Microwave Irradiation an Alternative Source for Conventional Annealing: A Study of Aluminum Oxide Thin Films by a Sol-gel Process

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ABSTRACT

The lower temperature and shorter time with microwave irradiation might be ascribed to the activating and facilitating effect of microwave on solid phase diffusion. Using microwave-heating process, it is possible to achieve enhanced mechanical properties such as higher hardness, improved scratch resistance and structure texturing. In the present investigation, thin films of Al_2O_3 have been prepared by simple and cost effective sol-gel process on quartz substrates, and as deposited films are subjected to annealing in microwave irradiation at different powers. It is evident that there is a dramatic change in the mechanical properties of the films irradiated in microwave compared to the conventional annealing temperature.

Key words: microwave irradiation, annealing, sol-gel process, hardness, surface texturing

1 INTRODUCTION

Microwave irradiation is becoming an increasingly popular method of heating in the laboratory to synthesize biological [1], organic [2], and inorganic materials [3]. Coatings with surface laser treatments [4] or microwave exposure [5] leads to enhance mechanical and tribological properties. There has been less attention in the literature that sol-gel films treatment with microwave irradiation. In the recent years, many investigators have utilized microwave technique to synthesize powder perovskite solid compounds such as $LaCuO_4$ [6], and high temperature superconducting materials such as $YBa_2Cu_3O_{7-x}$ [7]. Present authors have also applied this technique on multilayers of Al_2O_3 / ZrO_2 deposited by a sol-gel process and found enhanced mechanical properties [8].

Unlike conventional annealing process, microwave technique offers a clean, cost effective, energy efficient, quite faster, and convenient method of heating, which results in higher yields and shorter time reactions. This will have strong impact on coatings applied in nanotechnology, microtechnology, and biotechnology industries. This could be a great advantage for the hard, protective, corrosion, abrasion, wear resistance, thermal barriers, optical, optoelectronic, microelectronic, polymer thin films that are applied on plastic, quartz, glass substrates where conventional annealing process is a limiting factor. Keeping in view the necessity of the coatings that are applied on plastic substrates, microwave irradiation has been chosen as an alternative method for annealing process. In the present investigation, thin films of Al_2O_3 have been deposited on quartz substrate at room temperature by sol-gel dip coating process. Two sets of films are treated as follows: one set by annealing at different temperatures ranging from 200 °C to 800 °C for 5 h in nitrogen atmosphere, and second set of films are exposed to (2.45 MHz) at different powers ranging from 140 W to 800 W for 10 min. The conventional annealed films as well as microwave-irradiated films have subjected to characterization for structural and mechanical properties.

3 EXPERIMENTAL PROCEDURE

The preparation and deposition of Al_2O_3 thin films by sol-gel dip coating process have been shown in the figure 1.

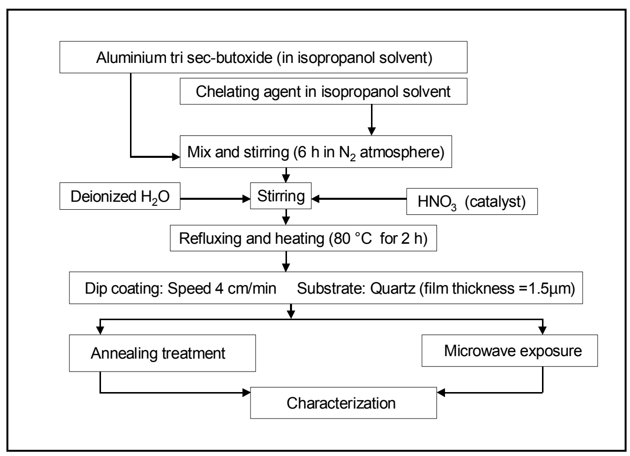

Figure 1: Flow chart for the preparation and deposition of Al_2O_3 thin films by sol-gel dip coating process

Calculated quantity of aluminum sec-butoxide (Chemat, 99.98 % purity) has been dissolved in isopropanol (99.99%) solvent along with acetylacetone as a complexing / chelating agent. The molar ratio of aluminum sec-butoxide and acetylacetone is 20:0.5. The contents are stirred at room temperature for about 6 h. To the above contents calculated quantity of HNO_3 is added drop wise as a catalyst and followed by deionized water using dropping funnel for stabilization and hydrolysis of the sol, respectively. Further the contents are refluxed at 80 °C for 2h to complete the reaction and later cooled to room temperature. The contents are filtered using Wattman filter paper in order to remove any particulates formed during the reaction. The obtained stock solution is used for the deposition of quartz substrates by dip coating process.

Cleaned quartz substrates (Ra = 1.4 nm) are clamped to pin and dipped in to the sol-gel stock solution at the rate of 4 cm/min. The process is repeated in order to get thickness around 1.5 microns. The deposited samples are subjected to two sets treatments as follows: one set by annealing at different temperatures ranging from 200 °C to 800 °C for 5 h in nitrogen atmosphere, and second set of films are exposed to (2.45 MHz) at different powers ranging from 140 W to 800 W for 10 min. The conventional annealed films as well as microwave-irradiated films have subjected to characterization for structural and mechanical properties.

4 RESULTS AND DISCUSSIONS

4.1 X-Ray Diffraction

XRD pattern for the Al_2O_3 thin films for both annealed and microwave exposed are shown in the figure 2a and 2b, respectively. The X-ray source is a sealed X-ray 1.5 kW Cu radiation (λ=1.5406Å).

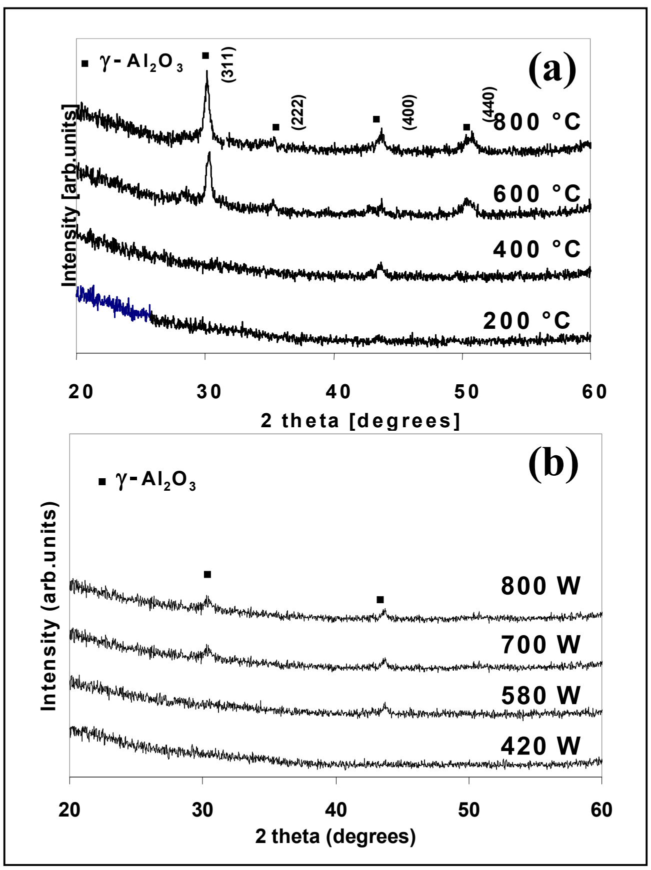

Figure 2: XRD pattern of Al_2O_3 thin films on quartz substrate by sol-gel dip coating process
(a) Annealed at different substrate temperatures
(b) Exposed to different microwave powers

Sharp and low intensity peaks belonging to γ-Al_2O_3 are observed in the annealed samples. Films annealed at 200°C are amorphous and as the substrate temperature increased from 400°C to 800 °C, γ-Al_2O_3 has grown preferentially in (311) orientation. On the other hand films exposed to 420 W and below have shown amorphous nature of γ-Al_2O_3 and as the power increased from 580 W and above there is slight formation of γ-Al_2O_3 in (311) and (400) planes. All peaks belonging to γ-Al_2O_3 phase are well matched with database in JCPDS (card #41-1432).

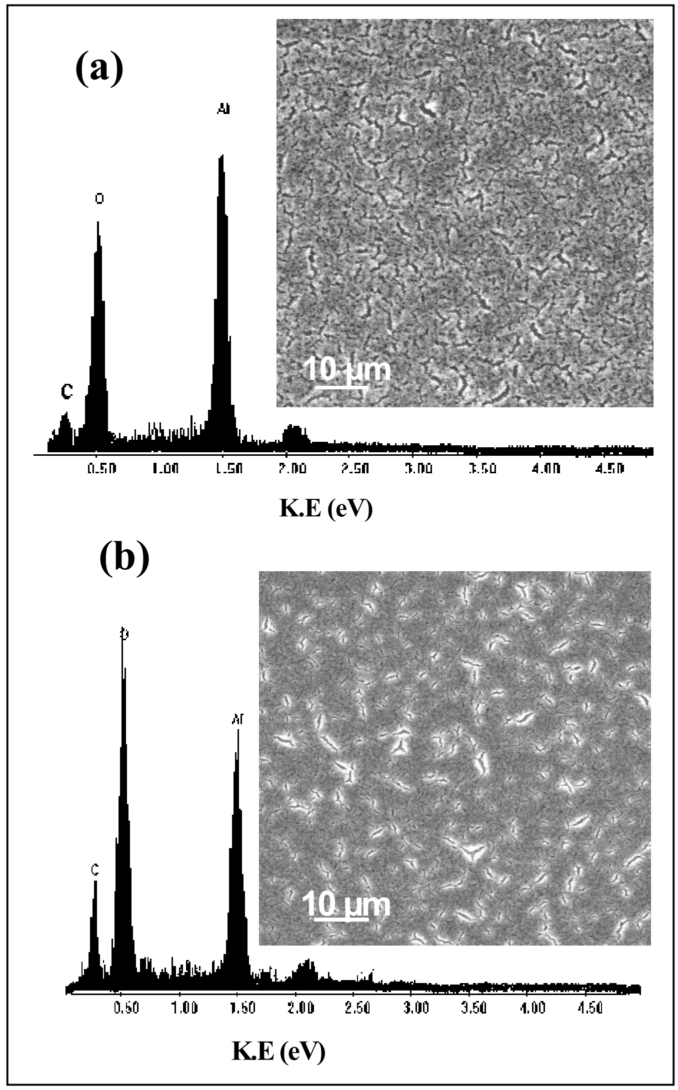

Figure 3: SEM-EDX pattern of Al_2O_3 thin films on quartz substrate by sol-gel dip coating process
(a) Annealed at 800 °C substrate temperatures
(b) Exposed to 800 W microwave power

4.2 Scanning Electron Microscopy

Scanning electron microscopy images and corresponding energy dispersive X-ray analysis of the Al_2O_3 thin films for the annealed and exposed to microwave are shown in the figure 3a and 3b, respectively. The presence of Al and O is evident in all the spectra with small amount of unburnt carbon in the films. Films annealed at different temperatures have shown dense structures with some cracks on the surface. The crack width ranges from 1 to 1.2 microns. On the other hand films exposed to different microwave powers have shown rupturing of the film in several areas. This may be due to abrupt heating of the film. The rupture width ranges from 0.5 to 1 micro in size.

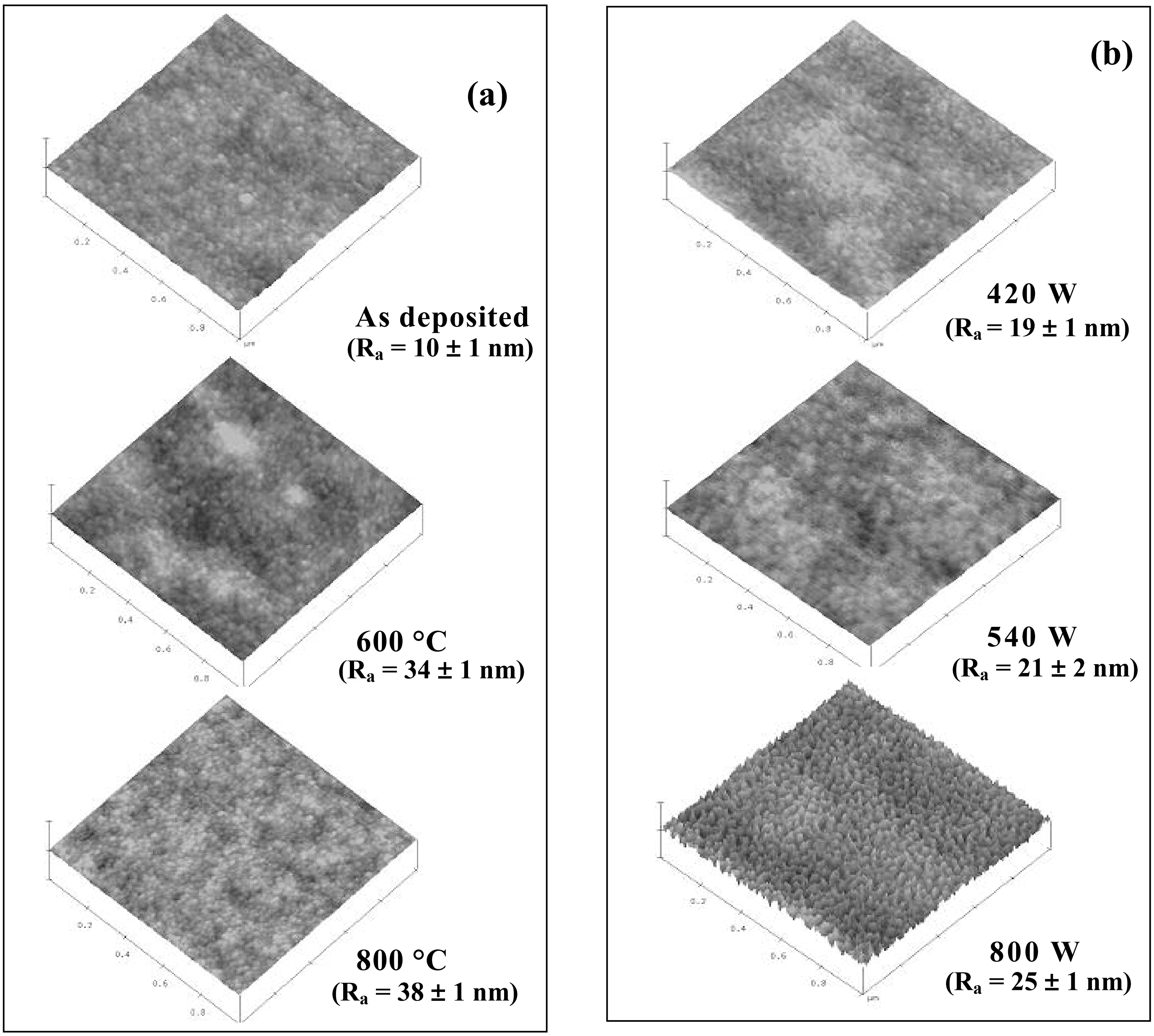

Figure 4: AFM topographical images of Al_2O_3 thin films on quartz substrate by sol-gel dip coating process
(a) Annealed at different substrate temperatures
(b) Exposed to different microwave powers

4.3 Atomic Force Microscopy

Roughness (R_a) and grain size of Al_2O_3 thin films are measured by atomic force microscopy technique. Films annealed at different substrate temperatures have exhibited fine spherical grain structure with size ranging from 12 ± 2 nm to 36 ± 2 nm with increasing annealing temperature. On the other hand films exposed to lower microwave powers (up to 420 W) have shown similar behavior to that of annealed films. With further increasing in microwave power (540 W) led to rupturing of the spherical structure in to open shell-like structures. At 800 W microwave power the open shell-like structures further opened to form needle -like structures. This suggests that one can change the surface structure or surface texturing by using microwave power.

4.4 Hardness

Nanoindentation measurements are performed with Berkovich indenter. The films are tested using a multiple loading sequence program with loading 5 mN. The maximum indentation depth is 260 nm, generally less than 10% of the typical film thickness. For each film 8 multiple loading indentations are measured each separated by 1000 microns. Al_2O_3 films have shown increase in hardness 2.3 to 4.4 GPa with increasing annealing temperature. On the other hand films exposed to microwave have shown hardness values from 4.2 GPa to 8.3 GPa with increasing power. This indicates that microwave irradiation is alone sufficient in order to get higher hardness compared to conventional annealing process. To understand whether this is surface effect or bulk, higher loads are applied up to 10 mN, where similar hardness (8.3 GPa) values are obtained with penetration depth of 340 nm for the film exposed to 800 W power, indicating the change in hardness is in bulk.

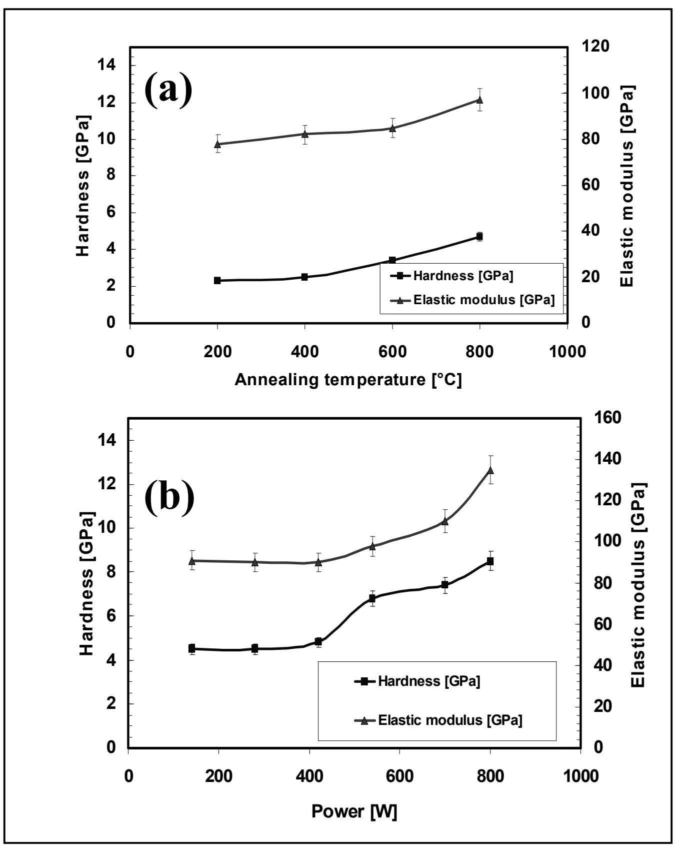

Figure 5: Hardness and Elastic modulus data of Al_2O_3 thin films on quartz substrate by sol-gel dip coating process (a) Annealed at different substrate temperatures (b) Exposed to different microwave powers

5 DISCUSSION

The ability of a material to absorb microwave energy is being expressed by its dielectric loss factor, which is always combined with the dielectric constant. In the present case, the plausible mechanism could be the conductivity of alumina increases with temperature as electrons are promoted into the conduction band from the O 2p valence band leading to increase in the dielectric constant. The increase in the dielectric properties with temperature is especially important in the microwave heating of solids, as it introduces the phenomena of thermal runaway. Microwave heating of alumina increases the temperature so too does the dielectric loss factor and heating becomes more effective which in turn has effect on the formation of dense structure causing increase in hardness of the alumina.

6 CONCLUSIONS

In conclusion, thin films of Al_2O_3 are deposited on quartz substrates at room temperature by sol-gel dip coating process and subjected to annealing at different temperatures and exposed to different microwave powers. The annealed films have shown γ-Al_2O_3 phase at and above 400 °C substrate temperature, whereas films exposed to microwave have exhibited low intensity γ-Al_2O_3 phase above 420 W microwave power. The films annealed at different temperatures are having grain size ranging from 12 nm to 32 nm with increasing substrate temperature. Films exposed to different microwave powers are having grain size from 12 nm to 20 nm. There is two fold increase in hardness, 8.2 GPa for the films exposed to microwave at 800 W compared to 4 GPa for film annealed at 800 °C.

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