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# Effect of oxygen pressure on preferential orientation, microstructure and functional properties of $Bi_{1.5}MgNb_{1.5}O_7$ thin films prepared by pulsed laser deposition

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ABSTRACT

Polycrystalline bismuth magnesium niobate ($Bi_{1.5}MgNb_{1.5}O_7$, BMN) thin films have been prepared by pulsed laser deposition at oxygen pressures in the range of 1–30 Pa. The degree of preferred orientation initially decreases and then increases as oxygen pressure is increased, as evidenced by X-ray diffraction measurements, revealing that a process of abnormal grain growth has occurred. The microstructures and dielectric properties of the BMN thin films are strongly dependent on the degree of preferred orientation which is influenced by oxygen pressure. The BMN thin films deposited at oxygen pressure of 10 Pa have the minimum degree of preferred orientation, while the thin films exhibit the highest dielectric tunability, the biggest dielectric constant and the lowest loss tangent. In addition, the frequency dependence of dielectric constant and loss tangent of BMN thin films deposited at different oxygen pressure is investigated as well.


## 1. Introduction

Over the past decade, dielectric thin films with electric field tunable dielectric constant have attracted much attention for applications in the electrically tunable devices in advanced radar and communication systems [1–3]. In such applications, it is desirable to possess a low dielectric loss and a large dielectric constant change ratio (tunability = $(\varepsilon_{max} - \varepsilon_{min})/\varepsilon_{max}$) by applying a relatively low electric field [4,5]. $Ba_{1-x}Sr_xTiO_3$ (BST) has attractive much attention as a promising candidate because of its unique combination of high dielectric constant and large tunability [6–9]. However, BST thin films have the essential problem of high dielectric loss [10,11]. Therefore, further explorations on alternative materials aims at those possessing high dielectric tunability associated with low dielectric loss.

The bismuth magnesium niobate ($Bi_{1.5}MgNb_{1.5}O_7$, BMN) thin films have been demonstrated to have medium dielectric constant (~100) and low loss (~0.005). In addition, the tunability as high as 39% has been observed for BMN thin films at room temperature [12]. These excellent dielectric properties make BMN an attractive material for tunable device applications. BMN thin films have been successfully prepared by sol–gel process, rf magnetron sputtering and pulsed laser deposition (PLD) methods [13–15]. Compared with other deposition methods, the PLD technique can provide excellent control of the stoichiometric composition of oxide thin films with many components, which is especially necessary for BMN thin films due to the high volatility of Bi [16,17]. Generally, the microstructure of the thin films is influenced by the growth temperature but is also affected by the oxygen pressure during the deposition, even when the thin films are grown at the same temperature. Furthermore, a deeper understanding and control of the structural ordering and morphology of these thin films is required for further improvements. In particular, it has been stated that the dielectric properties of BMN thin films drastically depend on their preferential orientation (i.e. texture) [14]. The thin film texture strongly influences the dielectric constant, which can affect the tunability. However, there is a lack of investigations addressing the role of texture's impact on microstructure and of detailed understanding of the role of preferential orientation in affecting the dielectric properties of the thin films. In this paper, we prepared cubic pyrochlore $Bi_{1.5}MgNb_{1.5}O_7$ thin films on Au-coated Si substrates by PLD. The dependence of the texture of BMN thin films prepared at different oxygen pressure is experimentally investigated by X-ray diffraction (XRD) measurements with the determination of the texture coefficients and degree of preferred orientation deduced from the Harris method [18]. The oxygen pressure (preferential orientation)

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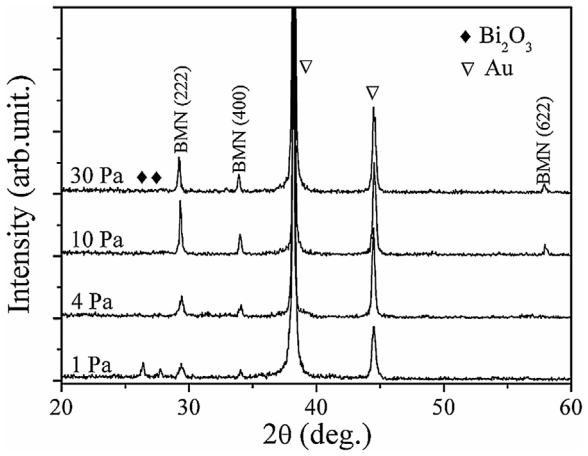


**Fig. 1.** The XRD patterns of the BMN thin films deposited on Au/Ti/$SiO_2$/Si(1 0 0) substrates at various oxygen pressures.

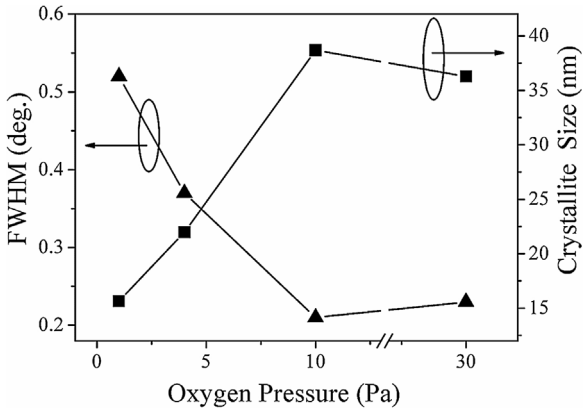


**Fig. 2.** Crystallite size and FWHM values of (2 2 2) diffraction peaks of BMN thin films deposited at various oxygen pressures.

dependent dielectric properties of the prepared $Bi_{1.5}MgNb_{1.5}O_7$ thin films are systematically investigated as well.

## 2. Experimental

The $Bi_{1.5}MgNb_{1.5}O_7$ (BMN) thin films were deposited on Au/Ti/$SiO_2$/Si(100) substrates by a PLD method. The BMN ceramic target was prepared by solid state reaction process with $Bi_2O_3$, MgO, and $Nb_2O_5$ as starting materials. To compensate the Bi loss during sintering, 10 at.% excess $Bi_2O_3$ was added. The weighted starting materials were mixed in an agate mortar for 4 h, pressed into 50 mm diameter and 4 mm thickness pellet at 20 tone, then the pellet was buried in the mother powder of BMN and sintered at 1150 °C for 4 h in air. The Au/Ti/$SiO_2$/Si(100) substrates were cleaned in an ultrasonic bath with alcohol for 30 min. Sintered BMN pellet were used as a target for laser ablation by pulse laser deposition using a KrF excimer laser with a wavelength of 248 nm, a pulse width of 30 ns and a repetition rate of 5 Hz. The substrates are fixed at an on-axis distance of 5 cm from the target and the deposition is done. The laser radiation is impinged on the target at 45° with respect to normal in a dynamic flow of oxygen. The substrate temperature was 700 °C. Before irradiations, the deposition chamber is evacuated down to a base pressure of $3 \times 10^{-4}$ Pa. The BMN thin films are deposited at different oxygen pressure viz. 1, 4, 10, and 30 Pa and the deposition rates were 15, 12, 11 and 8 nm/min, respectively. After deposition, the thin films deposited at higher temperatures are cooled to room temperature at the same oxygen pressure. The thin films have a typical thickness of about 300 nm obtained from the step height measurement instrument.

The crystallinity was determined by X-ray diffraction using a (Rigaku D/MAX–RB, Akishima, Tokyo, Japan) system equipped with a Cu–Kα radiation source (1.542 Å). The morphologies were investigated by field emission scanning electron microscopy (SEM) (FESEM; Hitachi, S-4800, Japan). The thickness was measured by Alpha-Step D-100 profilometer (KLA-Tencor, CA, USA). For electrical measurement, Au top electrodes with 0.2 mm in diameter were patterned by lift-off process to form the metal–insulator–metal type capacitors. The dielectric properties and tunability were measured at room temperature by LCR analyzer (TH2828S, Tonghui Electronics, Shenzhen, China) and precision LCR meter (Aglient 4285A, Santa Clara, CA, USA).

## 3. Results and discussions

Fig. 1 shows the XRD patterns of the BMN thin films deposited on Au/Ti/$SiO_2$/Si(100) substrates at various oxygen pressures. It can be seen that all the BMN thin films are crystallized and exhibit a cubic pyrochlore structure. However, the phases of $Bi_2O_3$ can be detected in the XRD patterns the second phase can be detected for the thin films deposited at oxygen pressure of 1 Pa. For BMN thin films deposited at low oxygen pressure (<4 Pa) the volatile Bi element reacts with oxygen to form $Bi_2O_3$. Consequently, a secondary phase of $Bi_2O_3$ can be detected in the XRD patterns for the thin films deposited at oxygen pressure of 1 Pa. For BMN thin films deposited at high oxygen pressure (≥4 Pa), the high oxygen pressure could inhibit evaporation of Bi element during the deposition process. Therefore, the formation of single-phase BMN is observed. As shown in Fig. 1, it also suggests that the oxygen pressure play an important role on the crystallization of the BMN thin films. In $Bi_{1.5}Mg_{1.0}Nb_{1.5}O_7$ cubic pyrochlore, the strongest peak is the reflection of the (2 2 2) plane and the second strongest peak is the reflection of the (4 0 0) plane. With the increase of the oxygen pressure, the reflection intensity of the (2 2 2) peak initially increases, reaches a maximum at 10 Pa, and then decreases with further increasing oxygen pressure to 30 Pa. For BMN thin films deposited at low oxygen pressure, there exist secondary phases and lots of oxygen vacancies, thus resulting in the fact that the BMN thin films have poor crystalline quality. However, the observed decrease in the diffraction peak intensity at higher value of oxygen pressure could be due to the reduction of plume size. This leads to reduction of the adhesion coefficient for the source element that arrives at the substrate and formation of defects in thin films [19]. The BMN thin films would not be well crystallized, thereby degrading the crystal quality of film as the oxygen pressure increases beyond an optimal pressure. In addition, the adatoms have a smaller diffusion path length at higher oxygen pressure, thus this reduction in surface adatom mobility can also lead to poor crystallinity [20,21]. Here, in our experiment, the 10 Pa is the critical oxygen pressure.

Fig. 2 displays the full width at half maximum (FWHM) values of (2 2 2) diffraction peaks of BMN thin films grown at various oxygen pressures. The value of FWHM for the BMN thin films decreases gradually and reaches its' minimum at the oxygen pressure of 10 Pa. When the oxygen pressure is higher than 10 Pa, the FWHM value begins to increase. It is well known that the FWHM values are related with the crystallization of the thin films [22]. The FWHM values in Fig. 2 indicate that the BMN thin films at the oxygen pressure of 10 Pa have better crystallization. This consists well with the above XRD analysis results.

In order to attain the detailed structure information, we calculated the crystallite size from the (2 2 2) orientation according to the Scherrer's formula [23,24].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$