Intrinsic Stress of Bismuth Oxide Thin Films: Effect of Vapour Chopping and Air Ageing

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Abstract Bismuth oxide thin films of thickness 1000 Å have been prepared by thermal oxidation (in air) of vacuum evaporated bismuth thin films (on glass substrate) at different oxidation temperatures and duration. Both the vapour chopped and nonchopped bismuth oxide thin films showed polycrystalline and polymorphic structure. The monoclinic bismuth oxide was found to be predominant in both the cases. The effect of vapour chopping and air exposure for 40 days on the intrinsic stress of bismuth oxide thin films has been studied. The vapour chopped films showed low (3.92 – 4.80 × 10⁹ N/m²) intrinsic stress than those of nonchopped bismuth oxide thin films (5.77 – 6.74 × 10⁹ N/m²). Intrinsic stress was found to increase due to air ageing. The effect of air ageing on the vapour chopped films was found low. The vapour chopped films showed higher packing density. Higher the packing density, lower the film will age. The process of chopping vapour flow creates films with less inhomogeneity i.e. a low concentration of flaws and non-planar defects which results in lower intrinsic stress.

1. Introduction
Bismuth oxide thin films have been reported for numerous applications such as gas sensor, electrochromic material, optical coatings, ceramic glass manufacturing and a good opto-electronic material [1-3] due to its interesting properties such as refractive index, photoconductivity, energy gap and dielectric permittivity. It is well known that it has five main crystalline phases with two nonstoichiometric phases, denoted by α-Bi₂O₃, β-Bi₂O₃, γ-Bi₂O₃, δ-Bi₂O₃, ω-Bi₂O₃ and nonstoichiometric phases are Bi₂O₂.33, Bi₂O₂.75. The α-Bi₂O₃ has monoclinic structure and δ-Bi₂O₃ having FCC structure are more stable at normal atmospheric conditions. The β-Bi₂O₃ with tetragonal crystal structure and γ -Bi₂O₃ with BCC structure are metastable phases for temperature less than 750 K. Each phase possesses the distinct crystal structure and physical properties.

Number of techniques has been reported for the deposition of bismuth oxide thin films such as pulsed laser deposition, reactive magnetron sputtering, chemical method, chemical bath deposition, spray pyrolysis and electrodeposition. Very few reports are available on the thermal oxidation (in air) of evaporated Bi which is studied by Leontie et al [2, 4-7]. Most of these reports are on the optical and structural properties. To the authors’ knowledge, no reports are available on the intrinsic stress of bismuth oxide thin films.

Vapour chopping technique developed in our laboratory has proved to improve the quality of thin film deposits [8-14]. Due to vapour chopping, packing density, adhesion, refractive index, optical band gap increases whereas intrinsic stress decreases. Also vapour chopped films show smaller ageing...
(in moisture and ambient air) effect. In this paper, we report the intrinsic stress of bismuth oxide thin films and the effect of vapour chopping technique and ambient air ageing (at room temperature) for 40 days on the intrinsic stress.

2. Experimental
Bismuth oxide thin films have been prepared by thermal oxidation (in air) of vacuum evaporated ($10^{-5}$ mbar) bismuth thin films onto thin glass cover slip substrates. The metallic bismuth (99.7 % pure) was used as the source material. As deposited (nonchopped) bismuth films and bismuth films deposited by using vapour chopping technique (vapour chopped) were thermally oxidized (in ambient air atmosphere at room temperature) at different oxidation temperatures as 523 K, 573 K and 623 K for different durations as 30 min and 60 min. The thin glass cover slips of diameter 1.9 cm and thickness 0.022 cm were used for stress measurement. The intrinsic stress was measured using interferometric method. The schematic of intrinsic stress measurement method is shown in figure 1. The structural analysis was inspected by Philips X ray diffractometer (Philips PW 3710) and surface morphology by SEM (JSM 6360 JEOL, JAPAN). Thickness of films was $\sim$1000 Å, measured by Tolansky interferometric method.

![Figure 1: Schematic of intrinsic stress measurement method](image)

The vapour chopping technique has been reported to improve the quality of thin films. The arrangement consists of a vane of thin metal sheet of aluminium cut into circular shape of 10 cm diameter. This circular sheet was given a V-cut (155°) shape 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 was 5-6 rot/sec in all of the experiments done. As the chopper rotated, the filaments were exposed to the substrates. The vane was at the height of 10.5 cm from the source.
3. Results and Discussion
The structural studies on nonchopped and vapour chopped bismuth oxide thin films have been reported in earlier reports [11, 12] where stable monoclinic Bi₂O₃ was observed to be predominant along with nonstoichiometric Bi₂O₂.₃₃. The dominant phase of -Bi₂O₃ was found only in nonchopped film. The surface morphological studies showed the smoother surface in vapour chopped film with crystallite size ~ 28 nm than those in nonchopped film with crystallite size ~ 24 nm.

The intrinsic stress values obtained for nonchopped and vapour chopped bismuth oxide thin films are tabulated in table 1.

From this table, it is clearly seen that the intrinsic stress of vapour chopped films are smaller than those of nonchopped films. It is seen that the stress is a temperature dependent property. The stress was found to decrease with increasing oxidation temperature and duration. Decrease in stress due to increase in oxidation temperature has been reported by us [14]. It is also seen that the vapour chopped films oxidized for 30 min has lower stress than the nonchopped films oxidized for 60 min. Intrinsic stress has correlation with adhesion of thin film where highly adhesive film shows smaller intrinsic stress. The vapour chopped films showed higher adhesion than those of nonchopped films.

Table 1: Intrinsic stress of nonchopped and vapour chopped bismuth oxide thin films.

| Oxidation time (min.) | Oxidation temp. (K) | Stress (× 10⁹ N/m²) | Nonchopped | Vapour chopped |
|-----------------------|---------------------|----------------------|------------|----------------|
|                       | 523                 | 6.74                 | 4.80       |                |
| 30                    | 573                 | 6.49                 | 4.58       |                |
|                       | 623                 | 6.05                 | 4.02       |                |
| 60                    | 523                 | 6.58                 | 4.71       |                |
|                       | 573                 | 6.21                 | 4.33       |                |
|                       | 623                 | 5.77                 | 3.92       |                |

Table 2 gives the intrinsic stress values after ambient air ageing for 40 days. From the table 2, it is seen that the intrinsic stress of both the nonchopped and vapour chopped films increases due to ambient air ageing. But it is clearly seen that the ageing in vapour chopped films is smaller than those in nonchopped films.

Table 2: Intrinsic stress of nonchopped and vapour chopped bismuth oxide thin films after ambient air ageing.

| Oxidation time (min.) | Oxidation temp. (K) | Stress (× 10⁹ N/m²) | Nonchopped | Vapour chopped |
|-----------------------|---------------------|----------------------|------------|----------------|
|                       | 523                 | 9.58                 | 6.01       |                |
| 30                    | 573                 | 9.33                 | 5.87       |                |
|                       | 623                 | 8.95                 | 5.48       |                |
| 60                    | 523                 | 9.41                 | 5.98       |                |
|                       | 573                 | 9.11                 | 5.63       |                |
|                       | 623                 | 8.80                 | 5.37       |                |

Generally, the vacuum evaporated thin films possess columnar microstructure interspaced with voids. Due to this, the adhesion of film decreases with increased stress. The vapour chopping technique provides growth flux interruption where columns are not allowed to grow tall or wide i.e. columnar growth of film is avoided and a close packed structure is formed. This corresponds to increase in packing density. Higher the packing density, lower will be the stress. Due to this, adhesion increases with decreasing stress. The process of chopping vapour the flow creates films with less inhomogenety i.e. a low concentration of flaws and non-planar defects which results in lower intrinsic stress. Due to exposure to ambient air, there is absorption of moisture in the film due to capillary effect
which causes decrease in adhesion and increase in stress. There is also an interaction of air molecules with the film molecules which causes chemical change in the film causing changes in the optical and mechanical properties of the film. The detailed discussion on the effect of vapour chopping technique is discussed elsewhere [8-14].

4. Conclusion
Polycrystalline and polymorphic bismuth oxide thin films have been prepared which showed the oxidation temperature and duration dependent intrinsic stress property of the film. The ambient air ageing effect was to increase the stress of both the nonchopped and vapour chopped films. The vapour chopping technique was found to lower the stress of bismuth oxide thin films as well as to reduce the ambient air ageing effect. These vapour chopped films can have applications in hard coatings.

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