Obtaining thin layers of ZnO with magnetron sputtering method

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Abstract
This paper presents research results on the obtaining of ZnO thin layers using a method of physical vapor deposition, namely magnetron sputtering. They used two types of ZnO targets sintered and non sintered. Deposit layers was done by magnetron sputtering method in argon atmosphere. Rigorous characterization of the deposited layers was performed by analysis of electron microscopy SEM and HRTEM.

Keywords: magnetron sputtering, thin films, ZnO

INTRODUCTION

Metal oxide thin films are used in many applications including solar energy devices, catalytic and photocatalytic processes, light emitting devices, fuel cells, etc These metal oxide films are prepared by a great variety of methods such as sputtering, pulsed laser deposition, chemical vapor deposition (CVD) sol-gel and spray pyrolysis (SPy) The last three methods are considered as chemical, because one or a series of chemical reaction have to take place in order to prepare an oxide thin film. A lot of different precursors have been used for the preparation of metal oxide thin films through the chemical methods. However, in the literature there is a lack of a thermodynamic analysis for the selection of an adequate precursor for obtaining a desired metal oxide film.[12]

Oxide semiconductors and are also called ceramics semiconductor. Generally they are polycrystalline materials with particle size between 1 and 10μm. Particle interface properties and plays an important role in both the study and application of these materials. In this context, control of particle composition and microstructure, especially particle interface, the most important problems encountered in developing these materials. Has been established that particle interface is associated with the controlled loading of the material structure defects, interface scattering particles is way different impurities, segregation, precipitation and oxidation properties of these materials affects the particle interface. Some examples of oxide semiconductors (band size is specified in parenthesis prohibited) Cu2O (2.1 eV) Bi2O3 (2.8 eV), ZnO (3.4 eV), SnO2 (3.7 eV), BaTiO3 (3 eV), SrTiO3 (3.3 eV) or LiNbO3 (4 eV). These materials are used for various electronic devices and sensors such as PTC thermistor, varistor (voltage resistance characteristics current-linear but symmetrical) which is used to protect electronic devices and circuit, capacitor with high dielectric constant which can be used in structures type MOS gas sensors and electro-optical modulators [1].

Recently, zinc oxide has attracted attention to the scientific community as "future material". It is still an exaggeration, because since 1935 this compound has been studied closely because much of the industry and our daily life is based on him. Interest revived for ZnO growth was possible because of ever more powerful technology for fabrication of single crystals and epitaxial layers deposited for the manufacture of electronic and optoelectronic components based on ZnO [2].

Metal oxide semiconductor films have been widely studied and have received considerable attention in recent years due to their optical and electrical properties. Some of them are good candidates for transparent conductive oxide films. Among them, ZnO is one of the metal oxide semiconductors suitable for use in optoelectronic devices. It is an alternative material to tin oxide and indium tin oxide, which have been most used to date [1]. ZnO is an n-type wide band gap semiconductor (Eg = 3.2 eV), the large exciton binding energy of 60MeV at room temperature and its electrical conductivity is due to intrinsic and extrinsic defects. The conductivity of pure ZnO was produced by the former defects such as zinc excess at the interstitial position and the lack of oxidation.

As pure ZnO thin films are sensitive to oxidation, absorption of O2 in the films is inclined to decrease the electrical conductivity. In cases of doped ZnO with different dopants, the electrical properties are enhanced by extrinsic defects and these trials have been attempted. Additionally, electrical properties of ZnO could be modified by thermal treatment in a reducing atmosphere. The optical properties of ZnO were mainly affected by a surface morphology and the change of the optical energy band gap followed heavy doping.

The morphology was also modified by thermal treatment in a reducing atmosphere and by an appropriate doping process .

ZnO is one of the metal-oxide semiconductors that has been utilized to be very useful functional materials for devices such as UVlight emitters, varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensing, solar cells and structural materials such as window material for display. As grown ZnO usually exhibits n type conductivity with a wide band gap. The n-type conductivity might be cause by intrinsic defects, interstitial zinc and oxygen vacancies. Its electrical conductivity can be increased by doping with group III elements such as aluminium, boron, gallium and indium, or group VII elements such as fluorine [10]

Manipulation of ZnO nanostructure to be various structures such as prismatic, needle-like, tetrapods , nanorods , nanobelts , nanotubes , nanocombs by various physical and chemical techniques attracts researchers to study their still-unknown properties. Among these various fabrication techniques, wet chemical route such as sol-gel, solvothermal, selfassembly, self-organization and chemical bath deposition, promises to be simpler, less-energy demand, less expensive which is more profitable for large-scale production.[11]

With a difference of 3.4 eV between the conduction band and valence energy extraction and high, approx. 60 meV at room temperature, zinc oxide, as GaN is important for optical applications in the UV. However comparative ZnO has several advantages but GaN, of which the most important is that the energy in large crystals can grow. Other qualities are those that can be used to retain the radiation, biocompatible materials, etc. Together, these qualities makes him the preferred candidate from the different components to Diodes ultraviolet sensors and nanostructured display.

Research on ZnO continue strong as ever faced difficulties in making such p-ZnO were exceeded. We move towards a near future in which ZnO is an integral part of many functional devices and "exotic."

Zn affinity for O_2 is much larger than the elements of subgroup I-a, but lower than those of subgroup III primary (Al, Ga, In). Outdoor burning is obtained ZnO zinc, used in dyeing and painting as zinc white. ZnO, wurtzitei structure, is white and yellow hot cold without changing their crystal structure.

In normal physical conditions, ZnO crystallizes Wurtz structure [3-4]. This network is hexagonal, belonging to the space and is characterized by P63mc interconnection of two sub networks of Zn^{2+} and $O^{2-,}$ every each zinc atom is surrounded by a tetrahedron of oxygen ions and vice versa. Wurtzitei structure is a hexagonal structure type compact Ababa. Network of hexagonal cell parameters are a = 3.2495 Å and c = 5.2069 Å, with a density of 5.605 g/cm3.

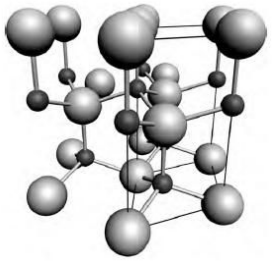


Figure 1. Hexagonal structure of wurtzitei.

Oxygen atoms are shown as large spheres and the Zn atoms as small spheres. It highlighted an elementary cell [1].

Thin film Zinc oxide exhibits excellent piezoelectric properties for surface acoustic wave (SAW) and for optical devices [9].

In addition to phase Wurtz, also ZnO crystallizes cubic, like sodium chloride. Zinc oxide is stable cubic structure but only increased the sodium chloride structure is a met stable phase, forming high pressure ~ 10 GPa and can not be stabilized epitaxially. Theoretical calculations show that a fourth type cubic phase cesium chloride can be formed at high temperatures [4].

ZnO is a semiconductor with an energy band at 3.37 eV at room temperature. The most common applications are electronic ZnO LEDs and laser diodes since the excitation energy is 60 meV. This energy is expected to grow by epitaxial deposition. It was also proposed as spintronics amplifications shows ferromagnetism at room temperature. ZnO layers deposited by magnetron sputtering usual method [5] or CVD.

THEORETICAL CONSIDERATIONS

The term "magnetron" was originally used to describe microwave tubes used in radar applications generation. It is still used for this purpose and system manufacturer uses microwave plasma source power "magnetron" to give rise to plasma. Magnetron same effect found in these tubes can be modified so that it becomes a very effective cathode sputtering. This cathode operates as a diode.

Sputtering is one of the most common methods to deposit thin layers and films. Its popularity comes from simple physical process involved, technical versatility and flexibility to adapt to individual requirements. The technique is widely used in semiconductor, photovoltaic cells and the automobile. Magnetron configured using static magnetic field on the cathode. The magnetic field has field lines parallel to the cathode surface. Secondary electrons which are emitted from the cathode during ion bombardment are forced to move the magnetic field perpendicular to both fields (normal to the surface) both magnetic and electric. It is known as ExB drift. Because it is floating movement of electrons change direction which is parallel with the initial cathode surface and come to change direction 90° from the magnetic field. If the magnetic field is set correctly, the ExB drift can be arranged to close the cycle of secondary electrons to form a floating current [6]

Sputtering techniques. These mainly include DC sputtering technique limited the spread of conductive and RF sputtering targets, which may be scattered and

conducting targets. Sputtering techniques, in terms of evaporation rates, rivaling the best methods. One disadvantage is the poor's sputtering using the target under certain conditions. High deposition rates are often disadvantaged by the fact that the region where the plasma is focused by electric and magnetic field interaction is limited in comparison with total area of the target. Suitable target is preferentially consumed in a certain area, usually annular.

DC sputtering is one of the simplest techniques. The only limitation is that non-conductive targets can not be scattered by this technique. It can not be used for jet sprays, especially when the target is contaminated and lead to the isolation of the target surface connections.

Target as payment is made of material that will be covered substrate and connected to a power source capable of providing a voltage kilovolts order. Added substrate facing the target. Depending on the film that is desired, the substrate can be cooled or heated water at a certain temperature. As can be electrically grounded. After providing pressure and filling the cavity's sputtering gas, usually argon, a negative potential is applied on target to give rise to plasma.

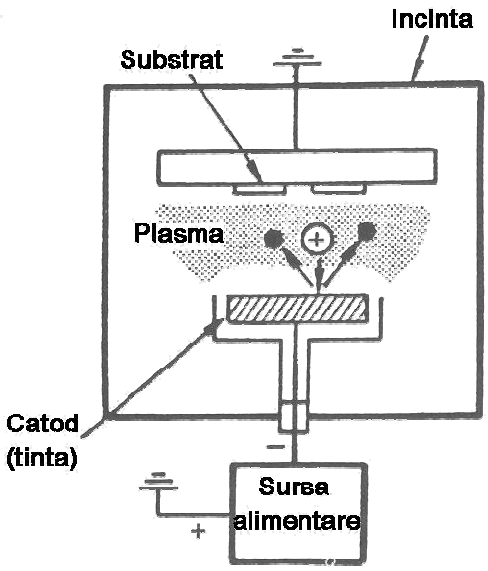


Figure 2. Schematic view of a DC magnetron sputtering operation: electrical connection

Positive ions from the plasma bombard the target surface and neutral atoms are expelled from the target surface and then condense on the substrate to form thin film.

EXPERIMENTS

To obtain thin layers by magnetron sputtering method have been made targets two types of ZnO: sintered and sintered powder we used to produce samples of zinc oxide in the form of disk used as targets magnetron sputtering to deposit was purchased from Umicore Zinc Chemicals. Type ZnO powder is HP, with particle sizes of the order microns with a purity of 99.995%.

Of zinc oxide powder was sampled a sample for characterization by X-ray diffraction characteristics Diffractometer used: Diffractometer Bruker-AXS X-ray type D8 Advance X-ray tube with Cu anode, Ni filter, goniometry vertically operating parameters: accelerating voltage 40kV / 40mA and current, θ-2 θ scan - normal incidence.

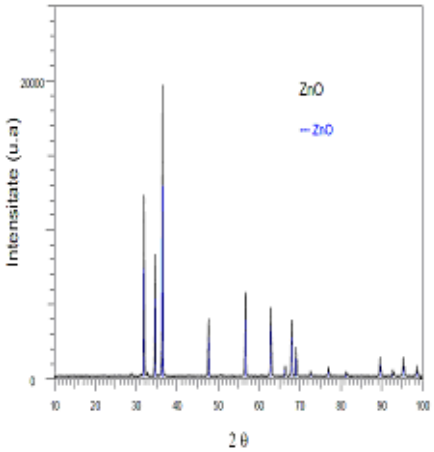


Figure 2. X-ray Diffraction spectrum of ZnO powder .

The sample was scanned θ-2θ - normal incidence, step 0.04°, scan speed: 2s/pas, domain registration: 10° - 100°. Identification was made with zinc oxide database International Centre for Diffraction Data. Corresponding sheet zinc oxide sample examined: PDF Number: 00-003 - 0888. Zinc properly examined this file has the following structural physical characteristics: system: hexagonal compact symmetry group: P63mc and cell parameters: a = 3.2495 Å and c = 5.2069 Å.

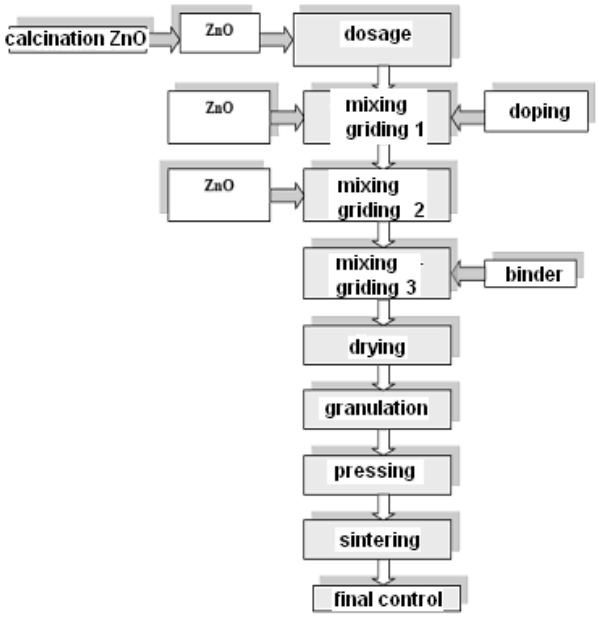


Figure 3 Process flow diagram
the for obtaining the target of zinc oxide

Oxide materials, advanced purity (≥ 99.99% ZnO) were processed by traditional ceramic process technology. To achieve the desired physical properties of ceramic material, each stage of their development is very important and has been monitored carefully. Figure 3 is shown the flow diagram followed technology for obtaining metal oxide ceramic targets. Technological stages critical pressing ceramic powder preparation and sintering heat treatment.

Zinc oxide, is mixed in several stages to obtain better mixing as the powder. This mixing, performed in pa alcohol medium in the grinding chamber of polyamide agate ball hard and guarantees uniform mass of material. In the last stage of mixing the binder is added to the pressure in the form of 8.5% solution of polyvinyl alcohol in distilled water. Homogenization was performed for 8 hours at 60 rpm.

After mixing the wet material was dried in an oven at 80-100 ° C for 4-5 h and finally granulated on a sieve of 0.9 mm. Powders were prepared for pressing discs compacted form in diameter Ø = 43.5 mm and height h = 3-4 mm. Pressure applied by press 10 tf. Type used press: Type MEYER, press double effect with lower punch thrown, the field pressures: 0-50 t.

During the heat treatment for sintering pressed discs are transformed into solid ceramic bodies. Sintering heat treatment was carried out at a temperature of 1200^{o}C, with a duration of one hour of landing in a sintering furnace LENTON mark EHF 18 / 3. In this process the powder particles to unify diffusion and grow well developed granular form. Figure 4 illustrates the temperature chart - thermal treatment of sintering time used.

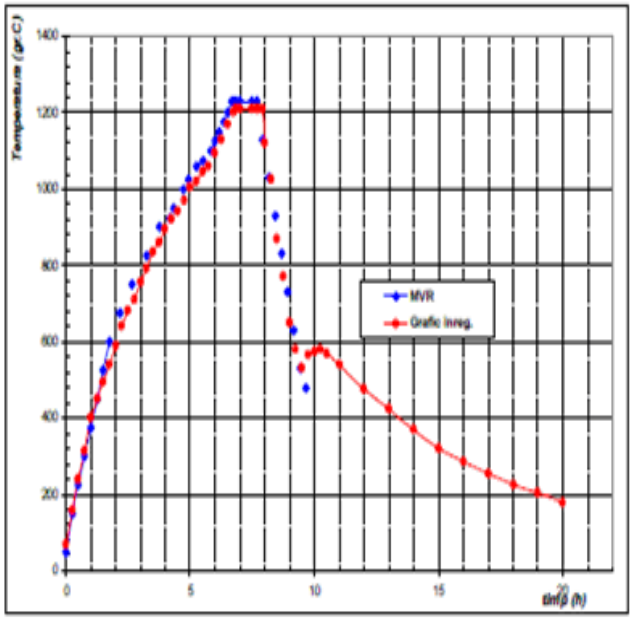


Figure 4 Technological flow chart of processing of zinc oxide target.

Preparation of samples for RF magnetron sputtering deposition method:
A zinc oxide targets sintered we do not need special preparation; B sintered zinc oxide targets were prepared for deposition by adjusting disk girls.
Zinc oxide sintered discs were polished on Struers polishing machine as [8]

SiC abrasive paper, P500, lubricant water, 150 rpm until they become flat surfaces SiC abrasive paper, P1000, lubricant water, 150 rpm, 1 min.

After polishing, the sintered zinc oxide targets have ultrasonic for 10 min. in ultrasonic bath using demonized water.

After drying in the air, the sample was handled with tweezers and caught the magnetron cathode mounting device. The substrate used was rectangular glass slide.

Substrates used for deposition of thin films are subject to cleaning in two stages: cleaning and alkaline cleaning Simple Standard Standard RCA1. These technological processes designed to remove small particles of impurities that are present on the substrate suparafata.

The material constituting the substrate (glass) samples are made (1x2 cm). Their handling is done with antistatic tweezers.
Simple standard cleaning is done in several stages:
1. Sample cleaning in trichlorethylene: substrate with a quantity of tricloetilena and place in a glass Berzelius (the amount should be sufficient to cover the sample) and ultra soneaza for 5 minutes with ultrasonic bath Elmasonic X-tra 70H.
After the substrate was cleaned with trichlorethylene is carefully handled and removed from the antistatic solution with tweezers and allowed to dry for 10 seconds, after which the liquid is introduced in the next stage.
2. Repeat operations from step 1 with the differences: the reagent is acetone used for cleaning and ultrasonic time is 3 minutes.
3. Repeat operations from step 1 with the difference that the liquid is deionized water used for cleaning.
After the substrate has passed through three stages of the standard single pass cleaning under running deionized water for 30 seconds, and then leave 10 seconds to dry then proceed immediately or at an RCA standard alkaline cleaning or deposit.
The substrate used for deposition of thin layers is subjected to standard alkaline cleaning RCA1. This operation consists of cleaning technology in a single step using a solution

NH4OH: H2O (deionized): H2O2 = 1: 5: 1, heated to 70-85oC for 10 minutes.

After drying in the air, the substrate was handled with tweezers and the mount caught the magnetron deposition. To obtain ZnO thin oxide layers has experienced RF magnetron sputtering technique. Equipment magnetron sputtering deposition technique VUP-5M is a system with three water-cooled magnetrons three lock operated by three devices, a fixed substrate with the possibility of driving through the device. Maximum temperature of the substrate which is 350° C can be achieved.

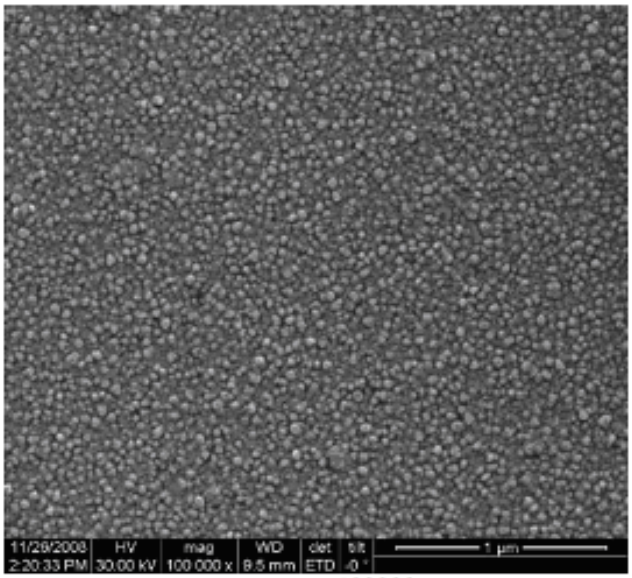
1. RF magnetron sputtering deposition in argon atmosphere of ZnO target non sintered;

2. RF magnetron sputtering deposition in argon atmosphere of sintered ZnO target.

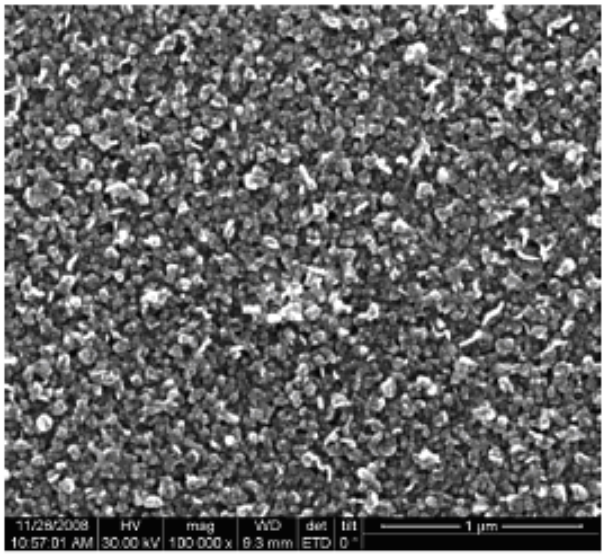
Samples were then subjected to investigate by electron microscopy and atomic force. Deposits of zinc oxide

sintered target, were not conclusive. One reason it may be too much energy required target evaporation. On the other hand deposition of zinc oxide target non sintered was a successful way, and we believe that while an innovative way. There are references in literature lost for. Rigorous characterization of the deposited layers was performed by analysis of electron microscopy SEM and HRTEM.

The transmission electron microscope High resolution Tecnica G2 F30 - Fei Company Investigation samples was done by transmission electron microscopy with high resolution (HRTEM) Tecnica type G2 F30 1A linear resolution and a resolution of 1.4 Å punctual. Scanning electron microscope Quanta Inspect F - Fei Company Investigation samples was performed with Quanta scanning electron microscope equipped with F INSPECT emission electron gun in the field - EGF (Field Emission Gun) with resolution of 1.2 nm-ray spectrometer the energy dispersive X (EDAX) with resolution of 133 eV at MnK. To investigate the scanning electron microscope, samples were viewed at various magnifications different orders.

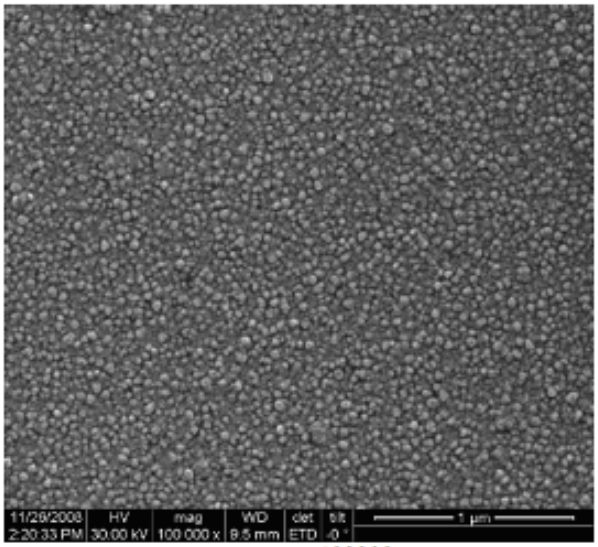


sample P11 100000x



sample P10 100000x

Figure 5. Comparative study of samples P10 and P11



sample P11 100000x

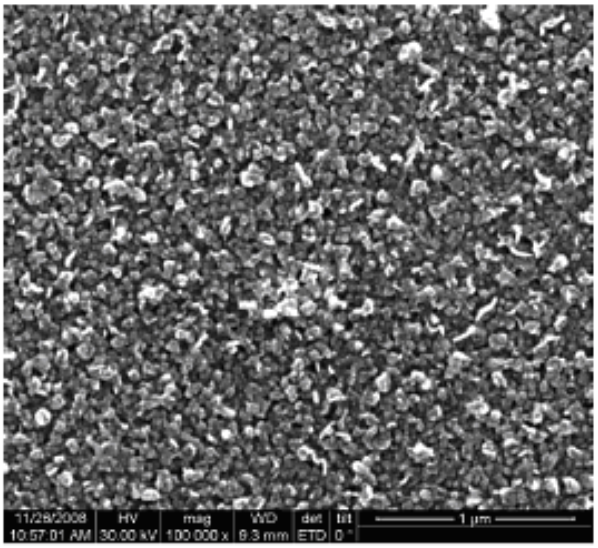
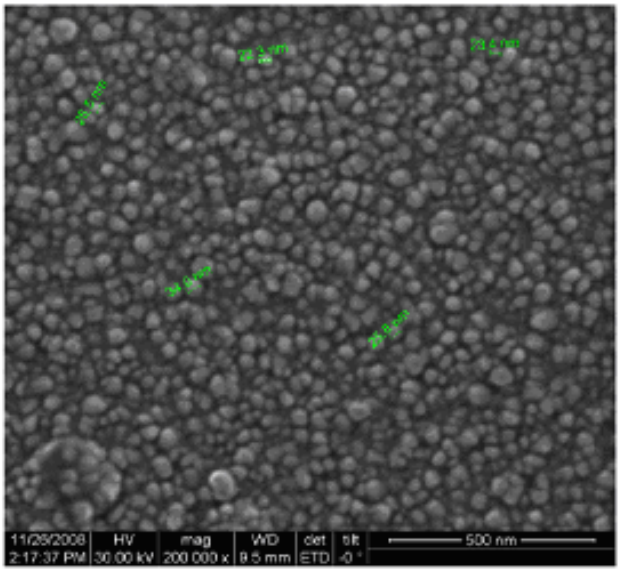


Figure 6. Comparative study of samples P10 and P11

Figure 6 reveals a good uniformity of layers deposited in both cases. The samples are differentiated as a layers morphologically. P11 sample shows a granular appearance, with nearly spherical grains, while sample P10 are rather part of the columnar oxide grains.



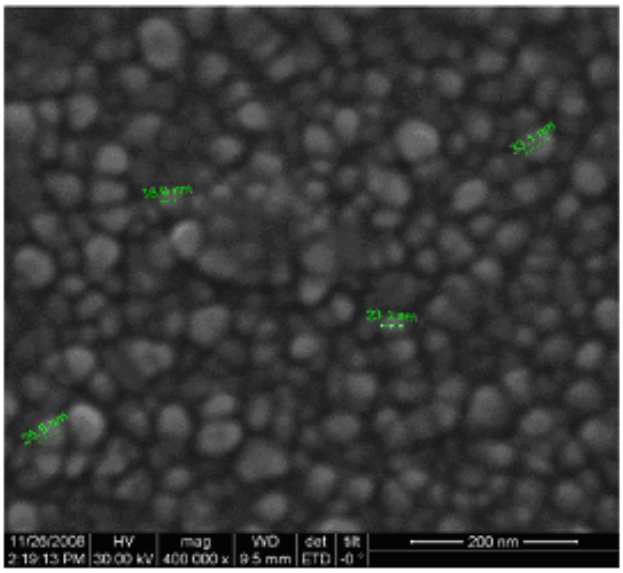


Figure 7. Sample P11 grain distribution layer comprised in the range 22-33nm.

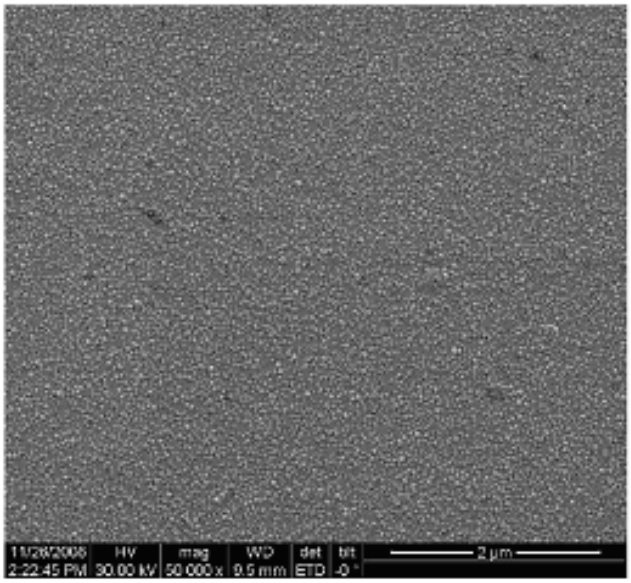


Figure 8. Sample P11-50 000x zoom.

Note the uniformity of deposit thin layer

If the sample is observed by SEM image P11 from a distribution of grain on thin film included in the range 22 -33 nm. This proof stands P11 nanocrystallites with sizes below 50nm. P11 sample families also plan highlighted corresponding phase crystalline ZnO with a hexagonal crystal lattice. Very important is the fact that although P10 and P11 samples differ in terms of method of production, structural analysis shows as if both layers have a hexagonal crystal lattice of zinc oxide.

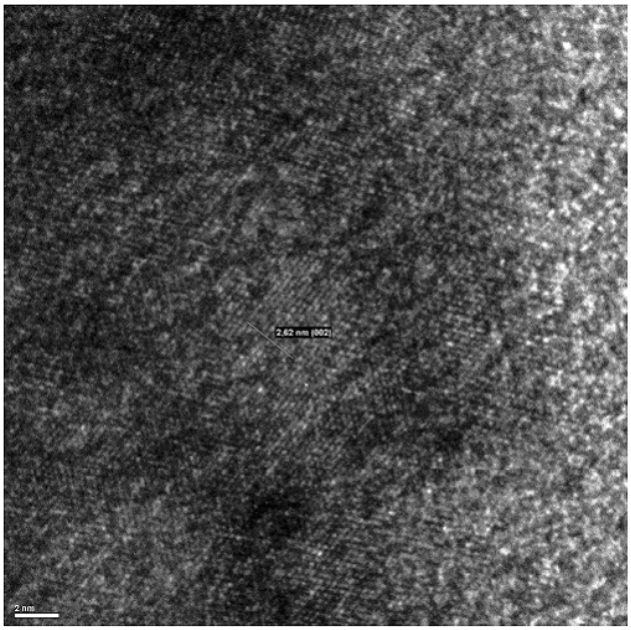


Figure 9. Image sample P10 by transmission electron microscopy of high resolution (HRTEM).
Families of crystalline planes highlighted with corresponding phase ZnO hexagonal crystal lattice.

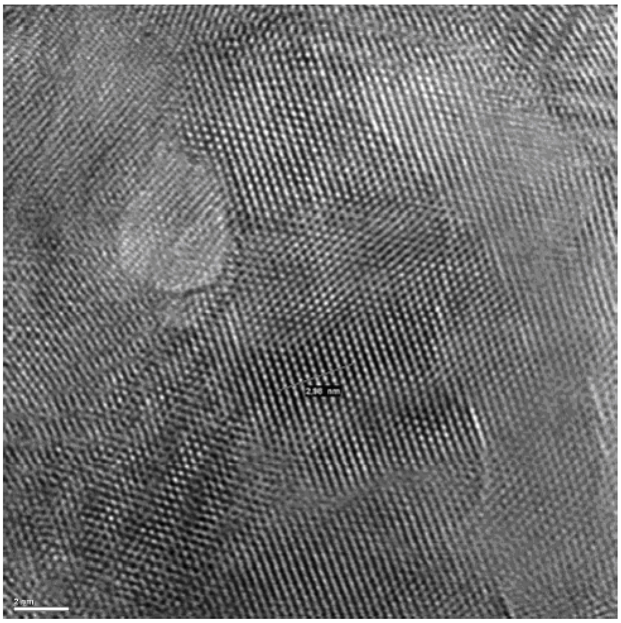


Figure 10. Image sample P11 By transmission electron microscopy of high resolution (HRTEM). Distance of 2.98 angstrom (the figure is measured 10 distances between plans = 2.98nm) crystal planes corresponding family

Sample P10 grain distribution layer comprised in the range 20 nm. By transmission electron microscopy image in bright field (TEMBF) show a characteristic appearance of granular film with nanometer grains (below 20nm). P10 sample distance of 2.98 angstrom (the figure is measured 10 distances between plans = 2.98 nm) corresponds to the family of crystalline planes (100) - HRTEM analysis.

Indexing electron diffraction image of sample present in sample P10 shows Zn0 phase with hexagonal crystal lattice. Sample P10 - families of crystalline planes highlighted with corresponding phase ZnO hexagonal crystal lattice

CONCLUSIONS

Zinc oxide 99.995% high purity can be obtained appropriate targets for achieving thin zinc oxide layers by RF sputtering method. Zinc oxide powder-type ZnO HP Umicore Zinc Chemicals, has been investigated by X-ray diffraction After investigating it shows the following structural characteristics: system: hexagonal compact; group symmetry: P63mc, cell parameters: a = 3.2495 Å and c = 5.2069 Å.

Zinc oxide powder was processed by a traditional ceramic process by mixing in a planetary ball mill using polyvinyl alcohol as binder. Were formed by pressing targets non synthesized diameter approx. And height 40mm max. 4 mm.

To experienced deposition of ZnO thin layers on glass support.

RF magnetron sputtering method has proved a versatile method which can achieve ultra uniform and adherent layer of ZnO. Deposition of zinc oxide targets does not produce desired results. Most likely is because energy is needed to process too much o get quality layers; Deposit of zinc oxide layers generates ultra non sintered targets, uniform, transparent and adherent to the substrate. This is confirmed by subsequent investigations scanning electron microscopy. Distribution layer, as seen from SEM examination is uniform. SEM analysis of samples P10 and P11 there is a good uniformity of layers deposited in both cases. As layers are differentiated morphologically. P11 sample shows a granular appearance, with nearly spherical grains, while sample P10 are rather part of the columnar oxide grains.

Sample P10 thin films contained in grain distribution range 20 nm. P10 sample distance of 2.98 angstrom (the figure is measured 10 distances between plans = 2.98 nm) corresponds to the family of crystalline planes (100) - HRTEM analysis.

Sample P10 - families of crystalline planes highlighted with corresponding phase ZnO hexagonal crystal lattice If the sample is observed SEM image P11 from a distribution of grain thin films included in the range 22 -33 nm. If this proof stands P11 nanocrystallites with sizes below 50nm. P11 sample families also plan highlighted corresponding phase crystalline ZnO with a hexagonal crystal lattice Very important is the fact that although P10 and P11 samples differ in terms of method of production, structural analysis shows as if both layers have a hexagonal crystal lattice of zinc oxide

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