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Role of Annealing Temperature on Morphology of Alumina Thin Film Prepared by Wet-Chemical Method

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Abstract: In this paper, we reported the compositional, morphological and structural properties of the alumina(Al_2O_3) thin films prepared by sol-gel technique and annealed between 800 °C to 1200 °C for 1-hour in an air atmosphere. The deposited films were polycrystalline in nature. Thin films were found uniform and adherent to the alumina substrate. Effect of annealing temperature on structural parameters such as pore size and surface area were calculated. The result indicates that pore size and surface area was decreased by increasing annealing temperature. The material characterization was done by field emission scanning electron microscope (SEM), atomic force microscopy (AFM) and Brunaur, Emmet and Teller (BET). *Copyright © 2015 IFSA Publishing, S. L.*

Keywords: Sol-Gel, Alumina, Thin films, Porosity.

1. Introduction

Thin film technology was found to be in many applications [1-4], including microelectronics, optics, magnetic, hard and corrosion resistant coating, micro-mechanics etc. [5-7]. Progress in each of these areas depends upon the ability to selectivity, and controllability on deposited thin film thickness ranging from tens of angstroms to micro meter with specified physical properties. This, in turn, requires control often at the atomic level of film microstructure and microchemistry. Several methods have been followed to prepare alumina thin films such as sputtering [5], chemical vapour deposition, molecular beam epitaxy method [6-7], spray pyrolysis technique [8] and sol-gel process [9-14]. Among the available techniques, the sol-gel process is undoubtly the simplest and the cheapest one. The advantages of the sol-gel methods are its versatility and the possibility to obtain high purity materials (shaped as monolithic blocks, powders or thin films), the composition of which may be perfectly controlled.

Alumina thin films have a tremendous potential for commercial exploitation. Thin films technology, in particular, is being actively applied in the development of moisture sensor devices [15-16] given such that sensors depend largely on moisture-surface interaction due to its porous structure. Thin film moisture sensors have potential advantages of fast response time and importantly, the potential for miniaturization via integration with IC-based technology leading to low power consumption, high reliability, improved selectivity and reduced cost. The porous thin film provides high permeability and large surface area. To obtain these requirements, it is necessary to control pore surface area, pore size and its distribution.

The present study demonstrates the preparation of alumina thin films by sol-gel technique and report the investigation about the influence of annealing temperature on the surface area and porosity of alumina thin film.

2. Experimental Details

2.1. Synthesis of Precursor Solution

Aluminium sec-butoxide, 95 %, $Al(OC_4H_9)_3$, (Alfa Aesar) was used as starting material, and nitric acid was used as peptizing agent for the preparation of a boehmite sol by sol-gel method [17-19]. The alumina substrate was dip coated with the boehmite sol with withdrawn speed of 50 mm/min. followed by annealing at 800-1200 °C with a heat rate of 100 °C/hr. for 1 hour. For development of crack free thin film over the alumina substrate zeta(ζ) potential of the sol was controlled to +19 mV by adding HNO_3 for uniform dispersion of the sol particles as shown in Fig. 1. From the zeta potential data lower pH values promise better dispersing efficiencies with respect to higher surface charges yielding more intensive repulsive forces. A pH range of 2.0-3.0 appears to be the most beneficial working range in dispersing process of boehmite.

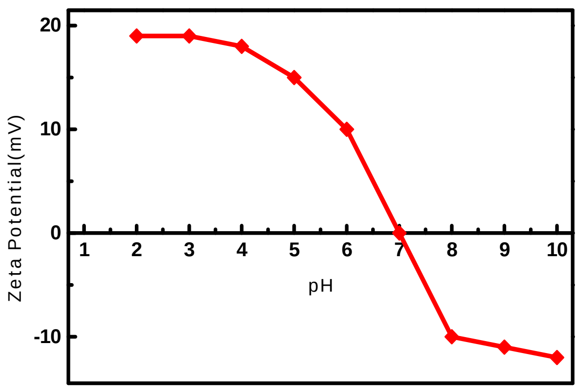

Fig. 1. Zeta potential curve of boehmite.

3. Results and Discussion

3.1. Surface Area & Pore Size Analysis

Porosity, surface area and pore size distribution are the basic quantities to specify a porous material. Brunaur, Emmet and Teller (BET) method was followed to measure surface area and pore size distribution using surface area & pore size analyzer (NOVA 2000e Model). BET characterization of the thin films, having same number of coatings, was done by removing and crushing the annealed films from the substrate. As shown in Table 1 the BET surface area was reduced as the annealing temperature shifted from 800 °C to 1200 °C.

Table 1. BET Analysis for surface area, pore size, and porosity present in alumina thin film annealed at different temperature.

No. of Coating	Heat (°C)	BET Surface Area (m^2/g)	Average Pore Diameter (nm)	Porosity (%)
8	800	150.11	6.62	70
8	900	120.23	8.21	60
8	1000	101.23	12.30	50
8	1100	90.45	15.66	40
8	1200	50.30	4.23	20

3.1.1. Effect of Annealing Temperature on the Pore Size Distribution

In the case of pore size distribution sometimes it happens that all the grains in the film merge together at higher temperature as a result of that all the pores are disappeared from the film or very few pores with very small size are available. However in some cases pore size increases at higher temperature due to the development of much more course pores. More micropores become mesopores and mesopores becomes macropores after exposure to higher annealing temperature.

3.1.2. Effect of Annealing Temperature on the Porosity

The effect of annealing temperature on porosity is shown in Table 1. The values of porosity was calculated by using the method which was proposed by De Lange [20]

$$\varepsilon(\%) = \frac{v_p}{v_p + 1/\rho} \times 100\%,$$

where v_p is the micro pore volume (ml g^{-1}), ρ is the density of the solid phase (g ml^{-1}), and ε is the porosity (%). The decrease in porosity is due the micro pore volume (v_p) that decreased with elevated temperature because more micro pores evolved to form meso and macropores at higher temperature.

3.2. Surface Morphology of the Films

In Fig. 2, (a), (b), (c), (d), and (e) represents the SEM images of alumina thin films annealed at 800 °C, 900 °C, 1000°C, 1100°C, 1200°C respectively. The SEM pictures clearly shown that the crystallite size increases with an increase in the annealing temperature. Surface morphology has shown that the particle sizes are the function of the annealing temperature. It has been observed that an increase in the annealing temperature leads to an increase in the crystallite size and decrease in surface area.

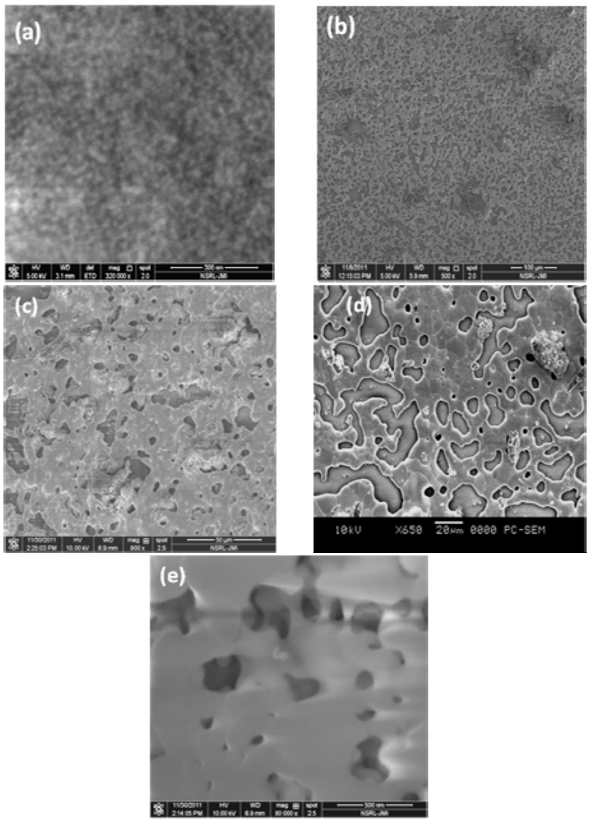

Fig. 2. Scanning electron micrograph of the top surface of alumina thin film annealed at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, and (e) 1200 °C.

The roughness of the film surface was checked by AFM (Solver Next, NT-MDT) measurements as shown in Fig. 4. The contact mode measurement was followed with the tip radius of 20 nm. The biggest cantilever deflection was 10 nm. In Fig. 3, (a), (b), (c), (d), and (e) represents the AFM images of alumina thin films annealed at 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C respectively. From the AFM images it was concluded that the roughness or surface area of the alumina film was reduced with increasing the annealing temperature.

4. Conclusion

The change in morphology was observed by BET, AFM and FESEM observation. Alumina thin films were prepared on alumina substrate by sol-gel technique which is simple and an inexpensive method. From SEM it was confirmed that alumina films were nonstochiometric, which are suitable for moisture sensing application. The films fired in the temperature range of 800-1200 °C, were found polycrystalline. The pore size decreases with an increase in the firing temperature hence specific surface area decreases. Film fired at 800 °C observed optimum surface area than further elevated temperatures. The film fired at this temperature may be suitable candidate for sensing applications.

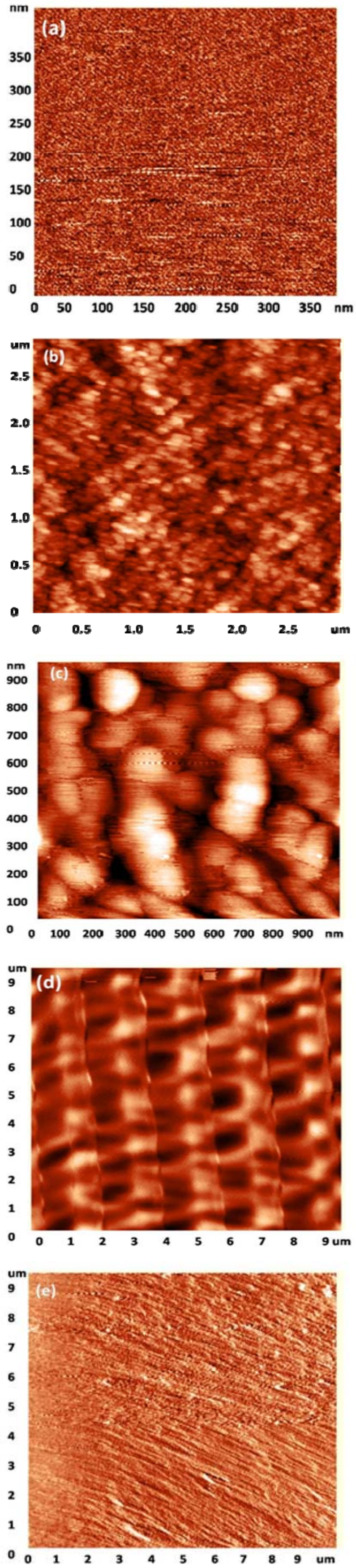

Fig. 3. AFM morphology of alumina thin film annealed at (a) 800 °C, (b) 900 °C, (c) 1000 °C, (d) 1100 °C, and (e) 1200 °C.

References

[1]. I. Strawbridge, P. F. James, Thin silica films prepared by dip coating, *J. Non-Cryst. Solids*, 82, 1986, pp. 366-372.

[2]. C. J. Brinker, A. J. Hurd, K. J. Ward, in Ultrastructure Processing of Advanced Ceramics, eds. J. D. Mackenzie and D. R. Ulrich, *Wiley*, New York, 1988, p. 223.

[3]. H. Schroder, Physics of Thin Films, *Academic Press*, New York-London, Vol. 5, 1969, pp. 87-141.

[4]. H. Dislich, Sol-gel: Science, processes and products, *J. Non-Cryst. Solids*, 80, 1986, pp. 115-121.

[5]. L. L. W. Chow, M. M. F. Yuen, P. C. H. Chan, A. T. Cheung, Reactive sputtered TiO_2 thin film humidity sensor with negative substrate bias, *Sens. Actuators B: Chemical,* 76, 2001, pp. 310-315.

[6]. G. Gordillo, C. Calderon, Properties of ZnO thin films prepared by reactive evaporation, *Solar Energy Mater. Solar Cells*, 69, 2001, pp. 251-260.

[7]. C. K. Ong, S. J. Wang, In situ RHEED monitor of the growth of epitaxial anatase TiO_2 thin films, *Appl. Surf. Sci.* 185, 2001, pp. 47-51.

[8]. B. J. Lokhande, P. S. Patil, M. D. Uplane, Deposition of highly oriented ZnO films by spray pyrolysis and their structural, optical and electrical characterization, *Mater. Lett*. 57, 2002, pp. 573-579.

[9]. H. Tang, K. Prasad, R. Sanjines, F. Levy, TiO_2 anatase thin films as gas sensors, *Sens. Actuator B,* 26-27, 1995, pp. 71-75.

[10]. C. Garzella, E. Comini, E. Tempesti, C. Frigeri, G. Sberveglieri, $Ti0_2$ thin films by a novel sol-gel processing for gas sensor applications, *Sens. Actuator B: Chemical,* 68, Issue 1-3, 2000, pp. 189-196.

[11]. T. Tsuchiya, T. Emoto, T. Sei, Preparation and properties of transparent conductive thin films by the sol-gel process, *J. Non-Cryst. Solids* 178, 1994, pp. 327-332.

[12]. S. Basu, M. Saha, S. Chatterjee, K. K. Mistry, S. Bandhapadhyay, K Sengupta, Porous ceramic sensor for measurement of gas moisture sensor in the ppm range, *Mater. Lett.* 49, 2001, pp. 29-33.

[13]. S. Basu, S. Chatterjee, M. Saha, S. Bandopadhyay, K. K. Mistry, K. Sengupta, Study of electrical characteristics of porous alumina sensors for detection of low moisture in gases, *Sens. Actuators B: Chemical*, 79, 2001, pp. 182-186.

[14]. J. Wen, V. J. Vasudevan, G. L. Wilkes, Abrasion resistant inorganic/organic coating materials prepared by the sol-gel method, *Journal of Sol-Gel Science and Technology*, Volume 5, Issue 2, 1995, pp. 115-126.

[15]. Debdulal Saha, Santanu Dasb, Kamalendu Sengupta, Development of commercial nanoporous trace moisture sensor following sol–gel thin film technique, *Sens. and Actuators B: Chemical*, 128, 2008, pp. 383–387.

[16]. Lokesh Kumar, Debdulal Saha, Shakeb A. Khan, Kamalendu Sengupta, and Tarikul Islam, A medium-range hygrometer using nano-porous thin film of γ-Al_2O_3 with electronics phase detection, *IEEE Sensors Journal*, Vol. 12, No. 5, May 2012, pp. 1625-1632.

[17]. B. E. Yoldas, Alumina gels that form porous transparent Al_2O_3, *J. Mater. Sci.,* 10, 1975, pp. 1856-1860.

[18]. B. E. Yoldas, Alumina Sol Preparation from Alkoxide, *Am. Ceram. Soc. Bull,* 54, 1975, pp. 289-290.

[19]. B. E. Yoldas, Transparent activated nonparticulate alumina and method of preparing same, US Patent No. 3941719, 1976.

[20]. De Lange R. S. A., Hekkink J. H. A., Keizer K., Burggraaf A. J., Microstructural Properties of non-supported top layers obtained by the sol-gel process, *Journal of Non-Crystalline Solids*, 195, 1996, pp. 203-217.