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Variation in mechanical properties with substrate temperature of SbTi thin film deposited by RF sputtering technique

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ABSTRACT

Nanoindentation technique has been used to determine the mechanical properties of bismuth layered structure ferroelectric thin films, which have been shown to be promising for MEMS based devices used in sensing, actuation and energy harvesting, especially at elevated temperatures. SBTi (SrBi4Ti4O15) is a promising layered ferroelectric material and thin films of this composition are deposited on amorphous fused silica substrates by rf sputtering technique varying the substrate temperature from 600–725oC. The crystal structure and surface morphology of SBTi thin films are characterized by X-ray diffraction and atomic force microscopy. Depth- sensing nanoindentation system is used to measure the mechanical characteristics of SBTi thin films. Nanoindentation measurements reveal that the Young's modulus and hardness of SBTi thin films are related with grain size and crystal orientation which in turn depend on substrate temperature. The increase in mechanical properties with grain size is observed, indicating the reverse Hall-Petch effect. Furthermore, hardness and Young's modulus of the (119) oriented films were higher than those of (0010) oriented films. The tribological properties of these films are confirmed by performing the scratch tests on the same films. Copyright © 2014 VBRI press.

Keywords: RF sputtering; crystal orientation; mechanical properties; tribological properties.

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Introduction

In the recent years, bismuth layer-structured ferroelectrics (BLSF) have attracted much attention for their potential use in high-temperature piezoelectric devices because of their relatively high Curie point (Tc), ferroelectric random access memories, lead free composition and excellent fatigue endurance property **[1]**. Fatigue characteristics of PZT thin films in different crystallographic orientations were studied **[2]**. It is well known that piezoelectric coefficients depend on the mechanical coefficients which are related to the mechanical state of the materials **[2]**. Moreover, the mechanical behavior plays a crucial role in the delamination, cracking or fracture, and polarization fatigue of the multilayer thin film structures **[3-5]**. Consequently, the investigation on the mechanical properties of the bismuth layer-structured ferroelectric thin films is of practical importance in various situations and particularly for the design of piezoelectric devices. The importance of such films have now increased with their potential for application in MEMS devices where they can be used not only for sensing and actuation but also for energy harvesting even at elevated temperatures. These applications require a closer study of the mechanical properties of the deposited thin films like the extent to which these material properties depend on the substrate, crystallographic orientation, grain size, process conditions and the deposition route.

It has been suggested that ferroelectric thin films prepared by different methods usually have different textures or preferred crystal orientations which affects the ferroelectric and mechanical performances of the films. Some groups have examined the effect of grain size and crystal orientation on the mechanical properties of PZT thin films by nanoindentation procedure **[6-8]**. However, there is less focus on nanomechanical properties of Bi-layered ferroelectrics than on their ferroelectric and dielectric properties. It is quite important to understand the mechanical behavior of Bi-layered ferroelectric films, especially because they are related to the piezoelectric coefficients. SBTi is a well known piezoelectric **[9]**, the mechanical behavior of SBTi in thin film form open window for applications as actuators, sensors and transducers.

Experimental

Preparation

Initially, the sputtering chamber was evacuated to a base pressure of 4x10-6Torr after loading the cleaned substrates on to the substrate holder placed inside the vacuum chamber. All the films were deposited at a fixed power density of 3Wcm-2. A working pressure of 20 mTorr was constantly maintained using a mixture of high pure (99.9%) argon and oxygen. The target to substrate distance was fixed at 5cms. To vary the degree of crystallanity, the deposition temperature (Td) was varied from 600 – 725^{o}C. It was observed that without any heating, the un-cooled substrate temperature increased to about 120-130^{o}C during the deposition, presumably due to ion bombardment. The thicknesses of the thin films were around 500 ±10 nm. Prior to every deposition, the substrates were stabilized at the respective Td for an hour and rate of increase in temperature was about 10^{o}C/min. To measure the mechanical and nano tribological properties of the films, nanoindentation and nanoscratch tests were performed using a Berkovich diamond tip respectively.

Characterization

In this paper, crystalline structure, surface morphology and mechanical behavior of SBTi thin films prepared by RF magnetron sputtering method are evaluated using GI-XRD (Bruker D8 Discover with Cu Kα=1.5405Ao source), atomic force microscopy (Model SPA400 of SII Inc, Japan-AFM) and Hysitron Nanomechanical system (Tribo Indentor, 900 series, USA). The thicknesses of the films are measured using surface profilometer (Model XP-1, Ambios Technology, USA). Cadmium acetate [$Cd(CH_3COO)_2$], Sodium sulphide nanohydrate ($Na_2S.9H_2O$) procured from Aldrich Chemical Co. Ltd., and Manganese acetate [$Mn(CH_3COO)_2$] purchased from Fisher Scientific Co. Ltd., were used as starting materials in this study. Mn doped CdS powders were synthesized according to the reported method **[12]** in our laboratory. All solvents and reagents obtained from commercial source were of analytical reagent (AR) grade and used as received.

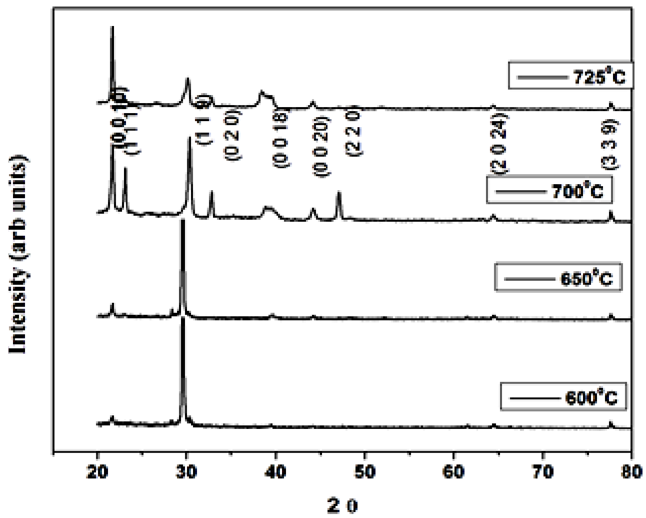

Fig. 1. XRD pattern of SBTi films.

Results and discussion

Structural properties

The X-ray diffractograms of the SBTi thin films deposited at different substrate temperatures on amorphous fused silica substrates were shown in **Fig. 1**. As evident from **Fig. 1** films deposited at higher substrate temperature were crystallized into an obvious pervoskite phase with a standard orthorhombic structure. As the substrate temperature increased, growth of grain orientation changed from (119) to (0010) orientation. In detail, films deposited at 600^{o}C shows polycrystalline nature prominent peak (119) orientation together with its 2-order (0010) and films deposited at 650oC shows same nature but intensity of the peak (119) increases along with (0010). Further increasing of substrate temperature i.e., at 700^{o}C the intensity of the (0010) peak is almost equal to the intensity of the (119) peak and films deposited at 725^{o}C shows the intensity of the (0010) peak dominated the intensity of the (119) peak. This shows that the substrate temperature plays a pivotal role in determining the orientational properties of the films. The lattice distortion as a function of substrate temperature is shown in **Table 1**. It was calculated as;

$$\delta = d - d_{hkl}/d_{hkl} \quad (1)$$

where d is the lattice spacing calculated from measured 2θ value of the XRD peak and dhkl is the ideal lattice spacing of the single crystal **[9]**.

Table 1. Lattice distortion values for films deposited from 600 to 725^{o}C.

Substrate temperature (ºC)	Lattice distortion
600	-0.027
650	-0.023
700	-0.002
725	0.008

Atomic force microscopy

The microstructures of the SBTi thin films as a function of substrate temperature were examined by atomic force microscope images. The surface morphology of the SBTi films deposited at different substrate temperature is show in **Fig. 2(a-d)**. The average grain size and roughness as a function of substrate temperature are shown in **Table 2**. It can be observed that the surface morphologies vary from with the substrate temperature. While deposited at 600^{o}C, the film has smooth and amorphous nature. Films deposited at 650 & 700^{o}C, the grains growth increases and roughness increases. This is due to the mobility of species adsorbed onto the substrate becomes higher and thus induces a higher speed of the coalescence of grain islands as the substrate temperature increases **[10]**. Further increase in temperature to 725^{o}C, the direction of the grain growth is in different orientation compared with other film orientation along with secondary growth. These results are supported to the XRD pattern of the films.

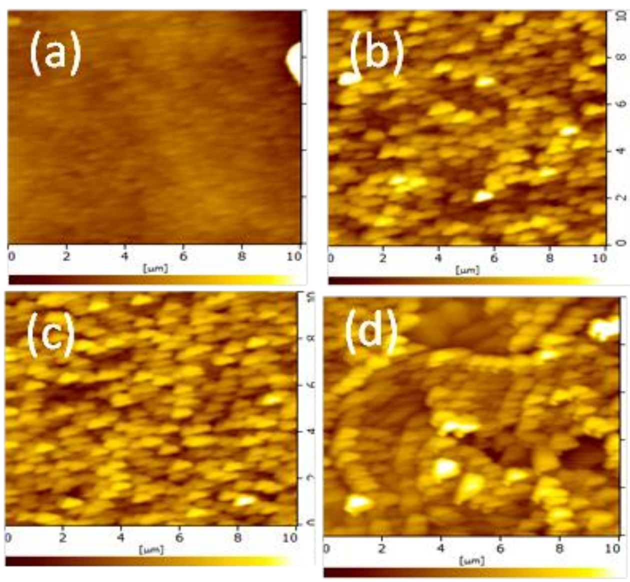

Fig. 2. AFM images of the SBTi films deposited at different temepratures (^{o}C) (a) 600, (b) 650, (c) 700, (d) 725.

Table 2. Average grain size and rms roughness of the SBTi thin films.

Sub. Temperature (^{o}C)	600	650	700	725
Ave. grain size (nm)	215	276	311	372
rms roughness (nm)	8.5	8.2	9.6	15

Mechanical properties

Nanomechanical properties, such as hardness and Young's modulus were obtained by nanoindentation (using a Triboscope from Hysitron Inc., USA). Load-controlled indentation testing followed a trapezoidal loading profile with a 10sec peak load hold time. The peak loads ranged from 10 to 2000 µN. Load-displacement curve is shown in **Fig. 3**. The presence of discontinuities in the load-displacement response reveals information about cracking, delamination, and plasticity in the film and substrate **[11]**. In present study, no discontinuity was observed in the load-displacement curve which indicates that both films were grown without cracks. Films were deposited at substrate temperature from 600-725^{o}C. The hardness and Young's modulus of the films are shown in **Fig. 4** & **5**. As the substrate temperature increased up to 700^{o}C, the Young's modulus (100-128GPa) and hardness (6.3-7.8GPa) is increased with respect to grain size. Further increase in substrate tetmperature (725^{o}C), the hardness and Young's modulus values are decreased. This shows that the deposition temperature plays a pivotal role in determining the mechanical properties of the films. This is due the porosity of the films by evaporating the Bi at high temperatures which generates the non-stoichometry of the films. It was clearly seen in hardness and Young's modulus graphs of the films deposited at 725^{o}C. As the contact depth increases, the hardness and Young's modulus value decreasing which indicated that these films are porous and less packing density results in decreasing mechanical properties though their grain size is more. On other hand, the orientation of the films deposited at 725^{o}C exhibited the (0010) direction which is different from the direction (119) of films deposited at 600-700^{o}C. From above results we can conclude that the mechanical properties are strongly depend on porosity and orientation of the films with respect to substrate temperature. The same trend was observed by **[12]**.

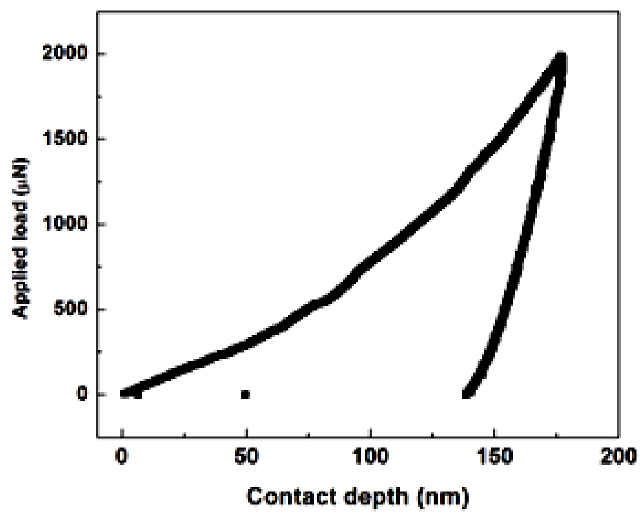

Fig. 3. L-D curve of SBTi thin films.

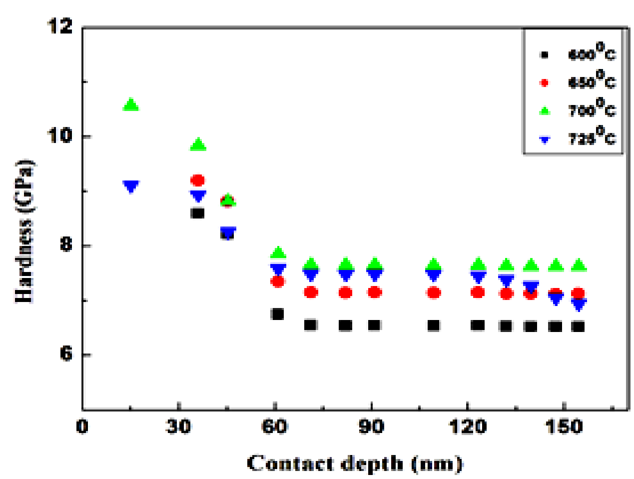

Fig. 4. Hardness as a function of contact depth.

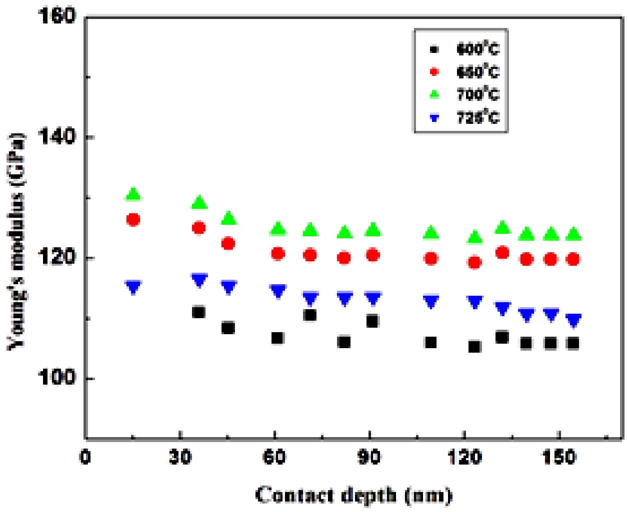

Fig. 5. Young's modulus of SBTi thin films.

The friction coefficient of the films deposited at 600-725°C are shown in **Fig. 6**. The values of the friction coefficient decreased as the deposited temperature increased up to 700°C. Films deposited at 725°C shows the high coefficient of friction which indicates that these films are having porosity.

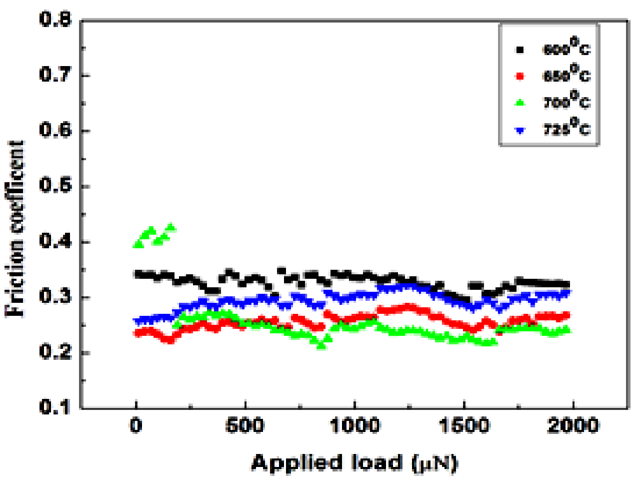

Fig. 6. Friction coefficient of SBTi films.

In order to have further proof for the above observations, scratch test for the same samples was carried out. Nanoscratch provides the capability to investigate modes of deformation and fracture that are not possible using standard indentation technique **[13]**. Nanoscratch is accomplished by applying a normal load in a controlled fashion while measuring the force required to move the tip laterally across the sample. The friction coefficient F is defined as –

$$F = PL/PN \qquad (2)$$

where PL denotes the lateral load and PN indicates the normal load. It is well known that the coefficient of friction is a material property. Coefficient of friction is almost constant as the contact depth increases for all the films. This indicates that the deposited film exhibits the uniform thickness and adhesion between the films and substrate is good throughout the film. As the substrate temperature increased to 700°C, the friction coefficient is decreased. Further increases in temperature, coefficient of friction increased due to less hardening of the films. It can be concluded that the films deposited at 700°C exhibited the less coefficient which means these films having higher hardness and Young's modulus. These results are in well support to the above hardness and Young's properties.

Conclusion

In summary, single phase SBT ($SrBi_4Ti_4O_{15}$) layered structure ferroelectric thin films were successfully deposited on amorphous substrates by varying the substrate temperature. XRD pattern revealed that all films are crystallized into orthorhombic structure and changes its orientation as the substrate temperature increases. The observed grain size and surface roughness is increased as the substrate temperature increased. As the substrate temperature increases, grain growth orientation changes from (119) to (0010) orientation which indicate that substrate temperature play an important role to obtain preferred orientation. It was observed that the mechanical properties were strongly depended on substrate temperature with respect to grain size and orientation. Nanoscratch test was confirmed the dependence of mechanical properties on substrate temperature.

Acknowledgements

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