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Variation of structural and surface properties of RF sputtered aluminum oxide (Al_2O_3) thin films due to the influence of annealing temperature and time

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Abstract: Aluminum oxide (Al_2O_3) thin films were deposited on Si (111) substrates by using RF magnetron sputtering of Al_2O_3 target in Ar atmosphere. The synthesized films were annealed in the temperature range of 200 to 600°C in nitrogen (N_2) environment for 2 and 4 hours. Variations in these structural and surface properties of the films were investigated using X-ray diffraction (XRD) and atomic force microscope (AFM). XRD analysis reveals that the synthesized films are in polycrystalline form with preferential orientation along (111) plane. By increasing the annealing temperature, the crystallite size of films was found to increase, whereas the micro-strain and dislocation density were decreased. The decrease in micro-strain and dislocation density was ascribed to the reduction in the lattice strain. The surface roughness of the films was increased with the increase of the annealing temperature, which was attributed to the films' grains growth and also with the increase in RF sputtering power.

Keywords: RF Sputtering, Aluminium Oxide, Thin Film

1. Introduction

Al_2O_3 thin films have received growing attention of researchers worldwide because of their unique properties in terms of chemical inertness, mechanical strength and hardness, high abrasion and corrosion resistance, as well as its high electrical breakdown field and high dielectric constant [1 - 2]. Owning to these excellent properties, Al_2O_3 thin films are widely used in various mechanical and microelectrical applications such as protective coatings, diffusion barriers, electronic seals, dielectric layers, optical layer, etc. [3].

Al_2O_3 films can be fabricated with several methods such as atomic layer deposition (ALD), electron beam (e-beam) evaporation, chemical vapor deposition (CVD), filtered cathodic vacuum arc and sputtering [4 - 5]. Among these techniques, sputtering is known to be a simple, low temperature, and cost-effective large-area deposition technique. It is one of the most effective technique to make amorphous materials which are difficult to be vitrified by an ordinary melting method. Using this technique, Al2O3 films can be synthesized by sputtering of either an Al target in Ar: O_2 mixtures (reactive sputtering), or by the sputtering of an Al_2O_3 target in pure Ar or Ar: O_2 mixtures (non-reactive sputtering) [6]. Target poisoning and arcing are the main disadvantages of the reactive sputtering technique. In general, the growth of Al_2O_3 film by non-reactive sputtering is a less complex process as compared to the reactive sputtering. Some of the previous work regarding the synthesis of Al2O3 films using reactive and non-reactive sputtering has been described below.

Li *et al.* reported the formation of Al_2O_3 films on n-type Si (100) substrates through reactive sputtering of Al target in O_2 environment. They found that by variation in the oxygen concentration does not significantly affect the bonding structures and densities. However, the incorporation of argon into the film was found to be detrimental to surface passivation [7]. Similarly, Kakati *et al* made the study on the effect of sputtering power and gas pressure on surface characteristics of Al_2O_3 films deposited through reactive sputtering [8]. In another work, Panitchakan *et al* described the formation of Al_2O_3 films on Al_2O_3-TiC substrates by using non-reactive RF sputtering and it was found that the surface roughness of the films are greatly influenced by the sputtering power [9]. Kijima *et al* also examined the effect of

sputtering pressure on the O/Al ratio of Al_2O_3 films for non-reactive RF sputtering [10].

The literature described above shows that the Al_2O_3 films synthesized through sputtering are found to be amorphous in nature [7 – 10]. However, synthesis of polycrystalline Al2O3 films on Si substrates has not been reported before. Therefore, in the present work, Al_2O_3 films have been prepared on Si substrate through non-reactive RF magnetron sputtering in Ar atmosphere. In this article, the effect of annealing temperature and time has been investigated on the formation of Al2O3 films. In addition, the influence of RF sputtering power on the changes in surface roughness of Al_2O_3 film has been also reported.

2. Experiment Procedures

Al_2O_3 films were prepared by RF magnetron sputtering system from an Al_2O_3 sputtering target with a nominal purity of 99.99% and thickness of 3mm. The substrate used was n- type silicon wafers (Si) (1cm X 1cm) with (111) plane orientation and resistivity of 1-10 Ω cm. These wafers were cleaned using the RCA method. The RCA clean is a standard set of wafer cleaning steps which need to be performed before deposition process. The RCA method was carried out in 3 steps. In the first step, Si (111) substrates were heated in the solution of NH_4OH, H_2O_2 and H_2O with a ratio of 1:1:5 at 75°C for 10mins. For the oxide strip purpose, the samples were then cleaned in the (1:50) HF and H_2O solution. For the third step, the wafers were heated in the HCl, H_2O_2 and H_2O solution with a ratio of 1:1:6 at 75°C. The substrates finally were rinsed in deionized water and dried by using N_2 gas. The sputtering gas used was argon (Ar) with a purity of 99.99%. The chamber was evacuated to base pressure of $3.78x10^{-5}$mbar. Prior to deposition, the target surface was cleaned by the argon ions (Ar^+) at power of 40W for approximately 15 min. The sputtering process was performed at room temperature with working pressure and substrate bias voltage of $3.33x10^{-3}$ mbar and 250V respectively. The deposition of the films was completed in 75 minutes. All the samples were deposited about 110 nm of aluminium oxide films. The details of sputtering conditions in this experiment are described in the table 1. The deposited films were annealed in a ceramic tube furnace at a temperature range of 200 to 600°C under nitrogen (N_2) atmosphere for 2 and 4 hours respectively. The post annealing process was carried out to improve the film properties.

***Table 1**. RF sputtering conditions for deposition of Al_2O_3 films.*

Parameters	Values
Target sputtering power	200 & 250W
Substrate bias voltage	250V
Flow rate of argon (Ar)	18 sccm/s
Operating Pressure	$3.33x10^{-3}$mbar
Deposition time	75min
Annealing time	2 & 4hours

The structural properties of Al_2O_3 films were examined by X-ray diffractometer (XRD) operating with CuKα radiation at 40kV. The average dimensions of crystallites and lattice strain were determined by the Scherrer method from the broadening and shift of the diffraction peaks taking into account the instrumental broadening. Atomic force microscopy (AFM) was used to investigate the surface topology of deposited films and calculate the surface roughness of the films.

3. Results and Discussion

Fig. 1 and 2 reflect the XRD scan of annealed-Al_2O_3 thin films annealed at 200°C, 400°C and 600°C for 2 and 4 hours. The figures reveal that the synthesized films are in polycrystalline form. In Fig. 1 there are four peaks which appear at 31.10°, 33.20°, 36.01° and 39.22° corresponding to (111), (107), (200) and (222) planes of aluminium oxide (Al_2O_3) respectively. Similarly, identical peaks with the same corresponding planes are observed. Moreover, the increase in the annealing temperature also demonstrates sharper and narrower peaks. Besides that, the peak intensities are also increased. With the increase in annealing time from 2 to 4 hours, a different kind of aluminum oxide film is observed. From fig. 2, only three peaks at 31.22°, 33.33° and 36.14° are observed which belong to (111), (107) and (200) planes respectively. As the annealing temperature increases from 200 to 600°C, the peak intensities are also increased. However at 600°C, broadening of peaks is observed. The figures also indicate peak shifting as a result of the increase in annealing temperature.

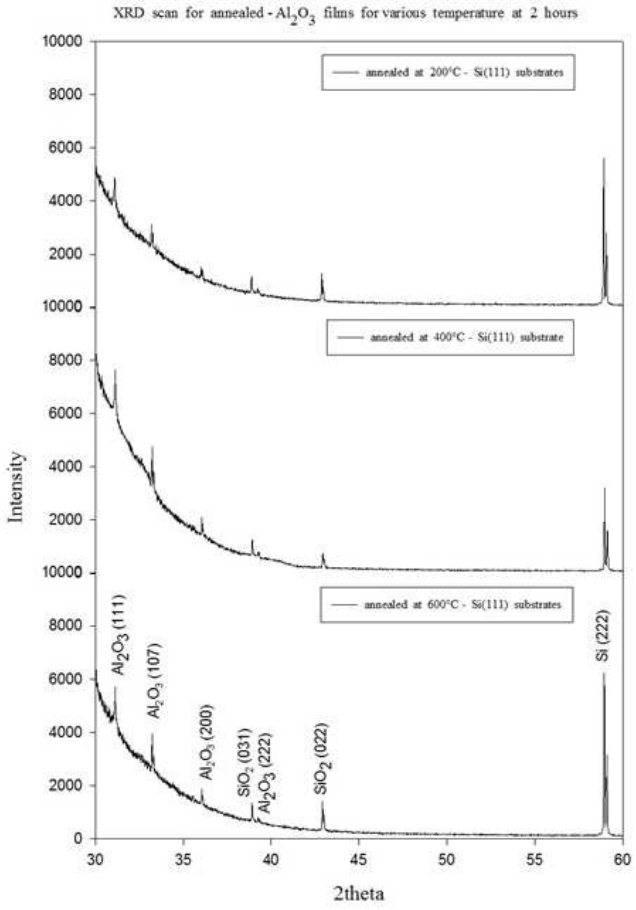

***Figure 1.** XRD scan of Al_2O_3 thin films for various annealing temperature at 2 hours.*

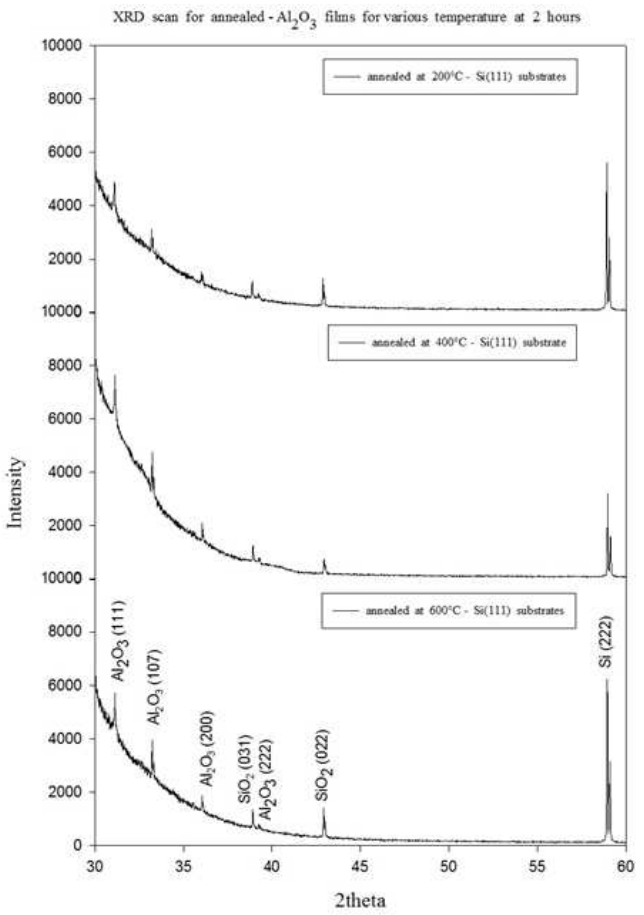

Figure 2. *XRD scan of Al_2O_3 thin films for various annealing temperature at 4 hours.*

At the annealing time of 2 and 4 hours, the peak intensities increase as the annealing temperature is increased from 200 to 600°C. This behavior is attributed to rearrangements in the atomic structure which improves the crystallinity of the films [11]. Moreover, it is observed that there is shifting in the position of peaks as the annealing temperature is increased from 200 to 600°C. The occurrence of shifting peaks is probably due to the release of intrinsic strain through annealing process. The shifting of peak positions also indicates that the films are in a uniform state of stress [12]. The occurrence of peak broadening can be due to the changes of lattice structure in the synthesized films. There are two reasons for the line broadening: (i) crystallite size which is caused by the finite size components diffracting incoherently with respect to one another and (ii) strain which is caused by the non-uniform displacements of the atoms with respect to their reference lattice position [13]

The structural parameters of the annealed - Al_2O_3 films are presented in table 1. The crystallite size is calculated by using Scherrer formula [14]:

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

where D = crystallite size (nm)

λ = wavelength of x-ray (1.5406 Å)

β = full width at half maximum (FWHM) of the peak (rads)

θ = Bragg angle (rads)

Table 2 indicates that when the annealing time increases from 2 to 4 hours, the crystallite size also increases. The increase in the crystallite size is due to a decrease in internal strain as a result of crystal point defects, surface defects and dislocations [15].

Table 2 also shows that as annealing temperature is increased from 200 to 400°C, the crystallite size is also increased. However, with the increase of annealing temperature from 400 to 600°C, the crystallite size is found to be decreased. The decrease in the crystallite size is ascribed to an increase of strain in the film caused by a change of crystal structure. With the increase of the annealing temperature to 600°C, the reduction in crystallite size is observed, which is attributed to the strain relieved crystals reduced in size and have enough energy to move towards low energy surface sites forming a more dense and compact film. [16] This reason is in accordance with the increased in values of micro strain when the annealing temperature increase from 400 to 600°C. Although it has to be considered that the XRD peaks can be broadened by stress and defects present in the films which affects the FWHM, and thus the real values of the crystallite size can be different from the calculated values [17].

In order to determine the preferential orientation of synthesized Al_2O_3 films, Harris analysis was performed by using the following relation [14]:

$$Pi\ (TC) = N\ (I_i/I_0) \ /\ \sum_n (I_i/I_0) \quad (2)$$

where Pi = texture coefficient of the plane I

I_i = measured intensity

I_0 = the intensity of the JCPDS diffraction pattern of the corresponding peak

N = number of reflections considered for the analysis

Table 2 summarizes the values of texture coefficient (TC) for the films. From the tables, it can be seen that the preferential orientation for the synthesized Al_2O_3 thin films is (111) plane as the value of texture coefficient for (111) plane was the highest among the plane orientation and this calculation was compatible with the XRD spectra obtained. The XRD spectra of the films indicate enhanced intensities for the peaks corresponding to (111) plane which also mention the preferential orientation along the specific plane by compared to the XRD pattern of cubic structure (JCPDS 01-075-0277). The relative intensity of the peaks corresponding to the (111) plane increase with increasing annealing temperature. It is believed that the preferential orientation is due to the minimization of surface energy and internal stress [18].

The micro strain value (ε) and dislocation density (δ) were calculated from the following formulas [14]:

$$\varepsilon = \beta\ /\ 4\tan\theta \quad (3)$$

where ε = micro strain value

β = full width at half maximum (FWHM) of the peak (rads)

θ = Bragg angle (rads) and

$$\delta = 1\ /\ d^2 \quad (4)$$

where δ = dislocation density

d = crystallite size

From tables 2, the micro strain and dislocation density values of the films are found to be decreased as the annealing temperature increases. The decrease in the dislocation density of Al_2O_3 films with increasing annealing temperature is because the annealing temperature plays a remarkable role in reducing the defects in the film which contributes to an increase in the crystallite size. For the same reason the micro strain in the film will decrease with increasing annealing temperature [19]. As a result of increase in annealing temperature, it is also believed that the reduction of lattice imperfection which originated from lattice misfit in the film leads to the decrease in micro strain and dislocation density

Fig. 3 and 4 represents the surface topography of the annealed-Al_2O_3 thin films for various temperatures at 2 and 4 hours respectively. Figure 3(a) – 3(c) shows that at 2 hours annealing time, there are agglomerations of Al_2O_3 particles at the film surface although the annealing temperature increase from 200 to 600°C. Figure 4(b) and (c) shows that at annealing temperature of 400 and 600°C, clusters of Al_2O_3 particles formed at the surface. It is deduced that longer period of annealing time is required for Al_2O_3 particles to be distributed uniformly across the film surface.

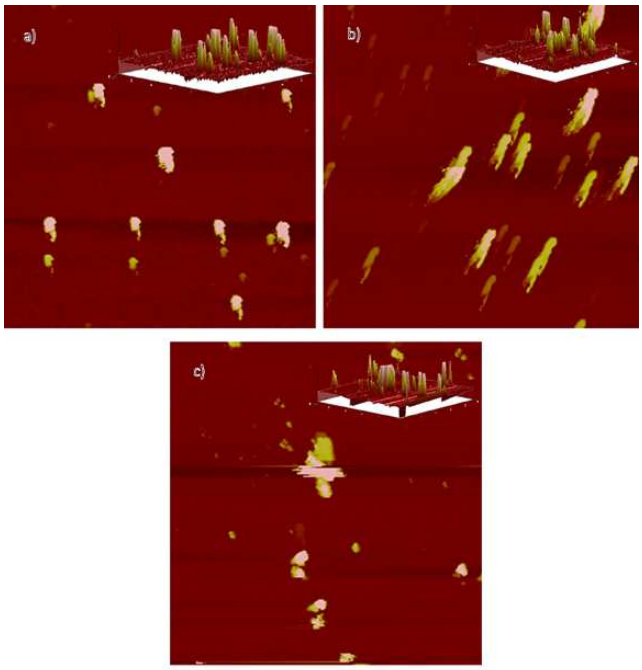

***Figure 3**. The AFM images of synthesized-Al2O3 thin films annealed at temperatures: (a) 200°C, (b) 400°C, and (c) 600°C at 2hrs respectively.*

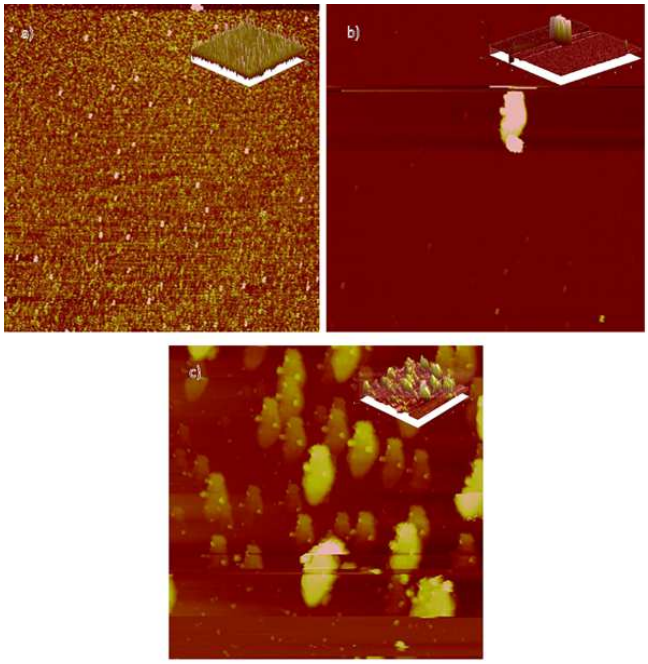

***Figure 4.** The AFM images of synthesized-Al2O3 thin films annealed at temperatures: (a) 200°C, (b) 400°C, and (c) 600°C at 4hrs respectively.*

Table 2 represents the average roughness of the annealed-films for various annealing temperature which determined from the surface analysis. The table reveals that with the increase in annealing temperature, the average roughness of the films also increase. The increase in average roughness is due to the grain growth and this reason is compatible with the increase in values of crystallite size. As a result of the grain growth in preferential orientation along (111) plane, the roughness increased as the annealing temperature increases from 200 to 600°C. With the increasing annealing temperature, the atoms have sufficient energy to occupy the energetically favorable site in the crystal lattice and eventually grains with lower surface energy become larger [20]. Thus this could be explained in terms of grain growth which yields an increase in surface roughness.

From the tables, it is also found that the increase in rf sputtering power lowered the average roughness of the films. It is believed that the low roughness at high rf power is attributed to the densification of the deposited films. However, when the annealing temperature increases, the average roughness also increased. One possible factor is the kinetic energy of deposited species increase with the RF sputtering power enhance the atom mobility in local regions [21]. The increasing kinetic energy increases probability of incident particle for surface diffusion which in turn, promote the grain growth, as a result the roughness of films increase.

***Table 2.** Structural parameters of annealed-Al_2O_3 thin films for different annealing temperatures at 2 and 4 hours.*

Annealing time (hrs)	Annealing temperature (°C)	Label	Crystallite sizes (nm)	Texture coefficient (TC)	Micro strain ($x10^{-3}$ lin^{-2} m^{-4})	Dislocation density ($x10^{13}$ lin/m^2)	Roughness (nm)
2	200	(111)	85.88	2.57	1.505	13.5	0.502
		(107)	115.12	0.67	1.053	7.54	
		(200)	116.00	0.21	0.966	7.43	
		(222)	117.11	0.54	0.830	7.29	

Annealing time (hrs)	Annealing temperature (°C)	Label	Crystallite sizes (nm)	Texture coefficient (TC)	Micro strain ($x10^{-3}$ lin^{-2} m^{-4})	Dislocation density ($x10^{13}$ lin/m^2)	Roughness (nm)
4	400	(111)	104.37	2.54	1.191	9.17	2.180
		(107)	140.50	0.49	0.826	5.06	
		(200)	141.58	0.27	0.751	4.98	
		(222)	106.75	0.68	0.910	8.75	
	600	(111)	114.52	2.61	1.127	7.62	7.360
		(107)	115.16	0.54	1.049	7.54	
		(200)	87.01	0.31	1.287	13.2	
		(222)	58.57	0.68	1.759	29.1	
	200	(111)	85.91	2.30	1.498	13.54	0.295
		(107)	86.37	0.45	1.399	13.40	
		(200)	116.05	0.23	0.962	7.425	
	400	(111)	139.75	2.25	0.923	5.120	1.930
		(107)	140.49	0.45	0.862	5.073	
		(200)	141.57	0.29	0.791	4.989	
	600	(111)	85.89	2.23	1.502	13.55	3.91
		(107)	115.13	0.50	1.051	7.544	
		(200)	116.02	0.26	0.964	7.429	

4. Conclusion

Al_2O_3 thin films were synthesized on Si (111) substrates and were subjected to annealing in the temperature range of 200 to 600°C at 2 and 4 hours. XRD spectra of the synthesized films reveal that the films are in polycrystalline form with the preferential orientation of (111) plane. With the increase in the annealing temperature from 200 to 600°C, crystallite size was increased which was attributed to the decrease in internal strain of the films. With the increase in annealing temperature from 200 to 600°C, the dislocation density and micro-strain of the films were found to be decreased. AFM results indicated that with increase in the annealing temperature, the surface roughness was increased which was attributed to the grains growth. However, the decrease in the surface roughness was related to increases in RF sputtering power.

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