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Chemical Vapor Deposition of Aluminum Oxide Thin Films Using a Low-cost Direct Liquid Injection Delivery System: An Educational Laboratory Experiment

Serrano Pérez Edgar[1,*], Serrano Pérez Javier[2], José Manuel Juárez García[3], Juárez López Fernando[1]

[1]Instituto Politécnico Nacional, CIITEC, Cerrada de Cecati, Sta. Catarina, D.F. 02250, México
[2]Universidad Tecnológica de Tecámac, Carretera Federal México - Pachuca, Predio Sierra Hermosa, Tecámac, Estado de México
[3]Centro Nacional de Metrología, Km 4.5 Carretera a Los Cués, CP 76246 Municipio El Marqués, Querétaro, México
*Corresponding author: kolben88@yahoo.de

Abstract The chemical vapor deposition is an attractive technique for the growth of thin films and coatings, mainly focused in applications of wear protection, corrosion and microelectronic. This technique has received special attention because allows to deposit thin films and coatings on complex substrates with irregular geometry. The laboratory experiment presented includes a delivery system based on an electro mechanical injector, denominated direct liquid injection, an updated variant of the classical chemical vapor deposition process with the aim of providing a more constant vapor phase for the process. Although it's numerous advantages, the high price for this equipment represents a barrier for the widespread of this technique in academic environments. The accessible materials used for this experiment setup allows building the setup in laboratories and facilities of universities and research centers focused on nanotechnology and materials science. The experiment setup has been successfully build and is used as a compressive hands-on tool to teach undergraduate, master and doctorate students the direct liquid injection chemical vapor deposition technique.

Keywords: *direct liquid injection, chemical vapor deposition, alumina*

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1. Introduction

Chemical vapor deposition is a useful process which allows the growth of thin films and coatings from the thermal decomposition of a vaporized precursor on a surface. Very few reports dealing with educational experiments for the chemical vapor deposition technique have been presented [1,2]. In this work a variant of the technique is based on an electronically pulsed injection control with the aim of providing a constant vapor phase to the chamber and obtaining uniform thin films. The direct liquid injection metal organic chemical vapor deposition (DLI-MOCVD) can be defined by the particular way in which the precursor is delivered to the reaction chamber. In this technique the injection of a precise amount of atomized liquid or solid precursor dissolved in a convenient organic solvent is transported by mean of a carrier gas [3,4]. The small volume of the atomized liquid droplets allows a fast vaporization in a thermally heated chamber prior to be carried by an inert gas. As in noted, the chemical vapor deposition technique is an important technique used for research laboratories and industrial applications but this technique seems to be reserved for specialized environments and is not commonly found in undergraduate practices [2]. Additional work must be developed in order to explain as far as possible the multiple variants and advantages of each particular variant of the process. As can be noted, the nature of this experimental setup requires expensive specialized equipment which usually can't be reached by undergraduate and graduate students. In this work is presented the direct liquid injection variant of the chemical vapor deposition process from a practical educational point of view. aluminum oxide is an attractive material to be deposited in the form of thin films and coatings due to its wear resistance and protection against corrosion and oxidation [5,6,7,8]. For this experimental set up the selected precursor is Aluminum isopropoxide, an easy to handle, cheap non-pyrophoric white powder which can be dissolved in the majority of apolar solvents. Although this advantages, alkoxides usually are moisture sensitive, moreover the heating and cooling during sublimation could result in ageing of the precursor, and this makes the process non-reproducible under the same conditions after the precursor has been exposed to thermal changes [9]. In this sense, the direct liquid injection system reduces this drawback; the precursor is dissolved and confined in a pressurized vessel under an inert gas atmosphere in order to prevent the contact with moisture. The thermal heating of the precursor takes places an instant after is atomized to the vaporizing chamber reducing drastically the ageing of the precursor. This configuration results in an easy controllable thin film deposition under safe conditions.

In this article a low-cost experimental educative system is described to deposit alumina thin films. Although the objective is not mainly obtain high quality films, this approach results attractive for the best understanding of the MOCVD chemistry in a safer and more controllable way. The experiment has been successfully included in the course “Introduction to nanotechnology” as part of the Master in Advanced Technologies program held at the IPN CIITEC, Mexico.

2. Experimental Section

The experiment section has been developed for students of introduction to the nanotechnology courses. The easy operation by mean of an electronic controller allows that the experiments can be developed for individual or pairs of student. The configuration has allowed to students to manipulate chemicals such as metal organic precursor and organic solvents in order to prepare the solution which is pressurized and electronically pulsed injected to the vaporizing chamber. The polished samples should be prepared by students after depositions. The module is easy to operate and has been designed in order to produce thin films and coatings in a safe and controllable way. This experiment is ideal for being used in the inclusion of students of material science at undergraduate and graduate courses. Students in this experiment were directly enrolled in preparation activities such as precursor handling in a glove box and solution preparation with a convenient molar concentration, sample cleaning and optimizing the deposition process. The experimental set up can be easily be modified in order to use different metal organic precursors; liquid and solid powder can be diluted in an organic solvent. The diagram of the experimental set-up components is shown in Figure 1.

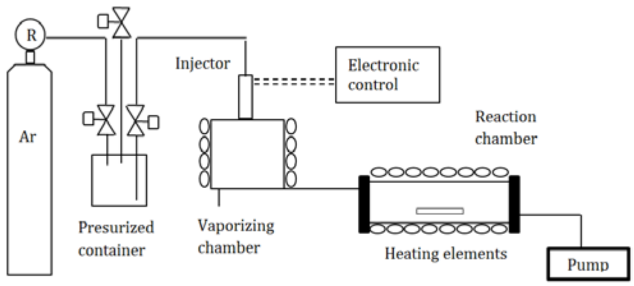

Figure 1. Schematic of the DLI MOCVD reactor used to deposit aluminum oxide thin films

In order to obtain precise data for the experimental set-up for process optimization, the solution container must be graduated to know the precise amount of precursor injected to the vaporizing chamber. The volume of the precursor solution with a known concentration must be measured before and after each deposition. The flow can easily be modified changing the time on and frequency parameters of the electronic control injector. As volume in a period of time can be measured, the gas phase flow can be computed for a mass balance, allowing interdisciplinary interaction for numerical modeling. Samples must be weight before and after depositions in order to know the gain weight and compute an average thickness. Numerical data can be fitted to experimental set ups in order to obtain a kinetic modeling which allows to improve uniform depositions under complex geometries [10,11]. A photograph of the DLI-MOCVD apparatus can be seen in Figure 2.

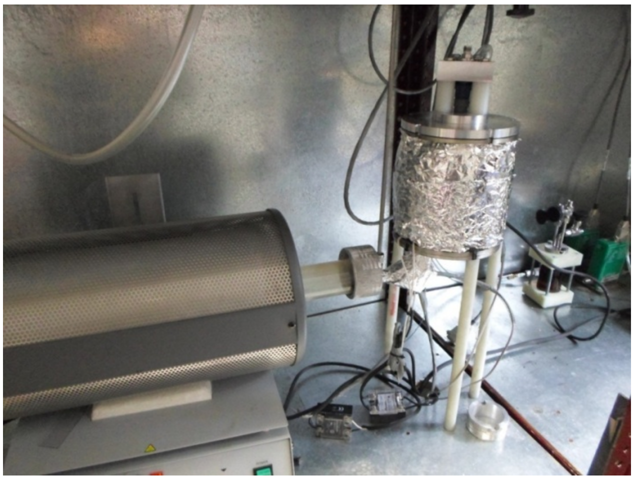

Figure 2. DLI MOCVD experimental reactor used to deposit aluminum oxide thin films

Depositions can be performed over a short period of time around 15-30 minutes. The heating of the chamber and vaporizer could take 25 minutes. Solution preparation can be prepared by a professor ahead of time if desired. Once deposition run has finished, it must be considered to take some minutes for the substrates cooling and removal from the inner chamber. As soon as the samples are removed, an optical inspection allows to initial characteristics of the films. Results can vary in a wide spectra of experimental set ups, from conformal uniform films to powder formation as residues of parasitic gas phase reactions. Sometimes thickness could be optically estimated looking at the color of the film. Some amorphous thin films, such as aluminum oxide and titanium dioxide exhibits different colors in function of the thickness of the sample after obtain the characteristic color of the material, usually before the thin film reach 1000 nm.

3. Characterization of Thin Films

Characterization can be performed to obtain further information of the films, such techniques includes reflectometry (thickness) and SEM (morphology), TEM (interface between substrate and the film), XPS analysis for elemental composition and stoichiometry. The thin film performance can be assessed in order to understand its behavior under mechanical, chemical (corrosion) and optical applications. These studies are not necessary for novice student which begins to understand the metal organic chemical vapor deposition mechanism. In the present work, the SEM micrograph shown in Figure 3 has revealed the topology of the thin film. The Figure 4 shows the EDS performed to the sample. Both analyses have been performed to a pure magnesium sample covered with an aluminum oxide thin film processed at 370 °C using aluminum isopropoxide and H_2O as reactive atmosphere under vacuum regime.

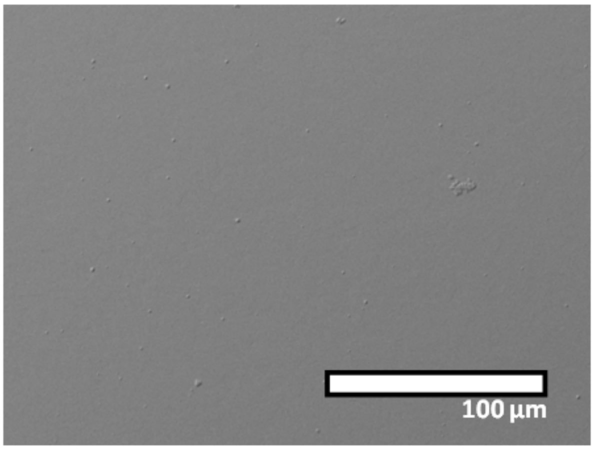

Figure 3. Scanning electron micrograph of an aluminum oxide thin film deposited on a pure magnesium sample

The SEM micrograph has revealed a smooth crack free surface with a granular morphology. The Energy dispersive X-ray Spectra has revealed aluminum, oxygen and carbon as constitutive elements on the film surface as can be seen in Figure 4.

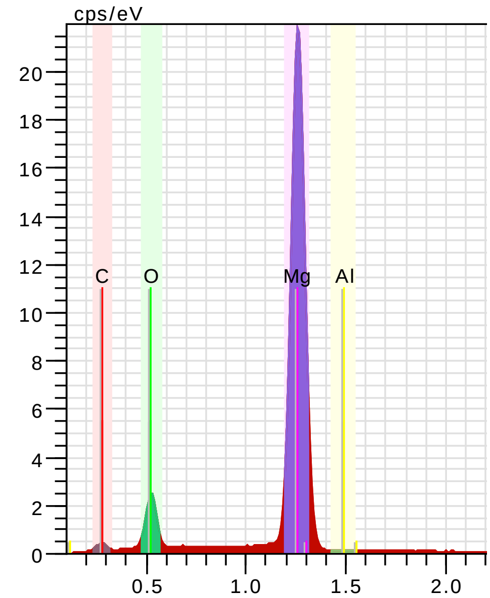

Figure 4. Energy dispersive X-ray Spectra of an aluminum oxide thin film deposited on a pure magnesium sample.

As an additional characterization tool, the element mapping has been revealed the elemental distribution in the thin film. Aluminum seems to be uniformly distributed in the sample around a rich oxygen surface as is shown in Figure 5.

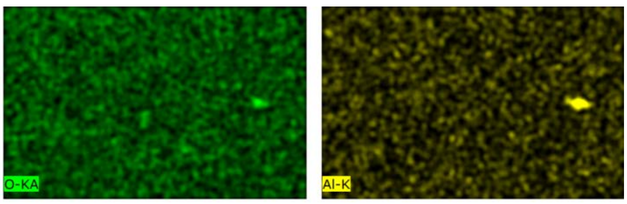

Figure 5. The Energy dispersive X-ray Spectra element mapping of an aluminum oxide thin film deposited on a pure magnesium sample. a) Oxygen b) Aluminum

4. Results

In this work the practical experience for student in the alumina thin film deposition combines process and chemical engineering abilities to perform a laboratory experimental practice; this allows gaining in the understanding for the chemical vapor deposition mechanism by mean of the practical approach. It is noted that students usually wanted to increase the thickness the thin films modifying operational parameters such as flow rate temperature and solution concentration. Novice students have shown significant increase in the understanding in the process which begins which the precursor transport to the vaporizer via liquid injection; the atomized solution droplets reaches the vaporizing chamber and the gas phase is transported by a carrier gas to the thermally heated reaction chamber. They have noted that in the reaction chamber a surface reaction takes place in order to obtain the alumina thin film deposition as product of the precursor decomposition.

4.1. Post-Lab Questions for Teacher and Student Feedback

To be solved individually

1. Draw the tetramer structure of the ATI in organic solvents
2. What does it means ATI can remain as a super cooled liquid?
3. What is the vaporizing and decomposition temperature of the ATI?
4. Draw the possible mechanism of the alumina thin film deposition, from precursor injection to removal of the sub products.
5. Look at the surface of you sample, Does it have powder? Which color does it have and how could you explain this color appearance? Does the film conformal?

To be solved in group

1. How the precursor “ageing” effect does modifies the reproducibility of the experiments?
2. Which are the main advantages of replacing sublimation and bubblers technologies for a direct liquid injection?
3. What are the energies of O-C and Al-O bands, which relation does it have with the precursor decomposition?
4. Which variable(s) do you consider have a strong effect on the deposition rate?
5. How could you improve the experimental setup?

5. Conclusion

The experimental set up combines a wide spectrum of laboratory techniques from the use of a glove box, sample and solution preparation and the use of electronic controllers to regulate the operational process; such as temperature, mass flow rates and injection parameters. Students can easily modify experimental parameters such as, liquid injection parameters (time open and frequency) or/and temperature of the chamber. After several assays, students have noticed the several influence of the temperature profile in the deposition rate. New ideas are depicted in order to determine which variable could reach a better quality or increase the thickness on the film, immediately students want to take in practice to solve its doubts. A first looking for the resulting samples can bring out an opportunity to see the color changes at the surface of the sample; this makes an initial idea of the product obtained, where a good result could bring the idea to go further with film deeper characterization. Usually amorphous alumina thin films with a thickness below of 1000 nm presents different transitional colors to the eyes. Particular characterization can be performed with additional collaborators which moreover, it brings the opportunity for students to know the measurement instruments which usually are just oriented for a scientific group.

Hazards

Alkoxide precursors and solvents must be handled carefully. Aluminum isopropoxide, a white powder precursor is toxic for health and ciclohexane a flammable toxic solvent must be far away from ignition sources. The argon pressurized container must have a protective coating as it could explode by mean of the pressure. Reactor chamber and vaporizer will be hot; student must to be careful of not touch this surfaces. Gloves, laboratory coat and glasses are required for all manipulations.

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