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Surface morphology of r.f. sputtered bismuth titanate thin films

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Bismuth titanate ($Bi_4Ti_3O_{12}$) thin films were prepared by the r.f. sputtering technique. A bismuth-rich target was used to compensate for the loss of bismuth during deposition. Studies on many films, deposited under various conditions, showed that existence of non-uniform erosion leads to many surface morphological features. This varying surface structure is a consequence of the resputtering process. Because the microstructure has a significant effect on the films electrical/optical response, a knowledge of its dependency on process parameters is an important step towards device development.

1. Introduction

Ferroelectric bismuth titanate ($Bi_4Ti_3O_{12}$) with a mica-like morphology belongs to the large family of layer structure oxide compounds. With its high electrical breakdown property, $Bi_4Ti_3O_{12}$ is a good candidate for thin-film capacitors. Device applications using its switching and optical properties were reported by Cummins [1, 2]. $Bi_4Ti_3O_{12}$ also has potential as a non-volatile high-density memory. For all of these applications it is important to have a knowledge of the microstructural behaviour of bismuth titanate thin film. This has been attempted in the present study by investigating the proclivity of the material for resputtering.

Epitaxial $Bi_4Ti_3O_{12}$ thin-film preparation on MgO and epitaxial platinum was reported by Takei *et al.* [3]. Films were prepared using both reactive triode and r.f. sputtering with various target compositions. Preparation of bismuth titanate thin films, on various substrates, with a dielectric constant comparable to its single crystal value, was also reported by Ghosh *et al.* [4]. The r.f. sputtering technique with a hot-pressed ceramic target of composition $0.8Bi_4Ti_3O_{12} + 0.2Bi_{12}TiO_{20}$ was used for deposition.

During the process of film preparation, several morphological variations in the films were observed. The observed profound effects of preparation parameters on the film microstructure are reported. The effects of microstructure on the dielectric properties of the film were significant and have been reported elsewhere [4]. Bismuth titanate was deposited under various deposition conditions and resputtering effects were investigated. The results obtained were compared with the prediction of the model developed by Cuomo *et al.* [5, 6].

2. Experimental procedure

Bismuth titanate thin films were deposited by r.f. sputtering a 2 in. diameter target in an argon:oxygen mixture atmosphere. $Bi_4Ti_3O_{12}$ films were prepared using a wide range of sputtering parameters. Deposition time, r.f. power level, partial gas pressure, and substrate temperature were all varied. After mounting clean substrates, the system was pumped down to an initial background pressure of 1.2×10^{-6} torr. In a hot deposition scheme (i.e. increased substrate temperature) this process was followed by heating the substrates to the desired temperature (maximum temperature 552 °C). The system chamber pressure was also stablized at 20 mtorr by the introduction of sputtering gas into the system. Three methods of film characterization were used. A profilometer (Talysurf 10) was used for measuring variations in film thickness as a function of radial distance from the centre of the target, by measuring the step height from the film to an area that had been covered by a thin glass wafer during deposition. In the second method, the development of surface morphology due to resputtering was studied using a scanning electron microscope (SEM). The third method of characterization was a visual observation of the sputtered films. As reported [7], any texturing of the film surface due to resputtering could often be observed visually.

3. Results and discussion

Substrates directly under the target, especially in a ring-shaped area under the edge of the target, are generally affected by resputtering. The development of surface morphology features and variation in film thickness was observed in substrates placed in this area.

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The intensity and type of effect, resulting from resputtering, were found to vary as functions of the sputtering parameters as well as the location of the substrate. Fig. 1 shows the electron micrographs in which the range of micro-effects (i.e. the development of surface morphology features) observed in bismuth titanate films can be seen. All three films were prepared at 100 W with 20 mtorr gas pressure (50:50, O_2:Ar) for 5 h. As indicated in Fig. 1, the only variable was the relative position of the substrates (preparation geometry) with respect to the centre-line of the target. The change of substrate temperature also induced a wide range of micro-effects as shown in Fig. 2. These films were deposited under similar deposition conditions (mentioned above) but this time the variable was substrate temperature.

In addition to the substrate position and substrate temperature, a change in the microstructure resulting from a change in r.f. power as depicted in Fig. 3, and from a change in partial gas pressure (Fig. 4) was also observed. The change in partial gas pressure also induces nonstoichiometry and is evident in the black colour of the film, compared to light yellow for stoichiometric bismuth titanate.

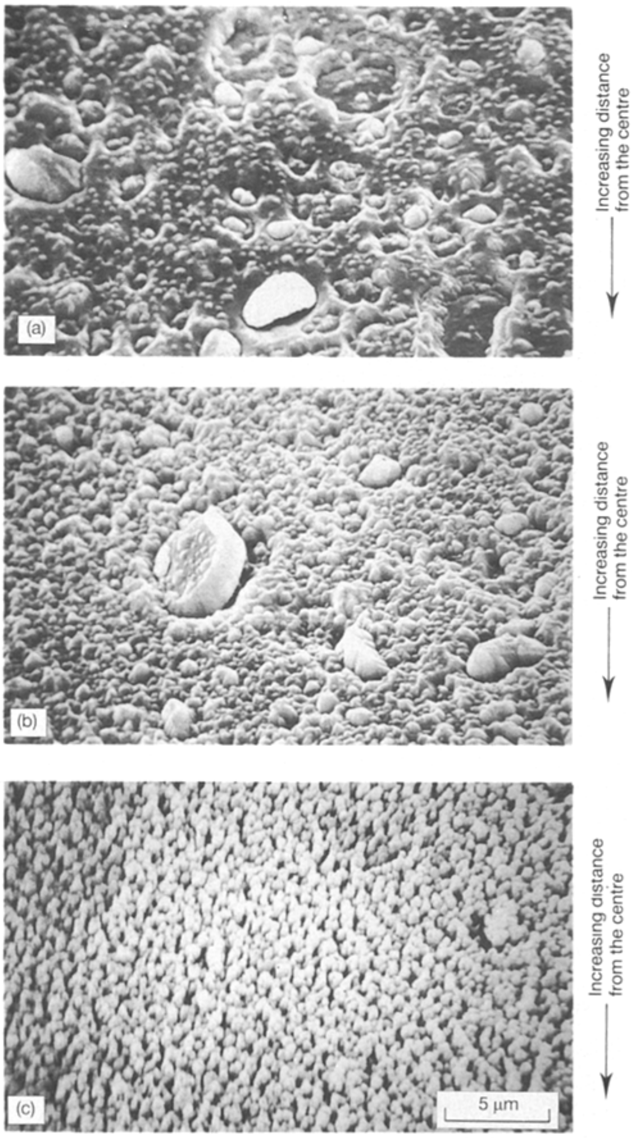


Figure 1 Effect of preparation geometry on the microstructure of $Bi_4Ti_3O_{12}$ thin films.

A significant variation in film thickness (macro-effect) was observed, as shown in Fig. 5, caused both by the change of substrate temperature and the relative position of the substrates.

The judgment on the presence of resputtering, its intensity and type of effects was made based on the three methods of observation: scanning electron micrographs, thickness profiles, and visual observation. On the micrographs evidence of resputtering would be seen through the formation of surface morphology features such as etch pits. For the thickness profile graphs, drops in thickness under the edge of the target indicated resputtering. Visual observation of the substrate indicate a change of colour in the resputtered area. These areas where resputtering had occurred also agree with the results of profilometer and/or scanning electron micrographs.

Resputtering of a growing film can occur due to a number of bombardment processes, e.g. bombardment of the material by energetic positive ions extracted from the discharge by a negative bias at the substrate [8, 9], high-energy elastically back-scattered particles [10], and bombardment by negative ions originating near the target surface, generally at a high negative potential, and accelerated across the dark space [8]. In particular, under certain conditions, the growing film can be resputtered at the same rate by which it grows and can even lead to resputtering of the substrate [11]. Among the various processes the bombardment by negative ions appears to be the main cause of resputtering. Cuomo *et al.* [5, 6], developed a model which states that ionization potential, I_A, and electron affinity, EA_B, of target elements, A and B, can be used in the form $I_A - EA_B$ as a useful measure to predict negative ion production. According to their results, at about 3.4 eV or less, the probability of negative-ion formation is higher, resulting in a noticeable resputtering effect.

Negative-ion resputtering does not lead to uniform film erosion but rather results in isolated etch pits on the growing films. If the etch pits remain isolated they may not be seen optically and can easily go undetected unless explicitly sought. However, under high doses of ion bombardment the etch pits overlap and can lead to a variety of morphological structures such as ripples, dimples, needles, etc., which usually scatter light and are readily noticed [12, 13]. These etch pits have been observed in WO_3 films [14], although $I_A - EA_B$ for WO_3 is 6.5 eV, which is considerably higher than the threshold value of 3.4 eV proposed by Cuomo *et al.* [5, 6]. The reason for this, as explained by Giri and Messier [14], is that the resputtering rate is not large enough to prevent the film growth, but it is sufficient to cause localized structural defects, such as isolated etch pits. The value of $I_A - EA_B$ for bismuth titanate is 5.35 eV, lower than the $I_A - EA_B$ value of WO_3. Because resputtering has been observed in WO_3, it is probable that resputtering will occur during the deposition of $Bi_4Ti_3O_{12}$. Kester [7], also reported the probability of resputtering in bismuth titanate. Our current observations on various films, prepared

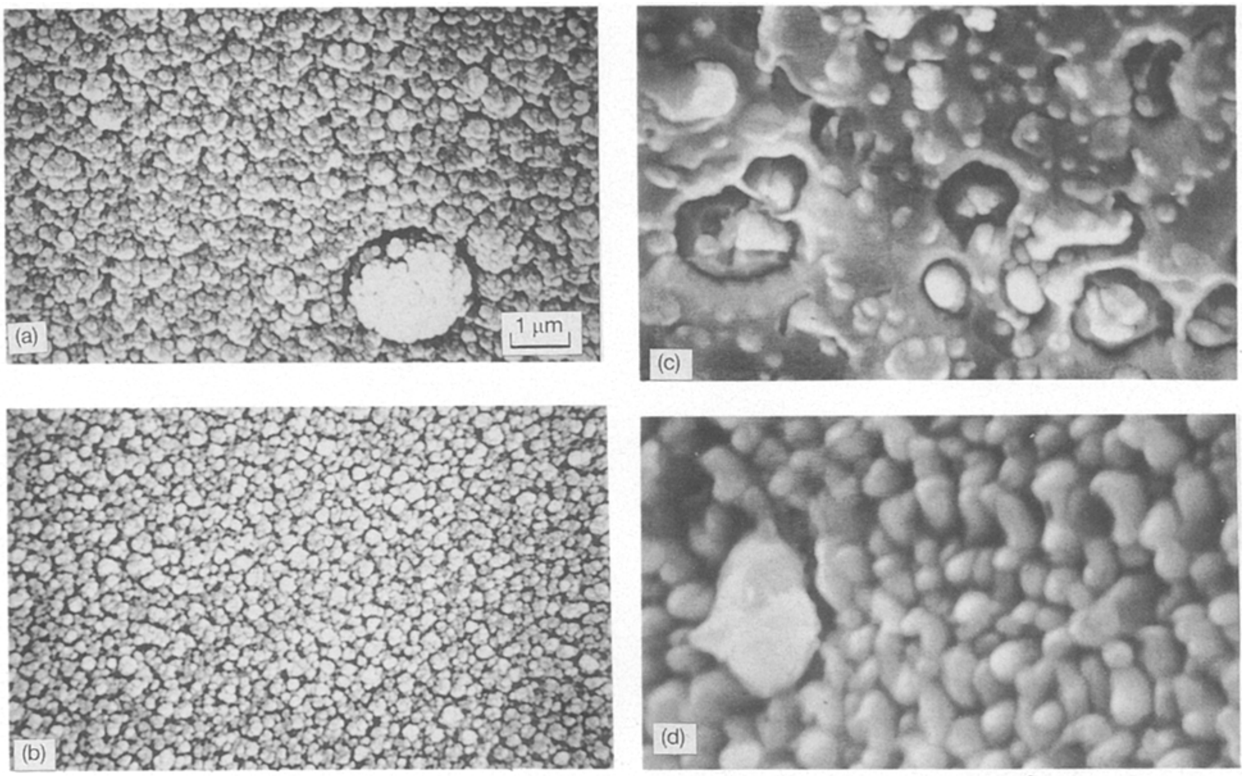
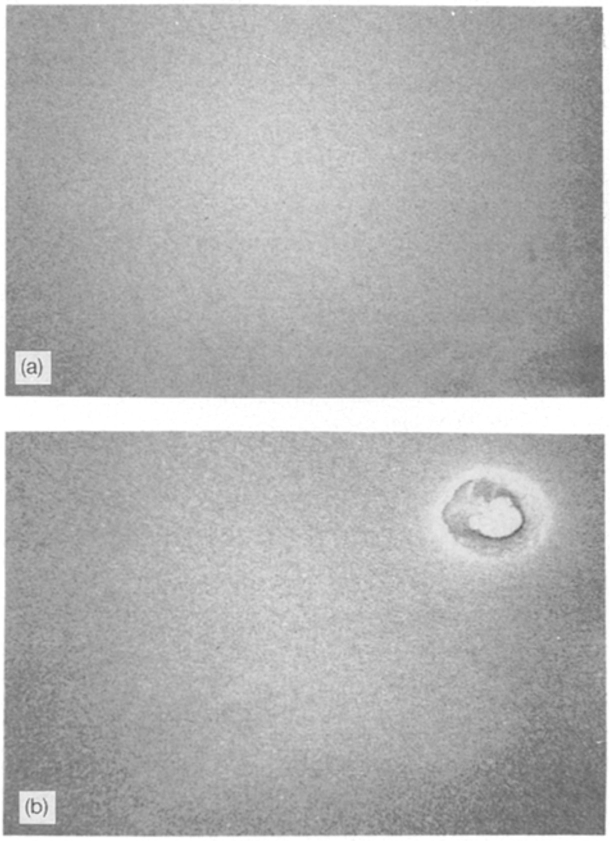


Figure 2 The microstructure of $Bi_4Ti_3O_{12}$ thin films deposited at different substrate temperature. (a) 325 °C, (b) 356 °C, (c) 414 °C, (d) 461 °C.



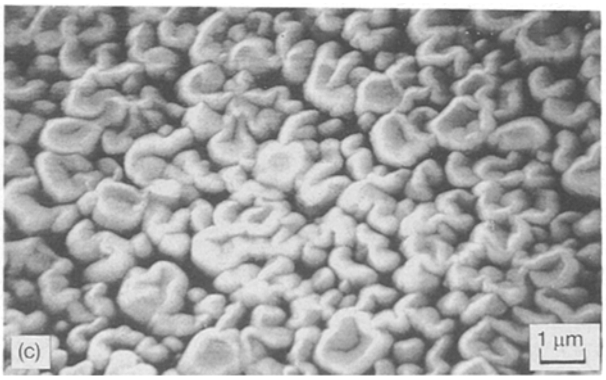


Figure 3 The variation in the microstructure of $Bi_4Ti_3O_{12}$ thin films due to the change in r.f. power. (a) 50 W, (b) 100 W, (c) 150 W.

under different conditions, confirm resputtering in $Bi_4Ti_3O_{12}$.

Our study indicates a significant effect of deposition parameters on resputtering, leading to various morphological surface features. In some cases, for example at low r.f. power level or a small change in partial gas pressure, no micro-effects occurred. The wide range of resputtering effects observed in this study, on both the macro- and the micro-level, lead us to conclude that the occurrence of resputtering, its intensity and the type of effect cannot be determined based on any one factor. Any model based on just one factor, such as the model by Cuomo *et al.* [5, 6], which was based on the material only, is limited. One other possible problem in evaluating the resputtering is that the stoichiometry of the material should be taken into account.

4. Conclusion

Bismuth titanate thin film prepared by the r.f. sputtering method exhibits various surface morphological features, resulting from non-uniform erosion of

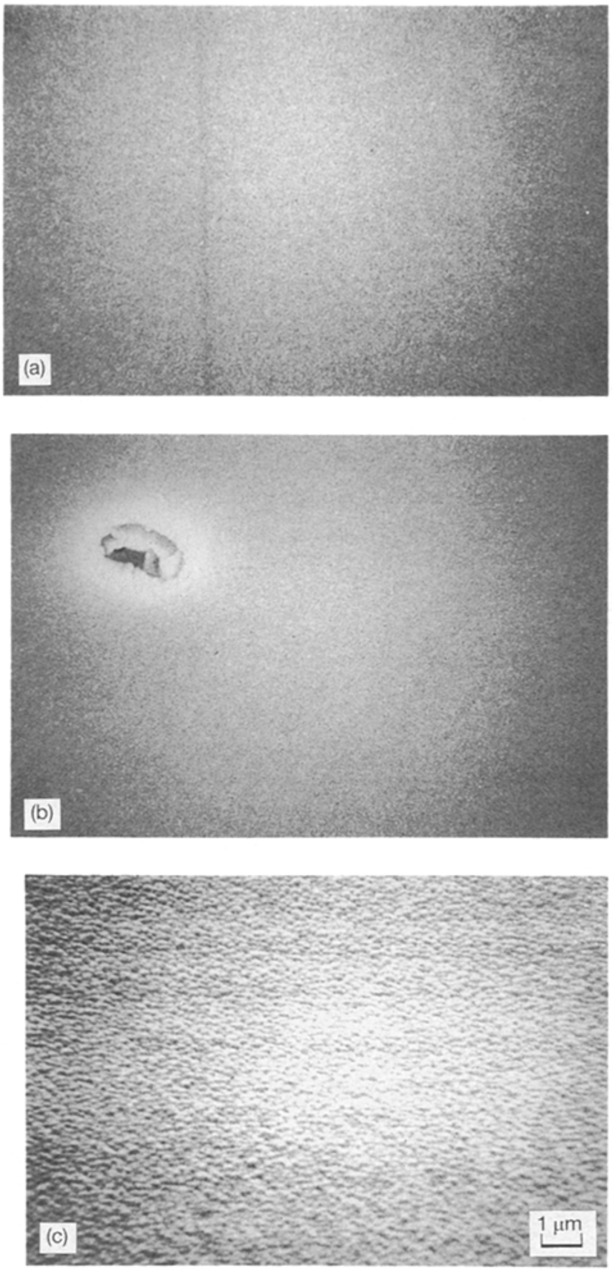


Figure 4 Effect of percentage change in argon pressure on the microstructure of $Bi_4Ti_3O_{12}$ thin films. (a) 10 mtorr, (b) 15 mtorr, (c) 20 mtorr.

the film due to the resputtering process. The effect of resputtering depends significantly on the deposition parameters. Results also indicate that many factors influence resputtering and that a model based on one factor, such as $I_A - EA_B$ value, cannot always predict the occurrence of resputtering.

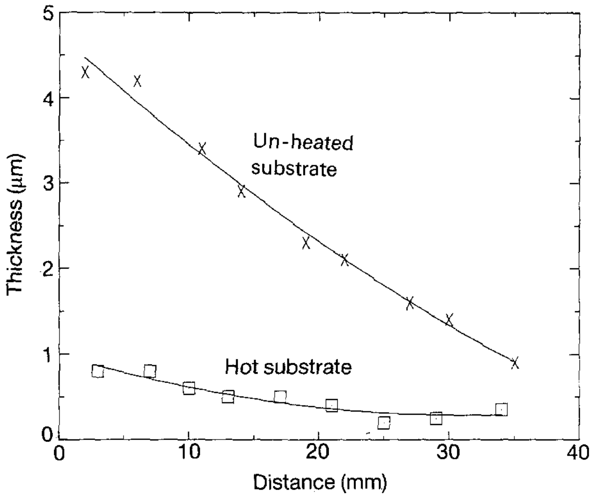


Figure 5 Thickness profile of $Bi_4Ti_3O_{12}$ thin films deposited on (X) unheated and (□) hot substrates. The thicker film is at the centre and the thinner film is near the edge.

Acknowledgement

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