

# Microstructural characteristics and carbon content of Al<sub>2</sub>O<sub>3</sub> films as a function of deposition parameters

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Microstructural characteristics and carbon content in aluminum oxide thin films deposited on silicon substrates are reported as a function of deposition parameters such as substrate temperature and molar concentration of the spraying solution. The films were deposited using the spray pyrolysis technique from a spraying solution of aluminum acetylacetonate (Al(acac)<sub>3</sub>), dissolved in *N,N*-dimethylformamide (*N,N*-DMF), at temperatures in the range from 500 to 650 °C. Water mist was added during the deposition process and no further post deposition thermal treatments were given to these films. The films have a stoichiometry close to that expected for Al<sub>2</sub>O<sub>3</sub>, although, residual carbon from the deposition process was found to be present in these films. The surface roughness of the films was less than 20 Å, with deposition rates up to 540 Å/min, low chemical etch rates and activation energies around 27.6 kJ/mol were also determined.

High resolution transmission electron microscopy observation of these films show the presence of a tiny 5Al<sub>2</sub>O<sub>3</sub>:H<sub>2</sub>O crystalline phase embedded in a dense amorphous matrix. It was found that the average crystallite diameter of this phase depended on the deposition temperature as well as on the molar concentration of the spraying solution.

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## 1. Introduction

Aluminum oxide thin films have received an increasing amount of interest because of their dielectric characteristics on different types of microelectronic devices [1, 2]. Aluminum oxide has excellent properties such as high chemical stability, high radiation resistance, high thermal conductivity and low permeability to alkali impurities. These films constitute an excellent candidate for applications on MOS (metal-oxide-semiconductor) structures as gate oxides among several other applications, such as passivation layers, dielectric films in chemical sensors and as hard coatings on several substrates [3,4]. Spray pyrolysis is a deposition technique that is frequently used for film deposition on applications that require large area and low cost process [5]. Within this approach, aluminum acetylacetonate, Al(acac)<sub>3</sub>, has been used as reagent to obtain amorphous Al<sub>2</sub>O<sub>3</sub> films at temperatures in the range of 380–490 °C [6]. However, the incorporation of residual carbon into the aluminum oxide films due to the chemical precursor, is a serious issue. Previous work have shown that the presence of carbon modifies the electrical conduction characteristics of these films [7]. In particular, the

resistivity of the films was found to decrease as the amount of carbon in the films increased.

In this paper, a study of the micro-structural characteristics, the stoichiometry and carbon content of spray pyrolysis deposited aluminum oxide thin films is reported for different deposition parameters. The structural characteristics were studied by transmission electron microscopy (TEM), where a crystalline phase embedded in an amorphous matrix was observed. The behavior of the crystallite average diameter, as well as the relative amount of residual carbon in these films was studied as a function of deposition temperature and in particular for the two largest concentrations used of the reagent organic salt in the spraying solution.

## 2. Experimental details

The spray pyrolysis deposition system has been described in detail previously [8,9]. It consists of an ultrasonic generator operated at 0.8 MHz for mist generation from a spray solution. The mist is transported to the substrate surface, located on top of a molten tin bath, to achieve the pyrolysis reaction. Air was used as

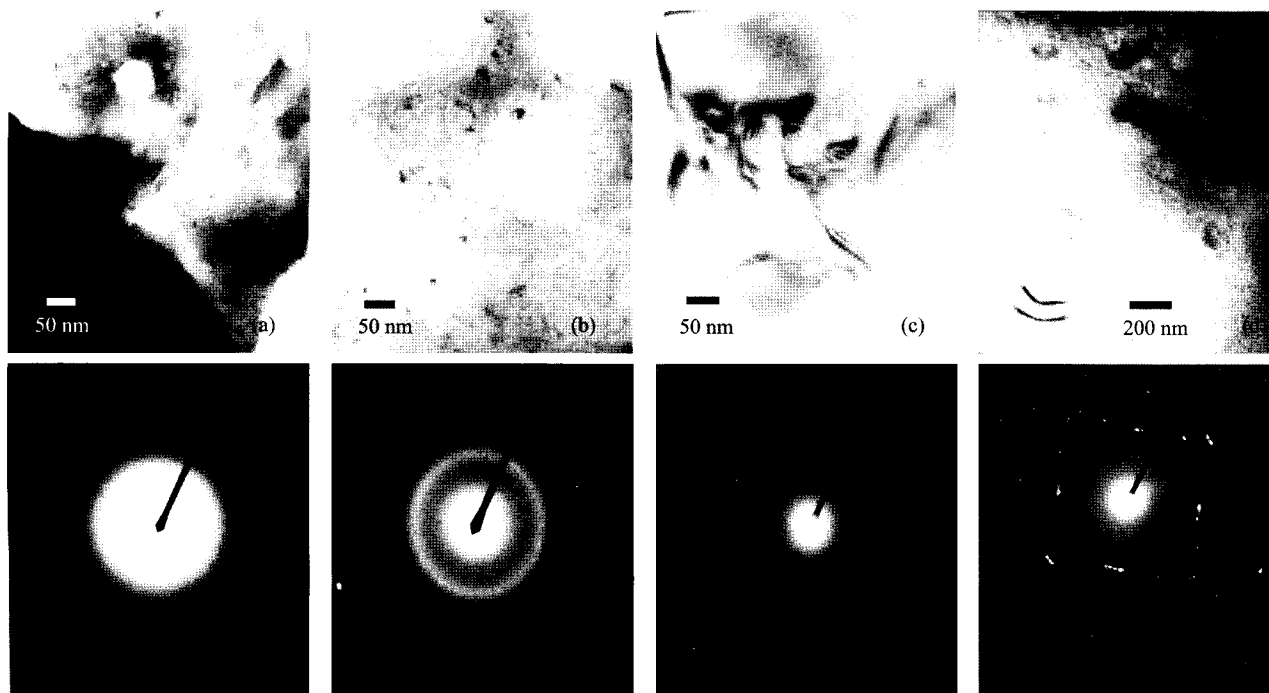


Figure 1 TEM micrographs and diffraction patterns for alumina thin films deposited at substrate temperatures of (a) 500 °C, (b) 550 °C, (c) 600 °C and (d) 650 °C with 0.36 M concentration of the spraying solution.

carrier gas at a flow rate of 8 l/min. Aluminum acetylacetonate, from Alfa Aesar, dissolved in *N,N*-dimethylformamide, from Mallinckrodt, was used as the spraying solution. Spraying solutions with reagent concentration of 0.03, 0.09, 0.15, 0.21, 0.30 and 0.36 Molar (M) were used for this work. The films were deposited with the addition of a stream of water mist in parallel to the spraying solution on *n*-type silicon (100) wafers of 0.1 and 200  $\Omega$  cm. The addition of water has been reported earlier to improve the overall physical characteristics of the aluminum oxide films deposited [1]. The substrate temperature during deposition was electronically controlled in the range from 500 to 650 °C. The chemical analysis was made employing a wavelength dispersive X-ray spectroscopy system trade Microspect model WDX-400 attach on a scanning electron microscope by Cambridge-Leica model stereoscan 440, using the Multielement X-ray Reference Standard (Microspec) Serial Number 0034, part No. 8160-53. The structural characterization was performed on both a conventional JEOL 1200 EM and a high resolution JEOL 4000 EX transmission electron microscope, and the average crystallite diameter was determined from the TEM micrographs using the ISIS IMQuant Oxford Instruments software package. Surface roughness was carried out in a Park Scientific Instruments Atomic Force Microscope. A single wavelength ellipsometer (633 nm), from Gaertner, was employed to measure the thickness of the films (in the range of 900–1100 Å). Etch rate measurements were determined using  $\text{H}_3\text{PO}_4$  at 60–70 °C as chemical etchant.

### 3. Experimental results and discussion

Fig. 1 shows the micrographs and the corresponding electron diffraction patterns for films deposited at (a) 500 °C, (b) 550 °C, (c) 600 °C and (d) 650 °C substrate

temperature. The TEM images show small crystallites embedded in an amorphous matrix with sizes that increase as the deposition temperature is increased. This behavior can be appreciated from the electron diffraction patterns as well. They show a cloud shape for the lowest deposition temperature (500 °C) and end up with a ring pattern made by spots for the highest temperature (650 °C). The high resolution transmission electron microscopy micrograph image (Fig. 2) shows tiny crystalline zones (around 20 nm in average) in amorphous films deposited at 550 °C with reagent concentration of 0.36 M. From the indexing of the diffraction patterns, these tiny phase corresponds to aluminum oxide hydrate of composition  $5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  with hexagonal unit cell, lattice constants  $a = 5.575 \text{ \AA}$ ,  $c = 8.76 \text{ \AA}$  according to the diffraction card ASTM 221119 [10]. Table I lists the ratio of oxygen to aluminum in atomic percent, for all films studied. It is observed that this ratio is close to the expected value of 1.50 for an  $\text{Al}_2\text{O}_3$  stoichiometry in all cases, although

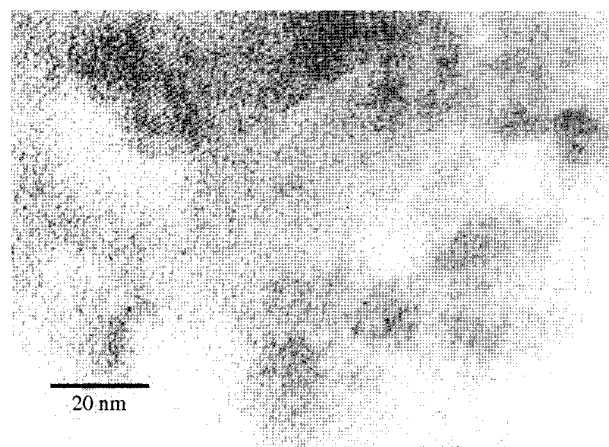


Figure 2 HRTEM image for a film deposited at a substrate temperature of 550 °C and 0.36 M concentration of the spraying solution.

TABLE I Ratio of oxygen to aluminum, in atomic percent as a function of the substrate temperature and molar concentrations in the spraying solution for aluminum oxide films

Mol	T = 500 °C	T = 550 °C	T = 600 °C	T = 650 °C	Average
0.03	1.66	1.73	1.83	1.79	1.75
0.09	1.63	1.61	1.70	1.72	1.66
0.15	1.65	1.69	1.69	1.75	1.69
0.21	1.71	1.76	1.77	1.68	1.73
0.30	1.52	1.54	1.52	1.59	1.54
0.36	1.69	1.59	1.50	1.69	1.62

TABLE II Carbon content in atomic percent, as a function of the substrate temperature and molar concentration in the spray solution for aluminum oxide films

Mol	T = 500 °C	T = 550 °C	T = 600 °C	T = 650 °C	Average
0.03	1.60	1.97	1.60	1.89	1.77
0.09	2.19	2.32	1.88	2.00	2.10
0.15	2.25	2.08	1.90	1.84	2.02
0.21	2.12	2.00	1.99	2.12	2.05
0.30	2.02	2.57	2.64	2.50	2.43
0.36	2.51	2.69	2.68	2.54	2.78

there is tendency to have a slight excess of oxygen. This oxygen excess could be due to the presence of the water molecule in the  $5\text{Al}_2\text{O}_3 : \text{H}_2\text{O}$  structure. Table II shows the atomic percent carbon content present in each film. The highest carbon content was found at the highest molar concentration of the spraying solution and a at substrate temperature of 550 °C.

Figs. 3 and 4 show the average crystallite diameter and the atomic percent carbon content as a function of substrate temperature during deposition for the most stoichiometry films (0.3 and 0.36 M, respectively). It can be observed that at low deposition temperatures there is an increasing behavior of both the carbon content and the average crystallite diameter, but for temperatures above 550 °C the carbon content starts to decrease while the average crystallite diameter continues to increase regardless of the molar concentration of the spraying solution. It should be stressed that the average crystallite diameter is strongly affected by the molar concentration

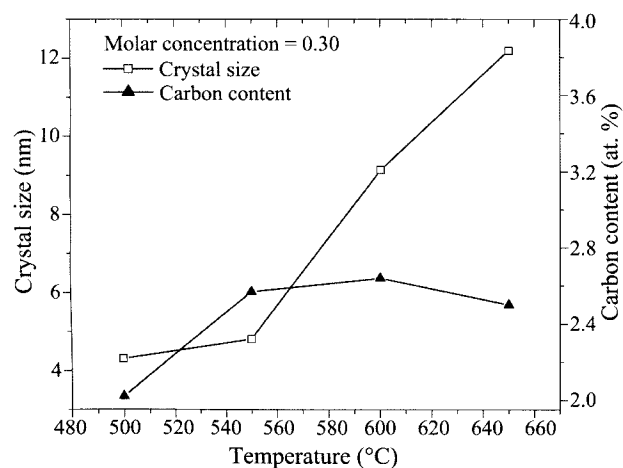


Figure 3 Variation of the average crystal size and carbon content as a function of the temperature for aluminum oxide films deposited with 0.36 M concentration of the spraying solution. The solid lines are only to guide the eye.

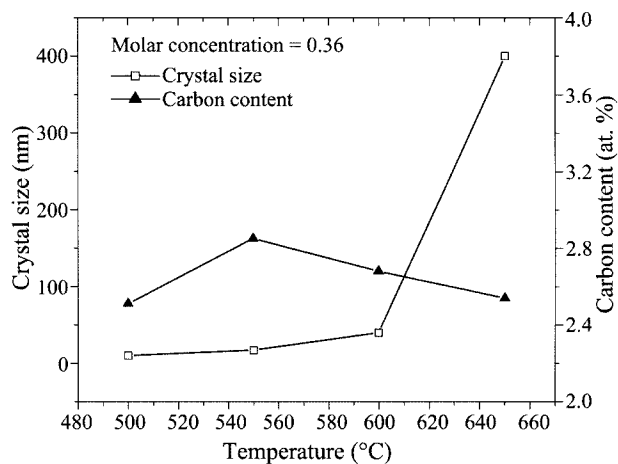


Figure 4 Correlation between the average crystallite size and carbon content and the substrate temperature for aluminum oxide films deposited with 0.36 M. The solid lines are only to guide the eye.

of the spraying solution, being up to more than one order of magnitude larger for the highest concentration and deposition temperature. On the other hand, the carbon content is less dependent on the molar concentration of the spraying solution, even though the highest carbon content still corresponds to the films deposited with the highest molar concentration of the spraying solution. It seems clear that the origin of the carbon impurities in the films is in the high carbon content of the reagents and solvent used for the deposition process. The dependence with deposition temperature of carbon content in the films could imply that at temperatures above 550 °C, a more efficient elimination of the carbon occurs, probably because an easier and/or more complete dissociation of the organic molecules involved. Also, at these temperatures the average size of the crystallites in the films starts to increase because a higher thermal energy is available. This process could also favor the segregation and elimination of carbon from the films.

Fig. 5 shows the surface morphology observed with atomic force microscopy of a film deposited with 0.03 M and at 600 °C. In general, the surface roughness of the films resulted extremely low for all the deposition conditions studied. Fig. 6 shows the films surface roughness as a function of the molarity of the spraying solution for samples deposited at 600 °C. The surface

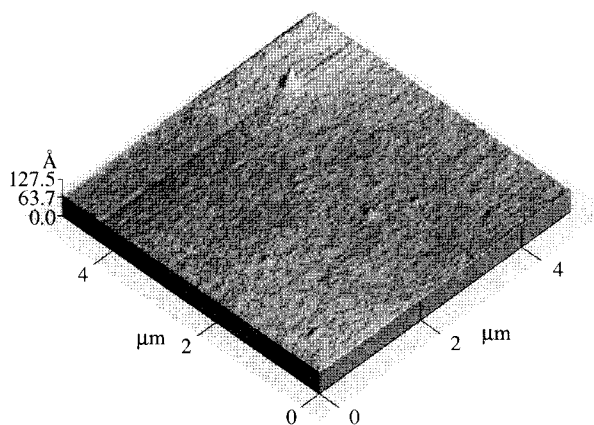


Figure 5 Morphology of the surface roughness for a film deposited at 600 °C, with 0.03 M concentration of the spraying solution.

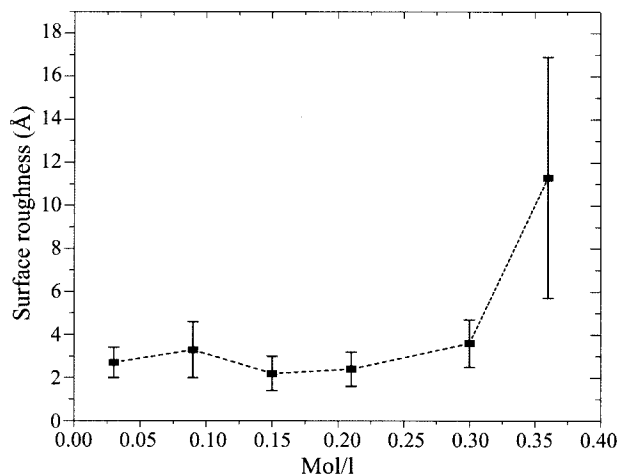


Figure 6 Mean square root surface roughness as a function of the spraying solution for samples deposited at 600°C.

roughness increases when the molarity of the solution increases. However, it was always less than 20 Å. The roughness values were similar to the one reported by Ott *et al.* [11] for aluminum oxide thin films deposited by the use of sequential surface chemical reactions, at much lower deposition rates. Thermogravimetric measurements on Al-acac show that this material is fully vaporized in the range of 145–283°C [7]. This could explain the low surface roughness values shown by these films, since the film deposition process is obtained from a vapor phase of the reactants, that usually results in an homogeneous and uniform deposition process. The increase in surface roughness of the films with 0.35 M concentration of Al(acac)<sub>3</sub> in the deposition solution, might be due to the increase in the growth rate of the films and/or to the decrease in the relative amount of water present during deposition of the films, since the rate of water mist used during the film deposition was kept constant for all the spraying solution concentrations. The deposition rate of the aluminum oxide thin films shown a gradual increase in the deposition rate with the increase of the molar concentration of the solution, this is illustrated in the Fig. 7. The activation energy for this deposition process of aluminum oxide films show in average an activation energy of 27.6 kJ/mol. This value is similar to the value of 28.0 kJ/mol reported when

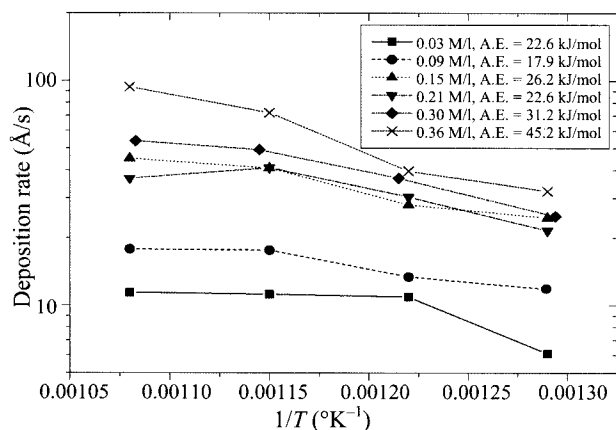


Figure 7 Deposition rate of the aluminum oxide thin films as a function of molar concentration.

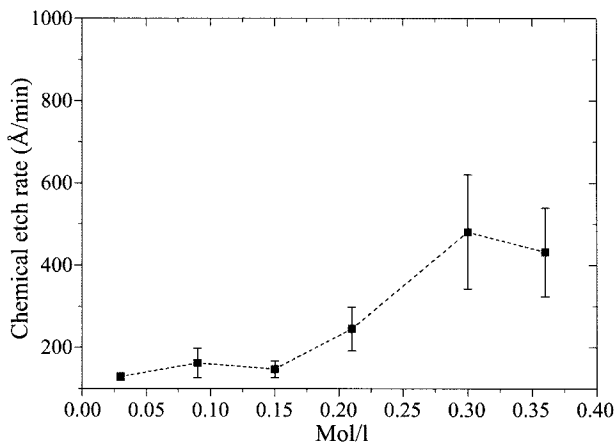


Figure 8 Chemical etch rate as a function of the spraying solution concentration for samples deposited at 600°C.

Al(acac)<sub>3</sub> is used to obtain aluminum oxide films using a low-temperature atmospheric-pressure chemical vapor deposition method [12].

Fig. 8 shows the chemical etch rate of the films using phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) as etchant. It is observed that there is a low etch rate for the films deposited with lower molar concentration than 0.20 M (129–162 Å/min). The etch rate for the films deposited with the larger molar concentration is of the order of 400 Å/min that is, more than double of the etch rate for concentrations below 0.15 M. The chemical etching values observed are comparable to those reported for high-quality aluminum oxide thin films deposited by CVD (180 Å/min)[12], giving a reference for these films quality. Since the etch rate is inversely related with the density of the films, that is, the lower the etching rate the more dense the film is, these films show in general good density characteristics that have a tendency to decrease as the molar concentration of the spraying solution.

#### 4. Conclusions

Aluminum oxide thin films obtained by ultrasonic spray pyrolysis from aluminum acetylacetonate and dimethylformamide on silicon substrates have been studied as a function of deposition temperature and spraying solution concentration. TEM observations have shown that these films are mainly amorphous with the inclusion of crystallites of the 5Al<sub>2</sub>O<sub>3</sub> : H<sub>2</sub>O phase. The size of the crystallites depends on the deposition temperature and the spraying solution concentration. The largest crystallites were observed in samples deposited at 650°C and the highest spraying solution concentration. The films resulted were dense (etching rates less than 500 Å/min in hot phosphoric acid), with a very low surface roughness (rms-roughness less than 12 Å), a stoichiometry very close to Al<sub>2</sub>O<sub>3</sub> and deposition rates up to 540 Å/min. Residual carbon (up to 2.69% at.) was found in these films. The maximum carbon content was obtained at 550°C and at the highest molar concentration. It has been determined that these films deposited under the proper conditions may have low roughness, high density, high depositions rates and structural characteristics which are required for a variety of applications such as optical coatings, protective films for chemical corrosion and

abrasive agents on metallic surfaces and as insulating layers in microelectronics.

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