Advanced Materials Research Vols. 750-752 (2013) pp 1891-1896
Online available since 2013/Aug/30 at www.scientific.net
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doi:10.4028/www.scientific.net/AMR.750-752.1891

The Influences of Oxygen Content on Microstructures and Optical Properties of Al_2O_3 Films Deposited by Oxygen Ion Beam Assisted Pulse Reactive Magnetron Sputtering

Jinxiao Wang[1,a], Zhimin Wang[1,b], Yi Wang[1,c], Kai Zhao[1,d],
Xiaomei Su[1,e], Hu Wang[1,f], *Yudong Feng[1,g]

[1]Science and Technology on Surface Engineering Laboratory, Lanzhou Institute of Physics,
Lanzhou 730000, China

[a]coldwind716@gmail.com, [b]wzm751219@sina.com,[c]Wangrui_781203@163.com,
[d]zhaokai_510@sina.com, [e]sxm_1873@sina.com, [f]57595095@qq.com, [g]fengyd2008@gmail.com

(*corresponding author)

Keywords: Oxygen ion beam; Pulse reactive magnetron sputtering; Al_2O_3 films; Oxygen content; Polyimide; Optical properties.

Abstract. Al_2O_3 films have been deposited at room temperature on polyimide substrates using oxygen ion beam assisted pulse reactive magnetron sputtering system in which aluminium sputtering is simultaneous with oxygen ion beam irradiation. A set of samples were prepared at different oxygen content and film characterizations have been carried out using X-ray diffraction (XRD) for film crystallization, atomic force microscopy (AFM) for surface morphology, and X-ray photoelectron spectroscopy (XPS) for elemental composition measurements and chemical bonding states. The films are smoother and near stoichiometric aluminum oxide as oxygen content increases up to 86%. All films are kept in amorphous structure. The optical properties of the films showed sensitive with oxygen content. Transparent films of refractive index 1.63 are obtained with a deposition rate as high as 70.3 nm/min by 86% oxygen ion beam assisted, which is about 5 times than the films by conventional reactive magnetron sputtering.

Introduction

Aluminum oxide (Al_2O_3) films have attracted great interest as a kind of important function material in a very large of of applications, such as micro-electronics, electroluminescent devices, optical wave guides and corrosion-resistant barriers, because of their high dielectric constant, high thermal conductivity, more radiation hardness and transparency over wide range of wavelength [1,2].

Various techniques have been used to deposit Al_2O_3 films such as magnetron sputtering(MS) [3-5], ion beam assisted deposition(IBAD) [6-8], pulsed laser deposition(PLD) [9], electron beam evaporation [10], chemical vapor deposition (CVD) [11], atomic layer deposition(ALD) [12] and Sol-Gel method(Sol-Gel) [13]. Pulse reactive magnetron sputtering is well known to yield films with high uniformity in large scale and be available abnormal discharge's suppression during dielectric film deposition. However, hysteresis phenomena still exist in the preparation process of Al_2O_3 films by pulse reactive magnetron sputtering. As a consequence, the pure Al_2O_3 film cannot be synthesized with room temperature and metallic sputtering mode, only with substrates heating in excess of 500℃ or target poisoned resulting in a rather low deposition rate. This limits the preparation and application of dielectric films on flexible polymer substrates. IBAD is not only able to synthesize compound films at very low temperature, but also can improve the properties of films with good adhesion of films to substrates and high density at low temperature, providing a promising application in preparation of structural films and functional films. Generally, oxide films are performed by electron beam evaporation with Ar ion beam assistance which exhibits low deposition rate and difficulty to control film composition. Therefore, it requires exploring a new preparation process, in order to decrease deposition temperature and increase deposition rate.

In the present study, Al_2O_3 films have been deposited at room temperature and high deposition rate by oxygen ion beam assisted pulse reactive magnetron sputtering system on polyimide substrates. The mixture gas of oxygen and argon have been bleeded into the ion source during deposition and films have been deposited at various oxygen content. We systematically investigate the influences of oxygen content on microstructures, surface morphology, optical properties and deposition rate of Al_2O_3 films using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), ultraviolet-visible-near infrared spectrometer, and so forth. The motivation of this study was to obtain the optimum oxygen content to achieve stoichiometrical Al_2O_3 films with good quality and optical properties at high deposition rate.

Experimental

The deposition of Al_2O_3 films has been carried out in a self-designed ion beam assisted pulse reactive magnetron sputtering system, in which the films can be synthesized with sputtering aluminum under simultaneous oxidation with oxygen ions produced by ion source. The vacuum system consists of a cryopump backed by a rotary pump and provides a backgroud pressure of better than 2×10^{-3} Pa. A metallic aluminum target with the purity of 4N has been employed which possesses of a 560mm by 80mm rectangular area. The power supply for sputtering used in the experiment is pulse power. Anode type linear ion source is equipped at a 45^o angle with magnetron target. High purity (99.99%) argon gas is bleeded to the target surface as sputter gas through aluminum tube and fixed at 15 sccm. The gas mixture of oxygen and argon is imported in the ion source. The oxygen content, which is defined as the ratio of oxygen flow rate to the total mixture gas flow rate of oxygen and argon bleeded into the ion source ($X_{O2}=O_2/(O_2+Ar)$), is varied in the range of 75%-90%. Two kinds of substrates are chosen, polyimide and quartz glass, to content the need of different test means (quartz glass for optical property measurements), located at 10 cm from the target surface. Before deposition, substrates are cleaned by Ar ion sputtering for 5 min to remove surface contaminant. For the present study, a set of Al_2O_3 films have been deposited at natural temperature condition (without any external heating) for 30 min and the depositions have been carried out at different oxygen content.

Film structure is analyzed by X-ray diffraction (XRD) with Cu Ka (Rigaku D/Max-rC). X-ray photoelectron spectroscopy (XPS) is used to evaluate elemental composition and chemical bonding states of the films. The optical transmission measurements are performed by means of an ultraviolet-visible-near infrared spectrometer. We carry out the envelop-method on the transmission spectra to obtain the variation curve in the optical constant of Al_2O_3 films as a function of the oxygen content. Deposition rate is deduced from profilometry measurements (Dektka8). Surface topography is investigated by atomic force microscopy (CSPM4000) working in contact mode to determine the deposition condition relevant to surface topology.

Results and discussion

Although oxygen gas is directly bleeded in the ion source during oxygen ion beam assisted oxidation process, the deposition zone of the metal film and the reaction zone of ion bombardment are not completely isolated, resulting in the mutually impact of cathode target and ion beam. Fig. 1 shows the hysteresis behavior of cathode target with ion source operated at V_a=200 V, I_a=1 A and conventional reactive magnetron sputtering. It can be seen that the poisoned point of cathode target with the assist of oxygen ion beam shiftes towards higher oxygen flow rate compared with conventional reactive magnetron sputtering (from 9.8 sccm to 11.4 sccm). The hysteresis effect still exhibits in the oxygen ion beam assisted process, and thus the cathode target should be operated before the transition point from the metal mode to the metastable transition mode. During ion beam oxidation process, the heavier argon ion bombardment provides better momentum transfer to ensure effective densification and makes the structure of the film more compact. The bombardments by oxygen ions enhances the reactivity between aluminum and oxygen atoms and are propitious to form completely oxidized films. Therefore, changing the mixture of ratio of oxygen and argon ions in the beam resultes in different properties of the oxide films [14].

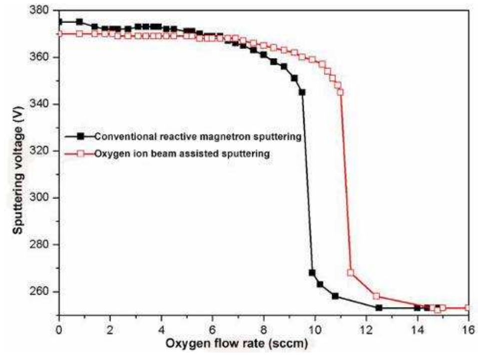

Fig. 1. Hysteresis behavior of oxygen ion beam assisted sputtering operated at V_a=200 V, I_a=1 A and conventional reactive magnetron sputtering.

XRD patterns obtained from Al_2O_3 films are shown in Fig. 2 with the variation of the oxygen content 75%-89%. It is found that all the films show no significant diffraction peaks, indicating that an amorphous structure is former. The changing of oxygen content in our experiments doesn't promote the transformation of films from amorphous to crystalline.

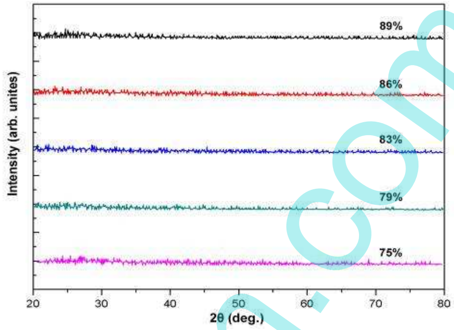

Fig. 2. XRD patterns obtained from Al_2O_3 films deposited with 75%—89% oxygen content

XPS spectra of Al 2p photoelectrons measured from films are shown in Fig. 3 with a variation of the oxygen content from 75% to 89%. The spectrum can be separated into two Gaussian components which corresponded to metallic state at binding energy of 72.8eV and Al_2O_3 oxide state at binding energy of 74.7eV, respectively [15-17]. Here it is noted that oxygen content could lead to significant influence on the composition of the films. As the oxygen content increases, the intensity of aluminum form at lower binding energy wear off, and yet the intensity of Al_2O_3 form at higher binding energy strengthenes, resulting that two obvious peaks appeare in the Al 2p spectrum. Further increase in the oxygen content results in gradual disappearance of the peak at lower binding energy from the metallic state. In consequence, the Al 2p peak could be fitted with only one peak located at binding energy of 74.7 eV, showing that aluminum may be present only in Al_2O_3 form in the film. The peak from the films shiftes towards oxide state at higher binding energy with oxygen content increasing, showing that Al_2O_3 content in the film increased as the oxygen content increased. It is remarkable that stoichiometrical Al_2O_3 films are successfully achieved at oxygen content as high as 86%.

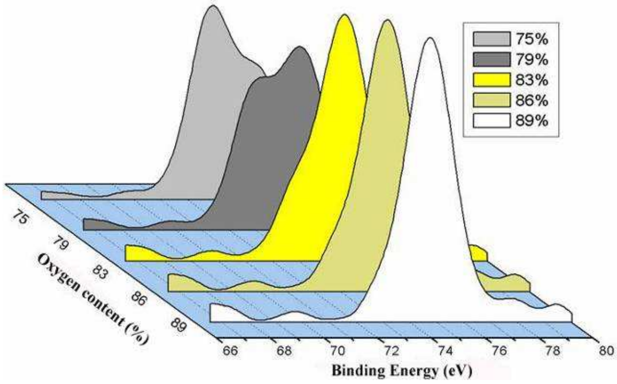

Fig. 3. XPS spectra of Al 2p photoelectrons measured from films deposited with a variation of the oxygen content from 75% to 89%.

Fig. 4 presents the transmittance spectrum of the Al_2O_3 films as a function of oxygen content of the assist ion beam. It is quite obvious that the transmittance of the film deposited at lower oxygen content, i.e. oxygen content at 75%, is far lower than the rest of the films deposited with higher oxygen content over the entire spectrum. It reveals that the film deposited at lower oxygen content at 75% does not entirely oxide, finally forming metal-dielectric mixture with high absorption. When the oxygen content increases larger than 86%, the transmittance spectrum of the films is consisted with theoretical optical spectrum, indicating that the film is totally stoichiometric and transparent over a wide range. This is consistent with the XPS analysis results.

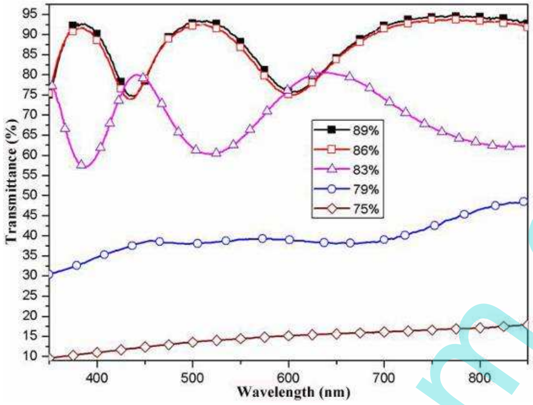

Fig. 4. Transmittance spectrum of Al_2O_3 films deposited as a function of oxygen content of the assist beam.

The optical constants at wavelength of 550 nm are calculated from the transmission curve using the envelop-method. Fig. 5 shows the spectral dependence of the refractive index n and the extinction coefficient k of Al_2O_3 films with various oxygen content. All values of n and k decrease with an increase of the oxygen content. Here it is noted that only 3% change of oxygen content can make great influence to the optical constants of the deposited Al_2O_3 films. The optical properties of the deposited films depend significantly on the oxygen content of the assist ion beam. The achieved refractive index is 1.63 which is comparable to that obtained by other film deposition methods [18].

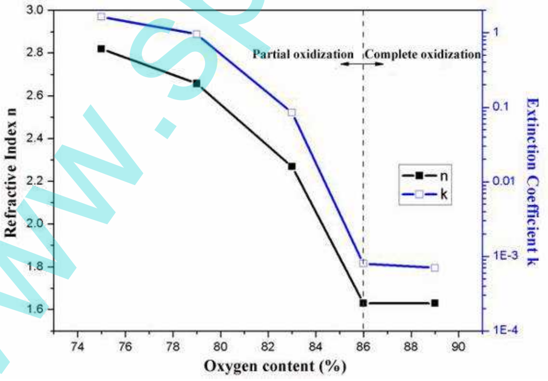

Fig. 5. Optical constants of the films with various oxygen content.

Fig. 6 presents deposition rate of the films with various oxygen content. The results show that the deposition rate was strongly correlated to oxygen content. It can been seen that the deposition rate increases slowly with the oxygen content increasing, and achieves the maximum of 70.3 nm/min (about 5 time faster than the deposition rate of 15.4 nm/min by conventional reactive magnetron sputtering) as the oxygen content increases up to 86%, but further increase in the oxygen content lowers the deposition rate. Obviously, as the oxygen content exceedes 89%, the deposition rate significantly decreases. This might be ascribed to the mutually impact of deposition zone of the metal film and the reaction zone in the vacuum chamber. As oxygen content increases, more oxygen ion diffuses from the reaction zone to the target surface, and then reactes with the cathode target surface to form an oxide layer. At an oxygen content of below 86%, the cathode target is operated in the metal mode. Since the flux of Al atoms diffusing to the substrate is almost changeless, the thickness of films increases, indicating that bombardments by oxygen ions enhances the reactivity between aluminum and oxygen atoms. When the oxygen content is in the range of 86%-89%, the Al cathode target is partially oxidized and operated in the metastable transition mode between the metal mode and the oxide mode, resulting in slight decrease of the deposition rate. The surface of the Al target is poisoned with the oxygen content in excess of 89%, leading to lower deposition rate.

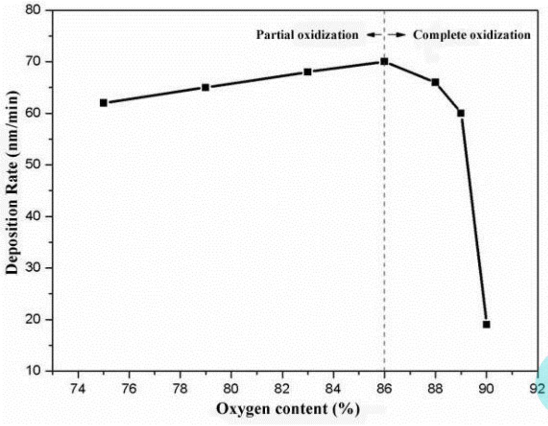

Fig. 6. Deposition rates of the films with various oxygen content.

AFM scans of the surface are carried out to determine the change in the surface topography of the films. Fig. 7 respectively shows AFM images of films deposited by conventional reactive magnetron sputtering, pure oxygen ion beam assisted and 86% oxygen ion beam assisted pulse reactive magnetron sputtering. It is observed that the surface of the film deposited with the assistance of oxygen ion beam is relatively dense and smooth. As expected, proper oxygen content of the assist ion beam leads to a further decrease of the surface roughness which is in favor for improving optical properties of films, and it can be attributed to the effectively bombardment of Ar ion on the film surface by driving a competition between ion erosion and surface diffusion. Therefore, it is believed that oxygen ion beam assistance technique can sufficiently improve uniformity and compactness of films.

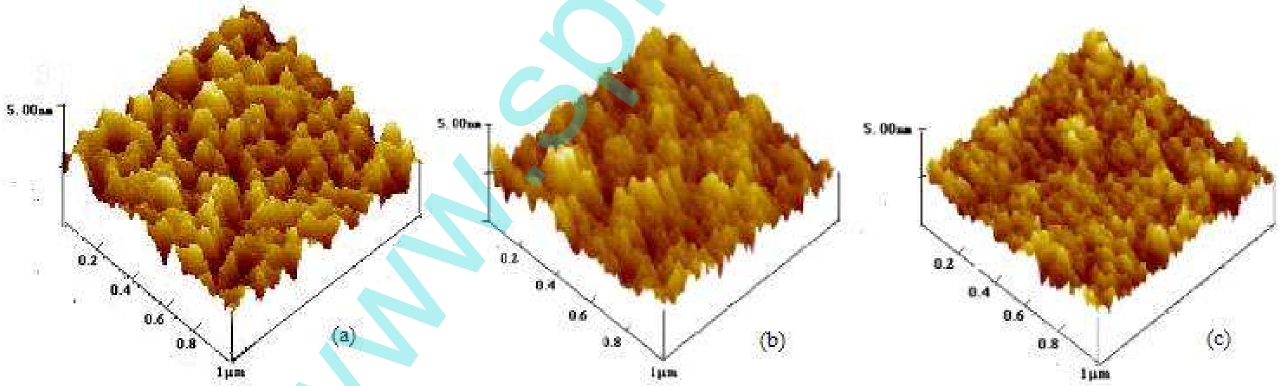

Fig. 7. AFM images of Al_2O_3 films deposited by (a) conventional reactive magnetron sputtering, (b) pure oxygen ion beam assisted and (c) 86% oxygen ion beam assisted pulse reactive magnetron sputtering, respectively.

Conclusions

Al_2O_3 films have been deposited on polyimide substrates by oxygen ion beam assisted pulse reactive magnetron sputtering at room temperature. It has been observed that the poisoned point of cathode target with the oxygen ion assist shiftes towards higher oxygen flow rate compared with conventional reactive magnetron sputtering (from 9.8 sccm to 11.4 sccm). Nearly stoichiometric composition is obtained with an oxygen content of over 86%, which indicates that the surface reaction of the aluminum atoms with oxygen molecules enhanced by bombardments of oxygen ions contributes to the film composition. All the films prepared with oxygen content show amorphous structure. The refractive index exhibits remarkable dependence on the oxygen content and refractive index as high as 1.63 is obtained. The highest deposition rate of 70.3 nm/min is achieved at the oxygen content of

86% which is 5 time faster than the deposition rate by conventional reactive magnetron sputtering. Proper oxygen content of the assist ion beam leads to a uniform, dense and smooth surface of the Al_2O_3 films due to the effectively bombardment of Ar ion. Finally it is believed that oxygen ion beam assistance technique allow deposition of aluminum oxide films on polyimide with a large scale thickness uniformity, smooth surface, high refractive index and deposition rate at room temperature.

References

[1] G.D. Wilk, R.M. Wallance, J.M. Anthony, J Appl Phys Vol. 89 (2001), p. 5243-5275.

[2] A.R. Phani, F.J. Gammel, T. Hack, Surface & Coatings Technology Vol. 201 (2006), p. 3299.

[3] A. Khanna, D.G. Bhat, A. Harris, et al., Surface & Coatings Technology Vol. 201 (2006), p. 1109.

[4] W.H. Ha, M.H. Choo, S. Im, J Non-Cryst Sol Vol. 303 (2002) , p. 78.

[5] J. Wang, Y.H. Yu, S.C. Lee, et al., Surface & Coatings Technology Vol. 189 (2001), p. 146.

[6] X. Ding, F. Zhang, X.Liu, et al., Thin Solid Films Vol. 346 (1999), p. 82-85.

[7] S. Aisenberg, F .M .Kimock, Mater. Sci. Forum Vol. 52 (1990), p. 1-40.

[8] Q. Wei, J. Narayan, Internationals Materials Reviews Vol. 4 (2000), p, 133-164.

[9] F. Di Fonzo, D. Tonini, A. Li Bassi, et al., Appl. Phys. A Vol. 93 (2008), p. 765-769.

[10] H.H. Huang, Y.S. Liu, Y.M. Chen, et al., Surface & Coatings Technology Vol. 200 (2006), p. 3309.

[11] S. Ruppi, A. Larsson, Thin Solid Films Vol. 388 (2001), p. 50.

[12] J.N. Ding, X.F. Wang, N.Y. Yuan, et al., Surface & Coatings Technology Vol. 205 (2011), p. 2846.

[13] B.L. Wang, X.H. Wu, Q.J. Liu, et al., Journal of Yunnan University Vol. A24 (2002), p. 56, In Chinese.

[14] D.M. Mattox, Surface & Coatings Technology Vol. 133-134 (2000) , p. 517.

[15] M.A. Signore, A. Rizzo, L. Mirenghi, et al., Thin Solid Films Vol. 515 (2007), p. 6798.

[16] J. Sjolen, L. Karlsson, S. Braun, et al., Surface & Coatings Technology Vol. 201 (2007), p. 6392.

[17] E.Valcheva, S. Dimitrov, D. Manova, et al., Surface & Coatings Technology Vol. 202 (2008), p. 2319.

[18] I. Shimizu, Y. Setsuhara, S. Miyake, et al., Surface & Coatings Technology Vol. 31 (2000) , p. 187-191.