Influence of oxygen gas pressure on phase, microstructure and electrical properties of sodium bismuth titanate thin films grown using pulsed laser deposition

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ABSTRACT
Na0.5Bi0.5TiO3 (NBT) thin films were grown with oxygen gas pressure in the range of 5 Pa and 100 Pa. NBT thin films grown at 30 Pa shows improved properties when compared to films grown at other pressures. This film exhibits single phase and good crystallinity. It has the highest dielectric constant of 754 and lowest dielectric loss of 0.21 at 1 kHz. It has the lowest leakage current of 2 × 10−6 A/cm² measured at 50 kV/cm electric field. The values of remnant polarization and coercive field, which were measured at room temperature, 10 V and 1 kHz, are 20 μC/cm² and 160 kV/cm respectively. Fatigue study reveals that remnant polarization (+Pr and −Pr) decreases by 15% after 10⁸ switching cycles.

1. Introduction
Currently, sodium bismuth titanate (Na0.5Bi0.5TiO3) also known as NBT has been attracting attention as a lead-free dielectric and ferroelectric material. It exhibits a higher Curie temperature (320 °C) which makes it suitable for dielectric and ferroelectric applications. Extensive investigations on bulk NBT have enabled thin film studies which lead to device applications. Various deposition techniques such as sol–gel process [1–6], r-f magnetron sputtering [7] and pulsed laser deposition [8,9] have been used to deposit NBT thin films. In our previous study, Taguchi method was used to optimize pulsed laser deposition (PLD) growth parameters in order to obtain single phase and high-quality NBT thin films [10]. Taguchi approach proved to be effective in terms of cost, time and effort. It significantly simplified the optimization procedure of PLD control parameters. However, it provided only the quantitative effect of the process parameter on the desired properties. Precisely for this reason, it was difficult to describe the effect of any single parameter on the quality of NBT thin films. The Taguchi analysis established that only two parameters namely substrate temperature, and oxygen pressure played a dominant role in deciding the quality of the thin films. In the current study, the effect of oxygen pressure on phase, microstructure and electrical properties of sodium bismuth titanate thin films grown using pulsed laser deposition technique has been investigated.

2. Experimental details
NBT thin films of thickness around 200 nm were deposited on Pt/TiO2/SiO2/Si substrate using optimized PLD control parameters. The optimized PLD control parameters include the distance between target and substrate (4 cm), substrate temperature (650 °C), laser pulse repetition rate (5 Hz), laser fluence (2 J/cm²) and pure NBT target. Oxygen gas pressure was varied in the range of 5 Pa and 100 Pa. A KrF pulsed laser with a wavelength of 248 nm (Lambda Physik Model CompexPro 102) was used for the growth process. Thereafter, top electrodes of Cr–gold having a 500 μm diameter were deposited on each sample by thermal evaporation method.

Solid state reaction process was used to prepare highly dense NBT target. Sodium carbonate (Na2CO3), bismuth oxide (Bi2O3), and titanium dioxide (TiO2) was used as starting materials. Homogenized powder was calcined in a furnace at 850 °C for 5 h. Thereafter, a pellet of 20 mm diameter and 3 mm thickness was prepared using the piston–mold process. It was sintered in a high-temperature furnace at the rate of 5 °C/min up to 500 °C. This temperature was maintained for an hour to remove the organic binder, followed by sintering at 1100 °C for 1 h.

The phase and crystal structure was examined using powder X-ray diffraction (XRD) method. Measurements were performed using a Philips XPert system. The X-ray source used for the measurement was
CuKα radiation (λ = 1.5405 Å) with a 0.02° step size and 60 second scan time per step. Surface morphology was studied using (JEOL JSM-7600F) field emission gun scanning electron microscopy (FEG-SEM). This system has a resolution of 1 nm and magnification range from 25 to 1,000,000×. It was operated at 10 kV. Surface topography was studied using atomic force microscopy (AFM) (Veeco nanoscope IV), which was operated in contact mode. Broadband dielectric spectrometer (Concept 80 system, Novo control GmbH, Germany) was used to measure dielectric constant and dielectric loss varying the frequency range between 1 kHz and 1 MHz. Hysteresis loop tracer (aixACCT System, GmbH) was used to study the ferroelectric properties and fatigue measurement of NBT thin films.

3. Results and Discussion

3.1. Structure and phase analysis

Fig. 1 exhibits the X-ray diffraction patterns for NBT thin films grown on Pt/TiO2/SiO2/Si substrate by varying pressure between 5 Pa and 100 Pa. It has been observed that, oxygen pressure plays an important role to stabilize the single phase of NBT. Peaks from impurity phases have been marked with an asterisk in the pattern. For the film grown at 5 Pa, the peak (117) has been observed at 30.16° which corresponds to Bi4Ti3O12 secondary phase (JCPDF No. 03-065-2527). It has higher intensity than the peak (110) of pure NBT phase. The intensity of peak (117) decreases while the intensity of peak (110) increases for the film grown at 10 Pa. Thin film grown at 30 Pa exhibits single phase and good crystallinity. Secondary phase Bi12TiO20 starts to appear with an increase in the oxygen pressure after 30 Pa. For the film grown at 100 Pa, the peak (220) seen at 24.76° and the peak (310) observed at 27.71° correspond to Bi12TiO20 secondary phase (JCPDF No. 00-034-0870) for Pt and JCPDS (01-072-1088) for Si. Highest intensity peaks of Si (211) is observed at 33.03°. Platinum peaks (111) and (200) have been marked with an asterisk in the pattern. For the films consist of the small fraction of secondary phases. X-ray diffraction pattern of Pt/TiO2/SiO2/Si substrate is indexed using JCPDS (01-087-0640) for Pt and JCPDS (01-072-1088) for Si. Highest intensity peak of Si (211) is observed at 33.03°. Platinum peaks (111) and (200) have been observed at around 39.89° and 46.39° respectively, which are merged with the peaks of NBT thin films as shown in Fig. 1. Other small intensity peaks observed in the XRD pattern are from TiO2 and SiO2.

Oxygen deficient BaTiO3 thin film was deposited at lower oxygen pressure by Zhao et al. [11]. The oxygen content in thin films was measured by Rutherford backscattering spectrometry. In the study, oxygen vacancies and interstitials oxygen ions were observed at lower and higher oxygen gas pressures respectively other than optimized pressure. In our study, similar defects might have caused charge fluctuations leading to fluctuation of composition of Na, Bi, and Ti in order to maintain balance. This leads to the appearance of secondary phases in NBT thin films deposited at lower and higher oxygen pressure other than 30 Pa oxygen gas pressure as shown in Fig. 1. The NBT thin films grown at lower oxygen gas pressure lose oxygen as a neutral atom leaving behind two electrons. The ionization of oxygen vacancies is represented using following defect equation.

\[ O_2^- + e^- \rightarrow O_2 \] (1)

\[ V_O^- + e^- \rightarrow V_O^0 \] (2)

\[ V_O^0 \rightarrow V_O^- + e^- \] (3)

These electrons seem to be bonded with Ti⁴⁺ in the form of

\[ Ti^{4+} + e^- \rightarrow Ti^{3+} \] (4)

Kröger–Vink notation has been used in above equations. \( V_O^- \) and \( V_O^0 \) represent the oxygen vacancies carrying one and two positive charges, respectively [12–14].

The formation of oxygen interstitials ions at higher oxygen gas pressure in the Bi₅Nb₂O₁₅ thin film grown using RF magnetron sputtering has been reported by Cho et al. [15]. It is represented using the following equation.

\[ \frac{1}{2} O_2^0 \rightarrow O_i^0 + 2 \ h \] (5)

where, \( O_i^0 \) and \( h \) represent the interstitial oxygen ions and hole respectively.

The relative volume percentage of the perovskite phase has been estimated from the intensity of the major X-ray diffraction peak of the secondary and perovskite phases. In our case, peak (117) of Bi4Ti3O12, peak (310) of Bi12TiO20 and peak (200) of NBT have been considered for this calculation. A commonly adopted method to study a relative change of volume fraction in the two phase systems of the perovskite phase is given by Eq. (6) [16,17].

\[ \text{Volume \% of perovskite} = \frac{I_{\text{perovskite}} (200)}{I_{\text{secondary (corresponding peak)}} + I_{\text{perovskite}} (200)} \times 100 \] (6)

It has been verified by Chen et al. [16] that this simplified formulation provides a realistic estimate for the relative change of volume fraction when compared to the values obtained from rigorous quantitative X-ray analysis methods. The volume percentage of the perovskite phase in the films grown under different oxygen pressures is calculated using Eq. (6). The variation of these values with increasing oxygen pressure has been shown in Fig. 2. It is noted that the volume percentage of the perovskite phase initially increased from 33% to 100% with an increase in the oxygen pressure from 5 to 30 Pa. Further, it decreased from 100% to 52% with an increase in the oxygen pressure from 30 to 100 Pa.
3.2. Microstructure analysis

Fig. 3 exhibits the FEG-SEM micrograph of NBT thin films grown on Pt/TiO2/SiO2/Si substrate at different oxygen gas pressures varying between 5 Pa and 100 Pa. Variation in the shape and size of the grains due to the difference in the oxygen pressure is in congruence with the reported literature. This is attributed to the interaction between the ablated ions or molecules with the oxygen [17–22]. The film grown at 30 Pa exhibits uniform and circular like grains observed at 105× magnification whereas other films show grains with disparate shapes and sizes. The film grown at 100 Pa exhibits hexagonal cylindrical and hexagonal spherical grains of size larger than 1 μm along with the small grains beneath it observed at 104× magnification. This is not observed in films grown at another pressure.

Fig. 4 shows the 2D AFM images of NBT thin films grown on Pt/TiO2/SiO2/Si substrate at different gas pressures varying between 5 Pa and 100 Pa. Films grown at pressure 5 Pa and 10 Pa exhibit root mean square (RMS) roughness of 3 nm and 4 nm respectively. It has an average grains size of around 80 nm. The film grown at 30 Pa has an RMS roughness of 4 nm. It exhibits a uniform circular like granular structure with an average grain size of about 100 nm. There is a significant increase in the roughness of the thin film grown at 100 Pa. This is due to the presence of the hexagonal cylindrical and hexagonal spherical grains of size larger than 1 μm, which are formed due to high oxygen pressure.

Fig. 5 exhibits a variation of the average grain size and RMS roughness with increasing pressure. It is observed that an increase in oxygen pressure leads to an increase in the average grains size and surface roughness of the films. Similar trend is observed for oxide thin films deposited using PLD, which has been reported by various authors [17–22]. It has also been reported that at high oxygen pressure, the energy of ablated species was lower because of scattering and multiple collisions between ablated and oxygen species. These species have been reported to nucleate on the surface due to the lower energy [17–23]. This leads to clustering and coalescing of small grains which results in the formation of hexagonal cylindrical and hexagonal spherical grains that have size between micron and sub-micron range. Similar to the reported studies, in this study, the above phenomenon seems to increase the surface roughness as well as the presence of particulates in the NBT thin films grown at high oxygen gas pressure.

3.3. Dielectric properties and leakage current

The electrical properties of the NBT thin films have been measured by metal–insulator–metal configuration, in which the thin films are sandwiched between bottom platinum and top Au/Cr electrodes. The variation in dielectric constant of NBT thin films grown at different pressure has been shown in Fig. 6(a). For the NBT thin films grown at 5 Pa, dielectric constant decreases steadily over the frequency range from 1 kHz to 1 MHz. NBT thin film grown at 10 Pa exhibits higher dielectric constant at 1 kHz compared to the film grown at 5 Pa. However, dielectric constant decreases significantly with an increase in the frequency range from 1 kHz to 1 MHz. The film grown at 30 Pa has the highest dielectric constant and negligible dielectric dispersion. This is attributed to a combination of single phase, good crystallinity and the better microstructure of NBT thin film. Significant decrease in the dielectric constant has been observed in the thin films grown above 30 Pa oxygen gas pressure. The film grown at 100 Pa exhibits lowest dielectric constant and dispersion in the frequency range from 1 kHz to 1 MHz. The variation in the dielectric loss of NBT thin films at different pressures varying between 5 Pa and 100 Pa have been shown in Fig. 6(b). Dielectric loss increases sharply with increasing frequency ranging from 1 kHz.
to 1 MHz for the NBT thin films grown at 5 and 10 Pa. The film grown at 30 Pa exhibits dielectric loss around 0.21 which is constant up to 10^5 Hz and increases at higher frequency. For the films grown at 50 and 100 Pa, dielectric losses are higher compared with the films grown for oxygen pressures at and lower than 30 Pa.

The variation of dielectric constant and dielectric loss of NBT thin films grown at different oxygen pressures measured at 1 kHz is shown in Fig. 7. The behaviour of dielectric constant and dielectric loss of NBT thin films is attributed to the appearance of secondary phases, surface morphology and roughness. The film approaches single phase with an increase in oxygen gas pressure up to 30 Pa and hence the dielectric constant increases. However, the dielectric constant decreases with further increase in the oxygen gas pressure above 30 Pa because of the appearance of secondary phases as shown in Fig. 1.

On the other hand, the dielectric loss increases sharply with an increase in the oxygen pressure up to 50 Pa, and remains almost stable with a further increase in pressure. This behaviour is attributed to the roughness of the thin films. The surface roughness is related to grain size that increases with an increase in pressure as shown in Fig. 5. The appearance of the defects at the interface of thin films grown at high oxygen pressure has been reported by Yao et al. [17]. The authors have stated that these defects can collect space charges at the interface of the thin films and led to formation of low resistance layer which were responsible for deteriorating the dielectric properties.

The plot of leakage current density with variation in the electric field for the NBT thin films grown at different oxygen gas pressures is shown in Fig. 8. The film grown at 5 Pa has higher leakage current density which is around 2 × 10^{-3} A/cm^2 at 50 kV/cm. However, it decreases to 2 × 10^{-6} A/cm^2 for the film grown at 30 Pa. This implies that a large
number of oxygen vacancies are present in the NBT thin films grown at lower oxygen gas pressure (below 30 Pa) which generate free electrons as discussed above using the defect Eqs. (1) to (4). These charge carriers are responsible for high leakage current in NBT thin films. Hence it is derived that increase in oxygen gas pressure (up to 30 Pa) improves electrical properties of the NBT films. However, it is noticed that the leakage current density increases with further increase in the pressure above 30 Pa. It is observed that the oxygen interstitial ions start to form in the films when the oxygen pressure increases above 30 Pa as discussed above using defect Eq. (5). The degradation of the electrical properties of the NBT thin films grown at higher pressure than 30 Pa is explained by the formation of oxygen interstitial ions. This ultimately results in the formation of secondary phases as shown in the XRD pattern. The increase in the leakage current density in the (Na$_{0.5}$K$_{0.5}$)NbO$_3$ thin films annealed at higher oxygen partial pressure due to oxygen interstitial ions has been reported by Kim et al. [24]. The presence of oxygen interstitial ions in the thin films annealed at higher oxygen partial pressure was confirmed by performing the Hall measurement.

3.4. Ferroelectric properties and fatigue measurement

NBT thin film grown at 30 Pa oxygen gas pressure has been considered further to study ferroelectric properties. Fig. 9 exhibits the electric polarization versus electric field response for Au/NBT/Pt capacitor measured at room temperature at 10 V and 1 kHz. The values of remnant polarization ($P_r$) and coercive field ($E_C$) are 20 μC/cm$^2$ and 160 kV/cm respectively. Fig. 10 exhibits the fatigue data measured for a film. Polarization has been measured up to $10^8$ switching cycles by applying 10 V. At 10 switching cycles; remnant polarization ($P_r$) is 20 μC/cm$^2$. After increasing switching cycles up to $10^8$, remnant polarization ($P_r$) decreases to 17 μC/cm$^2$. It means that, remnant polarization ($+P_r$ and $-P_r$) decreases by 15% after $10^8$ switching cycles.

4. Conclusions

NBT thin films have been grown on Pt/TiO$_2$/SiO$_2$/Si substrate using optimized PLD control parameters with varying the oxygen gas pressure from 5 to 100 Pa. It is observed that the oxygen pressure has a significant impact on their structural, microstructural and electrical properties. The formation of oxygen vacancies and interstitials oxygen ions arises at lower, and higher oxygen gas pressures respectively other than optimized pressure. Therefore, there is a fluctuation in the composition of Na, Bi, and Ti to maintain the charge balance. As a result, there is an
appearance of secondary phases in NBT thin films. NBT thin film grown at 30 Pa exhibits a single phase pseudo cubic perovskite structure. The microstructure study reveals that the grains size and roughness increase with an increase in the oxygen pressure due to increasing in the collisions between the ablated species and the oxygen species. The film grown at 30 Pa has grains of circular shape, average size of around 100 nm and roughness around 4 nm. Dielectric constant and loss of NBT thin film grown at 30 Pa is 754 and 0.21 at 1 kHz respectively, and leakage current is significantly less. The dielectric constant of (Na0.5Bi0.5)TiO3 thin films optimized using the Taguchi approach, Ceram. Int. 40 (2014) 2441.

In conclusion, optimum oxygen pressure is required to deposit high-quality NBT thin films. Any other pressure during deposition limits the performance of the film significantly.

Acknowledgements

This work is supported by a generous research grant from Directorate of Extramural Research & Intellectual Property Rights, Defence Research and Development Organisation, New Delhi. Authors wish to thank Industrial Research and Consultancy Centre (IRCC) and Sophisticated Analytical Instrument Facility (SAIF) facility available at IIT Bombay.

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