Formation of ZnO in or on glasses by using the Sol-Gel and Chemical Bath Deposition Techniques

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Abstract: - In the first part of this work was produced Zinc Oxide (ZnO) into a glass matrix by using the Sol-Gel Technique at room temperature, these materials were prepared using tetraethyl orthosilicate (TEOS) as precursor, the Zn ions were added before the jellification step trough an aqueous solution of zinc acetate. These glasses were characterized by X-ray diffraction, optic absorption, FT-IR and Raman spectroscopy. The X-ray patterns showed amorphousness. The optical absorption shows a shoulder in the UV range corresponding whit ZnO confined to the vitreous matrix. The spectra by FT-IR show characteristic vibrations of Si-O-Si with interaction Zn⁺². Raman scattering let us to identify and precise the formation of the ZnO. In the second part of this work was immersed glass substrates into an aqueous chemical bath with external controlled temperature, the chemical solutions contained in the bath were a Zn Ions source (ZnSO₄) 0.1 M, a pH 10 Buffer solution (NH₄Cl/NH₄OH), Ethanolamine to complex the Zn ions, and pure water, resulting ZnO films hexagonally structured with energy band gap of 3.3 eV, growing 1000 nm during 25 minutes followed of 60 minutes to 75°C and 85°C in the same chemical reaction.

Key-words: Glasses, Zn Ions, Zinc Oxide, Sol-Gel Process, Thin Films, Chemical Bath Deposition and semiconductors

1 Introduction

Zinc oxide has attracted a significant attention in the last decades because its wide band gap behavior which confers a host of potential applications in gas sensors [1], solar cells [2, 3], Catalysis [4], Organic light emitting diodes (OLEDs) [5], microelectronic devices how transistors [5-9], particularly a very interesting use of the ZnO is like electronic devices with highly nonlinear current-voltage relationships called Varistors [10-14]. At small applied electric fields, varistors are insulating; but at a fairly welldefined higher field, those switch to conducting and maintain a nearly constant field over many decades or magnitude orders of current. Most commercial, and military application varistors are based on polycrystalline, semiconducting ZnO with a variety of other oxide additives typically in the molar range of 100 parts per million to several percent. Their main application is in electrical circuits to limit or regulate the voltage that can be applied to other devices or components. While it is common for varistors to operate with current densities of 10^{-3} to 10 A/cm^2 , some others applications also require unusually high electric fields near 40kV/cm. With these high power conditions, it is perhaps not surprising those small flaws in the varistor result in breakdown, or a large irreversible change in their electrical and sometimes structural properties. The functional dependence of current on voltage in these devices is symmetrically bipolar that is due to an inherent property of the semiconductor from which it is made.

Several process using both chemical and physical methods have been reported for the production of these materials (ZnO and ZnO-composites) like tape casting[14], sol-gel[15-16], vapor-phase transport

method[17], chemical vapour transport (CVT) process, spray pyrolysis (SP)[18], sputtering, etc., either to produce powders, thin films, nanoparticles, nanorods, composites, etc. Particularly ZnOcomposites either using a matrix of glass, ceramic or polymeric, are very attractive since these composites offer many possibilities for creating new materials, especially for microelectronics and nanoelectronics industry, because through appropriate techniques can be homogeneously disperse the particles of the semiconductor (ZnO) in the matrix chosen. Furthermore, ZnO thin-film transistors (TFT) have recently received much attention due to their potentials toward a new driving component for liquid crystal display and other applications like solar cells, etc.

The purpose of this work is to study two alternative ways to prepare composites containing SiO₂ glasses and Zn ions or ZnO molecules. The first one, by using the sol-gel technique, is a way to prepare this kind of the required composites starting from TEOS as precursor, then the Zn ions are added trough an aqueous solution of Zn(CH₃COO)2•2H₂O in the process, before the gel formation. The process is carry on at room temperature and the complete process is as simple as the sol-gel technique. The second one, by Chemical Bath Deposition (CBD) technique using two reaction temperatures T₁ =75°C and T₂ = 85°C, during respective times of 25 minutes and 1 hour, in the same reaction.

2 Materials and Methods

The used chemicals compounds were reagent grade, but with purities between 98 to 99%. For the first composites were used Deionized Water, Absolute Ethanol, Tetraethyl Orthosilicate, Chlorhydric Acid and Zinc Acetate. For the second composites kind were used Deionized Water, Zinc Sulfate, Buffer Solution pH 10 (NH₄OH/NH₄Cl), Ethanolamine and Corning brand microscope slides as substrates.

2.1 Experimental Method to produce ZnO into a glass matrix by using the Sol-Gel Technique

Ten samples with different proportions of zinc ions were prepared, where the ZnO single molecules or nanoparticles were formed being embedded into the SiO₂ phase. The starting solutions were prepared by mixing TEOS, water and ethanol. This set of samples was prepared using a constant ethanol:TEOS volume ratio of 1:1 and a volume ratio of water : TEOS, 1:1. The solution was catalyzed with 50 drops of concentred HCl (or some dilution), in order to homogenize its phases, Sol formation. It is necessary to wait several days (7-15) to dry the monoliths. After jellification all samples were dried and/or ground to obtain a fine powder at room temperature. The zinc was incorporated into the samples, dissolving Zn (CH₃-COO)₂ into water and added to the starting solution. The amount of the zinc acetate varied from 0.1 M to 1.0 M, see Table 1.

Sample	TEOS	PureEthanol	ZnAc Dihydrated
1	10 ml	10 ml	10 ml, 0.1 M
2	10 ml	10 ml	10 ml 0 2 M
3	10 ml	10 ml	10 ml = 0.3 M
	10 ml	10 ml	10 ml 0.4 M
4	10 ml	10 mi	10 ml, 0.4 M
5	10 ml	10 ml	10 ml, 0.5 M
6	10 ml	10 ml	10 ml, 0.6 M
7	10 ml	10 ml	10 ml, 0.7 M
8	10 ml	10 ml	10 ml, 0.8 M
9	10 ml	10 ml	10 ml, 0.9 M
10	10 ml	10 ml	10 ml, 1.0 M

Table 1. Formulation and proportions of the Samples. The label each sample means the tenths of molar concentration in the sample.

A D8 Brucker Advanced equipment did the X-ray diffraction characterization, with a Cu source of 1.54 Å. The optical absorption was done in an S2000-UV-VIS Ocean Optics, Inc., and for the Raman spectroscopy was used a Raman Systems R-2000.

2.2 Experimental Method to produce ZnO on a glass substrate by using the Chemical Bath Deposition Technique

The samples were prepared by deposition of zinc oxide on glass substrate; we sent to analyze quantitatively the chemical composition of the substrates to a professional lab in Tucson, Arizona USA, Desert Analytics. In Table 2 is the information of that chemical composition of the substrates, Corning brand microscope slides.

Element	Concentration	Compound	Concentration
Al	0.702	Al ₂ O ₃	1.326
Si	34.039	SiO ₂	72.82
Na	8.527	Na ₂ O	11.494
Mg	2.478	MgO	4.108
S	0.107	SO_2	0.214
Р	0	P ₂ O ₅	0
K	0.696	K ₂ O	0.839
Ca	4.702	CaO	6.578
Fe	0	FeO	0
Mn	0	MnO	0
Ti	0.003	TiO ₂	0.005
0	46.131	Stoichiometry	-
Total	97.385	total	97.384

Table 2. Quantitative analysis and chemical composition of the Substrates sent to analyze to a professional lab in Tucson, Arizona USA, Desert Analytics.

Whereas, in Table 3 we tabulate the technical information of the provider of substrates.

Composition	Percent approx.
SiO ₂	73%
Na ₂ O	14%
CaO	7%
MgO	4%
Al_2O_3	2%

Table 3 Technical information published for the provider of substrates.

The chemical bath deposition (CBD) is used for deposition techniques that produce a solid film in a single immersion through control of the kinetics of formation of the solid. Film thickness and composition can be easily controlled by changing simple reaction parameters such as reactant concentration, reaction temperature and deposition time. The deposition medium for CBD consists of one or more salts of metal M^{n+} , a source for a chalcogenide (if the film to be deposited contains S, Se, etc), a source of oxygen for oxide films and a complexing agent (e.g. ammonia, NH₃, EDTA, sodium citrate, etc.) all mixed in aqueous solution.

For oxides, water normally provides the oxygen. The processes that occur in the CBD solution consist in general of the following five steps: (1) Time zero to equilibrium between the complexing agent and water; (2) Hydrolysis of the chalcogenide source (if the film is not an oxide); (3) Formation and/or dissociation of ionic metal–ligand complexes $[M(L)_i]^{n-ik}$, where L^{k-} denotes one of more ligands, and (4), (5) Formation of the solids. Step (4) consists of the oxidation of a metal hydroxide from the water release. Step (5) the controlled reaction of metallic cations either with ionic oxygen or chalcogenides ions by mean of release complexing agents.

Now schematically, CBD for oxide or sulfide films from a metal cation M^{n+} complexed by *i* ligands L^{k-} , can be depicted as follows (five steps):

1) Dissociation of water and Complexant-water equilibrium:

$$nH_2O \longleftrightarrow nH^+ + nOH^-$$
$$2(L)_i^{k-} + 2H_2O \longleftrightarrow 2(L)_i H^{-k+1} + 2OH^-$$

2) Thiourea hydrolyzes to form sulfides

$$nSC(NH_2)_2 + 2nOH^- \rightarrow$$

 $nS^{2-} + nCH_2N_2 + 2nH_2O$

3) Displacement of ligands:

$$nOH^- + M(L)_i^{(n-ik)+} \to M(OH)_n(s) + (L)_i^{k-1}$$

4) Deprotonation to form oxides

$$M(OH)_n(s) \rightarrow MO_{n/2}(s) + \frac{n}{2}H_2O$$

5) Total Reactions:

$$M(L)_{i}^{(n-ik)^{+}} + \frac{n}{2}H_{2}O \to MO_{n/2}(s) + nH^{+} + (L)_{i}^{k-}$$
$$M(L)_{i}^{(n-ik)^{+}} + nS^{2-} \to MS_{n/2}(s) + (L)_{i}^{k-}$$

The complexant is optional and is usually chosen based on the affinity of its ligands toward the metal. This makes step 3 the rate-determining step, adding a degree of control for thin film thickness. The hydrolytic process of reactions 4 and 5 can be accelerated by heating the solution, which induces deprotonation of the hydrated metal species (reaction (4)). This eliminates the need to use a base in reactions 4 and 5. For the oxide systems to be formed in this research work, hydrolysis can occur even in acidic solutions when the metal cation is easily hydrolysable, as in the case of some of the metals to be evaluated here $(Al^{3+}, Zn^{2+}, In^{3+})$. In contrast, CBD of non-oxides requires the addition of basic solutions. In all CBD processes, whether oxide or non-oxide, a solvated metal complex reacts with a chalcogenide source to form a desired solid product. The main difference is that for oxides, the "chalcogenide source" is water, so that tighter control must be exerted over just two parameters (pH, T) to achieve a similar degree of control over the rate of hydrolysis and, therefore, control over the film's microstructure and properties. For non-oxide films, the supply of chalcogenide anions can be controlled, in addition to pH and temperature, with the concentration of the chalcogenide source.

The practical procedure is too simple, consists to immerse the substrate into the solution (bath) containing an aqueous solution of complexed zinc sulfate, until the zinc oxide thin film is formed on the glass substrate.

Reagents used to deposit of ZnO thin films in a two-stage temperatures process; 25 minutes at 75°C and 1 hour at 85°C, in the same reaction bath:

- 36 ml of zinc sulphate (ZnSO₄) 0.1 M. Source metal.
- 12 ml of pH 10 controller buffer (NH₄Cl/NH₄OH).
- 18 ml of Diluted Ethanolamine in deionized water, 50%:50%. Complexing agent.
- Complete to a volume of 100 ml with deionized water.

This process has a singular complication as reaction condition which is: If we start to a initial temperature like the ambient, ~ 21 °C, it is necessary to consider a first reaction with small temperature gradient, until arrive to 75 °C, 25 minutes remaining in the latter, subsequently increasing the temperature to reach 85 °C for 1 hour.

Some equipment used to analyze this second kind of composite were: X-ray diffraction was done in a Philips X'Pert; studies of optical absorption UV -Vis was carried out using a UV-Vis spectrophotometer brand Perkin Elmer, Model 330; the image of the surface morphology, was performed with a scanning electron microscope brand Topcon SM-510 (SEM); the Raman spectra were obtained with the equipment Micro-Raman scattering brand LABRAM-Dilor. The thickness was done directly and enough accurate by using a profilometer brand Dekatar.

3 Results

Developed materials are of two types, so the presented results in this section will try to maintain a systematic independence

The monoliths of silicon dioxide with embedded zinc oxide particles are amorphous, they scatter the light and even some of them are opaque. The monoliths ere characterized by X-ray diffraction, UV-Visible and Raman spectroscopies, which below are explained in some detail. Similarly the growth Zinc Oxide Thin films on glass substrates led to a polycrystalline hexagonal structure, 1µm thickness and they were more completely characterized by X-ray diffraction, visible, Auger and Raman spectroscopies, and additionally its morphology was studied by scanning electron microscopy.

3.1 ZnO-Glass matrix composites by Sol-Gel Technique (SiO₂: ZnO)

Let us to begin with the commentary that the composites obtained had a drying time between 7 to 15 days. Also it is necessary to know that when added low proportions of zinc acetate, the composites were of a more translucent appearance, whereas that the obtained composites using the higher concentrations had opaque appearance.

We could have to measured more features for this material, but it is necessary to break the research in order to report some partial results if not this

The XRD patterns obtained showed that all the samples were amorphous compounds, as can be observed from Fig. 1. The behavior it is very similar between each gel, basically amorphous. However we can see that the wide band between $2\theta = 17-35^{\circ}$ is better defined with increase of content acetate of zinc. A little peak appears at $2\theta=34^{\circ}$, samples corresponding to 0.8 and 0.9 M, which can correspond to hexagonal ZnO structure. Here we can consider that the sensitivity of the XRD indicates the ZnO- Glass matrix composites have

not crystalline particles (SiO₂: ZnO).



Fig1. XRD patterns of glasses with zinc ions (ZnO), showing essentially the amorphousness of the samples.

Zinc oxide has a wide direct band gap of slightly bigger than 3 eV (\sim 400 nm). It is a great UV absorber. The Fig. 2 shows the absorption spectra with different contents of acetate of zinc. We can see an increasing of the optical absorption rising from 300 nm toward UV region in the graph. This plot also shows an absorption edge located at about 420 nm, (the inflection point), which means that ZnO is present in amorphous form in the samples.

They showed opaqueness lead to a diffuse detection of the intensity by the UV-Vis spectroscopy technique, but any way the main behave follows the same features of the involved material, we should not forget that this ZnO formation it is of very small and scattered particles. This also corresponds with the global amorphousness.



Fig. 2 Absorption spectra of glasses with zinc ions (ZnO), in the 245-500 nm range. All the samples, except the number 7 show typical ZnO behavior.

In Fig. 3 are shown the absorption spectra in the 425-640nm range, these spectra have a similar behavior for almost all samples. In fact absorption edges are weak in the zone of the 400-500 nm; from there the spectra behavior remains almost constant. The low intensities surely correspond with the opaqueness and to the dispersive of most of the samples.

Fig. 3 Absorption spectra of glasses with zinc ions



(ZnO), in the 425-640 nm range. Curiously, the labeled samples 1 and 2 begin an absorption edge

around 500 nm.

In the Figure 4 is shown the IR spectrum of eight of the ten studied samples. In order to understand the origin of the above glass structure in this spectrum is observed an intensive peak at 1100 cm⁻¹, which can be attributed to characteristic vibration of Si-O-Si bridges in the silica network [19-21]. The band seen at 965cm⁻¹, can be related to the Si-O-H stretching vibration [21-22], this peak increases as the concentration of Zn decreases, which is expected since the signal of the silicon bonded to hydroxyl groups would be more intense.

The band at around 800 cm⁻¹ observed for all the considered concentrations, vary likely due to interaction between Zn^{+2} and the silica glass network which can result between the two characteristic bands for silica at $800cm^{-1}$ and 470 cm⁻¹.



Fig. 4 Infrarred spectrum of our glasses with zinc ions (ZnO).

From the Raman spectroscopy patterns can be identified a signal corresponding to ZnO, see Figure 5, there are shown Raman spectra of as grown samples at room temperature; with different molar concentration. Two broad bands are shown, corresponding to ZnO (435 cm⁻¹) and SiO₂, as we already appointed. As it can be seen, small molar concentrations result in larger peak intensities. The peak at 435 cm⁻¹ is related with E2 mode for ZnO.

It is possible to use Raman Spectroscopy excited by laser light of various wavelengths to study LO and TO modes in polar and nonpolar semiconducting materials, the frequency variations of the LO and TO modes in polarized semiconducting material like ZnO Nano-Particles (NPs) have distinct physical origins to first order so we can do such an analysis from the experimental Raman spectra of ZnO Bulkpowder (BP) and NPs, excited by 514.5nm laser line, respectively. The first order Raman modes A1T, E1T, E2 (H), A1L and E1L are identified as the peaks at: 385, 426, 437, 572 and 584 c m⁻¹

On other hand, Zinc acetate in pure form shows a large peak in its Raman Spectra, located at 960 cm⁻¹, as it can be see Fig. 5. This peak is related with CHout of plane molecular stretching bond [24]. In our samples, this peak could disappear with a thermal annealing, due to breakage of the organic bonds by heating.

Samples in pure powder at RT show two Raman small signals at 435 cm⁻¹ and 556 cm⁻¹ corresponding to reported in other works [23]. Both peaks have a small intensity varying for different concentrations. The peaks at both positions are related with oxygen vacancies in ZnO [20].

ZnO can be derived in Sol-Gel procedures starting with TEOS. In this case, Raman spectra will show a broad band raising from 500 to 550 cm⁻¹ corresponding to SiO₂. This band can overlap the second mentioned Raman signal for ZnO.



Fig. 5. Raman spectra of our glasses with zinc ions (ZnO).

3.2 ZnO Thin Films on Glass substrate composites by CBD technique (ZnO/Glass)

Here we describe the specific characterization developed to study our second material, this material is inorganic semiconductor type metalchalcogenide and it is obtained in the form of thin films by the method of chemical bath deposition. Thanks to the versatility of this method or technique, it would be possible to vary a number of physical and chemical parameters that allow us to modify the properties of the obtained semiconductor.



Fig. 6. XRD pattern of our Zinc Oxide Thin Film on a glass substrate. Here can be observed the polycrystalline feature of the ZnO film and the amorphous feature of the substrate, like evolving broad band.

The XRD pattern in Figure 6 shows to us that the ZnO thin film onto glass substrate was polycrystalline; the diffractogram displays several sharp peaks. These peaks are related to the lattice spacing's 2.814Å to 2θ =31.77°, 2.603Å to 2θ =34.42°, 2.475Å to 2θ =36.25°, 1.911Å to

 $2\theta = 47.53^{\circ}$ and 1.624Å $2\theta = 56.6^{\circ}$, to which correspond to the (100), (002), (101), (102) and (110) planes of the hexagonal structure of zinc oxide (JCPDS card 36-1451). Therefore, the material synthesized has the hexagonal phase of the Wurtzite structure (space group: p63 mc) of ZnO (calculated cell constants: a = 3.24 Å, c = 5.20 Å). The strong and sharp peaks indicate that this as synthesized product is highly crystalline and pure. Also, it can observe a wide band around $2\theta=23^{\circ}$, this band corresponds to background of glass matrix (the substrate).

From a UV-Vis spectrometer we measure the absorbance, in Fig. 7. In this case the film is on the surface of the substrate, and then it can be measured or absorbance, or transmittance and also reflectance.

We can to observe a fast increasing in the absorption as we decrease the wavelength, in our study range, but an appropriate data treatment and some theoretical assumptions typical, allows us to obtain the energy band gap.



Fig. 7. Optical Absorption spectrum of our Zinc Oxide Thin Film on a glass substrate.

Using the fact that the ZnO is a direct bandgap semiconductor, it is possible to calculate the Energy bandgap (Eg) by using the optical absorption data. In the Fig. 8 the absorption data were treated and the Energy Band Gap was $\rm E_g{=}3.3~eV$



Fig. 8. Plot for the energy band gap calculations of our Zinc Oxide Thin Film on a glass substrate. $E_g=3.3 \text{ eV}$.

Using Auger spectroscopy we get the Fig. 9 where it is shown the presence of oxygen, zinc and carbon. It is considered that carbon is found as an environmental contaminant since CO_2 it is absorbed by the film. This confirms that DBQ is a very clean technique or selective, since it does not have other types of elements in the reagents.



Fig. 9. Detection of some chemical elements by Auger spectroscopy of our Zinc Oxide Thin Film on a glass substrate.

From the Raman spectroscopy pattern seen in the Fig. 9, it is possible to observe a wide band between 540-600 cm⁻¹, such has been reported as corresponding to the signal 570-580 cm⁻¹ of ZnO, with hexagonal structure [25]. This broad band can be produced by the phonons A1 (LO) to 574 cm⁻¹ and / or phonons E1 (LO) to 583 cm⁻¹.



Fig. 9. Raman shift of our ZnO thin film. It is corresponding with previous reported on literature.

The Fig. 10 shows the surface morphology obtained by SEM, which shows a uniform surface of the ZnO films. This material does not grow forming isolated aggregates; it can be observed a regular distribution of a kind of disordered cylinders with lengths between 0.5- $1.0 \mu m$.



Fig. 10. SEM micrograph of our Zinc Oxide Thin Film on a glass substrate.

This material is considered like photosensitive. In Fig. 11 we can see the ability to photo detect visible light, but the recombination time or time to stabilization of the material is too large, also from the same figure can be observed the jump of two orders of magnitude in about one or two seconds.



Fig. 11 Photoresponse versus time and light conditions of our Zinc Oxide Thin Film on a glass substrate.

4 Conclusion

Were obtained monoliths containing immersed nanoparticles of ZnO and also were obtained polycrystalline ZnO thin films deposited on Corning glass microscope slides substrates

The obtained glasses containing ZnO by the solgel technique were grown from TEOS as precursor, we think it is formed a porous or reticulated vitreous matrix containing ZnO nanoparticles in its pores. The glasses were amorphous, with stretching vibration of Zn-O and characteristic vibrations of Si-O-Si. So, the Raman spectrum identified the groups ZnO and SiO₂.

ZnO films were obtained by DBQ adjusting the reaction temperature to $T_1 = 75^{\circ}C$ during 25 minutes and to $T_2 = 85^{\circ}C$ during 60 minutes, in the same reaction, such films are white color, exhibit not so

good adherence to the substrate, are homogeneous enough, and are opaque's. These ZnO films were polycrystalline, its crystallites or grains have hexagonal structure, its estimated grain size was \sim 20 nm, the energy gap was 3.3 eV and its thickness was about 1000 nm.

The results obtained in this study are important given their potential implications for technological applications [26-29].

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