Thin films from different materials obtained by the Sol-Gel method: study of the morphology through Atomic Force Microscopy (AFM)

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Recently the obtainment of thin films is carried out by using different deposition methods, whether by chemical or physical methods. Thin films have been obtained of various materials with different characteristics and properties and it are used in different optical and electrical devices. Another important part in the study of thin films is the morphology that determines the properties of the film. The morphology of thin films varies according to the deposition technique. In this case, we present the morphology of various materials deposited on glass substrates using the sol-gel method, the synthesis was carried out using Spin Coating and Dip Coating techniques. The surface analysis of the films was done with an Atomic Force Microscopy (AFM). We present the surfaces of CuO-SiO\(_2\), FeO-SiO\(_2\) and ZnO obtained by the sol-gel method and deposited by Spin and Dip Coating techniques. Thin films of CuO-SiO\(_2\), FeO-SiO\(_2\) and ZnO were deposited using the Dip Coating technique, while the films of ZnO-1, ZnO-2 and ZnO-4 were deposited with the Spin Coating technique, in order to obtain different morphologies for the films. Some morphologies that we can find are seeds, triangles and wires for different deposited materials and depending of the morphology the optical and electrical properties of the films could be improved.

**Keywords** Thin Films, Sol-Gel, AFM, Morphology

### Introduction

Thin films are layers of any material deposited over different substrates to improve and achieve new properties that give better applications for some materials. We can find films of different thicknesses ranging from nanometers to micrometers. Recently the use of thin films is very extensive because it presents different properties and applications such as in electrical devices as light emitting diodes, liquid crystal devices, electrochromic and electroluminescent devices, anti-reflective films, interference filters, solar cells, magnetic films for data storage in computers, optical storage devices data as compact discs and computer memory applications [1]. There are many methods in order to obtain the thin films; one is the Sol-Gel method which relies on the use of inorganic or metal-organic precursors [2]. The most metal-organic precursors used are metal alkoxides because they react with water through the hydrolysis and condensation reactions lead to a solid amorphous metal. Either for inorganic or metal-organic precursors, the evolution of the structure of oligomers or polymers depends of the hydrolysis extent and the preferred coordination number or functionality of the metal. In the case of inorganic precursors, the extent of hydrolysis is generally controlled by the pH and for the metal organic precursor is controlled through the hydrolysis ratio H\(_2\)O/M [2]. On the other hand the methods of thin film deposition are very broad, because in the literature we found different methods to obtain thin films like electron beam evaporation, atomic layer deposition, DC/RF magnetron sputtering, etc. In this work we use the Spin Coating and Dip Coating technique to obtain thin films. The Spin Coating technique consists in the deposition of a small quantity of a solution on the center of a substrate, which is rotated at high speed in order to spread the slip by centrifugal force. The rotation is continued while the excess of solution is removed with the spinning until we obtain the desired thickness. [4]. There are two ways to apply the solution. The static application is the deposition of a small amount of solution in the middle of the substrate or close to it and then begins to spin; in the dynamic application the solution will be placed on the substrate while it is rotated at low speed. The final thickness is a function of the rotational speed, the concentration of the solution, molecular weight and time. And also it depends in much of how we apply the solution to the substrate, as well as the drying rate, both are affected by the viscosity of the solution, whereas the solution dries, the viscosity increases, to prevent that the solution be dispersed sufficiently well on the surface. If we give too high spin speeds and very long spin times we will obtain very thin films, however if you have very low speeds and very short times we will obtain very thick films. On the other hand, in dip Coating technique, the substrate is normally withdraw vertically from the coating bath at a constant speed. The moving substrate entrains the liquid in a viscous boundary layer that splits in two at the free surface, returning the outer layer to the bath. Since the solvent is evaporating and draining. The only requirements for successful Dip Coating are that the condensed phase remain dispersed in the fluid medium, that macroscopic gelation be avoided, and that the sol be sufficiently dilute so that upon deposition the critical cracking thickness not be exceeded. The final film microstructure depends on: a) the structure of the entrained inorganic species in the original sol, b) the reactivity of these species, c) the time scale of the deposition...
process and d) the magnitude of shear forces and capillary forces that accompany film deposition [2]. Once the thin films were obtained we may characterize it by different techniques, in order to know its crystallinity, explore their surface or to know their electrical and optical properties. One of the most widely used characterization techniques for the analysis of the surface of the thin films is the Atomic Force Microscopy. In the Atomic Force Microscopy the images are obtained by measurement of the force on a sharp tip, insulating or not, created by the proximity to the surface of the sample. This force is kept small and at a constant level with a feedback mechanism. When the tip is moved sideways it will follow the surface contours [5]. The Atomic Force Microscopy offers 3 different modes of operation: a) in the contact mode, the tip is brought into contact with the surface and the deflection of the cantilever is kept constant during the scanning; b) in the intermittent mode (tapping), the cantilever is oscillated at its resonant frequency. The probe lightly “taps” on the sample surface during scanning by maintaining constant oscillation amplitude a constant tip-sample interaction is maintained and an image of the surface is obtained. This mode allows high resolution of samples that are easily damaged [6]; c) in the Noncontact mode and oscillation probe is brought into proximity of (but without touching) the surface of the sample and senses the van der Waals attractive forces that induce a frequency shift in the resonant frequency of a stiff cantilever. Images are taken by keeping a constant frequency shift during scanning, and usually this is performed by monitoring the amplitude of the cantilever oscillation at a fixed frequency. The tip-sample interactions are very small in noncontact mode and good vertical resolution can be achieved, whereas lateral resolution is lower than in other operating modes [7]. In this paper we present images of the surface of different thin films obtained from Sol-Gel method and deposited with Dip Coating and Spin Coating techniques, the surface morphology of the thin films was observed by Atomic Force Microscopy (easyScan from Nanosurf) in contact mode with a maximum scanning speed of 1800 points per second.

Thin films obtained by DIP Coating

CuO-SiO$_2$

Using the Sol-Gel method with metal alkoxides was prepared a solution with cupric nitrate at different concentrations; films are obtained by the Dip Coating technique, where the substrate is withdrawn vertically from the coating bath an exit velocity of 0.37 cm/s. The substrates are coated with the solution only once and are subsequently given a heat treatment in a conventional furnace at a temperature of 350°C for 30 minutes. For many applications, subsequent heat treatment is required to achieve full densification and improve the crystallinity of the films [8]. The surface of the films is analyzed in the Atomic Force Microscopy, with a scanning area of 18.4 µm X 18 µm and shows a surface with particles in form of drops, these particles are oriented in the same direction and is not showing clusters. The size of these particles is among 1.8 y 2.5 µm (Figure 1). It has been reported the synthesis of copper oxide at temperatures of 300°C [9], in our case we found the particles on the surface correspond to these copper oxides. The most common applications that are given to the films of copper oxides are as antibacterial films, for example, O. Akhavan et al reported that thin films of copper oxide heat treated at 300°C exhibited a strong antibacterial activity against Escherichia coli bacteria. If the temperature of heat treatment is increase the antibacterial activity of the films decreased due to the penetration of the particles into the film [9]. On the other hand C. C. Trapalis et al, they obtained thin films of copper oxides using the Dip Coating techniques, the films were heat treated at 500°C so that they would from the metal particles, they report that the films have a high antibacterial activity that is improved with the increase of concentration of the metal and decreased with the increase of the heat treatment temperature [10].
For the synthesis of thin films of FeO-SiO$_2$ by the Sol-Gel method, we incorporated different concentrations of iron nitrate and we use a metal alkoxide to obtain these films. The deposition of the films was performed with an exit velocity of 0.37 cm/s. All the films were given a heat treatment of 300°C for 1 hour in a conventional oven. In the figure 2 we observed the films with a scanning area of 13.8 µm X 13.7 µm; these films were obtained with a concentration of 30% of FeO. We found a filled surface of particles in form of triangles, which are oriented in the same direction; the length of the sides of these triangles is between 1.4 y 1.6 µm. It has been found that some compounds such as MnO, CoO, NiO and FeO have a rocksalt crystallographic structure above the Néel temperature $T_N$ [11], so we assume that the particles found on the surface of the films are FeO. It has found a little similar morphology in the work of Yunxi Yao et al, on which they deposited FeO over Pt (001) although the films were grown by another procedure [12].

In the figure 3 we see the surface of another film with a concentration of 30% of FeO, the scanning area is 8.97 µm X 8.91 µm and we can see particles with triangle form all of the same length, there are also semi-spherical particles that are among the particles in form of triangles. The length of these triangles is between 2.3 y 3.2 µm, while the semi-spheres have sizes less than 1 µm. All the thin films obtained from iron nitrate have morphologies in the form of triangles, no matter the concentration used. Heat treatments were the same for all films, so the only difference between each thin film
is the amount of iron in the surface. Currently reported the use of iron oxides for applications in magnetic devices or for improving some properties, for example Linhua Xu et al, have reported ZnO thin films prepared by the Sol-Gel method which doped with different concentrations of Fe, this improves the crystallinity and orientation of ZnO thin films [13].

A ZnO solution was prepared by the Sol-Gel method and was deposited on glass substrates (previously cleaned) with an exit velocity 0.15cm/s. Four substrates were selected for to apply a first layer, with a drying time of 10 min at 150°C in a conventional plate. On each of the substrates a different number of layers were applied, obtaining thin films with 1, 2, 3, and 4 layers, giving the same drying time between each layer. Then they were heated at a 400°C for 2 hours [14]. By absorbing the films in the Atomic Force Microscopy, we found that the morphology of the films is in the form of threads which cover the entire surface of the substrate. In the figure 4 we have the image of thin film with 2 layers before and after the heat treatment. We can see how the thread morphologies are formed from the deposition of the first layer and the morphology is preserved with each deposited and the heat treatment does not affect the morphology of the thin films.

By absorbing the films in the Atomic Force Microscopy, we found that the morphology of the films is in the form of threads which cover the entire surface of the substrate. In the figure 4 we have the image of thin film with 2 layers before and after the heat treatment. We can see how the thread morphologies are formed from the deposition of the first layer and the morphology is preserved with each deposited and the heat treatment does not affect the morphology of the thin films.

The thin film with 4 layers is shown in figure 5 in an scanning area of 14.2μm X 14.1μm were we see that no matter the number of layers deposited on the substrate, the morphology is the same and these threads are accommodating each
The length of these threads has been found to be up to 12 µm and it is noticed that these threads are continuous so their actual length could not be measured accurately. The width of the thread before heat treatment was found to be between 0.5 and 0.9 µm and the width after the heat treatment didn't any change. So we concluded that the length and width value is independent of heat treatment and the number of layers deposited [14].

### Thin film obtained by Spin Coating

**ZnO-1**

A solution was prepared to obtain ZnO thin films. The deposit was made on these glass substrates using the Spin Coating technique at a rate of 3000 rpm for 20 s. Sixth substrates were coated rising the number of layers of 1 to 6. In Figure 6 shows the image of the films with 1, 2, and 3 layers, in the image a) Figure 6 we see the film with 1 layer and observed particles with a round form distributed on the surface, these particles are approximately between 0.8 y 1.2 µm. from the film with 2 layers to film 6 layers we found similarities on the surface. For films with 2 and 3 layers (Figure 6 a) and b)) it seems these particles are breaking from the center outward and are taking torus form. The length of these particles for the film with 2 layers is 0.8 y 1 µm, while for the particles of the film with 3 layers is approximately 1.1 y 2.7 µm.

In the Figure 7 we have films with 4, 5 and 6 layers, in the films with 4 and 5 layers that in some places of the surface we found torus-shape particles and other particles that have already been taken other forms. There also holes with different forms, the length of the holes are approximately 0.5 to 0.9 µm, while the particles on the surface are...
approximately 1.6µm. For the film with 6 layers (Figure 7c)) we observed that in some parts we found different particles to previous, now seems that the surface is cracked. The size of these holes is between 0.7 y 1.19µm.

![Figure 7.- Surface of the ZnO thin films with a) 4 layers, b) 5 layers and c) 6 layers](image)

**ZnO-2**

ZnO thin films were prepared by the Sol-Gel method, we use methylamine as complexing agent. The solutions were deposited on the glass substrates by a spin coater at a rate of 3000 rpm for 20 s. The surface is shown in Figure 8 with a scanning area to 5.9µm x 5.6µm, we found spherical particles distributed over the surface. These particles are between 1 y 5µm in length.

![Figure 8.- Surface of the ZnO thin film obtained by the Sol-Gel method](image)

**ZnO-4**

ZnO thin films were deposited on glass substrates using simple and low-cost Sol-Gel method; methylamine was used as complexing agent. The substrate was spin coated with the sol with a speed of 3000 revolutions per minute for 20s; four substrates were coated with four layers each one. Each coating of the substrate was first dried with a drying time of 10 min at 150°C in a conventional plate. Finally, the films were put into a furnace and fired at 200°, 300°, 400° and 500°C for each substrate. In figure 9 we have films with different heat treatments, where we observe that the difference in the heat treatment temperatures doesn’t affect the thin film morphology, because all thin films presents clusters on the surface, even before and after heat treatment.
Conclusions

Using the Sol-Gel method we deposited CuO-SiO$_2$, FeO-SiO$_2$ and ZnO thin films using the Dip Coating and Spin coating technique. Different speeds were used for the deposition of thin films obtained by Dip Coating technique and we obtain different morphologies for each thin films analyzed. In the thin films of CuO and FeO we assume that the surface particles are oxides of copper and iron. In the diffraction patterns of ZnO (no presented) thin films we found that the presence of ZnO on the surface. In the ZnO-3 thin films obtained by the Dip Coating technique we have seen morphology of thread form over the entire surface. These thin films were analyzed before and after heat treatment and the morphology was acquired since the time of deposit. For the films obtained with Spin Coating technique were obtained semi spherical particles no matter if the number of layers was increased; the spinning times were similar for all films. No matter the heat treatment, the morphology is the same and don’t change. For the ZnO-1 thin films the morphology was different, because the absent of agent complexing make that the morphology change compare to all ZnO thin films. We can do more changes in the metal concentration, deposit rates and times as well as heat treatment for studying change in the morphology and we can compared with other thin films already obtained for approach the change in the structural, electrical and optical properties.

References

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