Journal of Alloys and Compounds 503 (2010) 224–227

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Improvement in adhesion and decrease in stress of MgO thin films due to vapour chopping

Sikandar H. Tamboli [a], Vijaya Puri [b], Ravinder K. Puri [a,*]

[a] Vacuum Techniques & Thin Film Laboratory, USIC, Shivaji University, Kolhapur 416004, India
[b] Department of Physics, Shivaji University, Kolhapur 416004, India

ARTICLE INFO

Article history:
Received 18 February 2010
Received in revised form 22 April 2010
Accepted 29 April 2010
Available online 7 May 2010

Keywords:
Oxides materials
Thin film
Vapour deposition
Mechanical properties
X-ray diffraction

ABSTRACT

We report the enhancement of adhesion and reduction of stress of MgO thin films by using vapour chopping technique. Vapour chopped (VC) and nonchopped (NC) magnesium oxide thin films (thickness ~600 nm) have been prepared by thermal oxidation (in air) of vacuum evaporated magnesium films. The effect of oxidation temperature of 573, 623 and 673 K and duration 90 and 180 min on the adhesion and intrinsic stress of MgO thin films due to vapour chopping were studied. Adhesion and stress was investigated by direct pull off method and interferometric method respectively. Adhesion was in the range 27–54.8 $\times 10^4$ N/m^2 for vapour chopped thin films, as compared to 20.1–41.9 $\times 10^4$ N/m^2 of nonchopped MgO thin films. Intrinsic stress was found to decrease from 70.07 to 22.86 $\times 10^7$ N/m^2 for nonchopped and to 45.63 to 11.83 $\times 10^7$ N/m^2 for vapour chopped MgO thin films.

1. Introduction

Magnesium oxide is an interesting candidate for its application in recent advanced fields due to the high transparency [1], refractive index nearer to glass [2], high secondary electron emission property [3,4] and high density [5]. MgO plays an important role as protecting layer in ac plasma display panel (PDP). The exposure of the protecting layer to the discharge space has an influence on the discharge characteristic and lifetime of PDP; this layer has to be durable. Number of workers have studied magnesium oxide thin films deposited by magnetron sputtering [3,5], ion beam assisted deposition [2], spray pyrolysis [1] etc. Number of reports are available of MgO thin film as substrate for the deposition of perovskites thin film of oxide ferroelectric material [6] and for optical waveguide application [7].

The mechanical stability, durability and strong adhesion to the substrate are essential qualities of thin films for their device applications. The study of thin film adhesion is fundamental and of practical interest because it is related to the nature and the strength of the binding forces at the interface between the two materials in contact with each other. Stress of thin film is also well known, originated in thin films mainly due to dislocations, cracks and voids formation, impurities present in thin film or due to lattice mismatch and difference in thermal expansion of film–substrate interface. There is a need to study adhesion and stress of thin films while using the films for optoelectronics device fabrication e.g. plasma display panel. These are the fundamental microstructural properties on which the performance and lifetime of device depends. The adhesion and stress are interrelated to each other, so there is a need to investigate both the aspects simultaneously for improving the adhesion and reducing the stress in order to achieve a better device lifetime and performance.

Vapour chopping technique (with substrate at room temperature) developed at our laboratory has been reported to improve the adhesion of thin film coatings, it has given promising results for ZnS [8], bismuth oxide [9] and polymer thin films [10]. To the authors knowledge there are no reports available to date on the adhesion and intrinsic stress aspect of thermally evaporated magnesium oxide thin films deposited on glass substrate using vapour chopping technique. The aim of this work is to study the adhesion and stress of MgO thin films and the effect of vapour chopping on them.

2. Experimental

For obtaining vapour chopped (VC) and nonchopped (NC) magnesium oxide thin films, initially vapour chopped and nonchopped magnesium films (99.98%, Alfa Aesar) were deposited on glass substrates under vacuum of 10^{-5} mbar. Magnesium oxide thin films were obtained by thermal oxidation (in air) of nonchopped and vapour chopped magnesium thin films at different oxidation temperatures 573, 623 and 673 K and duration 90 and 180 min.

The vapour chopping technique [8] consists of a chopper which is a circular aluminum metal sheet of 10 cm diameter having a V-cut (155°) shape. This thin circular vane was fixed to a light aluminum rod attached to a motor. The rate of chopping in this study was 6 rot/s. As the chopper rotated, the filaments were exposed to the sub-

* Corresponding author. Tel.: +91 0231 2609245.
E-mail address: rkp_usic@unishivaji.ac.in (R.K. Puri).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.04.238

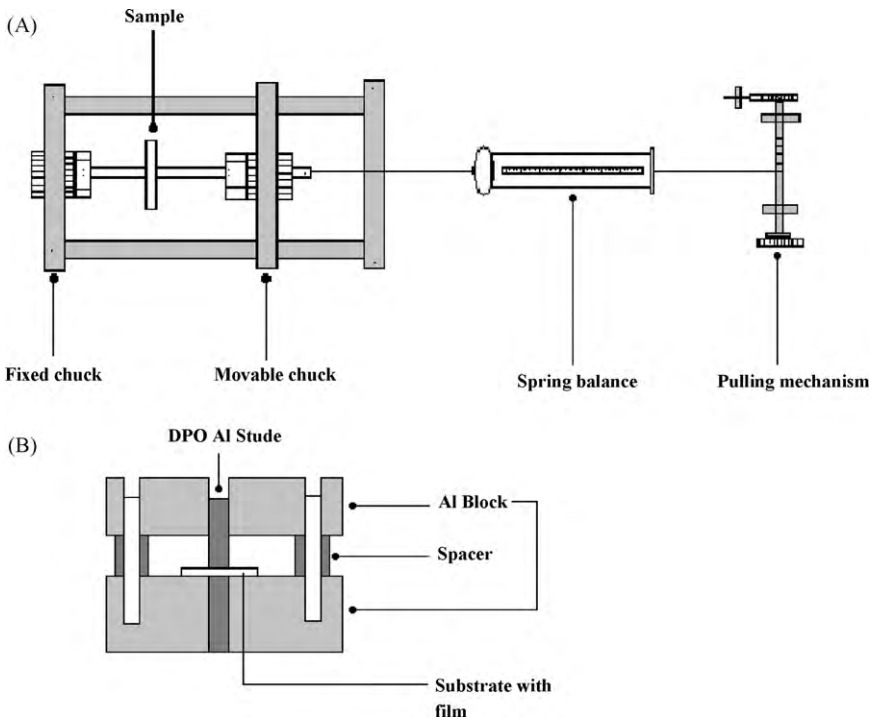

Fig. 1. Schematic diagram of direct pull off method for adhesion measurement.

strates. The vane was at the height of 10.5 cm from the source. The distance between source and substrate was 12.5 cm. Vapour chopping allows more time for the evaporated adatoms to settle on the substrate than the continuous arrival of evaporated adatoms on the nonchopped thin film. A decrease in the number of voids due to lateral surface diffusion of depositing particles in the film is obtained due to this.

The thickness of the films was 600 nm, as measured by Tolansky interferometric method. The structural analysis was carried out with a Philips diffractometer (Philips PW 3710) and surface morphology was inspected by SEM (JSM-6360 JEOL, Japan). Adhesion was measured by direct pull-off (DPO) method [8]. DPO method consist of two aluminium studs of 0.5 cm diameter and 5 cm length, movable and fixed hard metal chucks aligned along the direction of the axis, spring balance having maximum capacity 50 kg, pulling mechanism as shown in Fig. 1. Aluminium stud was attached to the front side of the film and back side of the substrate by using adhesive "Araldite". They were aligned properly by placing inside the special stud fixture and measurement was taken after 24 h.

Movable metal chuck was attached to the spring balance and the spring arm of the balance was attached to the pulling mechanism by flexible metal wire. The film attached with aluminium stud was placed in the metal chucks and pulled by using pulling arrangement. The adhesion of the film was calculated by measuring the load on the spring balance at the time of breaking off the film–substrate interface. The value of adhesion was calculated by using formula

$$\sigma = \frac{g \times F}{A}$$

where g is the force, F is the load in kg, A is the area of stud. The accuracy of this method is ± 9.81 kgf/m^2.

The stress of thin films was measured by interferometric method [8]. In this method the substrates were soda lime cover slips of diameter 1.9 cm and 0.022 cm thickness. This method works on the principle of Newton's ring. The stress was calculated by measuring the variation in diameter of Newton's ring before and after deposition. The stress was measured by the equation

$$S = \frac{Yh^2(K_x - K_y)}{6t(1-\upsilon)} \quad (1)$$

where Y is the Young's modulus, υ is the Poisson's ration, t is the film thickness, h is 0.022 cm (substrate thickness), K_x, K_y are the slope difference of plot $n\lambda/2$ vs radius Newton's ring of before and after deposition.

Thermal stress develops because of the difference between the thermal expansion of the film and the substrate. The thermal stress was calculated by equation [11],

$$S_{th} = (\alpha_f - \alpha_s)Y_f(T_d - T_m) \quad (2)$$

where α_f is the thermal coefficient of film, α_S is the thermal coefficient of substrate, Y_f is the Young's modulus for the film, T_d is the oxidation temperature, T_m is the temperature at the time of stress measurement (room temperature ~300 K).

The intrinsic stress occurs due to defects, microstructural variation, material phase transformation, voids formation during deposition or lattice mismatch between thin film–substrate interfaces. The intrinsic stress was obtained from equation [11],

$$S_{in} = S - S_{th} \quad (3)$$

3. Results and discussion

3.1. Structural

Fig. 2 shows the X-ray diffraction patterns of the vapour chopped and nonchopped magnesium oxide thin films oxidized at 673 K for 180 min. The broad peak between 20 and 30 (degrees) represents the hump of amorphous glass substrate. The dominant cubic (2 0 0) and (2 2 0) phase was observed in both chopped and nonchopped thin film. The peaks in vapour chopped films were more intense than those in nonchopped films. It was observed that the vapour chopped films were more crystalline than the nonchopped thin films. The increased intensity with reducing broadening of peak can be attributed to the improved crystallinity and more stoichiometric structure. No characteristic peaks of impurity and other phases were observed. The XRD patterns did not show evidence of the presence of magnesium metal, indicating complete oxidation of magnesium thin films to magnesium oxide thin films.

SEM of vapour chopped and nonchopped MgO thin films oxidized for 623 K for 90 min is shown in Fig. 3. The vapour chopped films show more uniform surface morphology as compared to the nonchopped films i.e. uniformity of thin film increases due to chopping. The film appears close packed due to vapour chopping. It is also seen that, the porosity of MgO thin films increases with increase in oxidation temperature. This might be due to evaporation of magnesium at higher temperature.

Fig. 4 shows the vertical crosssection of vapour chopped and nonchopped MgO thin films. It shows the vapour chopped thin films have uniform growth with minimum voids whereas nonchopped thin films showed clear columnar growth with larger cracks and voids.

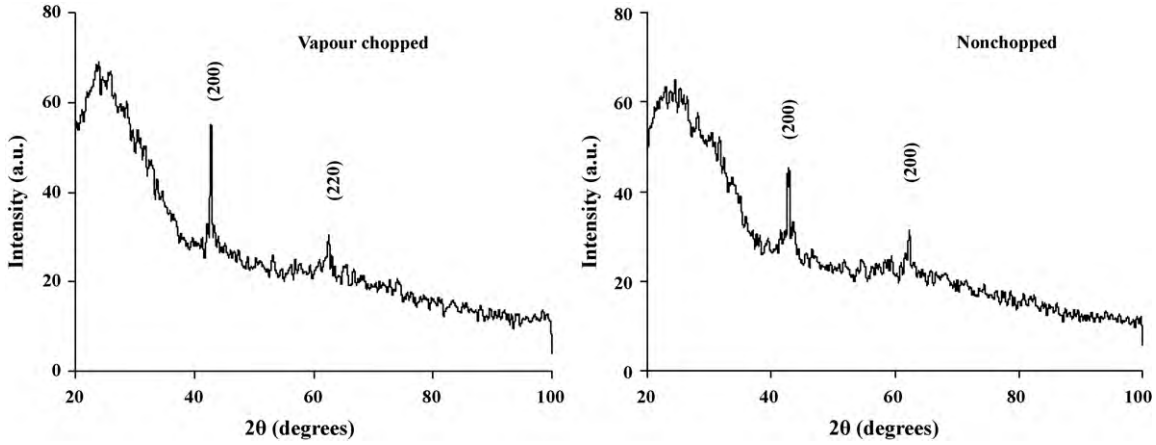

Fig. 2. XRD spectra of vapour chopped and nonchopped MgO thin films.

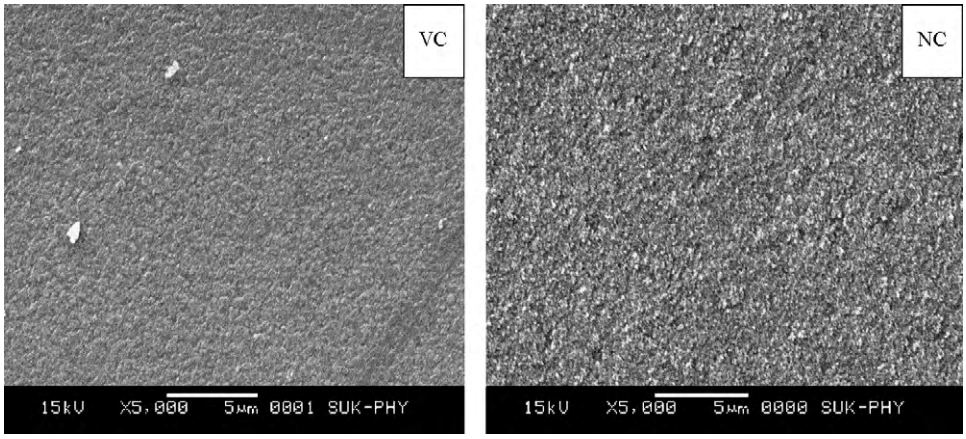

Fig. 3. Surface morphology of vapour chopped (VC) and nonchopped (NC) MgO thin films oxidized at 623 K.

3.2. Adhesion

Fig. 5 shows the adhesion of vapour chopped and nonchopped magnesium oxide thin films due to oxidation temperature and time. The adhesion of the MgO thin films on glass is quite high. It increases with increase in oxidation temperature and duration. Due to heating, mobility of adatoms as well as nucleation site increases and elimination of trapped excess vacancies occur which results in increased adhesion [9].

The adhesion depends to a large degree on the interface layer formed between the substrate and film. Good adhesion in vapour chopped thin films is promoted by improvement in crystal structure, low defect density and reduction of voids in the thin film. The vacuum evaporated thin films possess columnar structure. In nonchopped films, due to continuous arrival of adatoms, columnar growth of the film takes place (Fig. 4) and number of void increases which may further absorbs moisture from atmosphere. The overall effect is to decrease the adhesion of the film. Vapour chopping

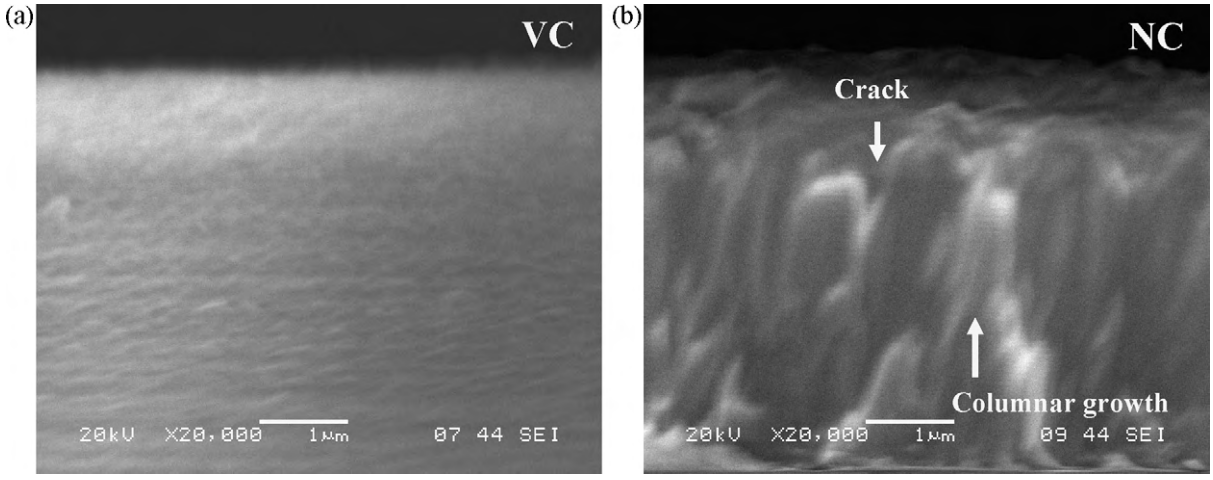

Fig. 4. Vertical crosssection SEM of (a) vapour chopped (VC) and (b) nonchopped (NC) MgO thin film oxidized at 623 K.

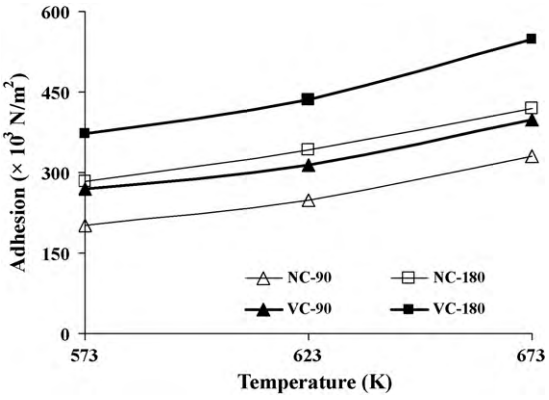

Fig. 5. Adhesion of vapour chopped (VC) and nonchopped (NC) MgO thin films for different temperatures and durations.

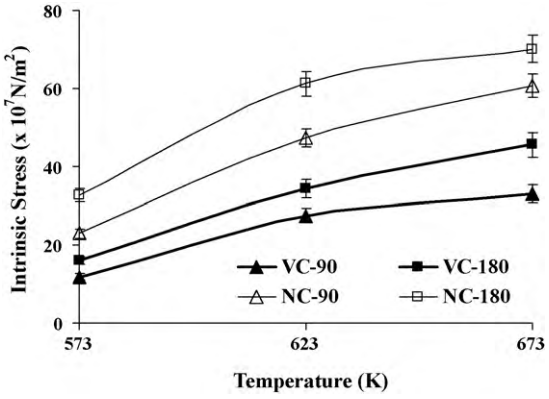

Fig. 6. Intrinsic stress of vapour chopped (VC) and nonchopped (NC) MgO thin films for different temperatures and durations.

allows more time for the adatom to settle and also increases number of nucleation sites. Decrease in the number of voids due to lateral surface diffusion of depositing particles in the film also take place which results in the increased adhesion [8,10]. Due to chopping a flux growth interruption takes place due to which columnar growth is interrupted (Fig. 4).

3.3. Intrinsic stress

Fig. 6 shows that intrinsic stress variation of vacuum evaporated vapour chopped and nonchopped magnesium oxide thin films. These are the values obtained by subtraction of thermal stress from total stress measured by interferometric method. Vapour chopped films showed less intrinsic stress than the nonchopped MgO thin films. Stress is related to crystal disorder, dislocations, voids [12] and density of thin films [13]. Vapour chopping technique helps in improving crystallinity and density of film and decrease in crystallite size, lattice disorder and voids in thin films resulting in decrease in intrinsic stress. At lower densities the stress distribution at the interface is sufficient to deform individual particles and affect the increment in intrinsic stress [14]. The dense vapour chopped MgO thin film with less voids showed lesser intrinsic stress than nonchopped thin films.

The calculated thermal stress from Eq. (2) [11] of vapour chopped and nonchopped MgO thin film is found to be 33.10, 22.40, and 12.97×10^7 N/m^2 for 673–573 K oxidation temperature respectively. For higher oxidation temperature thermal stress is higher. The vapour chopped and nonchopped thin films were oxidized simultaneously at the same temperature conditions for various oxidation temperatures, so the thermal stress at a certain oxidation temperature remains the same for both vapour chopped and nonchopped thin films, because it mainly depends on the difference between thermal expansion coefficient of the thin film material and substrate material. The changes in total stress might be due to the microstructural variations i.e. due to intrinsic stress originating during the thin film growth.

Adhesion and stress properties are interrelated with each other. Films having lower stress have higher adhesion whereas higher stress of thin film causes the reduction in adhesion. Figs. 5 and 6 show vapour chopped thin films have lower stress as well as higher adhesion. Simultaneously, during thermal oxidation, mobility of adatoms as well as nucleation sites increases due to heating and eliminating the trapped excess vacancies which increases the crystallinity and grain size. This growth of crystallinity and grain size creates more contact points at the film–substrate interface. The atomic volume and thermal expansion properties also changes due to heating. Adhesion is directly related to the interface contact point concentration, whereas atomic volume changes and thermal expansion leads to the stress due to cracks and void formation into the thin film. Higher adhesion prevents the crack formation while increase in cracks and voids reducing film–substrate interface contact points.

4. Conclusion

MgO thin films were successfully prepared by thermal oxidation in air of vacuum evaporated vapour chopped and nonchopped magnesium thin films. Vapour chopping technique increases the adhesion and decreases the stress of MgO thin films. The cost effective vapour chopping technique, can be used to obtain highly adherent thin film with lesser stress to improve the device performance and durability.

Acknowledgements

Mr. Sikandar H. Tamboli is thankful to Shivaji University, Kolhapur for Departmental Research Fellowship (DRF). Vijaya Puri acknowledges Research Scientists (C) award from University Grants Commission (U.G.C.), India.

References

[1] A. Raj, L.C. Nehru, M. Jayachandran, C. Sanjeeviraja, Cryst. Res. Technol. 42 (2007) 867.
[2] S.J. Rho, S.M. Jeong, H.K. Baik, K.M. Song, Thin Solid Films 355–356 (1999) 55.
[3] C. Park, J. Choi, M. Choi, Y. Kim, H. Lee, Surf. Coat. Technol. 197 (2005) 223.
[4] S.K. Ram, U.K. Barik, S. Sarkar, P. Biswas, V. Singh, H.K. Dwivedi, S. Kumar, Thin Solid Films 517 (2009) 6252.
[5] K.H. Nam, J.G. Han, Surf. Coat. Technol. 171 (2003) 51.
[6] Y. Yoneda, K. Sakaue, H. Terauchi, J. Phys.: Condens. Matter 12 (2000) 8523.
[7] F.J. Walker, R.A. McKee, H. Yen, D.E. Zelmon, Appl. Phys. Lett. 65 (12) (1994) 1495.
[8] P.V. Patil, R.K. Puri, Vijaya Puri, Mater. Chem. Phys. 49 (1997) 156.
[9] R.B. Patil, R.K. Puri, Vijaya Puri, Mater. Lett. 62 (2008) 198.
[10] J.B. Yadav, R.K. Puri, Vijaya Puri, Appl. Surf. Sci. 254 (2007) 1382.
[11] A.A. Hussain, J. Appl. Phys.: Condens. Matter 1 (1989) 9833.
[12] R. Koch, D. Winau, K.H. Rieder, Phys. Scripta T49 (1993) 539.
[13] A.K. Sinha, H.J. Levinstrin, T.E. Smith, J. Appl. Phys. 49 (4) (1978) 2423.
[14] A.S. Kao, M.F. Doerner, V.J. Novotny, J. Appl. Phys. 66 (11) (1989) 5315.