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Fabrication of Mg/Al_2O_3 Nanolaminates using DC/PDC Magnetron Sputtering to Evaluate the Effect of Oxygen Content and Total Pressure for Deposition of Thin-Films

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Abstract

Thin films have always shown high sensitivity to its deposition parameters and surface morphology. Magnetron sputtering is known for its high level of consistency in deposition and repeatability. In this study Mg/Al_2O_3 nanolaminates in a range of 10 to 40 nm were synthesized using Direct current and Pulsed DC sputtering techniques at room temperature on glass substrates and silicon substrate using different oxygen flow rates and varying total pressure conditions to understand its effect on deposition rates and roughness of thin films. It is observed that more power and resources consumed for higher deposition time. Roughness of the film is very sensitive for certain applications like corrosion, Lenses, Implants. Scanning electron microscopy (SEM), Atomic force microscopy (AFM) were used to characterize the morphology, structure of the thin films. Optical microscopy and X-ray reflectometry (XRD-XRR) techniques confirmed the optical density and thickness of the nanolaminates respectively. It is confirmed that as total pressure and oxygen flow rate rises deposition rate significantly goes down, that impacts deposition time and roughness of thin films.

Keywords: Thin-Films; Oxide Coatings; Flow rate; Total Pressure; AFM; SEM; XRR

1. Introduction

Surface morphology of thin films always been crucial for electrical, optical, mechanical and corrosion properties of nanolaminates[1]. Deposition parameters are playing vital role in fabrication of right choice chemistry and morphology. Pulsed DC and Radio frequency magnetron sputtering is most widely used method for oxide or ceramic thin film depositions[2-15]. For pure materials direct current magnetron sputtering is still the best choice[5, 16-20]. Magnetron sputtered thin films are found out to be most clean films as sputtering chambers reaches to ultra-high vacuum levels and stays there continuously without any trouble, that helps to clean chambers from any foreign particles before depositions. There are other thin films deposition methods like Atomic layer deposition, Pulsed layer deposition and Chemical vapor deposition etc. where in it is difficult to maintain consistency in one or other parameter. Among these methods, the magnetron sputtering process is advantageous for its large-area deposition ability of thin films with a relatively high deposition rate. For deposition of pure metals magnetron sputtering is more suitable than electrochemical process as it offers less environmental pollution[16].Alumina is always been first choice of researchers for biodegradable implant, semiconductor devices, optics, sensors as a protective coating because of its unique properties [21-29]similarly magnesium oxide finds its applications in variety of areas[28, 30, 31].Characterization of metals and metal oxides is always been area of interest for scientist as its reveals the structure, surface morphology of thin films. In this study Scanning electron microscopy (SEM) [32, 33]is used to understand the changes in surface

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structure after alerting the oxygen contents and pressures, to understand the change in surface roughness of nanolaminates atomic force microscopy is used[34, 35].

2. Material and methods

Multi-layered biodegradable thin films were deposited on glass substrates by DC, Pulsed DC (PDC) magnetron sputtering techniques using an AJA International, Inc. Model ATC 1800 F magnetron sputtering system. Prior to depositions, the glass substrates were cleaned in 100% ethanol using soft wipes and blown by air nozzle. The substrates were cleaned in situ using Ar^+ ion bombardment for 10 min [36].

A 30 nm thick base layer of Metal oxide was deposited prior to actual Mg/ Metal oxide bilayer deposition on glass substrate in order to avoid the effect of poor adhesion and pre-existing surface defects on glass surface. A 40nm thick Mg layer was deposited by DC sputtering method using 99.99 % pure magnesium target with 2 mTorr working pressure and 20 sccm Argon flow rate, DCXS-750-4 multiple sputter DC power supply from AJA International.inc. at 100W power for Mg Deposition is used. For depositing 20nm Metal oxide thin layer with PDC magnetron sputtering method, we used pure metal targets with 99.999% purity, oxygen flow rate 2 and 3 sccm were used and total pressure varied between 1 to 3 mTorr with interval of 0.5 mTorr. Metal oxide coatings were sputtered at frequency of 250 kHz with an Advance Energy Model Pinnacle Plus+ 5 kW pulsed DC power supply. We used fisher brand microscope cover glass of size 22 x 40 mm and 200 microns thick and deckglaser cover slips of 25 x 75 mm and 250 microns thick for all depositions. For SEM and AFM characterization experiments 500 nm thick Alumina layer were deposited on silicon substrates.

Deposition rates for Mg and Metal oxide were decided after rate optimization study. In order to get uniform thickness gun tilt calibration is done prior to experimentation, the distance between target to substrate and stage rotation speed were maintained 65 mm and 60 rpm respectively. Before deposition, vacuum chamber diagnostic was done with RGA 200 Mass spectrometer, we confirmed that there was no leak in the system and pressure of water, hydrogen, oxygen, carbon dioxide was well within $8x10^{-8}$ to $10x10^{-10}$ as they are the contributors for defects in thin film formation. The vacuum chamber base pressure was maintained at 10^{-8} torr throughout the experimentation.

2.1. Thin film characterization

The deposition rates of the Metal oxide coatings were calculated from the thickness of films, measured by modeling XRR data. The surface morphology and crystalline structure of the films were studied using Hitachi SU8000 scanning electron microscope (SEM) and Bruker D8 tool X-ray diffractometer (XRD) respectively[37] . The scanning electron microscope was operated at high magnification with a voltage of 2 kV and probe current of 5 mA. The X-ray diffraction experiments were performed using a locked-coupled scan with a scanning range (diffraction angle, 2θ) set between 20 and 80°. Optical Density of thin film coating is measured using Zeiss Axioimager M2m microscope[38].

3. Results and Discussion

3.1. Optimization of oxide coating

Table 1 Deposition parameters for Mg/Al_2O_3 bilayers with varying O_2

Sputtered Material	Deposited Material	O_2 flow rate(sccm)	Ar. Flow Rate (sccm)	Working Pressure (mTorr)	Deposition Rate (nm/sec)
Al	Al_2O_3	0.5	20	2	0.0881
		1	20	2	0.1225
		1.5	20	2	0.1117
		2	20	2	0.1013
		2.5	20	2	0.0820
		3	20	2	0.0713
		3.5	20	2	0.0311
		4	20	2	0.0095

Optimization of oxygen flow rates in case of Mg/Al_2O_3 bilayers is studied by varying O_2 flow rate during Al_2O_3 layer deposition[36]. Deposition parameters for this study are shown in Table1. Oxide coating were developed by optimizing oxygen flow rate while deposition process, for this optimization study we have introduced Oxygen from 0.5 sccm to 4 sccm with 0.5 sccm interval while Argon flow rate and total pressure 20 sccm and 2mtorr respectively kept constant[36].

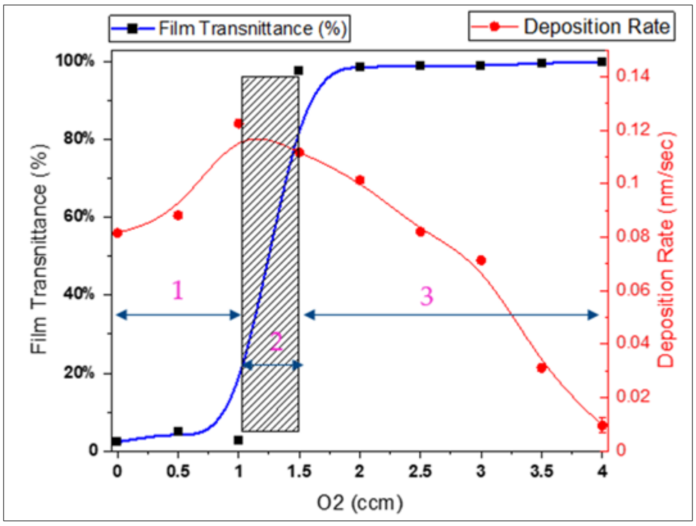


Figure 1 Effect of oxygen flow on deposition rate and optical transmission for the optimization of Al_2O_3 coating

From Figure 1 It is observed that up to 1 sccm coating is fully metallic but after 1 sccm it start to become semi-metallic and continues up to 1.5 sccm but thereafter it reaches in completely transparent regime that we called as oxide or ceramic material. While deposition rate gradually increased up to 1 sccm in metallic regime and thereafter gradually decrease up to 0.0095 nm/sec by 4 sccm of oxygen flow rate. For each oxide, the oxygen flow rate, total processing pressure and deposition rate were optimized using approach demonstrated in Figure 1.

The changes in optical properties of films grown at different content of oxygen were monitored to detect the transition from metallic films to oxides since oxides typically have low absorbance of visible light [39-41]. In absence of oxygen we received non-transparent metallic films (Metallic Regime). Increase of the oxygen flow rate activates process of metal oxidation and formation film consisting of metal and metal oxide mixture (Transition Regime). That results in increase of light transmission of the film due to partial replacement of opaque metallic phase by transparent oxide phase [39, 42]. Based on changes in thin film light transmittance the optimal oxygen flow rate was selected at the point where film become completely transparent (Oxide Regime). It is critical to select boundary condition between Transition and Oxide regimes at which deposition rate is still relatively high. Optimization efforts were focused on avoiding excessive oxygen flow, which can drastically reduce deposition rate due to creation of dielectric oxide layer on target material and consequently diminishing sputtering efficiency, leading to a phenomenon known as target poisoning [4, 43-45]. Other parameters that were optimized include RF-bias effect, argon flow rate, pulsing frequency and substrate cleaning in the sputtering chamber prior to deposition. Film transmission measurements were used for controlling oxidation process for Mg, Al. Formation of oxides was confirmed by x-ray diffractometry (XRD) and Electron Dispersive Spectroscopy (EDS) data[5, 46, 47]. Further total pressure variation study is done to see effect on quality of coating and deposition rate.

3.2. Optimization of total pressure

Total pressure of the magnetron sputtering system is responsible for evaluating the performance and transport mechanism of sputtering process[48]. This pressure not limited to purity and quality of thin films but also important factor or parameter in transport process of sputtered parameters[49].

Ultimately thin film growth rate indirectly depends upon energy of working gas ions, sputtering coefficient and sputtering rate. These parameters are contributing to enhance performance optimizing design with respect scattering of sputtered atoms and reducing total working pressure in sputtering deposition process[48]. It is confirmed after total pressure variation study, Deposition rates drastically goes down if there is small variation or increment on total pressure flow rate. In order to examine effect of change in process parameters alumina films were characterized using SEM and AFM as surface morphology plays a very important role in applications.

Table 2 Total pressure variation study table

Total Pressure(mTorr)	Ar. Flow Rate (sccm)	O_2 Flow rate (sccm)	FFT	Fit	Deposition Time(sec)	Deposition rate(nm/sec)
1	20	3	42.87	42.57	400	0.11
1.5	20	3	20.18	20.02	200	0.10
2	20	3	19.17	19.58	260	0.08
2.5	20	3	17.61	17.57	350	0.05
3	20	3	19.58	19.60	900	0.02

Alumina films were deposited on silicon substrate by cutting it in 5 x 5 cm size followed by cleaning in ultrasonic cleaner with pure ethanol for 10 mins, Silicon substrates were cleaned using soft wipes and smoothly blown with air before loading in load lock chamber. In-situ plasma cleaning is done on substrate before actual deposition for 6 min to make sure no foreign particles are present on the film. Before deposition it is confirmed that no other foreign particles and gases are present with mass spectrometer.

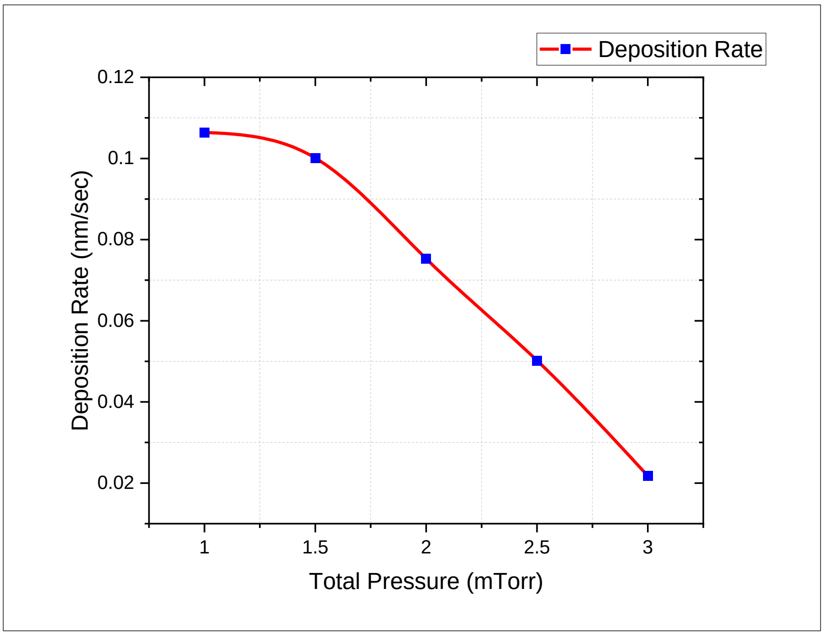


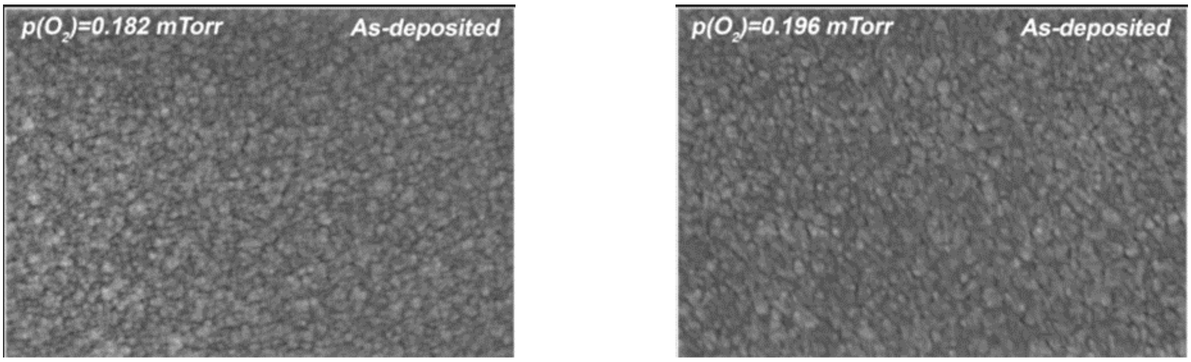
Figure 2 Effect of total pressure on deposition rate

Table 3 Alumina film deposition parameters

Layer Configuration			**Sputtering parameters**				**Flow parameters**			
Thin Film	**Target**	**Thickness (nm)**	**Source**	**Power (W)**	**Vtg. (V)**	**Frq. (KHz)**	**O_2 (sccm)**	**Ar. (sccm)**	**Pr. (mTorr)**	**T (Sec)**
Al_2O_3	Aluminum	500	PDC	100	400	250	2&3	20	1.5	5000

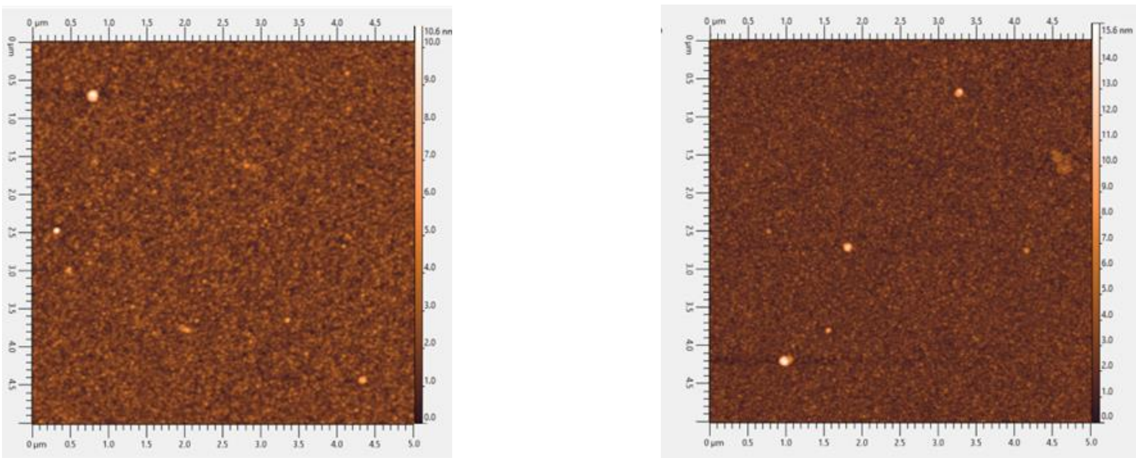
Pulsed DC magnetron sputtering process were used for depositing 500 nm thick alumina layer.99.5 % pure aluminum target with 2 and 3 sccm of oxygen level was used for reactive sputtering to be carried out.100W power with 250 KHz frequency were generated using 5000 W pinnacle source unit. 20 sccm of argon and 1.5 mTorr pressure successfully ignited plasma for eight successful depositions as per plan of alumina degradation study (Ref table no. 3).

A scanning electron microscope (SEM Zeiss Auriga FIB/FESEM with EDX) image in fig. 3 shows alumina coated on silicon substrate. The X-ray diffractometer (XRD) of alumina film not shown any crystalline phase in analysis. SEM and AFM observations confirmed very low nanoroughness of thin films that slowly increases with film thickness increase in the range 10-100 nm[9]. Roughness of the films increases with oxygen flow rates and total pressure figure 4. Not much change is observed in surface structure for 2ccm and 3cmm films figure 3. They exhibit very small density of topographical defects (bumps) that are results of inevitable adsorption of particulates from the air on substrate.



a b

Figure 3 SEM image in fig shows alumina coated on silicon substrate a) 2ccm flow b) 3 sccm flow



a b

Figure 4 AFM image shows alumina roughness on silicon substrate a) 2ccm flow b) 3 sccm flow

4. Conclusion

- Pulsed DC magnetron sputtering is the most suitable method for metal oxide deposition with controlled oxygen flow rate.
- Direct current magnetron sputtering is the most suitable method for pure metal deposition.
- Increase in oxygen flow rates lowers deposition rates or film growth rates.
- Purity and quality of thin films enhanced by optimizing total pressure.
- Surface roughness increases with increase in oxygen flow rate and total pressure.

Compliance with ethical standards

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Disclosure of conflict of interest

The author hereby declares that the published data in the manuscript have no conflict of interest against any parties. If at a later date, this is found, the full responsibility for this matter lies with the author.

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