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Research Article

Effect of Oxygen Mixing Percentage on Mechanical and Microwave Dielectric Properties of $SrBi_4Ti_4O_{15}$ Thin Films

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Aurivillus oxide thin films with nanostructures attained much interest due to their structural stability, outstanding ferroelectric, and dielectric properties. This manuscript reports the influence of oxygen mixing percentage (OMP) on structural, nanomechanical, and microwave dielectric properties of strontium bismuth titanate ($SrBi_4Ti_4O_{15}$) thin films. $SrBi_4Ti_4O_{15}$ films were successfully fabricated on fused silica substrates at room temperature, followed by annealed in a microwave furnace. The crystalline nature and purity of the phase was identified by X-ray diffraction. Nanomechanical properties of the $SrBi_4Ti_4O_{15}$ films were studied using nanoindentation and nanoscratch tests. The best nanomechanical (hardness ~6.9 GPa, Young's modulus ~120 GPa) properties were shown for films deposited around 50% of OMP. Microwave dielectric properties (dielectric constant and loss tangent at microwave frequencies 10 and 20 GHz) were extracted from the split postdielectric resonator technique.

1. Introduction

In recent years, the European Union has restricted the usage of lead (Pb) for the commercialization of devices due to environmental pollution and health problems from the toxicity of Pb. As a result, researchers have been paid great attention on layered Pb-free ferroelectric compounds due to their outstanding material properties like nontoxicity, high dielectric constant, and high fatigue endurance [1, 2]. These properties are very necessary and play a prominent role for device fabrications such as micro-electromechanical systems (MEMS), nonvolatile memory devices, and energy harvesting devices [3, 4]. However, finding of alternative materials to Pb is on high demand for applications like smart sensors, actuators, piezoelectric sensors, etc. In addition, Pb-free ferroelectrics are found to be good candidates for replacing Pb-based materials in order to reduce/overcome longstanding problems such as environmental pollution and health problems. Among the Pb-free ferroelectrics, $SrBi_4Ti_4O_{15}$ has been shown much interest due to the following material characteristics: (a) high Curie temperature, (b) fatigue-free, and (c) high spontaneous polarization along with its unique crystal structure [5, 6]. However, $SrBi_4Ti_4O_{15}$ does have certain limitations that have hindered its commercial development. Two significant limitations are its small remnant polarization and high processing temperature [7, 8]. These limitations have prompted researchers to explore effective methods with improved properties, such as chemical vapor deposition: sol–gel method and physical vapor deposition: laser deposition and sputtering. It has been reported that each method has its own advantages and disadvantages during material synthesis. Among them, radio frequency (RF) sputtering is a well-known fabrication technique

to deposit thin films while maintaining the parent stoichiometry of the material. In addition, in situ heating during the deposition is essential for reducing the processing temperature and enhances the crystalline quality of the films. With these advantages, RF sputtering has become a more recommendable technique to fabricate thin films for both industry and research purposes.

On the other hand, it was reported that $SrBi_4Ti_4O_{15}$ thin films were extensively studied, and various techniques have been employed to study their structural, morphological, dielectric properties at low frequency, ferroelectric, piezoelectric properties, etc. [9–11]. However, there are not many studies that specifically addressed the microwave dielectric characteristics. Studies on dielectric properties at microwave range will help us fabricate microwave devices like high overtone bulk acoustic resonators (HBAR). The potential uses of piezoelectric and dielectric thin films in microwave devices have pushed up research into the development of new materials, thin film production techniques, and optimization. It was known that the mechanical state of materials influences the piezoelectric coefficients [12, 13]. Therefore, obtaining superior mechanical and dielectric properties at microwave ranges is a difficult task. The combination of dielectric properties at the microwave range and good mechanical properties will create a new era of developments, especially in HBAR and microelectromechanical systems. For both current and future generations, there is a huge demand for materials with strong mechanical properties in the microwave frequency region for numerous device applications. Therefore, the present study focused on variation dielectric properties at microwave range and nanomechanical properties of $SrBi_4Ti_4O_{15}$ thin films while varying the oxygen mixing percentage (OMP) during the deposition. In addition, structural and morphological studies are investigated.

2. Materials and Methods

$SrBi_4Ti_4O_{15}$ thin films were fabricated on fused silica substrates by RF sputtering process. Highly densified lab-made $SrBi_4Ti_4O_{15}$ bulk ceramic having a purity of 95% was employed as a target for the deposition of the thin films. Substrates were cleaned thoroughly with ethanol in ultrasonication, followed by high-purity water before loading into the deposition chamber. In order to get rid of the adsorbed gas on the surface, the target was presputtered for about 10 min. Mass flow controllers were used to individually control the flow rates of the working gas, which was an Ar and O_2. The base pressure of the vacuum system was maintained at 2×10^{-5} mTorr for all depositions. The working pressure is set at 20 mTorr. The percentage of oxygen gas varied as 25%, 50%, 75%, and 100% from the base pressure. Power density was set at 4 W/cm^2, and substrate to target distance was 6 cm. As deposited, thin films were annealed in a microwave furnace at 550°C for this study.

The structural properties for the phase purity were characterized by X-ray diffraction (Bruker D-8 X-ray diffractometer, XRD). Surface morphology, such as grain growth, surface roughness, and grain size, was obtained from atomic force microscopy (AFM: SPA400 of SII Inc, Japan). Nanomechanical properties of $SrBi_4Ti_4O_{15}$ thin films were extracted from the load–displacement (L–D) curves at different loads using Triboscope nanoindenter (Hysitron Inc., USA). Using a measuring approach based on a split postdielectric resonator (SPDR), dielectric characteristics at the microwave region were measured [14].

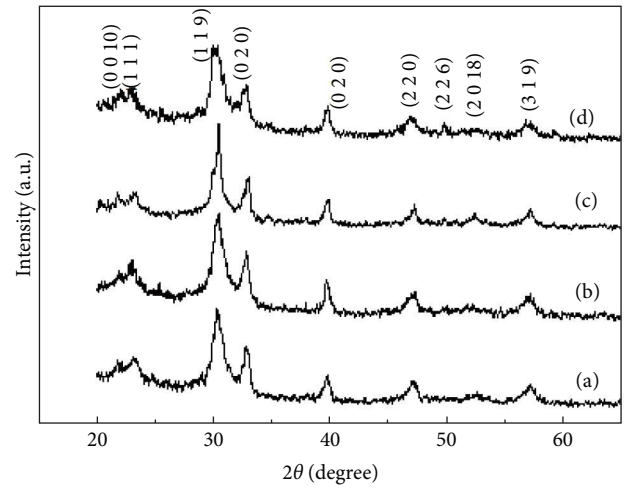

Figure 1: X-ray diffraction pattern of $SrBi_4Ti_4O_{15}$ thin films deposited at (a) 25%, (b) 50%, (c) 75%, and (d) 100% of OMP.

3. Results and Discussion

3.1. Structural Properties. Figure 1 displays the XRD patterns of $SrBi_4Ti_4O_{15}$ thin films that were formed at different OMPs and annealed in a microwave furnace at 550°C for around 20 min. From XRD patterns, it is clear that all the thin films are exhibited a polycrystalline nature with orthorhombic structure without any secondary phases and peaks in X-ray pattern resemble the typical JCPDS file (43-0973) and other reported literature [9, 15]. The peak broadening indicates that thin films are grown in a nanocrystalline nature due to variations of processing parameters. The average crystalline size of $SrBi_4Ti_4O_{15}$ thin films deposited at 25%, 50%, 75%, and 100% are found to be 28, 37, 25, and 20 nm, respectively. Films deposited at high OMP exhibited a more nanocrystalline nature due to the low rate of deposition. Overall, compared to other films, films that were deposited at 50% OMP showed a well-crystalline nature. XRD patterns revealed that the $SrBi_4Ti_4O_{15}$ thin films deposited at various OMPs have influenced the crystalline nature, and microwave annealing has reduced the crystalline temperature and time.

3.2. Morphological Studies. The surface morphology images of the $SrBi_4Ti_4O_{15}$ thin films deposited from 25% to 100% of OMP are shown in Figure 2(a)–2(d). These morphology images were captured from atomic force microscopy. From Figure 2, the grain growth and nanocrystalline nature of $SrBi_4Ti_4O_{15}$ thin films were supported with an XRD pattern. It was found that as the OMP varied from 25% to 100%, the grain size altered from 70 to 120 nm. The observed grain size of $SrBi_4Ti_4O_{15}$ thin films deposited at 75% and 100% OMP

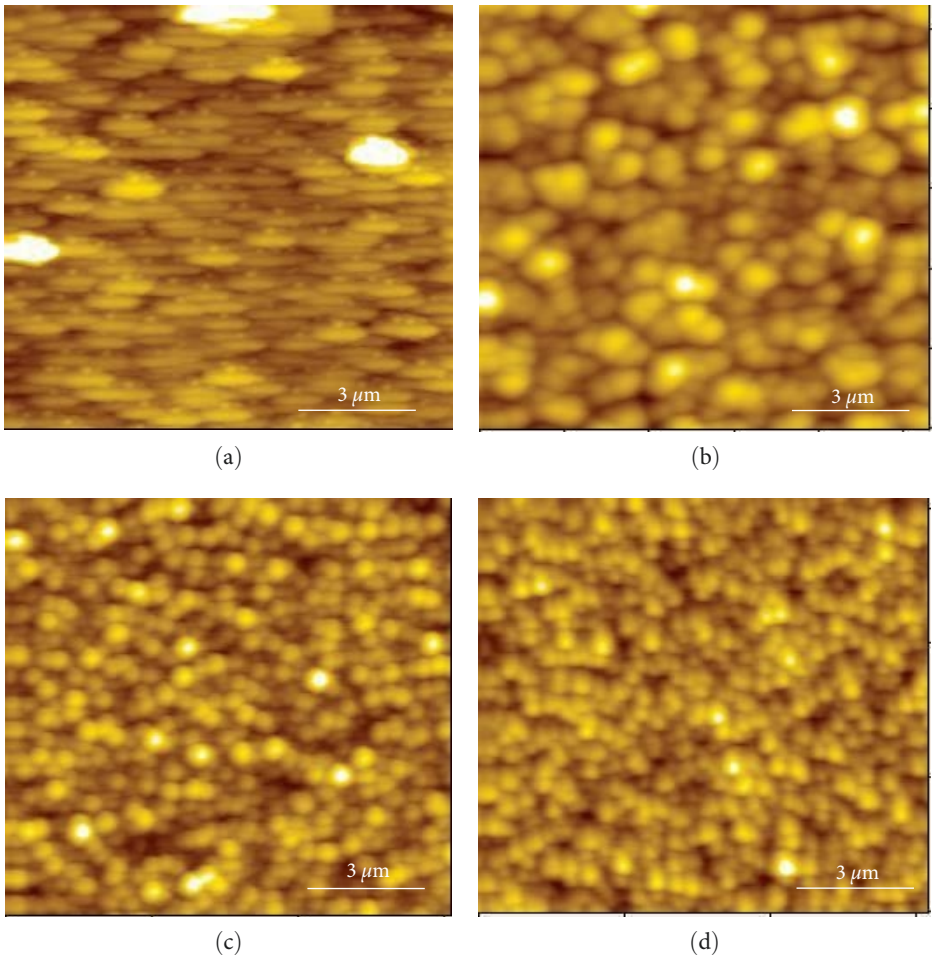

Figure 2: Surface morphology of $SrBi_4Ti_4O_{15}$ thin films of (a) 25%, (b) 50%, (c) 75%, and (d) 100% of OMP.

was less compared with films deposited at 25% and 50% OMP due to low rates of deposition, whereas oxygen species have less bombarding energy. The $SrBi_4Ti_4O_{15}$ films coated at 25%, 50%, 75%, and 100% of OMP have corresponding surface roughness values of 5.5, 6.1, 4.5, and 3 nm, respectively. During the thin film deposition, the adhesion of adatoms on the substrate surface, nucleation along the surface, and aggregation of adatoms to cause the origin of surface roughness. When the nucleation rate is slow, islands grow step by step, and as a result, the surface of thin film is smooth. Conversely, islands that form at a fast nucleation rate result in a thin film with a high surface roughness. Therefore, in order to suppress the surface roughness, the nucleation rate needs to be controlled during thin film deposition. Films deposited at lower OMP exhibit high roughness, and films deposited at higher OMP exhibit low roughness. Figure 2 shows that films that were deposited at 50% of the OMP showed well-defined grains that were consistent in size, very dense, and free of fractures. EDX analysis spectrum and elemental composition are presented in Figure 3 and Table 1, respectively.

3.3. Microwave Dielectric Properties of $SrBi_4Ti_4O_{15}$ Films. The OMP during deposition is shown to have the greatest impact

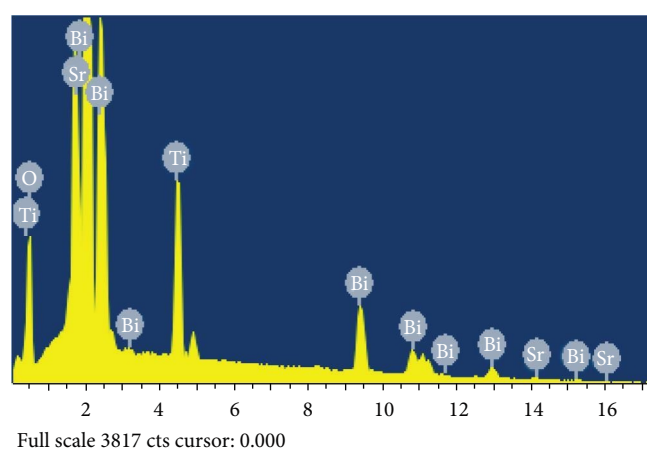

Figure 3: EDX spectrum of $SrBi_4Ti_4O_{15}$ thin films.

on the microwave dielectric characteristics of $SrBi_4Ti_4O_{15}$ thin films. The thin films are deposited at various OMPs varying from 25% to 100% in order to examine the influence of OMP. Using an SPDR approach, the microwave dielectric measurements of the permittivity and loss tangent of the deposited $SrBi_4Ti_4O_{15}$ thin films were performed at the

Table 1: Atomic percentage of each element of $SrBi_4Ti_4O_{15}$ thin films obtained from EDX analysis.

Element	Standard values (%)	Atomic % of $SrBi_4Ti_4O_{15}$ thin films
Ti K	16.66	16.34
Sr L	4.16	4.13
Bi M	16.66	16.46
O	62.49	62.31

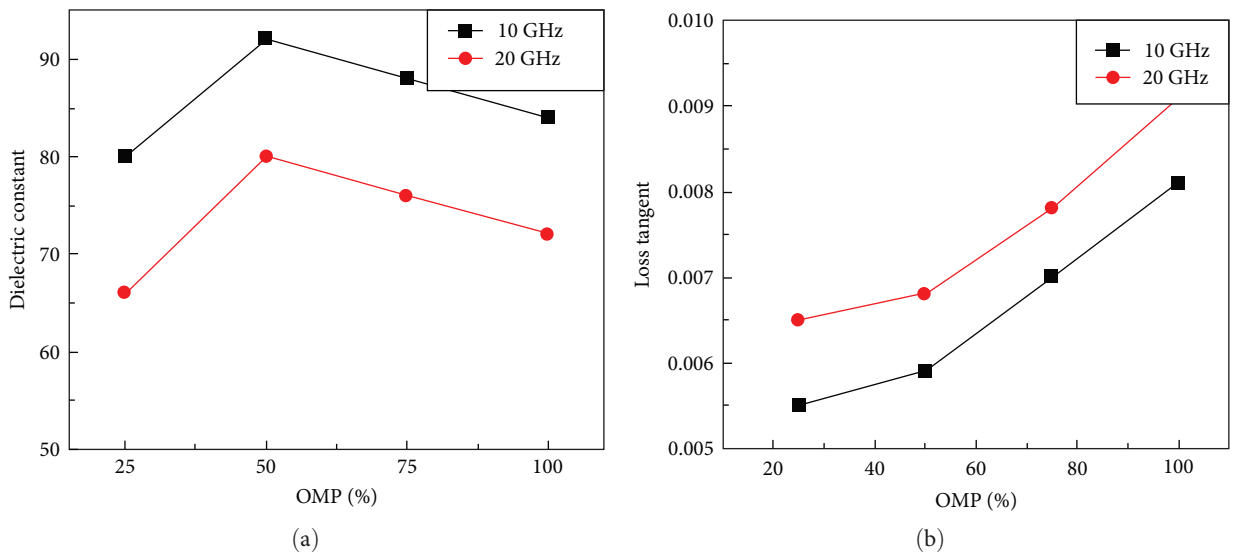

Figure 4: (a) Microwave dielectric constant and (b) loss tangent of the microwave annealed $SrBi_4Ti_4O_{15}$ thin films.

spot frequency of 10 and 20 GHz. This method is accurate and nondestructive for determining the dielectric properties of thin films at specific frequencies.

The dielectric properties at microwave frequency range as a function of OMP are shown in Figures 4(a) and 4(b). It has been found that the oxygen mixing fraction greatly influences the dielectric properties at the microwave range (dielectric constant and loss tangent (tanδ)). These results demonstrate that, in comparison to other films, the films deposited at 50% OMP had a high dielectric constant and low losses. Films deposited at higher OMP (75% and 100%) showed inferior dielectric properties due to a lack of well-defined crystalline nature, nonuniform grain growth, and small grain size. XRD and AFM analyses also support to microwave dielectric properties. Films measured at 10 GHz were found to exhibit high dielectric properties (dielectric constant ~92, loss tangent ~0.008) compared with films measured at 20 GHz. Due to the formation of oxygen vacancies, films formed at 25% OMP also showed lower dielectric properties than those deposited at 50% OMP. It is commonly known that when material porosity increases, the relative permittivity decreases. So, by minimizing the porosity, materials can produce good dielectric properties [16]. According to Wu et al. [12], dense microstructure improves dielectric characteristics. The films that were deposited at 50% of OMP would be suitable for MEMS and HBAR applications because they showed remarkable dielectric properties in the microwave range in addition to structural and microstructural properties.

3.4. Nanomechanical Properties of $SrBi_4Ti_4O_{15}$ Films. Nanomechanical properties of $SrBi_4Ti_4O_{15}$ thin films deposited at different OMPs were characterized using the nanoindentation technique. Since piezoelectric coefficients depend on mechanical coefficients, which are linked to the mechanical state of the materials, the mechanical properties of $SrBi_4Ti_4O_{15}$ thin films produced at various OMPs play a key role in the design of MEMS and HBAR devices. The penetration depth vs applied load was recorded using the L–D curves. The mechanical properties, such as hardness and Young's modulus, are extracted from L–D curves using Oliver and Pharr method. The L–D curves of $SrBi_4Ti_4O_{15}$ thin films deposited at different OMP are shown in Figure 5(a). For the present study, the applied load is ranged from 0 to 2,000 μN for the films. All L–D curves follow the same trend without any discontinuities, which indicates the films are lack of cracking and delamination [17–20]. The films deposited at 50% OMP exhibited the low indentation depth compared with other films, and films deposited at higher OMP showed less indentation depth due to the softness of the surface morphology. Additionally, films coated at 75% and 100% OMP showed discontinuity, indicating the presence of pores and an uneven microstructure in these films. Figures 5(b) and 5(c) show the values of the hardness and Young's modulus of $SrBi_4Ti_4O_{15}$ thin films, respectively. The hardness and Young's

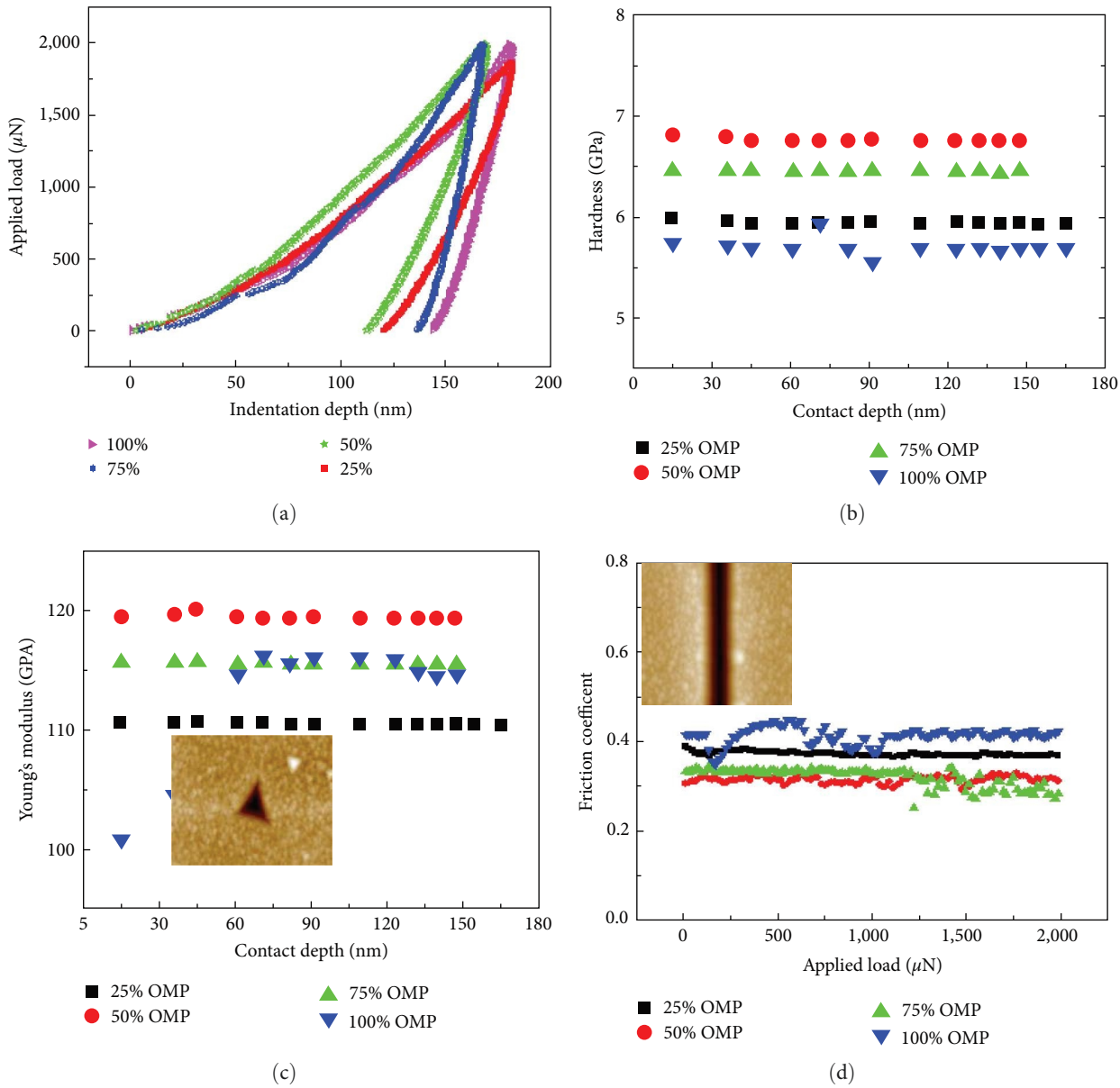

FIGURE 5: (a) L–D curves. (b) Hardness vs. contact depth. (c) Young's modulus vs. contact depth (inset: indentation image). (d) Friction coefficient vs. applied load (inset: scratch test image) of $SrBi_4Ti_4O_{15}$ films deposited at 25%–100% OMP.

modulus values were derived from an average of 40 indentations at different locations. Figures 5(b) and 5(c) show the hardness and Young's modulus of the films deposited at different OMP, films deposited at 50% OMP exhibited the best nanomechanical properties among other variants (Hardness: 6.9 GPa, Young's modulus: 120 GPa). Films deposited at 100% OMP showed inferior properties due to their microstructural nature and lack of preferred grain growth. The scanned image of the indentation test during the loading and unloading process has been shown in Figure 5(c) inset. In addition, a scratch test has been done for the same samples, and the results are shown in Figure 5(d). The scratch test is used to confirm the nature of adhesion between the substrate and thin films. The scratch test results demonstrate that the films deposited at 50% OMP have a highly adhesive nature compared with other components, since its friction coefficient value is less. Films deposited at 100% OMP exhibit a discontinuity nature. The results of the scratch test provided strong support for the indentation results. Overall, it can be concluded that the OMP is influencing the grain growth, grain size, and mechanical properties of $SrBi_4Ti_4O_{15}$ thin films.

4. Conclusions

$SrBi_4Ti_4O_{15}$ thin films with single phase and nanocrystalline nature were successfully obtained by controlling the OMP using the RF sputtering method. Films deposited at 50% of OMP revealed a well-defined surface morphology along with uniform grain size. The highest dielectric constant (~92) and low loss tangent (~0.008) was attained for films deposited at

50% OMP. The values of hardness (~6.9 GPa) and Young's modules (~120 GPa) are high among other films. Overall, the OMP has an influence on structural, microstructural, nanomechanical, and dielectric properties at microwave range. These sturdy properties are suitable for designing HBAR and MEMS-based devices.

Data Availability

Data will be available on request. For the data-related queries, kindly contact to Baseem Khan (baseem_khan04@yahoo.com).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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