

## FTIR and X-ray diffraction analysis of Al<sub>2</sub>O<sub>3</sub> nanostructured thin film prepared at low temperature using Spray pyrolysis method

Saif A. Naayi<sup>1</sup>, Azhar I. Hassan<sup>1</sup>, Evan T. Salim<sup>1,\*</sup>

<sup>1</sup>Laser Science and technology Branch, University of Technology, 10066 Baghdad, Iraq

### ABSTRACT

*Very simple and low-cost raw material was used to prepare Al<sub>2</sub>O<sub>3</sub> nano-thin films. Only Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 2-methoxy ethanol were used to prepare the required thin films employing spray pyrolysis method at low substrate temperature. The FTIR results ensure the formation of the Al-O bond which appears at different absorption peaks. Effect of substrate temperatures reveals the dependence of Al-O bond formation on the variation of substrate temperatures from 200 up to 400°C. This was confirmed by the x-ray diffraction results which ensure the formation of the Al<sub>2</sub>O<sub>3</sub> amorphous structure. SEM results ensure the formation of nanostructure Al<sub>2</sub>O<sub>3</sub> thin films*

### 1. INTRODUCTION

Aluminum oxide as a high-k gate dielectric material is of high desired in optoelectronic device applications. It has potentials ability to replace the SiO<sub>2</sub> buffer layer in the MOS device, MISIM device structures, and in ACTFEL devices [1, 2]. It has other important properties, such as low permeability, high thermal conductivity, proper hardness, very good thermal and chemical stability, and high radiation resistance [3, 4].

Al<sub>2</sub>O<sub>3</sub> also have a high refractive index, resistance against hostile environments beside it good transparency [1]. Due to these properties, Al<sub>2</sub>O<sub>3</sub> offer a broad range of industrial applications such as anti-reflection coating, anti-corrosive coatings, capacitance-humidity sensors, ICs heat sinks beside the fabrication of the different optoelectronic device such as thin-film transistors (TFTs), metal-oxide-nitride-semiconductor (SONOS) and complementary metal-oxide-semiconductor (CMOS) devices, [5- 8]

Various technique was employed to prepare Al<sub>2</sub>O<sub>3</sub> thin films such as CVD chemical deposition [11], metalorganic chemical vapor deposition (MOCVD) [3] electron beam deposition [12], magnetron sputtering [13], filtered vacuum arc [14], spray pyrolysis [1], plasma-enhanced chemical vapor deposition (PECVD) [15], sol-gel [16], PLD [17], aerosol-jet deposition (AJD) [18], atomic layer deposition (ALD) [19], and. Spray pyrolysis presents an efficient, inexpensive technique. It represents a simple, coast effective, and no vacuum is required [24].

It needs only decomposition of the fine droplets reaching to the heated substrate. Many researchers are interested in certain aspects of Al<sub>2</sub>O<sub>3</sub>. Shamala et al. [8,9] have complete an excellent work on achieving different characteristics but focused on electrical properties and its application as a humidity sensor. Duta et al. [10,20] characterized the morphological and structural aspects of Al<sub>2</sub>O<sub>3</sub> films as a solar thermal absorber.

\*For correspondence; Tel. + (964) 7715752087, E-mail: [evan\\_tarq@yahoo.com](mailto:evan_tarq@yahoo.com).

There are numerous works prepared alumina thin films using aluminium (III) acetylacetonate dissolved in different solvents [1,9,21,22], but in this work,  $\text{Al}_2\text{O}_3$  thin films were prepared using very simple raw materials included Aluminum nitride and 2-methoxy ethanol only at different substrate temperature. Were to the best of our knowledge this raw material was not extensively studied yet employing spray pyrolysis method. Structural properties of the films were examined using X-ray diffraction and FTIR analysis.

## 2. EXPERIMENTAL

$\text{Al}_2\text{O}_3$  thin films were deposited on a quartz substrate using a laboratory spraying system. A precursor solution of 0.1M contains aluminum nitrite ( $\text{Al}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) salt which dissolved with (10:40) 2-methoxy ethanol and deionized water. Quartz substrates were cleaned carefully using ultrasonic wave and ethanol to remove any contamination. The solution sprayed on the substrate at different substrate temperature (200, 250, 300, 350, and 400) °C. Optimized parameters of deposition are as follows: the solution flow rate was 5 ml/min, carrier gas was compressed air and nozzle to substrate distance was 30 cm.

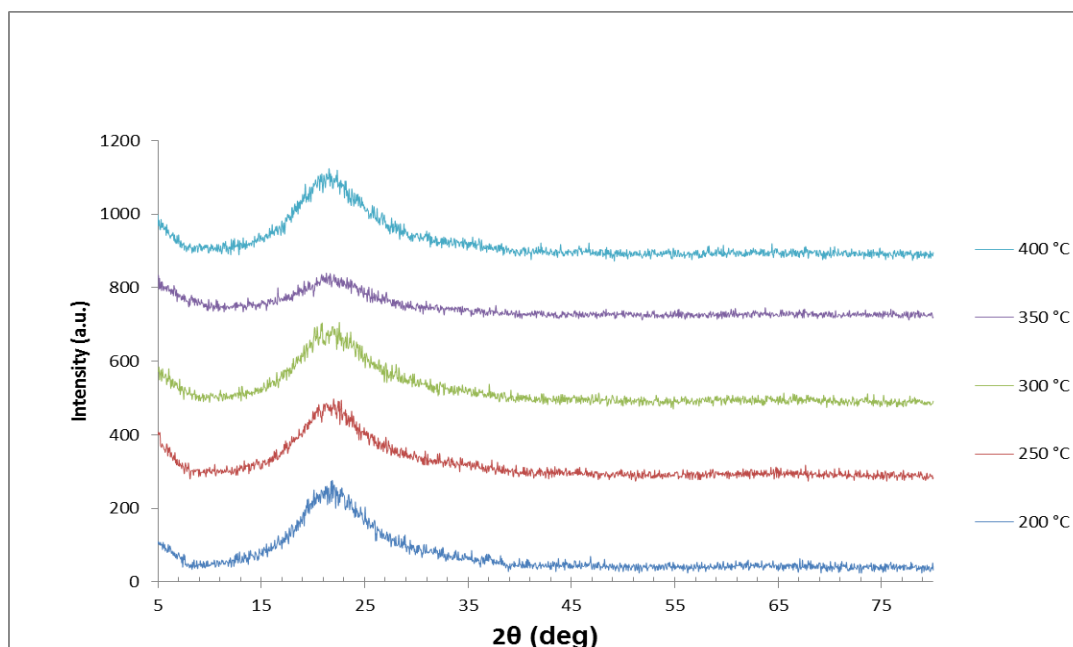
After the spraying process, the substrates were kept on the heater until cooled and reach room temperature to avoid any thermal stresses. The films structure were investigated using an X-ray diffractometer (XRD 6000, Shimadzu, Japan) with  $\text{CuK}\alpha$  line radiation ( $\lambda=1.5406 \text{ \AA}$ ) and Infrared spectrum of samples was recorded using a Fourier transformed infrared (FTIR) spectrophotometer.

## 3. RESULTS AND DISCUSSION

Effect of substrate temperatures (at low-temperature scale 200-400°C) on the structural properties is presented. XRD of the prepared aluminium oxide nanostructured thin films deposited at same molarities and different substrate temperatures are presented in Fig. 1. The obtained results ensure the formation of the amorphous  $\text{Al}_2\text{O}_3$  thin film. Apparently, the existed broad diffraction peak in at the low temperature of 200°C tend gradually to be narrower with higher intensity up to 250°C, beyond which the FWHM of the prepared sample start to increase and browed more reaching to 350°C. At 400°C the results reveal an enhancement in the structure of the obtained results since the direction peak shows an increase in the intensity and reduction in the FWHM which is related to the chemical pyrolysis of the raw material at high temperature.

In spite of that, the 400°C as a substrate temperature was not chosen as optimum temperature due to the very poor film adhesion to the substrate.

The obtained results agreed with other results ensure that alumina reveals an amorphous structure using any deposition methods at low deposition temperatures [1, 9, and 23].



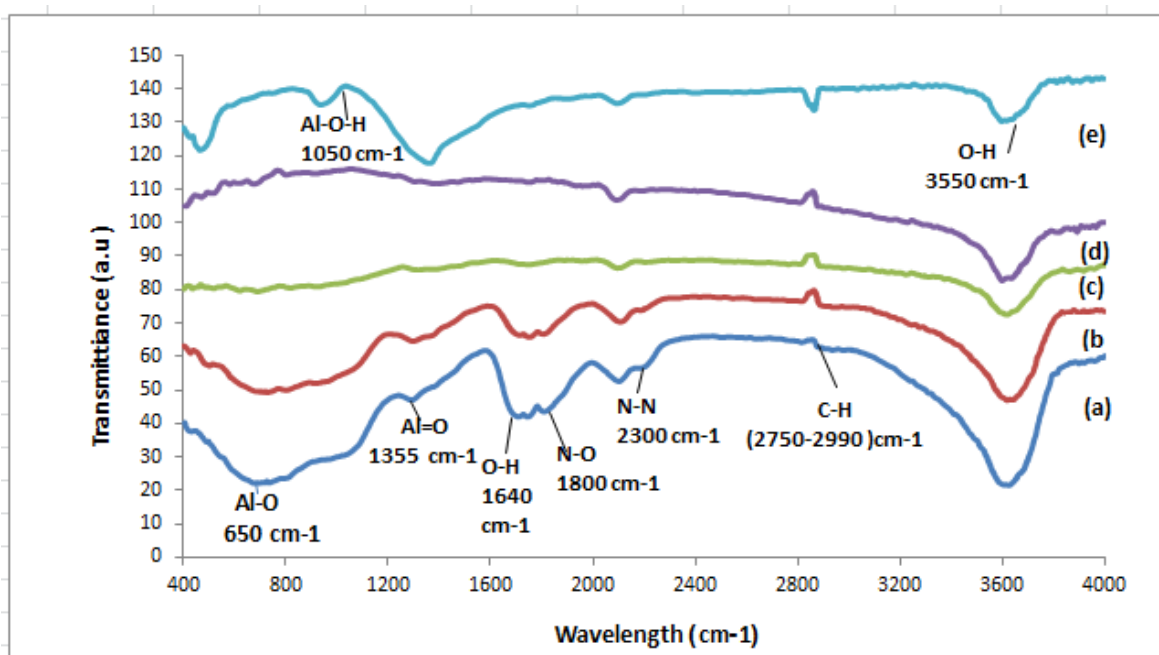
**Figure 1.** XRD results of prepared sample at different substrate temperatures

FTIR spectroscopy can be successfully applied to study the formation of the prepared oxides with nano crystalline sized. It is possible to characterize the surface state of nanosized objects deposition by spray pyrolysis, by IR spectroscopy with Fourier transformation in the range of 4000 - 400  $\text{cm}^{-1}$ . FTIR spectroscopy complements the information obtained from x-ray diffraction analysis. It represents the incorporation of all data that use to comprehend, analyze, and burnish more efficiently the structure of films [32-34]. The obtained absorption peak frequencies indicate the functional group's type that is present in the substance.

Fig. 2 represents the typical FTIR transmission spectra of the  $\text{Al}_2\text{O}_3$  thin films prepared at different substrate temperature; all samples were measured at room temperature. The results show the absorption peaks with different bands in the range between 400–4000  $\text{cm}^{-1}$ . This spectral region involves a lot of important stretch modes include carbon, hydrogen, oxygen and  $\text{Al}_2\text{O}_3$  bands which are obviously illustrated. The spectra below 1000  $\text{cm}^{-1}$  reveal general features of alumina, but in a closer look the absorption peaks about 600  $\text{cm}^{-1}$  assigned to amorphous aluminum oxide in all samples, at 200 °C in Fig (2-a) the absorption peaks at (430.1, 472.53, 607.54, 649.97, 688.54, 860.19)  $\text{cm}^{-1}$  wave number are related to the stretching vibrations mode of the Al-O band in alumina [1, 28, 29, 32]. At the same time, it could be noticed the increase in the intensity of the absorption peak by increasing the substrate temperature up to 250°C as shown in Fig(2-b), where a clear enhancement and distinction Absorption peak appeared at (430.1, 484.1, 617.18, 638, 650.23, 698.18, 781.12)  $\text{cm}^{-1}$  that confirm the formation of Al-O bonds. All absorption peaks presence in Fig( 2 -c,d) appeared at (487.96, 563.18, 613.32, 705.9, 790,79, 833.19, 460.96, 495.67, 541.96, 609.46, 700.11, 780)  $\text{cm}^{-1}$  are related to the stretching vibrations mode of Al-O bonds at 300 °C and 350°C respectively.

This figure indicates that when increasing temperature, the absorption peaks appear with smaller intensity due to the decrease in the thin film deposition probability and reduction in the chemical interaction ability which is responsible on the material formation. Figure (2-e)

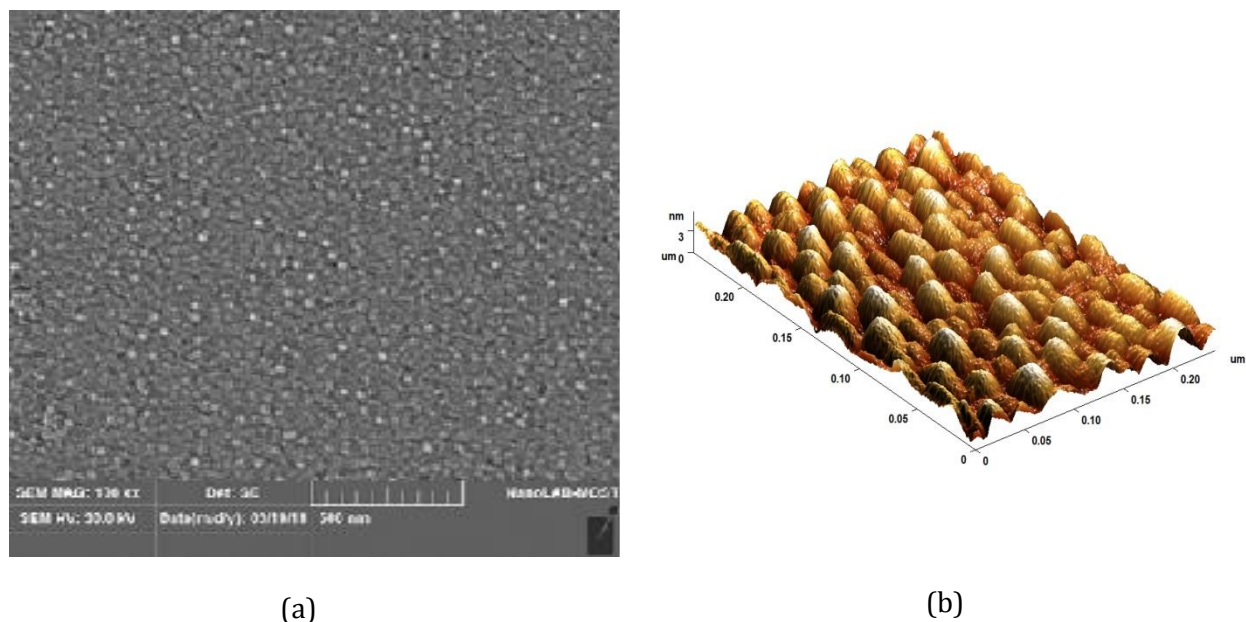
represented the FTIR result of the prepared thin film at 400°C, where absorption peaks appeared at (433.95, 457.1, 551.6, 594.03, 663.47, and 792.69)  $\text{cm}^{-1}$  wave number assigned the stretching vibrations mode of Al-O bonds. At this temperature we could recognize the presence of the absorption peaks at (1049.2, 1054.99, 1066.56, 1062.7, 1101.28)  $\text{cm}^{-1}$  wave number which are related to the symmetric bending of Al-O-H bond [25,26] which seem to be very weak at lower preparation below 400°C, and found to be very clear at 400°C. Also, the presence of the absorption peak at 1380  $\text{cm}^{-1}$  in the obtained results may be attributed to the incorporated of the neutral  $\text{O}_2$  species that adsorbed at the  $\text{Al}_2\text{O}_3$  thin films surface while the absorption peak at 1355  $\text{cm}^{-1}$  ensured the presence of Al=O bond as given else were [27,28]. Beside that the appearance of 1380  $\text{cm}^{-1}$  absorption peak is related to the chemisorbed oxygen atoms at the preparing films surface. All films reveal the presence of different bands such as the O-H extended band centred at the stretching 3420  $\text{cm}^{-1}$  wavenumbers and the bending mode at 1640  $\text{cm}^{-1}$  of the  $\text{H}_2\text{O}$  vibration modes.



**Figure 2.** FTIR results of prepared sample at different substrate temperatures

The large  $\text{Al}_2\text{O}_3$  surface area causes rapid adsorption of the water molecule from the environment. The O-H vibrational mode in the  $\text{Al}_2\text{O}_3$  thin films ranging from 3216 to 3644  $\text{cm}^{-1}$ ; this was predicted theoretically according to other work depending on the configuration and number of hydrogen atoms in the complex [29]. The wave number around (2750, 2990)  $\text{cm}^{-1}$  could be associated with C-H bonds from organic remains observed in samples calcined at all samples. The absorption peaks at (1425.3, 1494.73, 1548.73, 1480, 1525.59, 1529.45, 1421.44)  $\text{cm}^{-1}$  wave number are conforming to the stretching mode of the carboxyl group (C=O) bands [30]. There are in all samples bonds about 2300  $\text{cm}^{-1}$  correlating with  $\text{N}_2$  (N-N) bands. Many other peaks appear around 1800  $\text{cm}^{-1}$  when increasing temperature is related to stretching mode of the N-O bands. The result is expedient with other work [31].

Figure(3) shows the SEM results (a) of the prepared sample at optimum deposited substrate temperature which reveals the formation of Al<sub>2</sub>O<sub>3</sub> nanostructure thin films, a particles- like nano structure could be recognize. From these results the formation of homogenous, uniform and crack-free surface is clear. This was confirming also using AFM results (b), the obtained results show very uniform homogenous nanostructure.



**Figure 3.** SEM image of prepared Al<sub>2</sub>O<sub>3</sub> thin films

#### 4. CONCLUSION

Very simple raw material was used for the successful preparation of Al<sub>2</sub>O<sub>3</sub> nanostructured thin films at low substrate temperature; the obtained result reflected the preparation of amorphous thin films. A clear dependence of film structure with substrate temperature recognized through the FTIR result. A substrate temperature of about 250°C was found to be optimum substrate temperature. SEM and AFM results ensure the formation of nanostructured thin films.

#### REFERENCES

- [1] B. P. Dhongea, T. Mathews, S. T. Sundaria, C. Thinaharanb, M. Kamruddina, S. Dasha and A.K. Tyagia, 2011. Applied Surface Science. 258, 1091– 1096.
- [2] A.Huanosta, J.C.Alonso and A.Ortiz, 2001. Thin Solid Films. 401, 284–290.
- [3] S.K. Pradhan, P.J.Reucroft and Y.Ko, 2004. Surf. Coat. Technology. 176, 382-384.
- [4] T.Bostrom, G.Westin and E.Wackelgard, 2007. Sol.Energy Mater.Sol.Cells. 91, 38-43.
- [5] M. AguilarFrutis, M.Garcia, C.Falcony, G.Plesch and S.Jimenez Sandoval, 2001. Thin Solid Films. 389, 200-206.

- [6] G. Adamopoulos, S.Thomas, D.D.C. Bradley, M.A. McLachlan and T.D. Anthopoulos, 2011. Appl. Phys. Lett. 98, 1-3.
- [7] P.Vitanov, A.Harizanova, T.Ivanova and T.Dimitrova, 2009. Thin Solid Films. 517, 6327-6330.
- [8] K.S. Shamala, L.C.S. Murthy, M.C. Radhakrishna and K. Narasimha Rao, 2007. Sens. Actuators A. 135, 552- 557.
- [9] K.S. Shamala, L.C.S. Murthy and K. Narasimha Rao, 2004. Mater. Sci. Eng. B. 106, 269-274.
- [10] L. Isac, A. Duta, E. Purghel, G.C. Chitanu, S. Mitrea and I. Pelin, 2008. Phys. Status Solidi A. 205, 2413-2416.
- [11] N. Bahalawane, 2006. Surf. Coat. Technology. 200, 4097-4103.
- [12] D.W. Thompson, P.G. Snyder, L. Castro, L. Yan, P. Kaipa and J.A. Woollam, 2005. J. Appl. Phys. 97, 1-9.
- [13] C. Cibert, H. Hidalgo, C. Champeaux, P. Tristant, C. Tixier, J. Desmaison and A. Catherinot, 2008. Thin Solid Films. 516, 1290-1296.
- [14] Y.Y. Takamura, F.Koch, H. Maier and H. Bolt, 2001. Surf. Coat. Technology. 260, 142-144.
- [15] S. Konstantinidis, K.Jiang, A.Roobroek, F.Renaux and J.M. Schneider, 2011. Plasma Processes Polymers. 8, (7) 651-657.
- [16] K. Vanbesien, P. DeVisschere, P.F. Smet and D. Poelman, 2006. Thin Solid Films. 514, 323-328.
- [17] P. Katiyar, C. Jin and R.J. Narayan, 2005. Acta Materialia. 53, 2617-2622.
- [18] M. Lebedev, J. Akedo and T. Ito, J. 2005. Cryst. Growth 275, e1301-e1306.
- [19] M.D. Groner, S.M. George, R.S. McLean and P.F. Carcia, 2006. Appl. Phys. Lett. 88, 1-3.
- [20] E. Ienei, L. Isac, C. Cazan and A. Duta, 2010. Solid State Sci. 12, 1894-1897.
- [21] Aguilar-Frutis, Garcia, and Falcony, 1998. Appl. Phys. Lett. 14, 1700-1702.
- [22] J Guzm'an-Mendoza, M Garc'ia-Hip'olito, M Aguilar-Frutis and C Falcony-Guajardo, 2001. J. Phys: Condens. 13, 1700-1702.
- [23] Raid A Ismail, Evan T Salim, Walid K Hamoudi, 2013. Materials Science and Engineering: C. 33(1), 47-52..
- [24] A. B. Khatibani and S. M. Rozati, Bull., 2015. Mater. Sci. 2, 319-326.
- [25] M. A. Fakhri, Y. Al-Douri, U. Hashim, E. T. Salim, 2016. Advanced Materials Research. 1133, 457-461.
- [26] M.A. Fakhri, U. Hashim, E.T. Salim, Z.T. Salim, 2016. J. Mater. Sci. Mat. In Elec. 27(12), 13105-13112.
- [27] R. M. John and A. Jonathan P.D., 2005. J. Phys. Chem. 109, 9028-9034.
- [28] Evan T. Salim, Raid A. Ismail, Makram A. Fakhry, Y. Yusof, 2016. Int. J. Nanoelectronics and Materials 9, 111-122.
- [29] A.R. Choudhari and C.G. Takoudis, 2004. Thin Solid Films. 446, 155-159.
- [30] Makram A Fakhri, Evan T Salim, Ahmed W Abdulwahhab, U Hashim, Zaid T Salim, 2018. Optics Laser Technology. 103, 226-232.
- [31] V. Zdravkova, N. Drenchev, E. Ivanova, M Mihaylov, and K. Hadjiivanov, 2015. J. Phys. Chem.119, 15292-15302.
- [32] N.Avci, P. F. Smet, J. Lauwaert, H. Vrielinck and D. Poelman, J. 2011. Sol-Gel Sci Technol. 59, 327-333.
- [33] Makram A. Fakhri, Evan T. Salim, M. H. A. Wahid, U. Hashim, Zaid T. Salim, 2018. Journal of Materials Science: Materials in Electronics 29(11), 9200-9208.



[34] Makram A Fakhri, Evan T Salim, Ahmed W Abdulwahhab, U Hashim, Zaid T Salim, 2018. Optics Laser Technology. 103, 226-232