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Atomic Layer Deposition Al_2O_3 Thin Films in Magnetized Radio Frequency Plasma Source

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Abstract

Self-limiting deposition of aluminum oxide (Al_2O_3) thin films were accomplished by the plasma-enhanced chemical vapor deposition using trimethyl aluminum (TMA) and O_2 as precursor and oxidant, respectively, where argon was kept flowing in whole deposition process as discharge and purge gas. In here we present a novel plasma source for the atomic layer deposition technology, magnetized radio frequency (RF) plasma. Difference from the commercial RF source, magnetic coils were amounted above the RF electrode, and the influence of the magnetic field strength on the deposition rate and morphology are investigated in detail. It concludes that a more than 3 Å/ purging cycle deposition rate and the good quality of ALD Al_2O_3 were achieved in this plasma source even without extra heating. The ultra-thin films were characterized by including Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectric spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The high deposition rates obtained at ambient temperatures were analyzed after *in-situ* the diagnostic of plasmas by Langmuir probe.

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Keywords: magnetic enhanced RF; atomic layer deposition; Al_2O_3

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1. Introduction

In recent years, aluminum oxide (Al_2O_3) films have attracted more and more interest due to their excellent physical and chemical predominance [1], such as high dielectric constant (~9), large band gap (8.7eV), high field strength (6~8MV/cm) and the stability of chemical and thermal [2, 3]. The perspective applications of films include alternative dielectrics [4, 5], protective coatings [6, 7] and moisture permeation barriers [8, 9]. At present, a lot of methods were utilized to prepare Al_2O_3 films, such as chemical vapor deposition (CVD) [10], plasma enhanced chemical vapor deposition (PECVD) [11], and atomic layer deposition (ALD) [12]. Moreover, the ALD technology, one of the CVD methods, can deposit ultra-thin films with a high-quality and easily controllable thickness. The reported ALD methods were limited by the proper conditions like the window of growth temperature, however, all

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the surface reactions are saturated and film growth is self-limited but depending on the chamber temperature. With plasma assisted, it seems ALD can be processed in low temperature with still a high deposition rate, high quality, high conformality, and the controllable thickness.

In this study, we use plasma enhanced atomic layer deposition to deposit Al_2O_3 thin films, where trimethylaluminum (TMA) and O_2 are utilized as precursor and oxidant, respectively. Besides, the novel plasma source for the atomic layer deposition technology is confined by magnetic field and the discharge is at radio frequency (RF) plasma. The influence of the magnetic field strength on the deposition rate and morphology are investigated in detail.

2. Experimental details

Al_2O_3 films were deposited on p-type silicon (100) substrates which were cut into 5×5 millimeters pieces in a home-made PE-ALD system. TMA and O_2 were flowed in pulse mode as source materials to grow Al_2O_3, and a radio frequency supply as the power source. The magnetic coils enhancing radio frequency plasma source was amounted above the RF electrode as in figure 1 shows, and the magnetic field strength varied from 0 mT, 1.7 mT, 3.5 mT, and 5.0 mT were taken for the study of influence of magnetic field strength. The reaction pressure was around 0.2Pa, where Argon was used as the carrier and purge gas at flow rate set at 20sccm and 30sccm, respectively, whereas the flow rate of O_2 was 15sccm. The processing cycle for ALD- Al_2O_3 is: TMA flow time is 4s, Ar purge time is 20s, the O_2 pulse time is 10s, and the Ar purge time is 20s. The process was controlled by PLC system. Before the depositions, the Si wafers were rinsing in isopropanol to remove contamination and dust. After spin cleaning for 20s in isopropanol solve, the substrate surfaces were cleaned in piranha etch (H_2SO_4:30%H_2O_2 = 4:1 at 80℃) for 15min. The piranha etch removes both metal and organic contaminants without substantially increasing the microscopic roughness of Si (100) surfaces. Then the substrates were rinsed in de-ioned water again and then cleaned in 48%HF for 30s to remove the chemical oxide, at last the samples are rinsed more in de-ionized water.

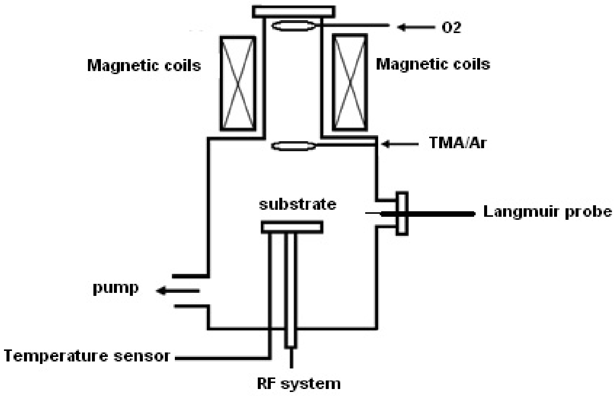

Figure 1. The schematic of PE-ALD system in BIGC

The as-deposited thin films were then characterized by including Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectric spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM). And the plasma parameters in the process were detected by Langmuir probe.

3. Results and Discussion

The growth rate of ALD- Al_2O_3 was measured by Dektec 150 (Vecco). Fig. 2a shows the variation in the film thickness as a function of the number of cycles on Si surfaces. One can see that the deposition rate is almost 0.39 nm/cycle in magnetized RF plasma enhanced ALD, which is very much faster than that in the other thermal or plasma enhanced ALD methods, like the films growth rate was 0.08 nm/cycle for thermal ALD in H_2O vapor, 0.06nm/cycle for thermal ALD in O_3 vapor, and 0.14 nm/cycle for ICP plasma enhanced ALD in O_2 [13]. It implies the magnetized plasma can significantly improve the deposition rate.

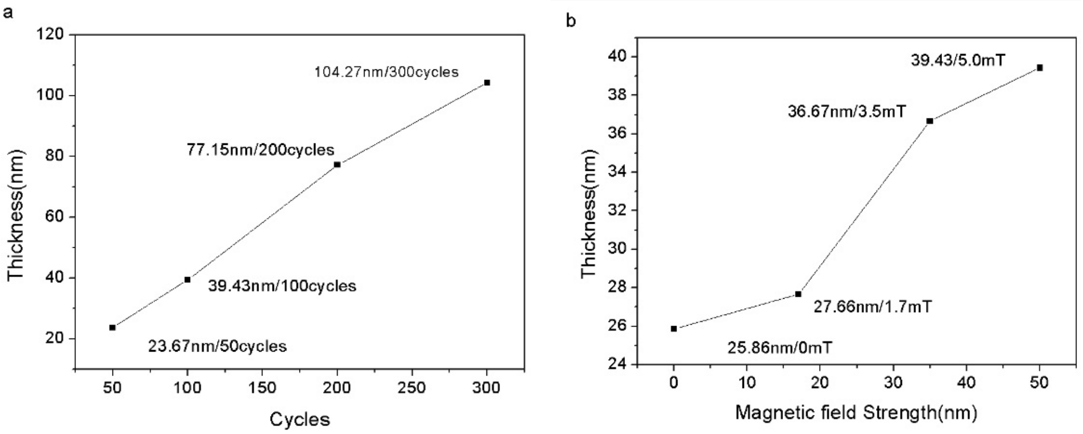

Fig. 2 (a)as-deposited film thickness versus the depostion cycle (50, 100, 200 and 300cycles); (b)influence of magnetic field strength on as-deposited film thickness (100 cycles)

The influence of magnetic field strength was performed and shown in Fig. 2b. It is found that the film growth per cycle is largely dependent on the magnetic field strength. It is 0.26nm, 0.28nm, 0.37nm, and 0.39nm/cycle corresponding to the magnetic field strength at 0 mT, 1.7mT, 3.5mT and 5.0mT, respectively.

The influence of magnetic field strength on the film chemical characteristics was analyzed by FTIR spectroscopy. It is noticed that all films are similar in chemical structures with the one grown at 0 mT as Fig.3 shows. The peak at around 537cm^{-1}, 721cm^{-1} and 830 cm^{-1} assumes to Al-O signal of amorphous Al_2O_3 in transverse mode ;The peak at 917 cm^{-1} is for longitudinal vibration modes associated with γ -Al_2O_3 [14].

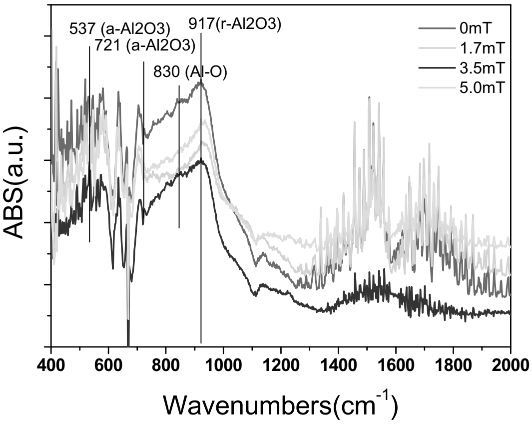

Figure 3. FTIR results of the samples deposition in different magnetic field strengths (RF 100W)

The surface morphologies were studied by atomic force microscope (AFM) (in tapping mode) and scanning electron microscope (SEM). Fig. 4 shows the AFM morphologies of films deposited under different magnetic field strengths. One can see that the ALD-Al_2O_3 films are excellent conformity and uniformity in large area. The root mean square (RMS) roughness of the as-deposited films are 0.53nm at 0 mT, 0.237 nm at 1.7 mT, 0.067 nm at 3.5 mT, 0.069 nm at 5.0 mT, which are remarkably smaller than those deposited by other deposition techniques, such as chemical vapour deposition (CVD) [15] and molecular beam epitaxy (MBE) [16]. This indicates that the magnetized plasma enhanced ALD method is very suitable for fabrication of the high-k materials which require excellent conformity and uniformity in large-area [17]. And it concludes that magnetic field has a big effect on the film roughness.

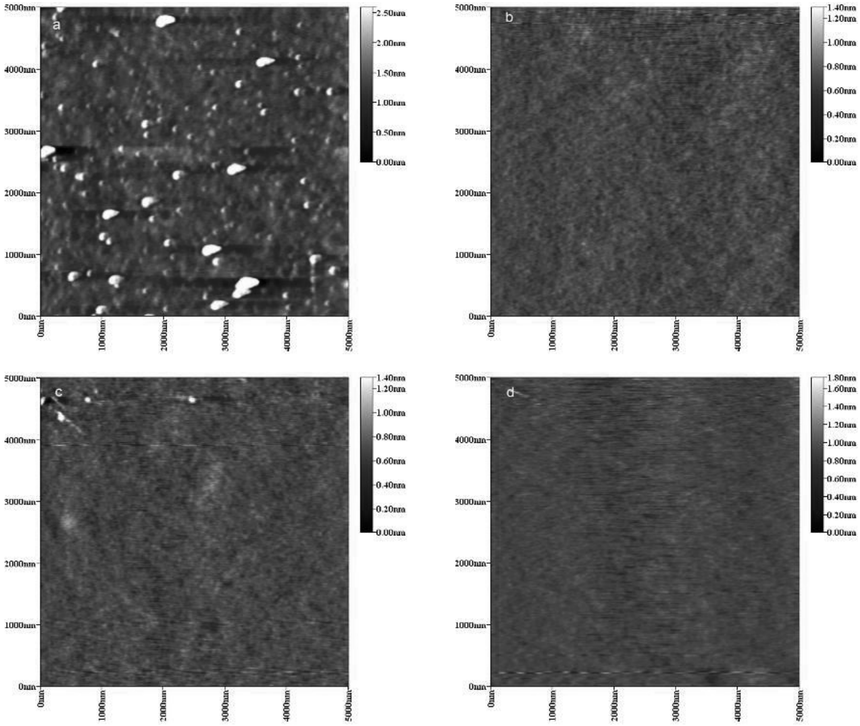

Figure 4. The influence of the magnetic field strength on the surface roughness. (a)0 mT/0.35 nm; (b)1.7 mT /0.237 nm; (c)3.5 mT/0.067 nm; (d)5.0 mT/0.069 nm

The as-grown thin film before and after annealing were studied by SEM. Fig. 5 shows that the surface is very smooth and the diameters of particles are relatively small before annealing. After annealing the particles were grown into big ones and the surface is rough due to the crystallization.

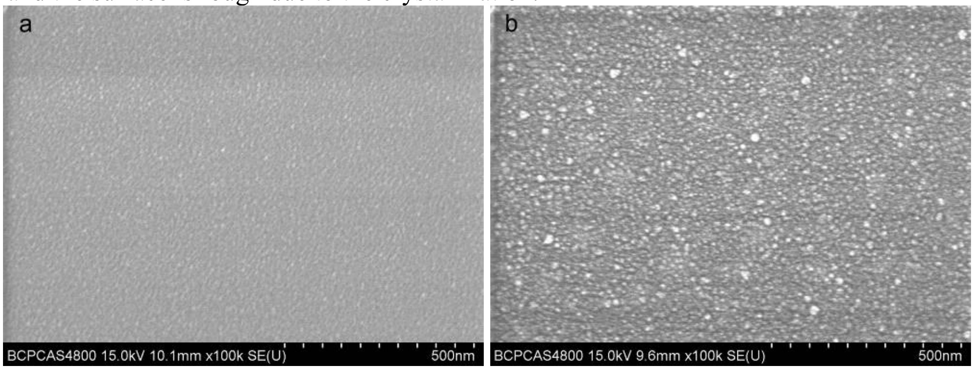

Figure .5 The SEM images of as grown Al_2O_3 thin film (a) before and (b) after annealing

In order to identify the composition of the films deposited in magnetized plasma enhanced ALD, X-ray photo spectroscopy (XPS) is used to analyze the elements in the films. The results are shown in Fig. 6 when thin films were deposited at 0 mT and 50 mT (all binding energies were referenced to the C1s hydrocarbon peak at 285 eV). As a result, Al2p (74.2 eV), Al2s (116.1eV) are appeared as expected, and the O1s (531.7 eV) is confirmed in the spectra. By calculation the atomic stoichiometeric ratios of oxygen to aluminium (O/Al) of the films at 0 mT and 5.0 mT were 3：2.14 and3：2.01, respectively. This means that the as-grown thin films are much more purity in magnetized plasma enhanced ALD.

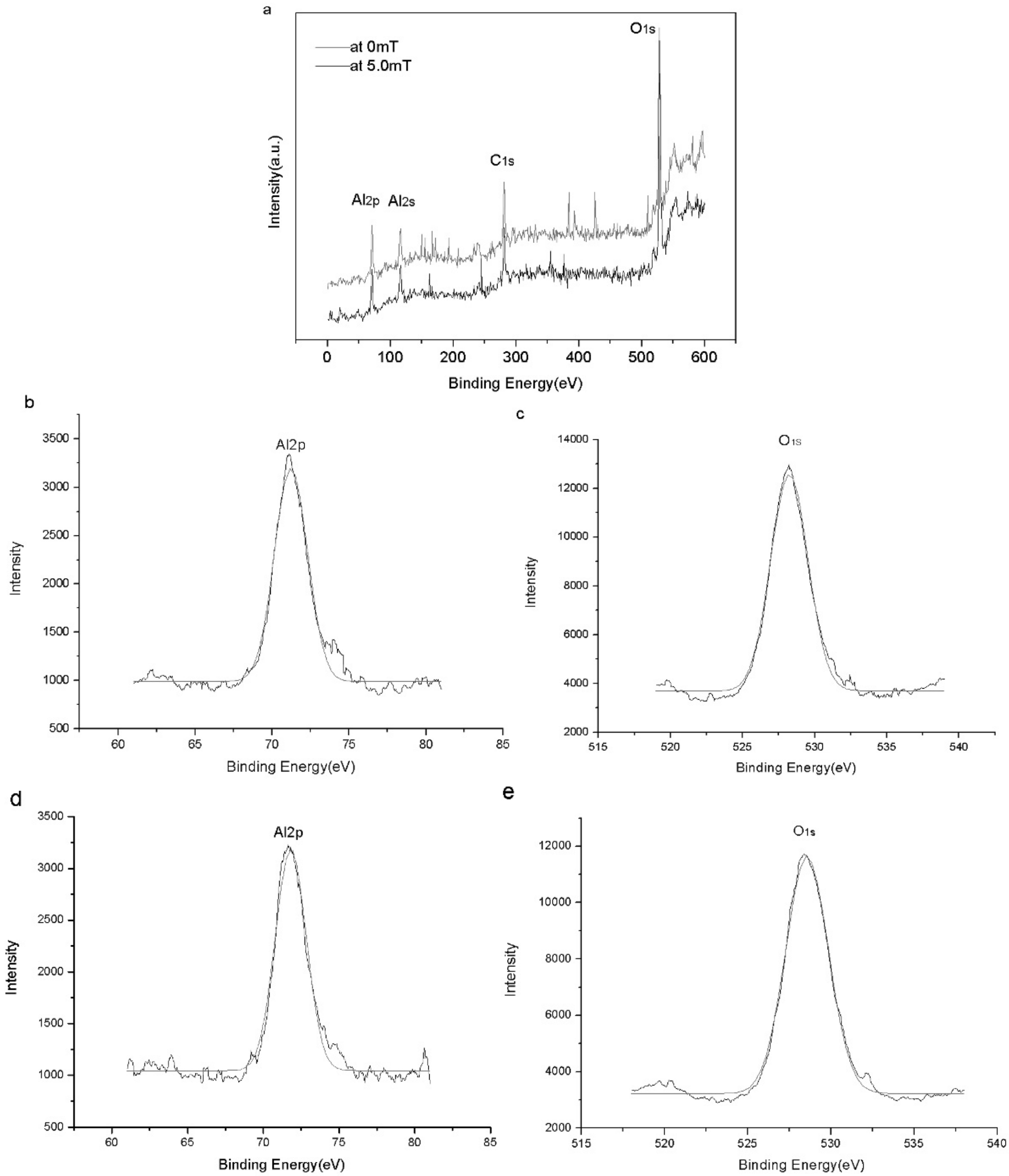

Figure 6. a-XPS for as-deposited Al_2O_3 thin film; b and c are the film deposited at 0 m T for Al 2p and O1s cores, respectively, O/Al=3:2.14; d and e are the film deposited at 5.0 mT for Al 2p and O1s cores, respectively, O/Al=3:2.01

The EDS in Fig.7 was also carried out to verify the elements detected by XPS. It is found that no C was detected in EDS pattern. It means that the TMA was completely decomposed and films are C-free by magnetized enhanced ALD technology.

In our research, magnetized plasma enhanced RF power show a specific role for the ALD- Al_2O_3. With the interaction of plasma, radicals were produced in this process, so the process does not need extra heating and the deposition process can be made in ambient temperature.

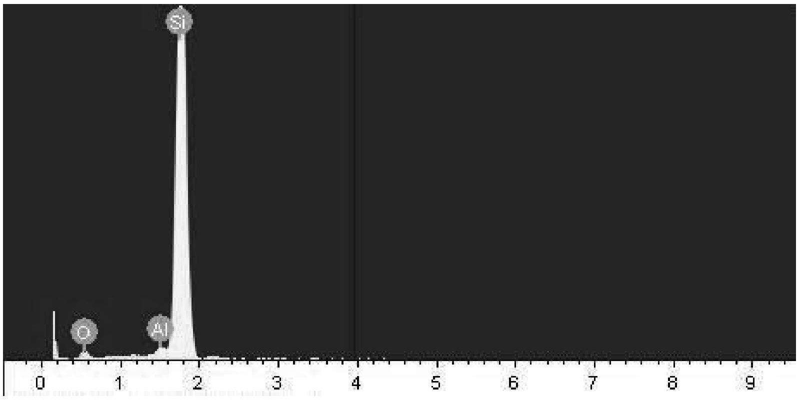

Figure 7. EDS pattern of as-grown Al_2O_3 thin film

The Fig. 8 shows the plasma parameters detected by Langmuir probe (Hiden, U. K.) when RF power was 100W. When the magnetic field strength increases, the ion densities in TMA pulse and Ar purge pulse become larger but not the ion density in oxygen plasma. It results that the amount of $AlCH_3$* radicals increases along with the magnetic field strength. When magnetic field strength is increasing, the collisions of electrons with gas particles become severe, and more and more gas molecules will be ionized. And in this case the amount of radicals will be concentrated, and with the increase of the amount of Ar^+ and its kinetic energy, the film growth in a competition of etching and growing process will lead to a lower RMS than that in other ALD process.

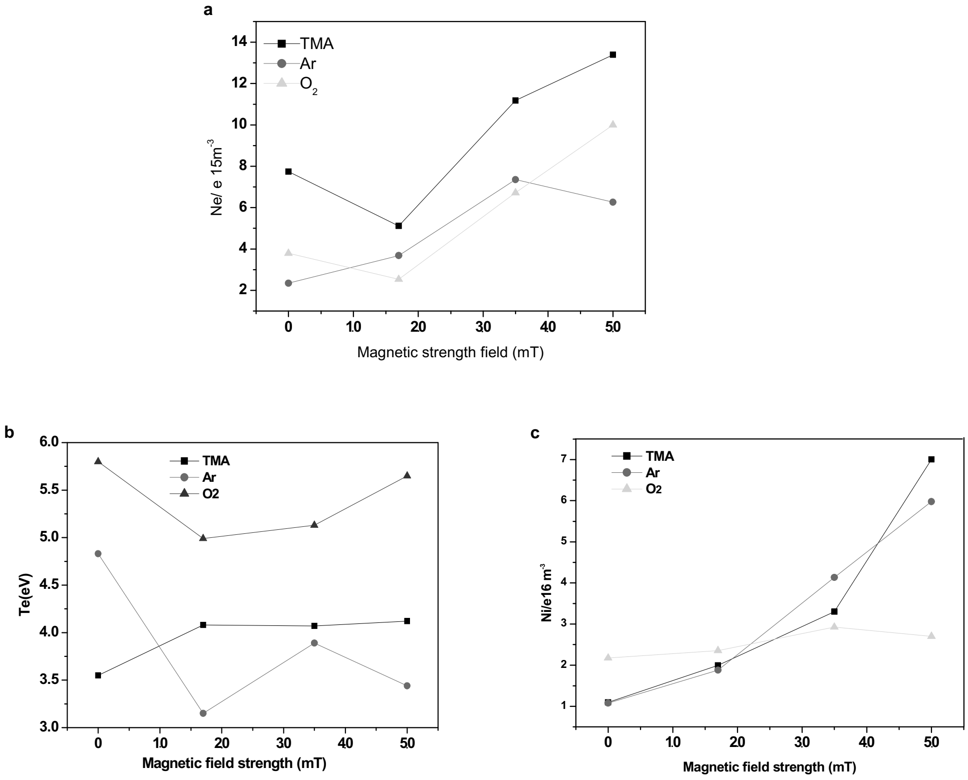

Figure 8. The Langmuir probe detection of (a) electron density; (b) electron temperature and (c) ion density (RF 100 W)

The possible film growth reaction can be summarized in the following reaction:

$2Al(CH_3)_3\,(g)+4O_2\rightarrow Al_2O_3(s)+2CO_2(g)+4CH_4(g)+H_2O(g)$

And this process may contain two half reactions:

a: AlOH* + Al(CH3)3(g) →AlOAl(CH3)2*+CH4(g)

b: AlCH3* + 4O* →AlOH* + CO2(g) + H2O(g)

From these reactions one can see that radicals play an important role for the film growth. Due to the absorb mechanism in ALD method, the saturation of the absorbed TMA is very important for the growth rate of ALD-Al_2O_3.

4. Conclusions

In this work we have successfully deposited Al_2O_3 thin films with TMA and O_2 as precursor and oxidant, respectively, in magnetized radio frequency (RF) plasma enhanced ALD. It is found that the magnetic field strength has a big effect on the deposition rate and morphology, and the ultra thin film shows a very low RMS value. It concludes that this novel method might be utilized to deposit high quality thin films instead of thermal ALD technology. The detailed work will be done later.

Acknowledgements

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References

[1] Scott F. Szymanski, Pieter Rowlette, and Colin A. Wolden, J. Vac. Sci. Technol. A, 26(4), 1079 (2008)

[2] J. Y. Lee, B. C. Lai, In Handbook of Thin Film Materials; Nalwa, H. S., Ed.; Academic Press: San Diego, 2002; Vol. 3, Chapter 1

[3] Yo-Sep Min, Young Jin Cho, and Cheol Seong Hwang, Chem. Mater. 17, 626-631(2005)

[4] T. M. Klein, D. Niu, W. S. Epling, W. Li, D. M. Maher, C. C. Hobbs, R. I. Hegde, I. J. R. Baumvol, and G. N. Parsons, Appl. Phys. Lett. 75, 4001 (1999)

[5] E. P. Gusev, M. Copel, E. Cartier, I. J. R. Baumvol, C. Krug, and M. A. Gribelyuk, Appl. Phys. Lett. 76, 176 (2000)

[6] O. Kyrylov, R. Cremer, and D. Neuschutz, Surf. Coat. Technol. 163, 203 (2003)

[7] A. N. Gleizes, C. Vahlas, M. M. Sovar, D. Samélor, and M. C. Lafont, Chem. Vap. Deposition 13, 23 (2007)

[8] P. F. Carcia, R. S. McLean, M. H. Reilly, M. D. Groner, and S. M. George, Appl. Phys. Lett. 89, 031915 (2006)

[9] E. Langereis, M. Creatore, S. B. S. Heil, M. C. M. van de Sanden, and W. M. M. Kessels, Appl. Phys. Lett. 89, 021915 (2006)

[10] A. R. Chowdhuri, C. G. Takoudis, R. F. Klie, and N. D. Browning, Appl. Phys. Lett. 80, 4241 (2002)

[11] P. Tristant, Z. Ding, Q. B. Trang Vinh, H. Hidalgo, J. L. Jauberteau, J. Desmaison, and C. Dong, Thin Solid Films 390, 51(2001)

[12] R. L. Puurunen, J. Appl. Phys. 97, 121301 (2005)

[13] Seung-Chul Ha,et al.,Thin Solid Films.472,252-257(2005)

[14] Y.T. Chu, et al., J. Appl. Phys. 64, 3727 (1988)

[15] Kobayashi N P et al.,Appl. Phys. Lett. 73 1553 (1998)

[16] A Corriona, F Wu, T Matesa, C S Gallinata, C Poblenza and J S Speck, J. Cryst. Growth 289 587(2006)

[17] L Zhang et al, J. Phys. D: Appl. Phys. 40, 3707–3713(2007)