XPS study of ZnO nanostructures prepared by laser ablation

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Abstract. The subject of the present work is different types of nanostructured ZnO films produced by pulsed laser deposition. The influence was investigated of the surface morphology on the physicochemical and optical properties of the nanostructured films. X-ray photoelectron spectroscopy was used to study the composition and chemical state of the nanostructured ZnO. The changes occurring on the surface of the films after prolonged exposure in air are considered in the light of practical applications of ZnO films. The change in the number of adsorbed species on the surface with the time affects the surface conductivity, the latter in turn modifying the optical properties of the samples.

1. Introduction

In recent years, the synthesis and modification of nanosized ZnO have been the object of comprehensive studies due to the wide range of possible applications in gas sensors, photocatalysts, chemical absorbents, solar cells, electrical and optical devices. However, in the case of nanostructured materials, undesired effects could be expected due to surface inhomogeneities, such as non-stoichiometry or selective adsorption of foreign species, in addition to the abrupt termination of the lattice periodicity. ZnO is known to adsorb readily atoms and, particularly, oxygen-containing species [1-3], which affect the surface conductivity of the nanostructures. The recent study of Yang et al. [4] indicated that the presence of OH⁻ and H⁻ species play a dominant role in facilitating surface recombination. Also, Bai et al. reported that a cover of hydroxyl groups on the surface of ZnO can inhibit the adsorption of ethanol [5], thus affecting the sensing properties. Besides, the possibility of interaction between chemical groups on the ZnO surface and the molecules that are to be detected can also influence the performance of a ZnO sensor. Our previous investigations showed that the gas sensing properties of the as-prepared sensor element may differ from those after a prolonged period of time. Therefore, investigating the influence of the adsorbed hydroxyl groups on the electronic and physical properties is necessary in view of the practical applications of ZnO nanostructures.

In the present work, the surface morphology and the electronic and optical properties of different types of ZnO nanostructured films were studied with the aim of monitoring the changes in the surface
composition, electronic configuration and optical properties after a prolonged exposure in air, depending on the nanostructure of the ZnO layers.

2. Experimental

Thin ZnO films were prepared on amorphous SiO₂ substrates by pulsed laser deposition (PLD). The third harmonic of a Nd:YAG laser (λ = 355 nm, τ = 18 ns full-width at half-maximum (FWHM), and repetition rate of 10 Hz) was used for ablation of a ZnO ceramic target. The target-to-substrate distance was fixed at 40 mm in a standard on-axis configuration. All experiments were performed in oxygen atmosphere. The substrate temperature was kept at 300 °C during deposition.

The nanostructured films were fabricated via a two step process [6,7]. As a first step, a thin ZnO film was prepared at high oxygen pressure in order to form growth nuclei. Oxygen pressures of 20, 50, and 100 Pa were used for preparation of three different types of nuclei. The laser fluence was kept constant at 2 J/cm². The second step consisted in the deposition of a ZnO film on the as-created nuclei. At this stage, the oxygen pressure was decreased to 5 Pa and kept constant to the end of the experiment. During the second step, laser fluence of 3.5 J/cm² was used.

The surface morphology of the samples was characterized by atomic force microscopy (AFM) using an Agilent 5500 microscope. The film composition and electronic structure were investigated by X-ray photoelectron spectroscopy (XPS). The measurements were performed on a VG ESCALAB II system using MgKα radiation with energy of 1253.6 eV. The binding energies (BE) were determined with an accuracy of ± 0.1 eV utilizing the C 1s line at 285.0 eV (from adventitious carbon) as a reference. The optical transmission spectra were obtained by illuminating the samples by a white-light source - halogen and Xe lamps. The light transmitted through the samples was detected by an HR 4000 Ocean Optics Spectrometer with optical resolution of 0.02 nm.

3. Results and discussion

3.1. AFM studies

The AFM images of the as-deposited ZnO nanostructured films are presented in figure 1.

![AFM images](image)

Figure 1. AFM images of ZnO nanostructured films prepared on the basis of different nuclei obtained at: (a) 20 Pa, (b) 50 Pa, and (c) 100 Pa oxygen pressure.

The surface morphology of the sample in figure 1a shows grains with clearly expressed spherical shape and mean grain-size in the range 60 - 110 nm. The grains are packed closely and are well distributed on the substrate with RMS surface roughness of about 10 nm. The scale bar in the AFM image (figure 1a) indicates a high peak-to-valley ratio. It is worth pointing out that the ZnO buffer layer deposited at 20 Pa oxygen pressure has the crystal structure as reported in our previous investigations [8]. The growth of the ZnO nanostructure follows the crystal nuclei.
The surface morphology of the sample prepared by a ZnO buffer layer deposited at 50 Pa is presented in figure 1b. The increase of the oxygen pressure applied during the buffer layer deposition leads to a change of the surface morphology, namely, a non-uniform structure with a larger grain-size in the range of 100–200 nm, in contrast with the sample shown in figure 1a. Additionally, the increase of the oxygen pressure worsens the crystal structure of the buffer layer. The further increase of the oxygen pressure applied during the buffer layer deposition (100 Pa) preserves the non-uniform structure of the surface morphology (figure 1c). In this case, the sample grain-size is ranging from 100 to 200 nm. Furthermore, at this high oxygen pressure the as-prepared buffer layer is practically amorphous. Again, one should point out that the difference in the surface morphology appears mainly between the film prepared on the basis of growth nuclei produced at 20 Pa (figure 1a) and samples prepared with growth nuclei obtained at higher oxygen pressures (figure 1b and c).

3.2. XPS studies

The composition and chemical state of the nanostructured film surfaces were studied by XPS. The asymmetric peak observed in the O1s region for all as-prepared samples (not shown) is resolved into two peaks by a Lorentzian - Gaussian spectral fitting. The peak with low binding energy (530.2 eV) corresponds to O\(^{2-}\) ions in a normal ZnO wurtzite structure, while the second one centered at 531.7 eV may be attributed to different kinds of species, such as adsorbed hydroxyl or/and carbonyl groups [9,10]. Also, some contribution to this peak may originate from O\(^{2-}\) ions in the oxygen deficient regions within the ZnO matrix [11]. However, it should be mentioned that the fitting of the O1s peak in the present study is in close agreement with that for a nanostructured ZnO film on a silica substrate [12], where the actual oxide stoichiometry is given as ZnO\(_x\)(OH)\(_y\).

Further on, we followed the changes in the intensity of the oxygen peak at 531.7 eV depending on the time of exposure in air. The XPS data are presented in table 1. Variation should not be expected in the oxygen vacancies concentration on the surface of the ZnO nanoparticles during a prolonged exposure. Therefore, the changes in the intensity of this peak are mainly related to variation in the concentration of the adsorbed oxygen containing species, most probably OH\(^{-}\) groups. In addition, the atomic ratio of crystal lattice oxygen to zinc on the surface of the distinct oxide nanostructures is lower than the stoichiometric value of 1.0. It is evident that there is pronounced oxygen deficiency in the films. This fact indicates that there are large concentrations of vacancies and unsaturated chemical bonds that can interact with other atoms.

| Samples with growth nuclei prepared at: | Exposure [days] | O\(_{\text{lat}}\)/Zn | O\(_{\text{OH}}\)/O\(_{\text{total}}\) | \(\dot{\alpha}\) [eV] |
|----------------------------------------|-----------------|-----------------|--------------------------|-----------------|
| 20 Pa O\(_2\)                          | as-dep          | 0.57            | 0.29                     | 2010.6          |
|                                        | 7               | 0.63            | 0.32                     | 2010.4          |
|                                        | 21              | 0.63            | 0.44                     | 2010.8          |
|                                        | 42              | 0.59            | 0.46                     | 2010.9          |
| 50 Pa O\(_2\)                          | as-dep          | 0.62            | 0.34                     | 2010.9          |
|                                        | 7               | 0.68            | 0.29                     | 2010.7          |
|                                        | 21              | 0.72            | 0.40                     | 2011.1          |
|                                        | 42              | 0.66            | 0.41                     | 2010.9          |
| 100 Pa O\(_2\)                         | as-dep          | 0.61            | 0.30                     | 2010.8          |
|                                        | 7               | 0.63            | 0.28                     | 2010.6          |
|                                        | 21              | 0.69            | 0.36                     | 2011.1          |
|                                        | 42              | 0.70            | 0.40                     | 2011.0          |
The chemical state of Zn in the ZnO thin film was analyzed in detail by investigating the Zn 2p core level and Auger Zn LMM peaks. These peaks show irregular shifts whose origin is associated with the electrostatic charging of the film surfaces during the acquisition of the spectra. In order to avoid these discrepancies, we used the modified Auger parameter $\alpha$ for more exact determination of the chemical state of Zn, thus eliminating the surface effects of the electrostatic charging. This parameter is defined as $\alpha = KE(\text{Zn } L_3M_{4,5}M_{4,5}) + BE(\text{Zn 2p}_{3/2})$, where $KE(\text{Zn } L_3M_{4,5}M_{4,5})$ is the kinetic energy of the Auger transition and $BE(\text{Zn 2p}_{3/2})$ is the binding energy of an electron in the core level [13].

The values presented in table 1 for the Auger parameter are in the range 2010.4 – 2011.1 eV. It is known that the $\alpha$ values located at 2010 and 2014 eV are characteristic of the oxidation state Zn$^{2+}$ and metallic state Zn$^0$, respectively [14,15]. Our values are consistent with the existence of Zn$^{2+}$, but the positive shift observed as the air exposure is increased is explained by charge transfer during the continuous adsorption of oxygenated species on the surface of the oxide nanostructures.

Table 1 also shows the values for the $O_{\text{OH}}/O_{\text{total}}$ intensity ratio depending on the time of air exposure. This dependence of the $O_{\text{OH}}/O_{\text{total}}$ intensity ratio is plotted in figure 2a for the three nanostructured films prepared on the basis of different nuclei. Clearly, the intensity ratio tends to saturate at prolonged exposure, suggesting that the chemical adsorption of the surface of the ZnO films is nearly saturated.

According to theoretical predictions, surface defects, such as oxygen vacancies, can dominate the electronic/chemical properties and adsorption behavior of metal oxide surfaces [16]. The film formed at the lowest oxygen pressure during the growth of nuclei exhibits the fastest increase compared with the films formed at higher oxygen pressures, indicating that more oxygen vacancies exist in the surface layers of the film.

The adsorption behavior of the films is compared with the variation of the modified Auger parameter in figure 2b. The Auger parameter has been recognized as a very powerful tool in acquiring information on the electronic interactions and the polarizability of the medium around the photoemitting atom [17]. In this plot, the film formed with growth nuclei at 20 Pa shows a lower degree of increase of the Auger parameter than the ones formed at higher oxygen pressures. As mentioned above, adsorption occurs at vacancy defect sites on the oxide surface. Charge transfer takes place, resulting in a change of the surface conductivity with the absorbed species gaining a negative charge; this causes the formation of a depletion layer on the surface of the n-type ZnO. The formation of this layer affects the photoemission process by increasing the relaxation energy, which leads to an increase of the Auger parameter values for the three samples in figure 2b. Thus, the variation of the Auger parameter reflects the variation of the surface conductivity as a result of increased number of...
adsorbed species. The nanostructured film with the highest number of oxygen vacancies exhibits the lowest conductivity change.

3.3. Optical studies
The optical transmission of the samples was measured during air exposure in order to investigate how the surface composition affects the optical properties of the samples. We followed the behavior of one fixed maximum in the transmission spectra as a function of the time of exposure in air; its shift is presented in figure 3. The shift in the maximum's position means that the optical density of the samples has changed [18]. Assuming that the samples thickness remains constant during exposure, this shift is probably due to the change in the refractive index of the samples. It should be mentioned that for all samples the behavior of the optical maximum shift follows the behavior of the $O_{\text{OH}}/O_{\text{total}}$ intensity ratio, presented in figure 2a. The change of the surface conductivity of the samples results in a variation of the optical properties, as it was previously reported [19]. The least change of the surface conductivity provokes the smallest shift in the maximum position.

Conclusions
We showed that the physicochemical properties of ZnO nanostructured films depend on the initial stages of growth. The analysis of the XPS data demonstrates that the amount of surface oxygen vacancies decreases with the increase of the oxygen pressure used for preparation of the initial growth nuclei. As the grain size of the zinc oxide films increases, their adsorption capability with respect to the hydroxyl groups is reduced. The changes in the intensity of the oxygen peak in the surface composition of the samples were observed depending on the time of exposure in air. The intensity ratio $O_{\text{OH}}/O_{\text{total}}$ tends to saturate at a prolonged exposure, suggesting that the chemical adsorption of the surface of the ZnO films is approximately saturated. The change of the number of adsorbed species on the surface during the exposure leads to a variation of the surface conductivity which affects the optical properties of the samples.

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