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Aluminum oxide thin films deposited on silicon substrates from $Al(NO_3)_3$ and an organic solvent by spray pyrolysis

M. Aguilar-Frutis[*, 1], **J. Guzmán-Mendoza**[1, 2], **T. Alejos**[1], **M. García-Hipólito**[2], and **C. Falcony**[3]

[1] Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del IPN, Legaria 694 Col. Irrigación, Del. Miguel Hidalgo C.P. 11500, Mexico DF, México
[2] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Del. Coyoacan C.P. 04510, Mexico DF, México
[3] Centro de Investigación y de Estudios Avanzados del IPN, Apdo. Postal 14-740, 07000, Mexico DF, México

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Aluminum oxide thin films were deposited on silicon substrates at temperatures in the range from 500 to 650 ºC, from $Al(NO_3)_3$ dissolved in N,N-Dimethylformamide and using the spray pyrolysis technique. The films of aluminum oxide resulted stoichiometric, amorphous and optically transparent in the visible spectrum, with a refractive index close to 1.66 when a 0.2 molar solution of $Al(NO_3)_3$ was used. The films as deposited had a surface roughness as low as 3.8 nm and were almost free of Al–OH bonds, depending on the experimental deposition conditions. The best films were incorporated in a Metal–Oxide–Semiconductor structure and were able to stand electric fields up to 2 MV/cm without destructive breakdown and a dielectric constant of 7.95.

1 Introduction

Aluminum oxide thin films have been studied recently because of their possible application as high dielectric constant layers on different types of microelectronic devices. Aluminum oxide thin films present high chemical stability and high radiation resistance, high thermal conductivity and low permeability to alkali impurities [1–4]. These characteristics make this material a good candidate for applications on Metal-Oxide-Semiconductor (MOS) structures, as high dielectric constant gate oxide, among several other applications; such as passivation layers and hard coatings on different surfaces [5]. All these applications require films with good homogeneity, high density and excellent dielectric characteristics as well as a low surface roughness. Aluminum oxide thin films have been deposited mainly from organic reagents [6–10], using a wide variety of deposition techniques; most of these techniques involve deposition from chemical vapors. Physical deposition processes have also been studied for this purpose [11–12]. The use of an organic reagent has the disadvantage of presenting both; complex chemical reactions as well as high cost of the reagent itself [13]. The deposition of aluminum oxide thin films from an inorganic salt as source of aluminum, such as $AlCl_3$, has also been performed by chemical vapor deposition [14–15]. However, when using $AlCl_3$ as source of aluminum, a complex deposition process involving high temperatures during deposition (in the range from 700 to 790 ºC) has to be implemented in order to obtain good film characteristics [14]. For some applications, the interest in obtaining aluminum oxide thin films at low temperatures is very important [16]. The spray pyrolysis technique has been de-

[*] Corresponding author: e-mail: mafrutis@yahoo.es, Tel.: (52) 55 5729 6000 ext. 67738, Fax: (52) 55 5557 5103

scribed previously [17]. In this technique an ultrasonic generator is used for mist production from a liquid solution. The generated mist is transported to a heated substrate, in order to achieve a pyrolysis reaction. In this deposition technique the deposition rate and film properties depend on a number of experimental parameters, such as the temperature of the substrate, the flow rates of the aerosol and carrier gas, the distance between the nozzle and the substrate, and the concentration of the reactants in the solution. In this work, we report the deposition of aluminum oxide thin films on silicon substrates with good optical, structural and electrical characteristics, from an inexpensive inorganic salt, as reactive source of aluminum, [$Al(NO_3)_3$], dissolved in an organic solvent, N,N-Dimethylformamide (N,N-DMF), and using the spray pyrolysis technique at temperatures below 650 ºC. Previous reports involving inorganic salts; such as $AlCl_3$ and $Al(NO_3)_3$ to prepare aluminum oxide thin films by spray pyrolysis have used water as solvent. In particular, when $Al(NO_3)_3$ is used to deposit Al_2O_3 films on glass substrates, the films are opaque, exhibit huge surface islands and a high surface roughness. Furthermore, due to the hydrophobic characteristic of silicon, it has been impossible to deposit these films on this type of substrate using $Al(NO_3)_3$ in a water based solution. $Al(NO_3)_3$ has also been used previously in the preparation of aluminum oxide powders by spray pyrolysis [18].

2 Experimental

Aluminum nitrate ($Al(NO_3)_3$) from Aldrich Chemical Co., dissolved in N,N-DMF, from Mallinckrodt, were used as spraying solution. Solutions with molar concentrations (M) of 0.10, 0.20 and 0.40 of $Al(NO_3)_3$ in N,N-DMF were prepared. The best characteristics were obtained with 0.2 M. All the films were deposited on quartz slides, n-type Si(100) wafers of high resistivity (200–300 Ω cm) and on n-type Si(100) wafers of low resistivity (0.1–10 Ω cm). The silicon substrates were given the RCA cleaning procedure before the deposition process [19]. The substrate temperature during deposition was in the range from 500 to 650 ºC. Air, at a flow rate of 14 liters/min, was used as carrier gas, during deposition of the films. The distance between the nozzle and the substrate was 0.5 cm, and the spraying solution containing the aluminum source reactant ($Al(NO_3)_3$ at different molar concentrations) is consumed at a rate of approximately 1 ml/min. The thickness and refractive index of the films were measured with a manual ellipsometer (at 630 nm) from Gaertner. A 750 Magna-IR NICOLET spectrometer was used for the infrared (IR) measurements. A scanning electron microscope (Jeol, JSM-6300) was used to plan view the surface of the films and also to carry out the chemical analysis by energy dispersive spectroscopy (EDS). The chemical composition measurements were performed at a beam accelerating voltage of 3 kV. An Al_2O_3 crystal was used as a reference for the chemical analysis, and the Voyager microanalysis system from Noran instruments was used for the chemical composition analysis. The surface roughness measurements were carried out on a Park Scientific Instruments atomic force microscope. A Dektak3 surface profiler system was also used to characterize the surface morphology of the films. Finally, the films with the best characteristics were incorporated into Metal-Oxide-Semiconductor (MOS) structures for their electrical characterization. For this purpose, a commercial equipment by Keithley Instruments was used.

3 Results and discussion

Figure 1 shows the deposition rate of the films synthesized with a 0.2 M solution as a function of the substrate temperature. Deposition rates up to 0.5 nm/sec, approximately, are obtained. Films deposited with a lower or a higher molar concentration, resulted in much lower deposition rates. In some cases the deposition rate was extremely low (films deposited with a 0.4 M at 600 and 650 ºC). The only adhesion test carried out on the films was the adhesive tape test, which they resisted without problem.

Figure 2 shows the refractive index for the films of aluminum oxide deposited with 0.2 M of $Al(NO_3)_3$ as a function of the substrate temperature. A maximum around 550 ºC, reaching a value close to 1.66, is observed from this plot. This value is similar to the one that has been reported for high quality aluminum oxide thin films [20]. Films deposited with larger or smaller molar concentrations resulted in a reduction

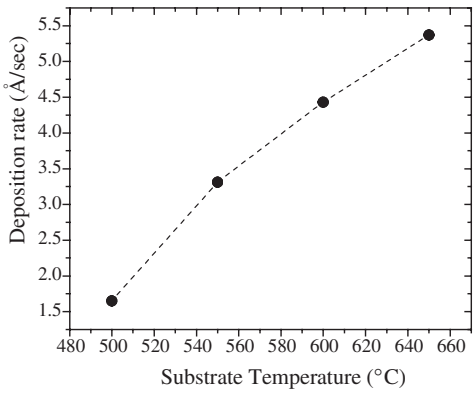

Fig. 1 Deposition rate as a function of the substrate temperature for the aluminum oxide thin films deposited with a 0.2 molar concentration of $Al(NO_3)_3$.

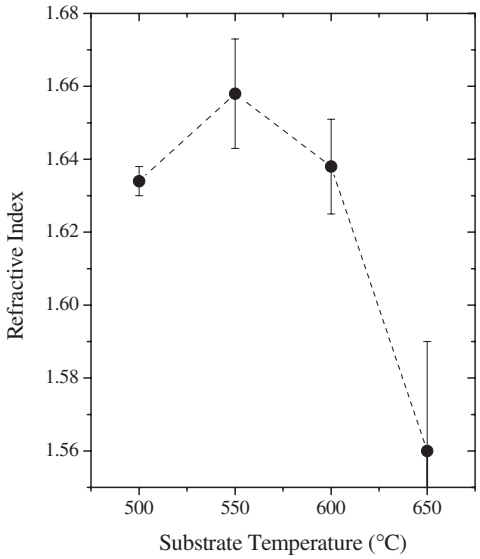

Fig. 2 Refractive index for the aluminum oxide films, as a function of substrate temperature, for the films deposited with a 0.2 molar concentration of $Al(NO_3)_3$.

of the refractive index with increasing substrate temperature. The surface morphology of the films, observed in plan view by SEM, is shown in Fig. 3, for the case of films deposited with a 0.2 M solution at 500, 550, 600 and 650 °C. In these images, a continuous film is observed in all cases. However, the formation of protruding features of Al_2O_3 (as determined by EDS) on top of the film was observed. The surface density and size of these features increased as the deposition temperature was increased. Figure 4

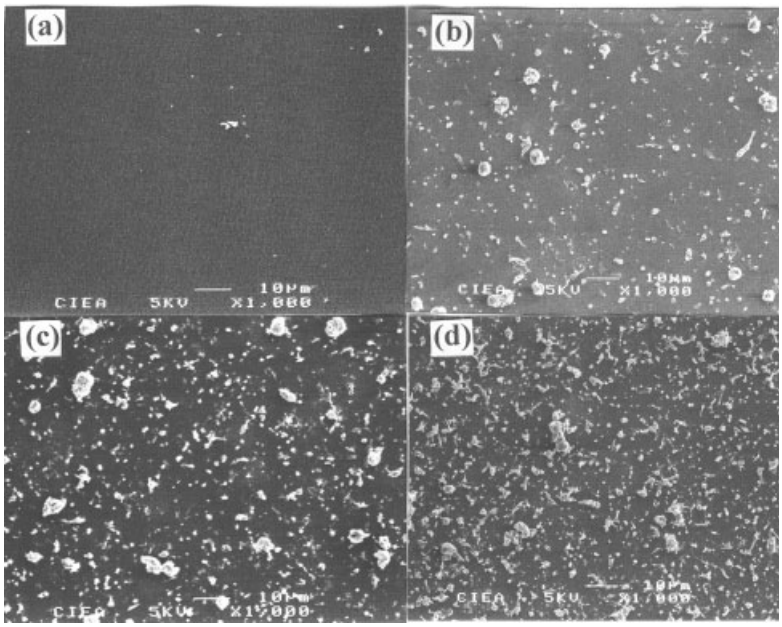

Fig. 3 Plan view surface morpholgy of the films deposited with a 0.2 molar concentration of $Al(NO_3)_3$ at temperatures of 500 ºC to 650 ºC (a–d).

Table 1 rms surface roughness (nm) of the films determined by Atomic Force Microscopy aluminum oxide films deposited from $Al(NO_3)_3$.

	500 ºC	550 ºC	650 ºC	Average
0.1 M	3.26	3.56	4.60	3.81 ± 0.53
0.2 M	18.9	7.8	28.1	18.27 ± 6.98
0.4 M	4.69	2.93	–	3.81 ± 0.88

shows the behavior of the maximum peak to valley vertical distance of these surface features as function of deposition temperature. The scan lenghts were of 100 μm and were performed on different places of the samples by profilometry. Figures 3 and 4 indicate that the films with more surface density of the protruding features show also a larger height distribution. Table 1 lists the rms surface roughness determined by AFM on the continuous film part over scanned areas ranging from 4 to 100 μm^2. Films deposited with 0.1 and 0.4 M present, in general, lower average surface roughness than that observed for films deposited with 0.2 M. However, for these experimental molar conditions (0.1 and 0.4) both, the deposition rate and refractive index were lower, compared with the films deposited with 0.2 M. Even though the surface morphology presented by the films deposited with 0.2 M is rough, it is lower than that observed on films deposited on glass when water is used as solvent for $Al(NO_3)_3$ (no film deposition is obtained on silicon due to the hydrophobic nature of this substrate under these conditions). It is also known that the surface morphology of the aluminum oxide films deposited on glass substrates, using $Al(NO_3)_3$ and water as solvent, is extremely irregular, presenting huge islands throughout all the surface. These results suggest that the role of the solvent during spray pyrolysis deposition of the film is very important.

The relative chemical composition of the films deposited with a concentration of 0.2 M, determined by EDS, shows that the stoichiometry is close to Al_2O_3 (the atomic oxygen to atomic aluminum ratio resulted in 1.51 ± 0.03). The infrared spectrum of a film deposited at 500 ºC and 0.2 M is shown in Fig. 5. This spectrum shows the characteristic Al_2O_3 band centered between 500 and 900 cm^{-1}. This band is an overlap of the O–Al–O bending mode that appears at 650–700 cm^{-1} and the Al–O stretching mode at 750–850 cm^{-1} [21]. The Al–OH band (3250–3300 cm^{-1}) is not present in this plot. This band however, was present for other molar concentrations or temperatures above 600 ºC, suggesting that some degree of porosity is present in those films. This behavior is in agreement with the results obtained for the refractive index. Al–OH bonds are not present when the films have a refractive index higher than

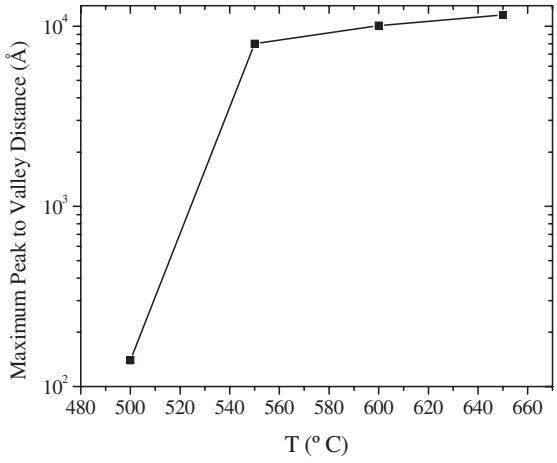

Fig. 4 Maximum peak to valley vertical distance of the films deposited at 0.2 M as a function of the substrate temperature.

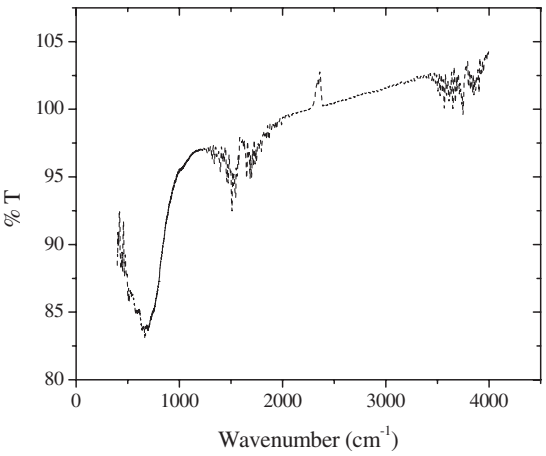

Fig. 5 Infrared spectrum of an aluminum oxide film deposited at a substrate temperature of 500 ºC with a 0.2 molar concentration of $Al(NO_3)_3$.

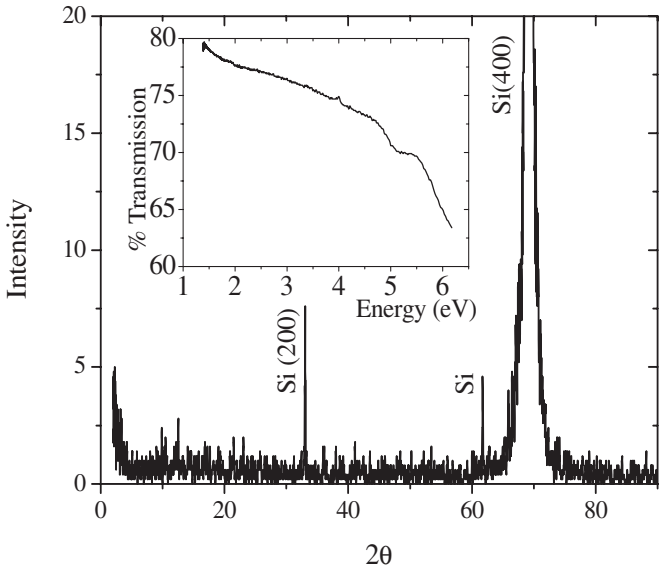

Fig. 6 X-ray diffraction pattern of a film deposited at 550 ºC. The inset shows the optical transmission measurements of a film deposited on quartz slides at the same temperature.

approximately 1.625, indicating a more compact film. According to Gladstone-Dale equation; the density $\rho = k(n-1)$, where n is the refractive index and k is a constant, therefore, the larger the refractive index, the higher the density of the film [20]. From these structural and optical characteristics, it is observed that those films deposited with 0.2 M of $Al(NO_3)_3$, present the best overall characteristics.

Figure 6 shows the X-ray diffraction pattern of a film deposited at 550 ºC and with 0.2 M. There are no diffraction peaks coming from the thin film of aluminum oxide. The only peaks observed are those found in bare silicon. This might indicate that the films are basically amorphous. The inset of Fig. 6 shows the optical transmission in the UV-Vis range, for a film deposited at the same temperature on a quartz slide, showing a % transmittance over 70% in the 1.5 to 4 eV range.

The films with the best overall characteristics (deposited at 500 ºC and with 0.2 M) were incorporated into MOS structures. Fig. 7 shows three consecutive $I-V$ ramps performed on a capacitor prepared with this type of films. It is observed that these films can stand electric fields up to 2 MV/cm. The inset of Fig. 7 shows the high frequency capacitance versus voltage curve of the same sample. The dielectric constant, obtained from the $C-V$ curve, for the films prepared with 0.2 M was 7.95 ± 0.66, correspond

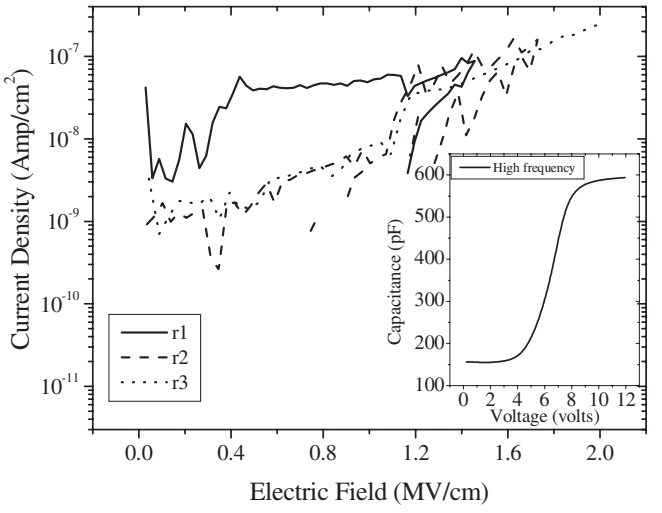

Fig. 7 Three consecutive ramp $I-V$ curves (r1, r2 and r3), performed on a MOS structure fabricated with a film deposited at 500 ºC and with 0.2 molar concentration of $Al(NO_3)_3$. The inset shows the high frequency capacitance versus voltage curve, performed on the same MOS capacitor.

ing to a good quality aluminum oxide film [22]. The electrical characteristics of the films deposited at higher substrate temperatures, for the same molar concentration, 0.2 M showed a lower dielectric strength. The good electrical performance of the films deposited at 500 ºC with 0.2 M, is probably due to the low density and size of surface features, as well as to their good optical and structural characteristics. Finally, the possibility of obtaining good properties for aluminum oxide thin films on silicon from $Al(NO_3)_3$ at low temperatures and without any further thermal treatment, is very important, since very scarce reports have been published for aluminum oxide thin films deposited with this type of inorganic reagent up to date.

4 Conclusions

Stoichiometric aluminum oxide thin films, deposited on silicon, by ultrasonic spray pyrolysis, were obtained for the first time, to our knowledge, from $Al(NO_3)_3$, as inorganic aluminum source, dissolved in an organic solvent (N,N-DMF). The importance of the solvent is such that made possible the deposition of films on silicon substrates, with good optical, structural and electrical characteristics. Amorphous, transparent and stoichiometric films with a refractive index close to 1.66 were obtained with a 0.2 M solution. The films as deposited resulted almost free from Al–OH bonds up to a substrate temperature of 550 ºC when they were deposited with this spraying solution molarity. The surface roughness of the films resulted in the range from 38 to 182.7 Å. The films as deposited (no further thermal treatment) are able to stand electric fields up to 2 MV/cm and show a dielectric constant of 7.95 ± 0.66.

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