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Short communication

Low temperature crystallized voltage tunable $Bi_{1.5}Cu_xMg_{1-x}Nb_{1.5}O_7$ thin films capable of integration with Au electrode

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Abstract

$Bi_{1.5}Cu_xMg_{1-x}Nb_{1.5}O_7$ ($x = 0$–0.1) (BCMN) thin films have been fabricated on Au/Ti/SiO_2/Si(1 0 0) substrates using a chemical solution spin coating process. Crystallization temperature is reduced and dielectric properties are improved when moderate Mg^{2+} is substituted by Cu^{2+} in $Bi_{1.5}MgNb_{1.5}O_7$ thin films. Optimized dielectric properties are obtained in $Bi_{1.5}Cu_{0.075}Mg_{0.925}Nb_{1.5}O_7$ thin films crystallized at a low temperature of 500 °C: dielectric constant $\varepsilon_r = 173$, dielectric loss tan $\delta = 0.0045$ at zero bias field and tunability $\eta = 39\%$, figure of merit FOM = 86.7 under an applied electric field of ~1 MV/cm. The combination of low fabrication temperature and favorable dielectric properties of BCMN thin films makes the integration with Au bottom electrode possible.

Keywords: Dielectrics; Thin films; Spin coating; Bi-based pyrochlore

1. Introduction

Dielectric thin films with voltage tunable dielectric constant have attracted much attention for applications in the electrically tunable microwave devices in advanced radar and communication systems. Ferroelectric $Ba_xSr_{1-x}TiO_3$ thin films have been widely investigated for its large tunability [1,2]. However, high dielectric loss and intrinsic hysteresis in the microwave region strongly inhibit their industrial applications [2]. The bismuth based cubic pyrochlore $Bi_{1.5}ZnNb_{1.5}O_7$ (BZN) and $Bi_{1.5}MgNb_{1.5}O_7$ (BMN) thin films have been attracting much attention as promising alternative tunable materials for their low dielectric loss and adequate tunability in the microwave region [3–11]. In most studies Pt bottom electrodes were used because of their chemical stability and ability to withstand the high-temperatures and oxidizing conditions during the fabrication process. One apparent drawback of Pt bottom electrodes is that the relatively high resistivity of Pt (~9.7 μΩ cm) will decrease Q value of the device in microwave region due to the conductor losses [12]. Concerning low resistivity and chemical stability, Au is an ideal candidate metal for electrode. Au has a lower resistivity (~2 μΩ cm) than Pt and is chemically stable even in oxidizing atmospheres. However, it is difficult to integrate BZN or BMN thin films with Au bottom electrode because the low melting temperature of Au (1064 °C) limits the high temperature processing. It was reported that Au thin films agglomerated and showed island-like structures after annealing at 600 °C [13]. According to this conclusion, the highest annealing temperature should be lower than 600 °C. However, in most studies annealing temperatures of BZN and BMN thin films are 600–750 °C [3,4,10,12]. So, reducing the processing temperature of BMN and BZN thin films or searching new low temperature crystallized thin films is of importance for improving the performance of devices.

$Bi_{1.5}CuNb_{1.5}O_7$ (BCN), similar to BMN in structure, is another Bi-based cubic pyrochlore compound [14]. And it is well known that Cu compounds often possess low melting point and low crystallization temperatures [15]. We therefore suggest that crystallization temperatures of BMN thin films might be reduced by substituting Cu^{2+} for Mg^{2+}. In this letter, we report the fabrication and dielectric properties of Cu partially substituted BMN thin films prepared on Au/Ti/SiO_2/Si(1 0 0) substrates using chemical solution deposition (CSD) process. Our results show that low loss and high tunability can be achieved in $Bi_{1.5}Cu_xMg_{1-x}Nb_{1.5}O_7$ (BCMN) thin films crystallized at 500 °C.

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2. Experimental procedure

For preparation of the BCMN precursor solution, high purity $Bi(NO_3)_3{\cdot}5H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$ and Nb_2O_5 were used as starting materials. Firstly, Nb_2O_5 was dissolved in hydrofluoric acid at 80 °C, and then ammonia water was added into the above solutions to form precipitates of niobic acid ($Nb(OH)_5$). The precipitates, $Nb(OH)_5$, were filtered off and washed with distilled water to remove H^+ and F^+ ions. The $Nb(OH)_5$ precipitates were dissolved in citric acid solution under stirring at 80 °C. Subsequently, stoichiometric amounts of $Mg(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$ and $Bi(NO_3)_3{\cdot}5H_2O$ were added to the niobium citrate solution under stirring. Finally, ethylene glycol was added to this solution to promote polymerization. The concentration of BCMN in the final solution was adjusted to approximate 0.12 mol/L. BCMN thin films were spin-coated onto Au/Ti/SiO_2/Si(1 0 0) substrates with the prepared solution at 3500 rpm for 30 s. The as-deposited films were heated at 500 °C for 1 min in O_2 atmosphere to remove the organics. The coating-heating procedure was repeated until the desired thickness was reached. Finally, the films were annealed at 500 °C for 30 min.

The thickness of the films was about 400 nm which was evaluated by a stylus profiler (Model D-100, KLA-Tencor Co., USA). The crystalline phase of BCMN thin films was characterized by X-ray diffraction (XRD, Model D/MAX-B, Rigaku Co., Japan) with Cu Kα radiation (40 kV, 150 mA). Surface morphology of the films was observed by an atom force microscope (AFM, Model easyScan 2, Nanosurf AG Co., Switzerland). For electrical measurements, Au top electrodes with a diameter of 0.2 mm were deposited by dc sputtering. After electrode deposition the films were heated at 450 °C for 20 s under N_2 flow to improve adhesion between the metal and films. The dielectric properties were measured using an Agilent HP 4285A precision LCR meter with 500 mV test oscillation voltage. The maximum dc bias field for 400 nm thick films was about 1 MV/cm.

3. Results and discussions

The X-ray diffraction spectra of the BCMN ($x = 0$, 0.025, 0.05, 0.075, 0.1) thin films annealed at 500 °C are shown in Fig. 1(a). No obvious diffraction peaks were detected in the unsubstituted BMN sample, which indicated that 500 °C was not sufficient to crystallize the amorphous BMN film. However, diffraction peaks related to cubic pyrochlore structure emerged in Cu^{2+} substituted BCMN thin films, which indicated that Cu^{2+} partially substituting for Mg^{2+} reduced the crystallization temperature of BMN thin films. Diffraction peaks intensities increased with increasing Cu^{2+} substitution content. BCMN thin films with $x = 0.05$–0.1 were fully crystallized after annealing at 500 °C for 30 min. There was no obvious shift of diffraction peaks when Mg^{2+} was partially substituted by Cu^{2+} as illustrated in Fig. 1(a), which indicated that the replacement of Mg^{2+} by Cu^{2+} leaded to no changes in the volume of unit cell of cubic pyrochlore structure. The reason might be the radius of

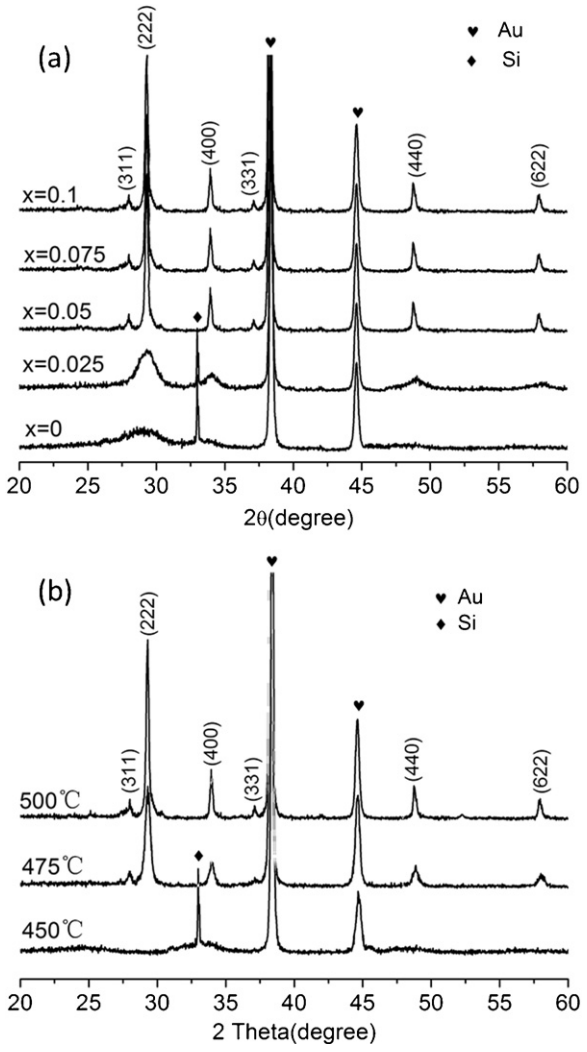

Fig. 1. XRD patterns of $Bi_{1.5}Cu_xMg_{1-x}Nb_{1.5}O_7$ thin films with different x annealed at 500 °C (a) and $Bi_{1.5}Cu_{0.075}Mg_{0.925}Nb_{1.5}O_7$ thin films annealed at various temperatures (b).

Mg^{2+} (0.72 Å) is similar to that of Cu^{2+} (0.73 Å) [16]. XRD data for $x = 0.075$ samples annealed at 450 °C, 475 °C and 500 °C were collected to study the influence of annealing temperature on the phase evolution (Fig. 1(b)). There is no evidence for crystallization in the films annealed at 450 °C. When the annealing temperature increased to 475 °C and 500 °C, cubic pyrochlore phase formed. Intensity of diffraction peaks increased with increasing annealing temperatures. No intermediate phase or additional phase was detected during the crystallization process.

The surface morphology evolution of the thin films annealed at 500 °C with different Cu substitutions is shown in Fig. 2. For BCMN thin films with $x = 0$ and 0.025, few crystallites formed after the annealing at 500 °C, which was consistent with the dominant amorphous phase shown by XRD results in Fig. 1(a). BCMN thin films with $x = 0.05$ and 0.075 show dense surface and round crystallites with average size of ∼80 nm and ∼127 nm respectively. Abnormal grain growth emerged and the shape of grain tuned to be trilateral in the $x = 0.1$ sample. Correlated with the grain growth, the root-mean-square (RMS)

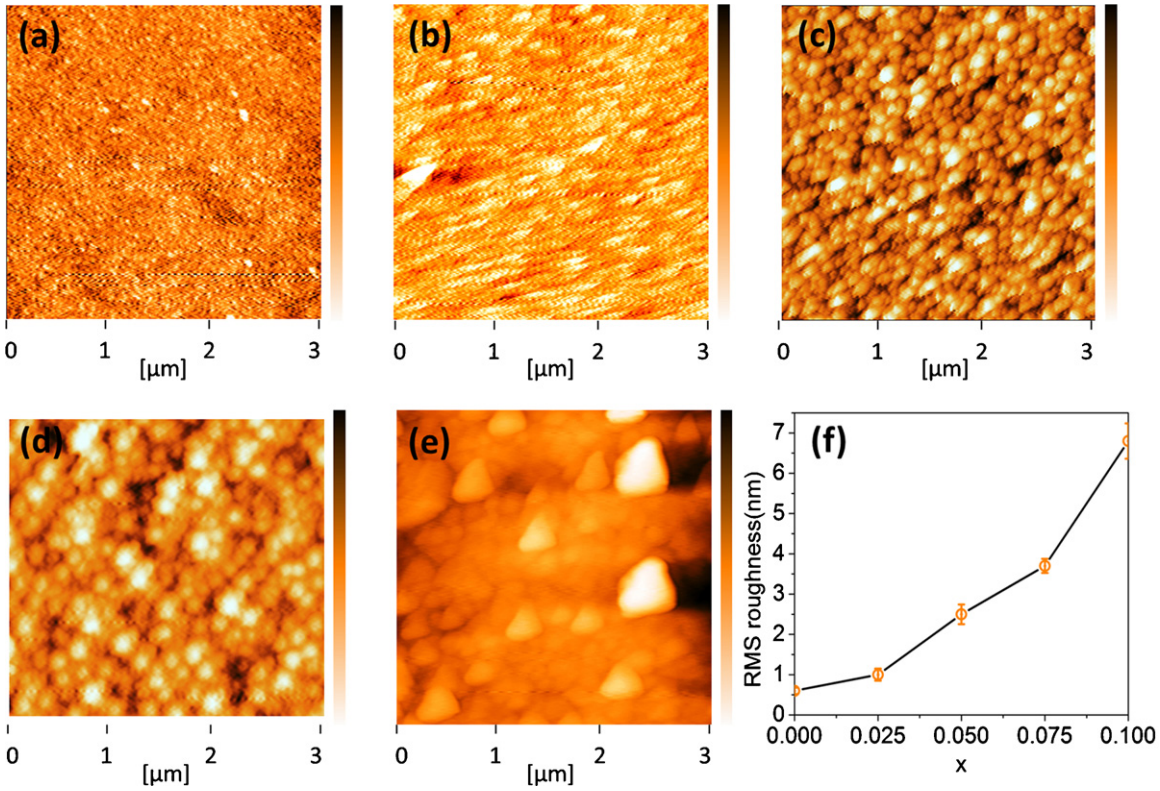

Fig. 2. AFM micrographs of $Bi_{1.5}Cu_xMg_{1-x}Nb_{1.5}O_7$ thin films annealed at 500 °C: (a) $x = 0$; (b) $x = 0.025$; (c) $x = 0.05$; (d) $x = 0.075$; (e) $x = 1$. The RMS roughness of BCMN thin films as a function of x is shown in (f).

surface roughness increased from 0.6 nm ($x = 0$) to 6.8 nm ($x = 0.1$) as illustrated in Fig. 2(f).

The compositional dependence of dielectric constant and loss tangent measured at 1 MHz are shown in Fig. 3. Effects of Cu^{2+} substitution on the dielectric properties of BCMN thin films could be separated into two parts. The dielectric constant of BCMN thin films increased and loss tangent decreased with increasing Cu content from $x = 0$ to $x = 0.05$, which can be ascribed to the transformation from amorphous to crystalline phase as illustrated in Figs. 1(a) and 2. When Cu^{2+} substitution contents increased from $x = 0.05$ to $x = 0.1$, both dielectric constant and loss tangent increased monotonically. This change

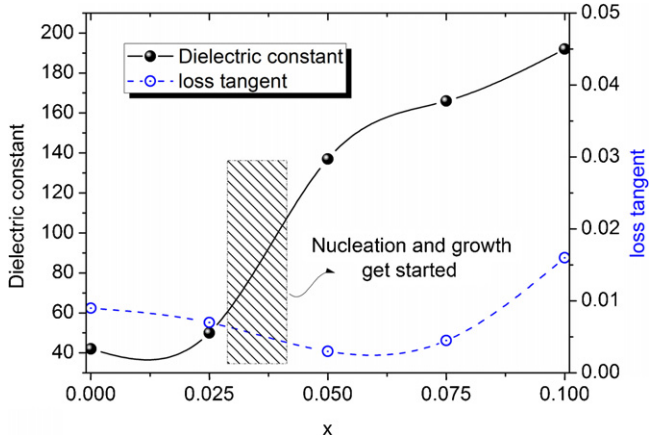

Fig. 3. Compositional dependences of dielectric constant and loss of $Bi_{1.5}Cu_xMg_{1-x}Nb_{1.5}O_7$ thin films measured at 1 MHz.

in dielectric properties of crystallized BCMN thin films ($x = 0.05$–0.1) might be explained referring to the dielectric properties of pure BMN and BCN ceramics. It was reported that both dielectric constant and loss tangent of BCN ceramic were higher than those of BMN ceramic [14]. This result is consistent with the effects of Cu substitution on dielectric constant and loss tangent of BCMN thin film (Fig. 3).

Fig. 4 shows the electric field dependences of the dielectric constant and loss tangent of BCMN thin films measured at room temperature. The tunability of the films is defined as $[\varepsilon(0) - \varepsilon(v)]/\varepsilon(0)$, where $\varepsilon(0)$ and $\varepsilon(v)$ are the dielectric constant at zero and a certain bias field respectively. At a bias filed of ~1 MV/cm, the tunabilities are 24%, 39% and 42% for BCMN films with $x = 0.05$, 0.075 and 0.1 respectively. Dielectric tunability in bismuth based cubic pyrochlores can be interpreted by a model of hopping dipoles in double-well potentials under the influence of random fields arising from chemical and displacement disorder of ions at A site [8]. The random fields and their interaction between these disordered sites are believed to be the major sources of the polarizability [3,17]. One possible cause of the tunability is that large fields applied to thin films effectively clamp out part of the polarizability [3]. Based on these mechanisms, it is reasonable to deduce that tunability of bismuth based pyrochlores might be improved by substituting randomly displacive ions on A sites using the one with higher polarizability because highly polarizable ions will promote the dielectric response [10]. In this study, the increase in tunability with increasing Cu content of BCMN thin films might be due to the higher polarizability of

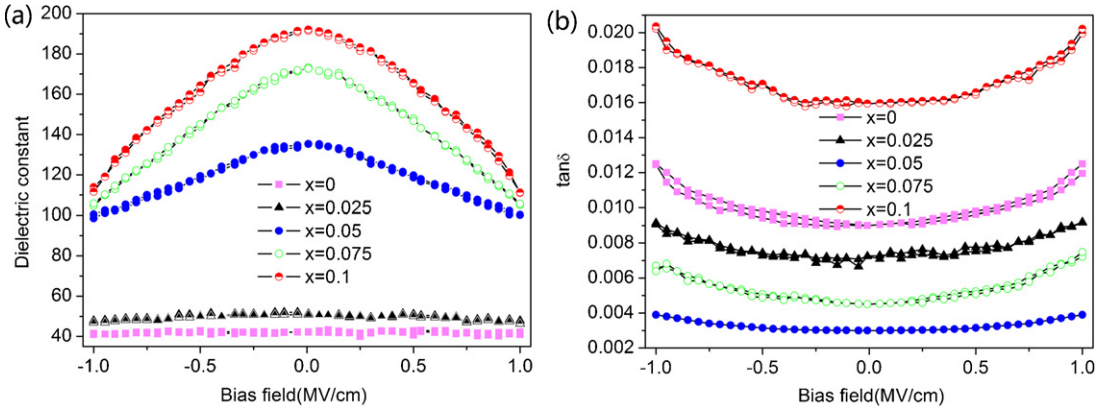

Fig. 4. Voltage dependence of dielectric constant (a) and loss tangent (b) of $Bi_{1.5}Cu_xMg_{1-x}Nb_{1.5}O_7$ thin films.

Table 1
Comparison of the annealing temperature and dielectric properties of BCMN ($x = 0.075$) thin films with those of BZN or BMN thin films.

Thin films	Deposition method	Annealing	ε	FOM at 1 MV/cm	Measurement frequency	Reference
BZN	CSD	750 °C	150	22	10 kHz	[4]
BZN	rf magnetron sputtering	700 °C	220	660	1 MHz	[5]
BZN	CSD	Laser plus 400 °C	156	50	100 kHz	[19]
BMN	rf magnetron sputtering	750 °C	86	133	100 kHz	[10]
BCMN ($x = 0.075$)	CSD	500 °C	173	86.7	1 MHz	This letter

Cu^{2+} (2.11 Å^3) than that of Mg^{2+} (1.32 Å^3) and the change of local random field [18]. However, fully understanding of the effects of Cu doping on the tunability needs more detailed structure data and dielectric relaxation investigation over a wide temperature range and a broad frequency range [8,11].

The figure of merit (FOM) defined as FOM = tunability/tan δ is frequently used to characterize the quality of tunable materials, which is a balanced combination of tunability and dielectric loss. Fig. 5 summarizes the tunability and FOM of BCMN thin films under a bias field of 1 MV/cm as a function of x. The optimal property was obtained for the BCMN ($x = 0.075$) thin films which give the largest FOM of 86.7 under a bias of 1 MV/cm.

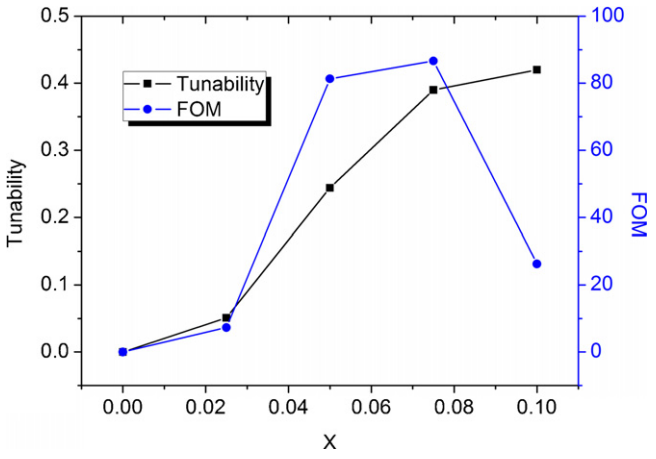

Fig. 5. Compositional dependences of tunability and FOM of $Bi_{1.5}Cu_xMg_{1-x}Nb_{1.5}O_7$ thin films.

Comparison of the annealing temperature and dielectric properties of BCMN ($x = 0.075$) thin films prepared in this letter with those of BZN or BMN thin films reported in the literature is shown in Table 1. The FOM of BCMN ($x = 0.075$) thin films is much higher than that of BZN thin films fabricated by the similar chemical method. Annealing temperature of BCMN thin films in this work is much lower than that of BZN and BMN thin films in most reported works except for the case using excimer laser annealing process [19].

4. Conclusions

In summary, structure and dielectric properties of BCMN thin films prepared on Au/Ti/SiO_2/Si(1 0 0) substrates using a CSD method were investigated. Crystallization of thin films was promoted by substituting Cu^{2+} for Mg^{2+}. When the Cu^{2+} substitution content increased to $x = 0.05$, BCMN thin films were fully crystallized by annealing at 500 °C for 30 min. Grain size and RMS roughness increased with increasing Cu content. BCMN ($x = 0.075$) thin films annealed at 500 °C exhibit dielectric constant of 173 and low dielectric loss of 0.0045 at 1 MHz. A high tunability of 39% and FOM of 86.7 were achieved under a bias field of 1 MV/cm. Low crystallization temperature and favorable dielectric properties make BCMN thin films attracting for tunable device applications.

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References

[1] A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh, N. Setter, Ferroelectric materials for microwave tunable applications, J. Electroceram. 11 (2003) 5–66.

[2] L.B. Kong, S. Li, T.S. Zhang, J.W. Zhai, F.Y.C. Boey, J. Ma, Electrically tunable dielectric materials and strategies to improve their performances, Prog. Mater. Sci. 55 (2010) 840–893.

[3] W. Ren, S. Trolier-McKinstry, C.A. Randall, T.R. Shrout, Bismuth zinc niobate pyrochlore dielectric thin films for capacitive applications, J. Appl. Phys. 89 (2001) 767–774.

[4] R.L. Thayer, C.A. Randall, S. Trolier-McKinstry, Medium permittivity bismuth zinc niobate thin film capacitors, J. Appl. Phys. 94 (2003) 1941–1947.

[5] J.W. Lu, S. Stemmer, Low-loss, tunable bismuth zinc niobate films deposited by rf magnetron sputtering, Appl. Phys. Lett. 83 (2003) 2411–2413.

[6] J.W. Lu, D.O. Klenov, S. Stemmer, Influence of strain on the dielectric relaxation of pyrochlore bismuth zinc niobate thin films, Appl. Phys. Lett. 84 (2004) 957–959.

[7] J. Park, J. Lu, S. Stemmer, R.A. York, Microwave dielectric properties of tunable capacitors employing bismuth zinc niobate thin films, J. Appl. Phys. 97 (2005) 084110.

[8] A.K. Tagantsev, J. Lu, S. Stemmer, Temperature dependence of the dielectric tunability of pyrochlore bismuth zinc niobate thin films, Appl. Phys. Lett. 86 (2005) 032901.

[9] H. Funakubo, S. Okaura, M. Suzuki, H. Uchida, S. Koda, R. Ikariyama, T. Yamada, Low strain sensitivity of the dielectric property of pyrochlore Bi–Zn–Nb–O films, Appl. Phys. Lett. 92 (2008) 182901.

[10] S.W. Jiang, Y.R. Li, R.G. Li, N.D. Xiong, L.F. Tan, X.Z. Liu, B.W. Tao, Dielectric properties and tunability of cubic pyrochlore $Bi_{1.5}MgNb_{1.5}O_7$ thin films, Appl. Phys. Lett. 94 (2009) 162908.

[11] J.C. Booth, N.D. Orloff, J. Cagnon, J. Lu, S. Stemmer, Temperature-dependent dielectric relaxation in bismuth zinc niobate thin films, Appl. Phys. Lett. 97 (2010) 002902.

[12] J.W. Lu, S. Schmidt, D.S. Boesch, Low-loss tunable capacitors fabricated directly on gold bottom electrodes, Appl. Phys. Lett. 88 (2006) 112905.

[13] K.C. Lee, N.H. Kim, B. H.O., H.W. Kim, Annealing effects on the structure properties of gold films on Si by the RF magnetron sputtering, Mater. Sci. Forum 475–479 (2005) 3923–3926.

[14] V.P. Sirotinkin, A.A. Bush, Preparation and dielectric properties of $Bi_{1.5}MNb_{1.5}O_7$ (M = Cu, Mg, Mn, Ni, Zn) pyrochlore oxides, Inorg. Mater. 39 (2003) 1130–1133.

[15] D. Zhou, H. Wang, X. Yao, Microwave dielectric properties and co-firing of $BiNbO_4$ ceramics with CuO substitution, Mater. Chem. Phys. 104 (2007) 397–402.

[16] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Appl. Catal. A 32 (1976) 751–767.

[17] S. Kamba, V. Porokhonskyy, A. Pashkin, V. Bovtum, J. Petzelt, Anomalous broad dielectric relaxation in $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ pyrochlore, Phys. Rev. B 66 (2002) 054106.

[18] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, J. Appl. Phys. 73 (1993) 348–366.

[19] J.-G. Cheng, J. Wang, T. Dechakupt, S. Trolier-McKinstrya, Low-temperature crystallized pyrochlore bismuth zinc niobate thin films by excimer laser annealing, Appl. Phys. Lett. 87 (2005) 232905.