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Mechanical properties of bismuth oxide thin films

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ABSTRACT

The bismuth oxides thin films have been prepared by thermal oxidation (in air) of vacuum evaporated vapour chopped and nonchopped bismuth films. Polycrystalline and polymorphic structure of bismuth oxide have been observed. The improved adhesion and decreased intrinsic stress of bismuth oxide thin films due to vapour chopping is reported. The effect of oxidation time, oxidation temperature and film thickness on the adhesion and intrinsic stress is studied. The response of these films to ambient air exposure for 40 days is also reported. Both the vapour chopped and nonchopped films showed decrease in adhesion and increase in intrinsic stress upon exposure to air. The effect of air ageing on the vapour chopped films was found lesser.

Keywords: ageing, mechanical properties, thin films, vapour chopping.

INTRODUCTION

Bismuth oxide thin films are used extensively for various applications [1-3] due to its peculiar properties. The properties of bismuth oxide thin films are strongly dependent on its preparation conditions. Bismuth oxide thin films can be prepared with different chemical and physical methods [3-8]. Number of reports is available on the optical and electrical properties of bismuth oxide thin films but the mechanical properties of these films have not been investigated much. Adhesion and intrinsic stress of thin films on substrates are very important for the stable operational characteristics of coatings. Various methods [9-14] exist for production of adherent coatings. Most of them involve either heated substrate or presence of energetic particles.

In our previous works [15-18], it was proved that vapour chopping technique (with substrate at room temperature) developed in our laboratory improves the properties of thin film deposits. In previous reports on vapour chopped oxide films [15, 16], the oxide films were directly deposited by electron beam evaporation and the vapour chopping technique was used while deposition of oxide film. In the present paper, the vapour chopping technique is used for depositing bismuth films and then thermal oxidation (in air) of bismuth films was done for obtaining bismuth oxide thin films. Leontie et al [5-7] and Gujar et al [8] have studied structural, optical and electrical properties of bismuth oxide thin films prepared by thermal oxidation of vacuum evaporated bismuth films. In this paper, we report the adhesion and intrinsic stress of bismuth oxide thin films prepared by thermal oxidation (in air) of vacuum evaporated vapour chopped and nonchopped bismuth thin films. The effect of ambient air exposure for 40 days (at room temperature), oxidation temperature and duration on adhesion and intrinsic stress is also reported.

MATERIALS AND METHODS

Bismuth oxide thin films have been prepared by thermal oxidation (in air) of vacuum evaporated (10^{-3} Pa) nonchopped and vapour chopped bismuth thin films on to glass substrates (Blue Star micro slides). The deposition method is a two step process. In first step, the bismuth thin films have been deposited by resistive heating method. In second step, these bismuth films have been oxidized in ambient air atmosphere at room temperature for different oxidation temperatures and duration to obtain bismuth oxide. The films deposited in this way are termed as 'nonchopped' films. Pure (99.7%) metallic bismuth (Balzers) was used as the source material. The vapour chopping technique consists of a vane of a thin metal sheet of aluminium cut into circular shape of 10 cm diameter. This circular sheet was given a V-cut (155 ^{o}) shape. The vane was at the height of 10.5 cm from the source. This thin circular vane was fixed to a light aluminium rod of 6.5 cm height. This aluminium rod was attached to the shaft of 3 V DC motor having a broad base so that it could be kept inside the vacuum system. The variable power supply of 0-4 V (DC) was used to vary the voltage by means of which the speed of rotation could be controlled and hence the chopping speed. The rate of chopping in this study was 5-6 rot/sec. As the chopper rotated, the filaments were exposed to the substrates i.e. bismuth was evaporated. The films deposited in this way are termed 'vapour chopped' films. The thin microscopy glass cover slips (Blue Star) of diameter 1.9 cm and thickness 0.022 cm were used for intrinsic stress measurement. After the deposition of nonchopped and vapour chopped bismuth films by vacuum evaporation, these films were thermally oxidized in ambient air atmosphere (at room temperature) at different temperatures of 523, 573, 623 and 673 K for different time periods of 30, 60 and 90 min. The onset of oxidation (formation of bismuth oxide) could be seen from the disappearance of bismuth and the film becoming transparent.

The thicknesses of the bismuth oxide thin films were 150 and 200 nm, measured by Tolansky interferometric method. The structural analysis was carried out with Philips X ray diffractometer (XRD) (Philips PW 3710) using a Cu target, at wavelength 0.154056 nm and surface morphology by scanning electron microscopy (SEM) (JSM-6360 JEOL, JAPAN). Adhesion was measured by direct pull off method [16] and intrinsic stress by interferometric method [17]. Adhesion and intrinsic stress of bismuth oxide thin films of 100 nm have been discussed elsewhere [17-19]. The adhesion and intrinsic stress measurements were made in ambient air atmosphere at room temperature.

RESULTS

3.1 Structural characterization:

Both the vapour chopped and nonchopped bismuth oxide thin films showed polycrystalline and polymorphic structure. Monoclinic bismuth oxide was found to be predominant in both (vapour chopped and nonchopped) the cases. Typical XRD patterns of nonchopped and vapour chopped bismuth oxide thin films of thickness 150 nm oxidized at 573 K for 60 min is shown in Figure 1. For the same oxide, many different surface structures and compositions exist and the surface phase one obtains depends largely on the preparation conditions. The vapour chopped and nonchopped films showed predominance of monoclinic Bi_2O_3 (031) phase. Both films (vapour chopped and nonchopped) showed the strong presence of $Bi_2O_{2.33}$ (101) and (107). The nonchopped bismuth oxide showed the presence of β-Bi_2O_3 (220) and (102) which was not observed in vapour chopped films. The XRD patterns do not show the presence of bismuth metal, indicating complete oxidation of bismuth to bismuth oxide thin films. The SEM images of nonchopped and vapour chopped bismuth oxide thin film of thickness 150 and 200 nm oxidized at 573 K for 60 min are shown in Figure 2. The nonchopped bismuth oxide thin films show nanorod like dumbel shaped structure. Gujar et al [8] observed well defined hexagonal, triangular and tetragonal crystals for thickness of 100 nm oxidized at 573 K.

The vapour chopped films show smaller grains as compared to nonchopped films. The average crystallite size as determined by conventional Scherrer's formula is ~ 30 and ~ 33 nm for nonchopped films and ~ 26 and ~ 29 nm for vapour chopped films at thickness 150 and 200 nm respectively. The crystallite size as obtained by X ray data also showed smaller size for vapour chopped films. The decrease in grain size due to vapour chopping has been reported by us previously for Al_2O_3 thin films also [16].

3.2 Adhesion

The adhesion has been plotted as a function of oxidation temperature. Figure 3 shows the adhesion vapour chopped and nonchopped bismuth oxide thin films. Irrespective of the oxidation time and temperature, the adhesion of the vapour chopped bismuth oxide thin films is higher than the nonchopped films. Even after 40 days ambient air ageing effect, this trend is maintained. The increase in adhesion due to vapour chopping is very much larger than the accuracy of the direct pull off method (± 9.81 Kg F/cm^2). From the Figure 3, it is seen that both the nonchopped and vapour chopped films oxidized for 60 min showed higher adhesion than the other films. It was observed that as the oxidation temperature increases, the adhesion also increases. The temperature of oxidation dependent adhesion is more prominent in the vapour chopped films as compared to those of nonchopped films. The films of thickness 200 nm have higher adhesion as compared to those of 150 nm. Increased adhesion has been observed at 150 and 200 nm as compared with those at 100 nm [18, 19]. An increase in adhesion with increase in thickness has also been reported for Al_2O_3 thin films also [16].

Due to ambient air exposure for 40 days (at room temperature), the adhesion was found to decrease. In general the decrease in adhesion was ~ 6 % for vapour chopped films and ~ 15 % for nonchopped films.

3.3 Intrinsic stress

Table 1 show the intrinsic stress of nonchopped and vapour chopped bismuth oxide thin films oxidized at different oxidation temperatures for 30 and 60 min. Since glass cover slip (thickness 0.022 cm) was used as substrate, the substrate deformed due to heating for 90 min. and also due to oxidation temperature of 673 K. The fringes could not be observed. From this table, it is seen that the intrinsic stress is smaller for vapour chopped films for all the oxidation temperatures and duration. The films of 200 nm thickness showed lesser intrinsic stress than those of 150 nm thickness. These films have lesser intrinsic stress as compared with those of thickness 100 nm [17]. In general the films oxidized for 30 min showed higher intrinsic stress than those oxidized for 60 min. Due to exposure to air for 40 days, the intrinsic stress was found to increase. The effect of ambient air ageing on the vapour chopped films was found smaller as compared to those of nonchopped films. The increase in intrinsic stress due to air exposure is larger for the nonchopped films.

Table 1: Intrinsic stress values of nonchopped (NC) and vapour chopped (VC) bismuth oxide thin films.

Oxidation time (min) ↓	Oxidation temp. (K) ↓	Intrinsic stress ($\times 10^9$ N/m^2)							
		Fresh Films				Air ageing films (40 days)			
		150 nm		200 nm		150 nm		200 nm	
		NC	VC	NC	VC	NC	VC	NC	VC
30	523	4.98	2.37	3.15	1.58	6.18	3.19	5.36	1.83
	573	3.54	1.86	2.38	1.53	4.90	2.23	3.72	1.80
	623	1.95	1.18	1.06	0.75	4.47	1.46	1.68	0.93
60	523	4.08	2.17	2.49	1.61	5.43	2.95	3.98	1.97
	573	2.63	1.67	1.88	1.27	4.06	2.18	2.02	1.64
	623	1.47	0.98	0.67	0.54	3.84	1.33	1.52	0.72

DISCUSSION

The polycrystalline and polymorphic bismuth oxide thin films were observed. So it is difficult to correlate the adhesion and intrinsic stress with the particular phase of bismuth oxide. The vapour chopped bismuth oxide thin films showed higher adhesion and lower intrinsic stress than those of nonchopped films. Most of the films oxidized for 60 min showed comparatively higher adhesion.

The intrinsic stress and adhesion was found to be lesser and higher respectively at thickness of 200 nm.

The adhesion of thin films is closely related to intrinsic stress. The intrinsic stress observed in both the nonchopped and vapour chopped bismuth oxide thin films were tensile in nature. Since the film is attached to the substrate and intrinsic stress is transmitted by virtue of its adhesion to this substrate, as intrinsic stress decreases, adhesion should increase. Our result show similar effect. During the process of oxidation, as the temperature of oxidation increases, substrate heating also taken place. Due to this a relief in strain energy takes place which also increases the adhesion. According to Loyd et al [21] heat treatment at moderately low temperatures can eliminate trapped excess vacancies which results in increased adhesion. The process of chopping the vapour flow creates films with fewer inhomogeneites i.e. a low concentration of flaws and non-planar defects. This results in decreased intrinsic stress and increased adhesion of the vapour chopped films. In the nonchopped films, owing to the continuous arrival of adatoms, they are frozen in to sites where they initially arrive, because of restricted mobility, self shadowing occurs and an anisotropic microstructure develops during deposition. Internal stresses are produced owing to incomplete structural ordering during film growth. It is well known that intrinsic stress decreases with increase in adhesion. The vapour chopped bismuth oxide thin films showed increased adhesion and decreased intrinsic stress. Enhanced adhesion and decreased intrinsic stress due to the increased mobility of adatoms and decreased void density due to lateral diffusion is well-known. Both the vapour chopped and nonchopped films showed higher adhesion and lower intrinsic stress at higher thickness. As thickness increases, the packing density of the films increases giving rise to increase in adhesion thereby decreases the intrinsic stress.

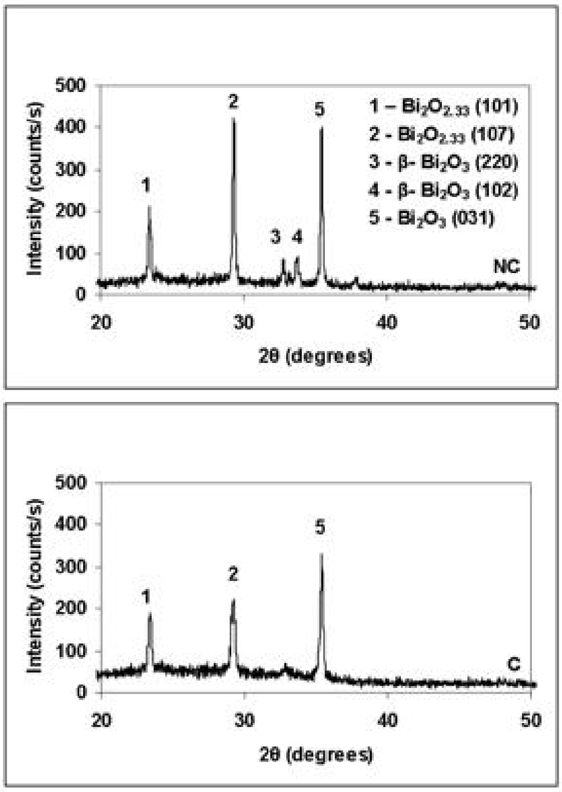

Figure 1 : XRD patterns of nonchopped (NC) and vapour chopped (C) bismuth oxide thin films oxidized at 573 K for 60 min. of thickness 150 nm.

The vapour chopped films showed higher packing density for Al_2O_3, ZnS and MgF_2 films as reported by us previously. The vapour chopped bismuth oxide films also showed higher packing density (~ 0.84) as compared to those of nonchopped bismuth oxide thin films (~ 0.76). Stress relaxation occurs due to morphological changes. The process of vapour chopping changes the morphology of the columnar structure of the film. Due to growth flux interruption, there is a change in the columnar growth of the films due to which a decrease in crystallite size is obtained.

The SEM and XRD data of the vapour chopped bismuth oxide thin films showed smaller crystallite size. Due to smaller crystallite size, there is a reduction in tensile stress. Due to vapour chopping fewer defects are produced and the long range crack propagation in the film is decreased. The intrinsic stress being lower and adhesion being higher in thicker (200 nm) films might due to the films having lower defects and voids. Exposure to ambient air atmosphere at room temperature increases the intrinsic stress and decreases the adhesion. The changes are smaller in the vapour chopped films. It is felt that absorption of moisture from air might be the major cause of the changes observed in the adhesion and intrinsic stress. The absorption of molecules such as water in voids causing increase in tensile stress has been reported [15]. An increase in tensile stress produces a decrease in adhesion. Since the vapour chopped films show a more close packed structure, the effects are smaller.

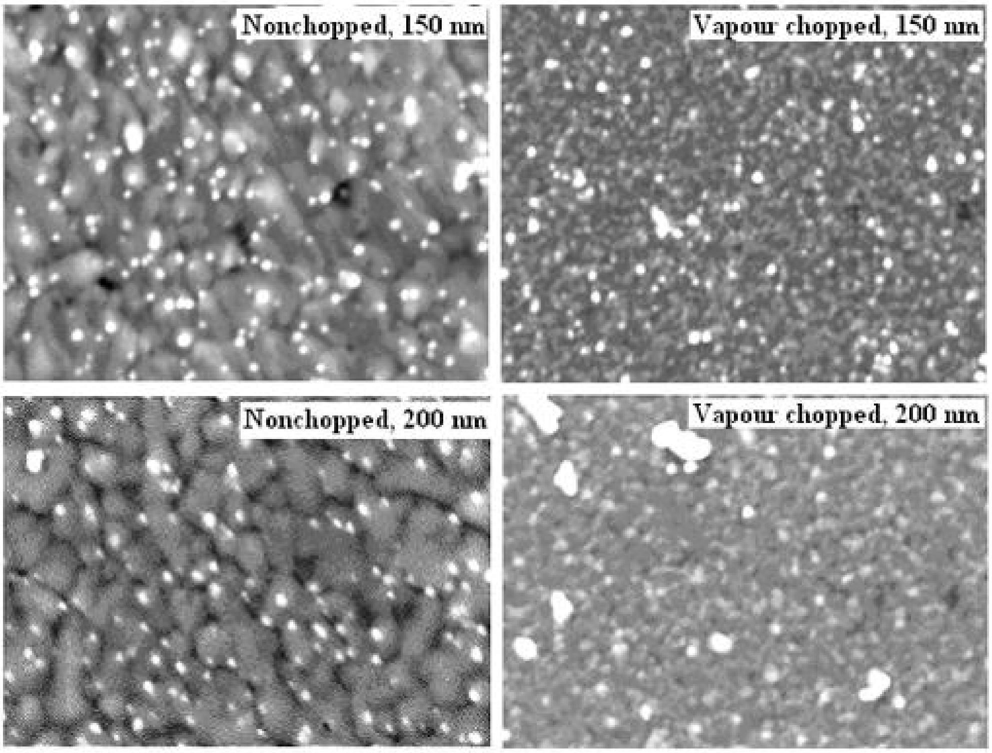

Figure 2: SEM images of 150 and 200 nm thick nonchopped and vapour chopped bismuth oxide thin films oxidized at 573 K for 60 min.

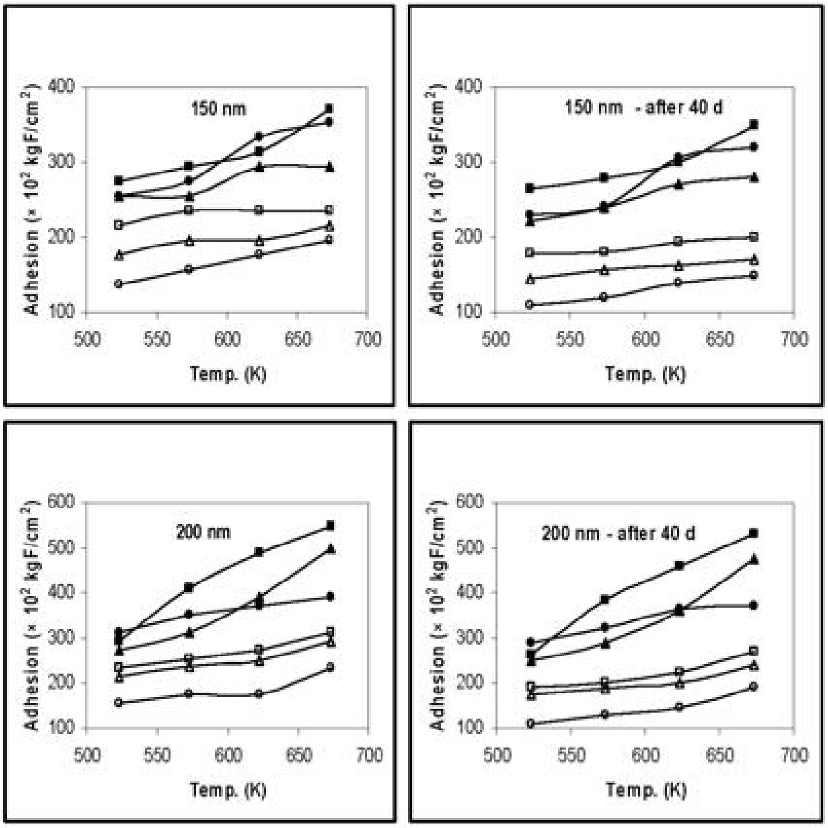

Figure 3: Adhesion as a function of oxidation temperature for as-prepared and aged nonchopped (hollow symbols) and vapour chopped (filled symbols) bismuth oxide thin films oxidized for (●, ○) 30, (■,□) 60 and (▲, Δ) 90 min.

CONCLUSION

Bismuth oxide thin films have been deposited by thermal oxidation (in air) of vacuum evaporated bismuth films. The effect of oxidation temperature and duration, thickness and ageing on adhesion and intrinsic stress has been studied. Films prepared using vapor chopping technique showed better properties. The vapour chopped bismuth oxide thin films showed higher adhesion and lower intrinsic stress than those of nonchopped films. The films oxidized for 60 min showed comparatively higher adhesion and lower intrinsic stress. The intrinsic stress and adhesion was found to be lower and higher respectively for the films of thickness 200 nm. The ambient air ageing study showed less effect on the vapour chopped films. This study indicates that the levels of intrinsic stress may be controlled to quite a good extent by the process of vapour chopping, whereby the adhesion improves drastically. Vapour chopping technique might be of great use in the development of low temperature deposition process for the production of durable hard coatings for optical purposes.

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REFERENCES:

[1] Fuentes OR, Aguilera ES, Velasquez C, Alvarado RO, Alonso JC, Ortiz A. *Thin Solid Films*, **2005**; 96,478.
[2] Wang SF, Yang TCK, Yang YR, Kuromitsu Y. *Ceram Int*, **2001**; 27,767.
[3] Leontie L. *Phys Low Dimen Struct*, **2006**; 2, 23.
[4] Leontie L, Caraman M, Visinoiu A, Rusu GI. *Thin Solid Films*, **2005**; 473, 230.
[5] Leontie L, Caraman M, Alexe M, Harnagea C. *Surf Sci*, **2002**; 507-510, 480.
[6] Leontie L, Rusu GI, *J Non Cryst Solids*, **2006**; 352, 1475.
[7] Leontie L, Caraman M, Deliba M, Rusu GI. *Mat Res Bull*, **2001**; 36, 1629.
[8] Gujar TP, Shinde VR, Lokhande CD. *Appl Surf Sci*, **2008**; 254, 4186.
[9] Schwarz B, Schrank C, Sittner CE, Pollach MS, Rosner M, Neubauer E, *Surf Coat Technol*, **2006**; 200, 4891.
[10] Schrank C, Schwarz B, Sittner CE, Mayerhofer K, Neubauer E. *Vacuum*, **2005**; 80, 122.
[11] Xu X, Tang Z, Shao J, Fan Z. *Appl Surf Sci*, **2005**; 245, 11.
[12] Fancey KS, Mathews A. *IEEE Trans Plasma Sci*, **1999**; 18, 869.
[13] Kinbara A, Baba S, Matuda N. *Thin Solid Films*, **1986**; 141, 229.
[14] Pulker HK, Reinhod M, Esposito R. *Lasers Optronics*, **1991**; 9, 51.
[15] Patil PV, Nerle UV, Puri V, Puri RK, *J Adhes Sci Technol*, **1996** ; 10, 156.
[16] Patil PV, Bendale DM, Puri RK, Puri V. *Thin Solid Films*, **1996**; 288, 120.
[17] Patil RB, Puri RK, Puri V. *J Phys Conf Series*, **2008** ; 14, 012036.
[18] Patil RB, Yadav JP, Puri RK, Puri V. *J Phys Chem Solids*, **2007** ; 68, 665.
[19] Patil RB, Puri RK, Puri V. *Mat Lett*, **2008** ; 62, 198.
[20] Patil RB, Yadab JB, Puri RK, Puri V. *Vacuum*, **2009**, 83, 1355.
[21] Loyd CJ, Nakahara SJ. *Electrochem. Soc*, **1978**; 125, 2037.