Surface characterization of ZnO transparent thin films

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Abstract. Zinc oxide transparent thin films (ZnO) with different thickness were prepared by dc magnetron sputtering and pulsed laser deposition (PLD) techniques using metallic and ceramic targets onto silicon and Corning glass substrates. Structural investigations carried out by Optical Microscopy (OM), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) have shown a strong influence of the target and deposition technique on the film surface topography. Film roughness (RMS), grain shape and dimensions were found to correlate with the applied deposition technique. On the films grown by PLD high oriented nanostructures were identified and XRD measurements proved that they have a polycrystalline structure following the characteristic zincite XRD spectrum, while the dc magnetron sputtered films were amorphous. Results revealed also that the target composition has a radical effect on film characteristics. In the case of thin films sputtered from a ceramic target AFM analysis has shown the presence of hexagonal shaped grains exhibiting a different surface behavior compared with the films grown from metallic target, the first being also the case of the PLD grown film surfaces. This work indicates that the film surface characteristics are strongly influenced by the deposition technique and conditions applied, thus providing a tool for the enhancement of the film sensing capabilities.

1.Introduction
ZnO is a very interesting material for many different applications in both microelectronic and optoelectronic devices. It is a wide-bandgap oxide semiconductor with a direct energy gap of about 3.37 eV. As a consequence, ZnO absorbs UV radiation due to band-to-band transitions [1], while it can be used as transparent electrode in solar cells and flat panel displays as well as for the fabrication of gratings in optoelectronic devices, window in antireflection coatings and optical filters. Furthermore ZnO is used as semiconducting gas sensor [2] due to its conductivity changes when exposed to oxidizing gases such as ozone. Many deposition techniques [2,3] have been applied for the production of ZnO in order to improve the properties of the films. Sputtering and PLD techniques are preferred among these techniques due to their high deposition rates, good film properties and process stability [1,2]. Due to the interest related to the specific properties of these transparent metal oxide thin films, recent studies are focused in the correlation of surface and interface topography with deposition parameters and physical properties [4]. In the present work, we report on the dependence of ZnO films...
surface topography, upon technique and target properties as applied in the case of dc magnetron sputtering and PLD preparation methods.

2. Experiment
The deposition of the ZnO films was carried out first in an Alcatel dc magnetron sputtering system using either 99.999% pure metallic target or a ZnO sintered ceramic target and secondly in a typical homemade PLD deposition chamber [1], using XeCl Excimer Laser 308 nm wavelength, in oxygen atmosphere. The base pressure in the dc magnetron sputtering chamber was about 5×10⁻⁷ mbar.

The films were deposited onto silicon and Corning 1737F glass substrates in an oxygen-argon atmosphere. The surface morphology (grain size and surface roughness) was measured with a Nanoscope III atomic force microscope (Digital Co. Instruments, USA) using a normal silicon nitride tip (125µm) in Tapping Mode scanning the surface with an oscillating tip to its resonant frequency (200-400 kHz). All measurements were made at room temperature (RT). In the present study the RMS roughness of the surface is defined as: \[ \text{RMS(nm)} = \sqrt{\frac{\sum (z_i - z_{ave})^2}{N}} \]

Grain radius and features dimensions were evaluated using the Cross Section Analysis Menu facilities of NanoScope III Program. Optical microscopy characterization was done with a Leica Optical Microscope using reflection mode and different magnifications. SEM characterization was made using a JEOL 840 SEM System. X-ray diffraction (XRD) using a Rigaku diffractometer with CuKα X-rays was applied in order to determine the crystal structure of the deposited films.

3. Results and Conclusions
The dc magnetron deposition constant parameters for both types of targets were the total pressure (8x10⁻³ mbar), the substrate temperature 27°C, and the film thickness ~100nm. In the case of metallic target, the depositions were done for two different plasma current settings (I₁=0.44A and I₂=0.25A) at different Ar/O₂ concentrations. The XRD measurements revealed that all the dc sputtered films (sputtered both from the metallic or ceramic target) show a preferred growth orientation along c-axis, i.e. (002) plane, which is perpendicular to the substrate (figure 1).

![Figure 1. The XRD spectra for ZnO films from a) metallic, b) ceramic targets](image)

AFM characterization of the film surfaces revealed that grain size seems to increase as the argon partial pressure increases for both I₁ and I₂. The roughness was found to increase in both plasma current sets I₁ and I₂. For high plasma current I₁=0.44A, grain radius increases from ~24 nm to ~31 nm as Ar partial pressure increases, and the surface roughness varies from ~1.33nm to ~3.43nm. For low plasma current I₂=0.25A, grain radius increases with Ar partial pressure from ~23nm to ~36nm, and the surface roughness varies from ~1.74nm to ~5.24nm. In both cases the films grown in 100% O₂ atmosphere show higher grain radius and roughness. The typical surface of thin films ZnO growth from metallic target is shown in figure 2.
In the case of ceramic target, the depositions were done for two different plasma current settings ($I_1=0.44A$ and $I_2=0.25A$) and different Ar concentrations in the deposition atmosphere. The characteristic of these films is the presence of grains of different dimensions with a strong tendency to form agglomerations as it is shown figure 3. The grain radius on these surfaces is varying from 10 to 80 nm. The height of the grains shows a slow increase when Ar concentration decreases, fact, which can be correlated with the effect of high-energy Ar$^+$ atoms bombardment. This is also reflected in the RMS variations from 4.48 nm for 100% Ar atmosphere to 1.40 nm at 80% Ar/20% O atmosphere.

Similar ceramic target material was used for ZnO thin films prepared by PLD technique. XRD measurements revealed that ZnO films deposited by PLD show a rather random orientation of the crystallites with (103) reflection displaying the higher intensity (see figure 4).

Surface characterization of thin films revealed different sample topography. The roughness of these films increases from about 0.60 nm to 13.95 nm. Correlated with high reactivity and very fast
processes during the laser ablation, a mean grain radius could not be defined due to the not regulated shape of the grain and dimensional unhomogeneity as shown in figure 5.

Figure 5. Images of ZnO thin films surface by PLD: a) optical (x20), b) SEM, c) AFM.

Features dimension on the ZnO thin films prepared by PLD technique is varying from 10 nm to 1µm and it can be well controlled though deposition parameters. The maximum film RMS was obtained in the case of nanostructured films with “nanospaghetti” behavior see figure 6.

Figure 6. Images of ZnO thin films surface by PLD: a), b) SEM, c) AFM.

The growth parameters are strongly influencing the characteristic parameters of the surface (i.e. crystalline orientation, grain radius and RMS). The preparation conditions determine the grain size and the crystallinity of the films, which reflects on the film physical properties. All these results, correlated with optical and electrical studies, give us the possibility to improve the sensing properties of our gas sensors.

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5. References
[1] Norton D P, Heo Y W, Ivill M P, Ip K, Pearton S J, Chisholm M F, and Steiner T 2004 Materials Today 34-40
[2] Subramanyam T K, Srinivasulu Naidu B and Uthanna S 2000 Cryst. Res. Technol. 35 10 1193-1202
[3] Vasco E, Zaldo C and Vázquez L 2001 J. Phys.: Condens. Matter 13 N° 28 L663-L672
[4] Suchea M and Kiriakidis G Correlation of Surface Characteristics of In and Zn Oxides by AFM: CAS 2004 Proc. Int.Conf. (Sinaia, Romania, 4-6 October 2004) pp 345-341