye.

**Figure 5.** Average diameter (left axis) and length (right axis) of ZnO nanorod arrays as a function of their density. The solid lines are drawn to aid the eye. The inset shows the average density of ZnO nanorod arrays as a function of the RF sputtered AZO thin film seed layer growth time. The solid line is a guide for the eye.

**Figure 6.** Typical grazing angle X-ray diffraction (GARXD) patterns of the different AZO seed layers grown onto FTO/glass substrates as a function of the seed layer growth time: t_{SL} = 5 min (black line), t_{SL} = 15 min (blue line), t_{SL} = 30 min (green line) and t_{SL} = 45 min (red line). Diffraction planes are indicated for ZnO. The inset shows a plot of the intensity ratio of the (0002) to (1011) diffraction peaks of ZnO as function of the seed layer growth time. The solid line is a guide for the eye.

Al^{3+} ions, the lattice constant is decreased, resulting in a shift toward higher diffraction angles.49,55 This diffraction peak corresponding to the (0002) crystal plane of ZnO appears as the strongest one, revealing the preferred orientation of the film along the c-axis (i.e. the (0002) crystallographic direction) of ZnO crystals. Moreover, it can be seen in Fig. 6 that the (0002) diffraction peak intensity increases as the seed layer growth time (seed layer thickness) increases. In order to characterize the evolution of the (0002) texture in the AZO seed layer, the intensity ratio I_{0002}/I_{1011} as a function of the seed layer growth time has been plotted as an inset in Fig. 6 (vide infra for more details about this working out). It can be seen that the increase of the (0002) texture is nearly linear with the seed layer growth time. This strong texture in [0001] direction will determine the quality of alignment. As a consequence, such a substrate could act further as a suitable platform for the development of orientated ZnO nanostuctures. The c-polar plane chemical reactivity has been found to be favorable for the growth of ZnO NRs in solution, and hence these planes may present preferential surface nucleation sites.56

**Figure 7** shows typical X-ray diffraction patterns of the ZnO NRAs obtained by electrodeposition on a naked FTO/glass substrate and onto different AZO thin film seed layers grown at different growth times (t_{SL}) onto an FTO/glass substrate as indicated, as well as the standard reference powder diffraction pattern for hexagonal ZnO. The X-ray diffraction peaks can be indexed to the hexagonal wurtzite ZnO structure (JCPDS file No. 06-0564), and to the SnO2 phase which comes from the FTO substrate. Seven diffraction peaks corresponding to the (1010), (0002), (1011), (1012), (1120), (1013) and (1122) crystallographic planes of the ZnO hexagonal wurtzite structure, can be clearly identified in X-ray diffraction pattern of ZnO NRAs grown onto a bare FTO/glass substrate. On the other hand, it can be noted the absence of (1010) ZnO diffraction peak in those X-ray diffraction patterns corresponding to ZnO NRAs grown onto the different seed layers under study. The large (0002) ZnO diffraction peak height confirms that ZnO nanorods are highly crystalline with an hexagonal structure and indicates obviously a preferential growth of the ZnO NRs perpendicular to the substrate, as confirmed as well by the FE-SEM images in Fig. 3. In fact, because ZnO nanorods are single crystal and contain the c-axis along their longitudinal axis, the crystallographic orientation degree of the samples may give a measure of the verticality of nanorods.32

Indeed, the intensity of the (0002) Bragg peak would be stronger for narrower angular distributions along the normal to the substrate. In order to characterize the evolution of this (0002) texture, we consider the intensity ratio I_{0002}/I_{1011}.56–58 Here I_{0002} and I_{1011} are the intensities...
of (0002) and (1011) diffraction lines. The ZnO (1011) line has been selected due to the fact that it is the strongest XRD line for standard ZnO powder with no preferred orientation. The value of $I_{0002}/I_{1011}$ from standard ZnO JCPDS values is 0.56. Figure 8 shows the intensity ratio $I_{0002}/I_{1011}$ calculated from the XRD data of electrochemically grown ZnO NRAs depicted in Fig. 7, as function of the seed layer growth time. It can be appreciated that these intensity ratio values are ca. 3.6 to 25 times higher than that of standard ZnO JCPDS one (0.56). These results confirm that the characteristics of the ZnO NRAs are well-shaped c-axis oriented hexagonal columns. Moreover, it can be seen that the degree of c-axis orientation of the electrodeposited ZnO NRAs increases for increasing seed layer growth times, and then saturates for times above 30 minutes, indicating an improvement in the vertical alignment of the ZnO NRs when the seed layer growth time increases. This behavior can be explained taking into account the texture evolution of the AZO seed layer, see inset of Fig. 6. It has been reported that the vertical growth rate of the ZnO NRs has a strong relationship with the [0001] orientation of the ZnO seed layer, and the orientations of the NRs prepared on non-c-axis-oriented ZnO thin films were poor compared to those on c-axis-oriented films. In the present case, an increase of the (0002) texture of the AZO seed layer results in the improvement of the c-axis orientation (i.e.: vertical alignment) of ZnO nanorods as is depicted in the inset of Fig. 8, and can be observed in Fig. 3. Thus, it must be concluded that this c-axis orientation of electrochemically grown ZnO NRAs is governed by the texture of the AZO seed layer, and it is enhanced when the seed layer texture along c-axis is strengthened.

The X-ray pole figures and $\psi$ scans for both families of planes (0002) and (1011) have been performed to characterize and to quantify the tilt angle of ZnO NRs with respect to the normal to the substrate surface. Figure 9 shows typical $\psi$ scans and pole figures (as insets), for the case of an electrochemically grown ZnO NRAs sample (AZO thin film seed layer, tSL = 30 min). X-ray diffraction pole figure measurements, shown in Fig. 9, confirm that the sample consists of quasi vertically aligned ZnO NRs. This is evidenced by the fact that the pole figure recorded for the ZnO (0002) reflection only exhibits a peak located at $\psi = 0^\circ$; meanwhile, the pole figure recorded for the ZnO (1011) reflection only exhibited a ring-distribution at about $\psi = 60^\circ$, corresponding to the angle between the (0002) and (1011) atomic planes in hexagonal wurtzite crystals, without any preferential distribution in the $\varphi$ axis. Moreover, the pole figure in Fig. 9a, for the (0002), corresponds to a narrow distribution. From the $\psi$ scan in Fig. 9a a FWHM of about 12° can be estimated, meaning that the c-axis of most of the ZnO NRs in the sample are aligned within ±6° from the substrate surface normal. The apparent anisotropy of the pole figure in Fig. 9b is due to the rectangular shape of the sample.

**Optical properties of the ZnO nanorod arrays.** The optical properties of ZnO NRAs are strongly influenced by light scattering. The general morphology of the NRAs, i.e. diameter (D), length (L), den-

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**Figure 7.** X-ray diffraction patterns of ZnO nanorod array samples electrochemically grown onto bare FTO/glass substrate, and onto different AZO/FTO/glass substrate thin film seed layers obtained at different growth times $t_{SL}$ as indicated. Diffraction planes are indicated for ZnO. Hexagonal wurtzite ZnO JCPDS pattern is also shown for comparison (ZnO JCPDS: thick black bars). (*, indicates the peaks originated from the SnO$_2$:F substrate).

**Figure 8.** Plot of the intensity ratio of the (0002) to (1011) diffraction peaks of ZnO from their respective XRD patterns of electrochemically grown ZnO NRAs depicted in Fig. 7, as function of the seed layer growth time. Inset shows this intensity ratio $I_{0002}/I_{1011}$ calculated from the XRD data of electrochemically grown ZnO NRAs depicted in Fig. 7, plotted as a function of this intensity ratio $I_{0002}/I_{1011}$ but for the AZO seed layer (see inset of Fig. 6). The solid lines are a guide for the eye.

**Figure 9.** $\psi$ scans and pole figures (insets) for: (a) (0002) and (b) (1011) Bragg reflections of a typical electrochemically grown ZnO NRAs sample (AZO thin film seed layer, tSL = 30 min).
sity (N) and order (or preferential growth direction of the NRAs) are determinant to ensure multiple scattering. The dominant phenomena will depend on the relation between NRAs geometry (D, L) with the wavelength (λ). For samples where λ is approximately equal to the NRAs geometry, the optical properties will be dominated by multiple scattering. Due to this scattering phenomenon, an enhancement in the absorption is observed as a consequence of an increased optical path in the sample. If the NRAs geometry is smaller than λ, then other mechanisms, like effective index of refraction gradient, are dominant. A diminution in the optical transmittance is observed for small diameter ZnO NRAs due to the disordered growth direction of the nanorods compared with the ordered samples. Moreover, multiple scattering shows a dependence on the length of the NR, particularly an increase in the scattering is observed for longer NRAs. Also, the diffuse reflectance spectra show an increment with the length of the NRAs and a red-shift in the peak position with the diameter. Another important parameter is the NRAs density in the samples, as the number of scattering centers depends on the number of NR per surface unity. However, as seen from Figure 5, the NRAs density is not an independent parameter of NR diameter and length. Finally, these multiple scattering phenomena produces the lost of interference effects in the spectra. As the geometry of the NRAs is a key feature in the optical properties of the different samples the following discussion was focused on the main differences in geometry between ZnO NRAs.

In Fig. 10 the visible TT and DR spectra for two selected ZnO NRAs samples are shown. Both spectra show the presence of the optical absorption edge of ZnO located ca. 370 nm (according to a bandgap energy of ca. 3.3 eV). As previously mentioned, the purpose of the optical characterization is to study the dependence of the optical properties with the morphology; therefore the main morphological parameters are reported in figure caption. As either sample have similar NR mean diameter D and density N, the main difference between the observed spectra of Fig. 10 could be caused by the different NR mean length L. It is important to point out that the samples of Fig. 10 do not only have similar N but also similar D. Note that while the changes in D and N are on the order of 15%, the one in L is almost 50%. The sample with the longer NR exhibits the smaller TT. This is in agreement with the enhancement in the scattering with the length of the NR. The small difference in N in the samples of Fig. 10 (higher for the one with shorter NRs) may partially compensate the previously observed tendency.

For further study these dependencies of the optical properties on the morphology and illustrate their combined effects, the DR spectra are also shown on Figures 10, 11 and 12. The DR spectra have a particularly an increase in the scattering is observed for longer NRAs. The dominant phenomena determinant to ensure multiple scattering. The broadening of the DR is roughly the same for both samples and this could be explained because the samples had almost similar D (see below when discussing Fig. 12). The DR have a behavior compatible with that of the TT spectra: the sample with the longer NRs shows the higher DR spectra. Thus, for longer NRs there is an enhancement of the scattering, increasing the diffused light and diminishing the transmittance.

To study the influence of the NR density Fig. 11 shows the DR of two particular samples with the same D, similar L but different N. The DR of the sample with the higher N has the larger DR, in spite of that its length is slightly smaller. Note that the change in L is less than 9% while that in N is about 25%. This can be understood thinking on the number of scattering centers available. With a higher density of NRs, more scattering centers are available, and the scattered light increases. Therefore a higher diffuse reflectance is expected. The inset of Fig. 11 shows the normalized curves of the ones shown in the main Figure 11. Once again (as in Fig. 10) it is seen that the shape of the DR spectra is almost the same for both samples. That means that both the length and density of the NRAs influence the absorption edge, a broad peak located ca. 450 nm for both samples in Fig. 10, and finally a slow decaying slope for longer wavelengths.

Figure 10. Total transmittance spectra (full curves) and diffuse reflectance spectra (dashed curves) for different ZnO NRAs samples with D = 80 nm, L = 520 nm, N = 2.3 × 10^9 cm^−2 (black curves) and D = 70 nm, L = 750 nm, N = 2 × 10^9 cm^−2 (gray curves).

Figure 11. Diffuse reflectance for different ZnO NRAs samples with D = 110 nm, L = 810 nm, N = 1.7 × 10^9 cm^−2 (dotted curve) and D = 110 nm, L = 880 nm, N = 1.3 × 10^9 cm^−2 (short dashed curve). The inset is a zoom of the normalized curves.

Figure 12. Diffuse reflectance for different ZnO NRAs samples with D = 50 nm, L = 420 nm, N = 3.2 × 10^9 cm^−2 (dot - dashed curve), D = 80 nm, L = 520 nm, N = 2.3 × 10^9 cm^−2 (dashed curve, same as in Figure 10), D = 110 nm, L = 880 nm, N = 1.3 × 10^9 cm^−2 (short dashed curve, same as in Figure 11). Upper inset is a zoom of the normalized curves while lower inset is the first derivative of main figure.
amplitude of these spectra but not their shape. As stated before, this shape is more dependent on the NR diameter D. For a clear study of this dependence of the optical properties with the morphology of the NRAs, in Fig. 12 different DR spectra are compared. These data corresponds to three different samples with increasing D and L, and decreasing N (in accordance with Fig. 5). All the spectra exhibit a peak located between 410 nm and 470 nm. That is, on the contrary as in Figures 10 and 11, the shape of the whole spectra changes in Fig. 12. There is a red-shift in the peak position and a broadening of the spectra (see Fig. 12 upper inset, which shows the normalized spectra). The normalization permits the solely study of the broadening and the peak position. These changes might be originated in the diameter variations between NRs. In present samples it goes from 50 nm for dot dashed curve, passing through 80 nm for dashed curve to 110 nm for solid curve, indicating an improvement in the vertical alignment of the ZnO NRs when the seed layer growth time increases. It must be concluded that this c-axis orientation of electrochemically grown ZnO NRAs is governed by the texture of the AZO seed layer, and it is enhanced when the seed layer texture along c-axis is strengthened. From X-ray pole figures it has been demonstrated that typically the c-axis of most of the ZnO NRs grown onto an AZO seed layer in the sample is aligned within ±6° from the substrate surface normal.

The influence of the morphology of the NRAs was clearly observed in their optical properties. In effect, the optical properties of these ZnO NRAs showed a distinctive dependence on the NR diameter, length and density which controls the size and quantity of scattering centers. Both NRs mean length and density increases light scattering, without greatly affecting the shape of the spectra (mainly for diffuse reflectance DR). Particularly, the DR intensity resulted to be more sensitive to NR density variations than to length or diameter variations. On the contrary the NR diameter affects directly the shape of these DR spectra: they red-shifts and broadens when NR mean diameter increases. A small influence in the UV edge due to size quantization may be also present. However a combination of effects is present, due to the correlation of these morphological parameters with the deposition parameters, mainly the seed layer growth time, which effectively controls the morphology of the samples. Moreover, these results indicates that multiple scattering in the NR array is a complex phenomenon where the control of the morphology is a key feature to achieve a good light management in the sample, for example, for an optimum solar spectrum harvesting.

Conclusions

ZnO NRAs have been grown by electrochemical deposition onto FTO/glass substrates with and without a RF sputtered AZO seed layer. The effect of the AZO thin film seed layer and its growth time onto the morphological, structural and optical properties of the resulting electrochemically grown ZnO NRAs have been studied. ZnO NRs with a single crystal wurtzite structure growing along the c-axis direction have been obtained for both FTO/glass and AZO/FTO/glass substrates. The results indicate that the ZnO NRs grown onto the different AZO seed layers exhibit smaller mean diameter and length than those grown onto the FTO/glass substrate, but the ZnO NR density presents an opposite behavior, by using a AZO seed layer the ZnO nanorod density can be increased by a factor of six. As a general rule, the ZnO NRs mean diameter slightly increases as the AZO seed layer growth time increases, but the length and density remain nearly constant. Both nanorod diameter and height have been found to be proportional to 1/N, in very good agreement with a growth process mass transport limited. From XRD study the large (0002) ZnO diffraction peak height confirms that ZnO nanorods are highly crystalline with an hexagonal structure and indicates obviously a preferential growth of the ZnO NRs perpendicular to the substrate. The degree of c-axis orientation of the electrodeposited ZnO NRAs increases for increasing seed layer growth times, and then saturates for times above 30 minutes, indicating an improvement in the vertical alignment of the ZnO NRs when the seed layer growth time increases. It must be concluded that this c-axis orientation of electrochemically grown ZnO NRAs is governed by the texture of the AZO seed layer, and it is enhanced when the seed layer texture along c-axis is strengthened. From X-ray pole figures it has been demonstrated that typically the c-axis of most of the ZnO NRs grown onto an AZO seed layer in the sample is aligned within ±6° from the substrate surface normal.

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