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RF Sputtered BZN Pyrochlore Thin Films for Voltage Tunable Dielectric Device Applications

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ABSTRACT

The BZN pyrochlore thin films were prepared on platinized Si substrates using a reactive RF magnetron sputtering. The structures, surface morphologies, dielectric properties and voltage tunable properties of films with deposition parameters were investigated. The BZN thin films have a cubic pyrochlore phase and secondary phases of zinc niobate, bismuth niobate when crystallized at 600℃ ~ 800℃. The dielectric constant and tunability of thin films are O_2/Ar ratio and post-annealing temperature dependent. The BZN thin films sputtered in 15% O_2 and annealed at 700℃ had a dielectric constant of 153, tan δ of ~0.003 and maximum tunability of 14% at 1,000kV/cm.

INTRODUCTION

Ferroelectric thin film such as $SrTiO_3$, $Ba_{1-x}Sr_xTiO_3$ has been exploited as voltage tunable dielectric materials [1-6]. Suggested applications of these thin films are planar capacitors, coplanar waveguides, tunable phase shifters and tunable filters, etc. But, ferroelectric thin films have an inherently capacitive hysteresis in the microwave region resulting in large dielectric losses. Therefore, it is necessary to develop new paraelectric tunable materials without hysteresis.

Bi_2O_3-ZnO-Nb_2O_5 (BZN) pyrochlore systems are paraelectric with medium dielectric constant and low dielectric loss [7]. There are two main phases in the BZN system depending on composition; a cubic pyrochlore structure(base composition of $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$)and pseudo-orthorhombic pyrochlore structure(base composition of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$). These two compositions are members of the general family of $(Bi_{3x}Zn_{2-3x})(Zn_xNb_{2-x})O_7$, with x=1/2 and x=2/3, respectively [8]. Previous studies on the BZN pyrochlore ceramics have been focused mostly on the applicability to low firing temperature multilayer capacitors as a bulk form [9]. Recently, several studies on the dielectric tunability and dielectric property of BZN thin film prepared by metalorganic deposition (MOD) [10] and pulsed laser deposition (PLD) [11] process has been reported. It was found that the composition of $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ thin films prepared by MOD process have voltage tunable dielectric properties, while the composition of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ thin films were nearly field independent. From a current industrial point of view, it might be necessary to investigate another process technique other than PLD or MOD process. In that case, the sputtering deposition technique would be another highly attractive process for commercial production.

In this work, we report on the fabrication and dielectric properties of BZN thin films by conventional reactive RF magnetron sputtering and the correlation between deposition parameters and the tunability of BZN thin films is also discussed.

EXPERIMENTAL PROCEDURE

The composition of $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ cubic pyrochlore target materials were prepared by a conventional mixed-oxide process and shaped into 2 inch disk. The BZN thin films were deposited by reactive RF magnetron sputtering with system geometry of target to substrate was off-axis type. The base pressure in the process chamber evacuated 3.0×10^{-6} Torr and high purity Ar and O_2 were used as sputtering and reactive gases respectively. The discharge was generated at a constant RF power of 150W and the flow rate of Ar were kept at a constant value and O_2/Ar ratios were variable in 5%, 10%, 15% and 20%, receptively, working pressure was maintained at 10mTorr using throttle valve. As a bottom electrode and substrate, (111) oriented platinum coated p-type Si wafers ($Pt/TiO_2/SiO_2/Si$) were used. The as-deposited films were amorphous and annealed at 600~800℃ for 3hr in air to have crystallized films with a pyrochlore structure. The thickness of the films prepared was 4,000~4,500 Å. The standard capacitor type Metal-Insulator-Metal (MIM) heterostructure devices were then fabricated for dielectric properties measurements. The silver dots of 250㎛ diameter as the top electrode were deposited by the thermal evaporation for electric contact probing.

The crystal structure of films was characterized by x-ray diffraction (XRD, Mac Science M18XHF) using Cu$K\alpha$ radiation and an Alpha-Step surface profiler was used for measuring the thickness of all the samples. The microstructure and surface morphology of the film was investigated by scanning electron microscopy (SEM, JEOL JSM-6330F) equipped with a field emission. The dielectric properties of the BZN films(capacitance(Cp) and dissipation factor(tan δ)) were measured with an Agilent 4294A precision impedance analyzer in the 40Hz-10MHz range with a 500mV root-mean-square(rms) oscillation voltage. Using the measured capacitances, the dielectric constants were calculated with the measured film thickness and top electrode area. The bias electric field dependence of the dielectric properties were measured in 1MHz with a maximum dc bias field was ±40V.

RESULTS AND DISCUSSION

Crystal structure

The XRD patterns of BZN films deposited with various O_2/Ar ratios and post-annealed at different temperatures are shown in Fig. 1. The films were amorphous at 500℃ and below. Films annealed at 600℃ were crystalline and showed a cubic pyrochlore structure and secondary phases. These secondary phases were indexed by orthorhombic zinc niobate phases: $Zn_3Nb_2O_8$ and $ZnNb_2O_6$. The films annealed at 700℃ have a pyrochlore structure while those annealed at 600℃ exhibit the zinc niobate structure with the $ZnNb_2O_6$ phase increasing significantly for 20% O_2. With increasing the annealing temperature up to 800℃, the BZN films started to contain small amounts of orthorhombic bismuth niobate phase ($BiNbO_4$) as well as even larger amounts of zinc niobate. These secondary phases are different from those found in MOD or PLD-BZN films [10-11].

Surface morphology

Fig. 2 shows surface micrographs of the BZN thin films deposited with O_2/Ar of 15% and annealed at different temperatures. It can be seen that grain size became about 30nm in average

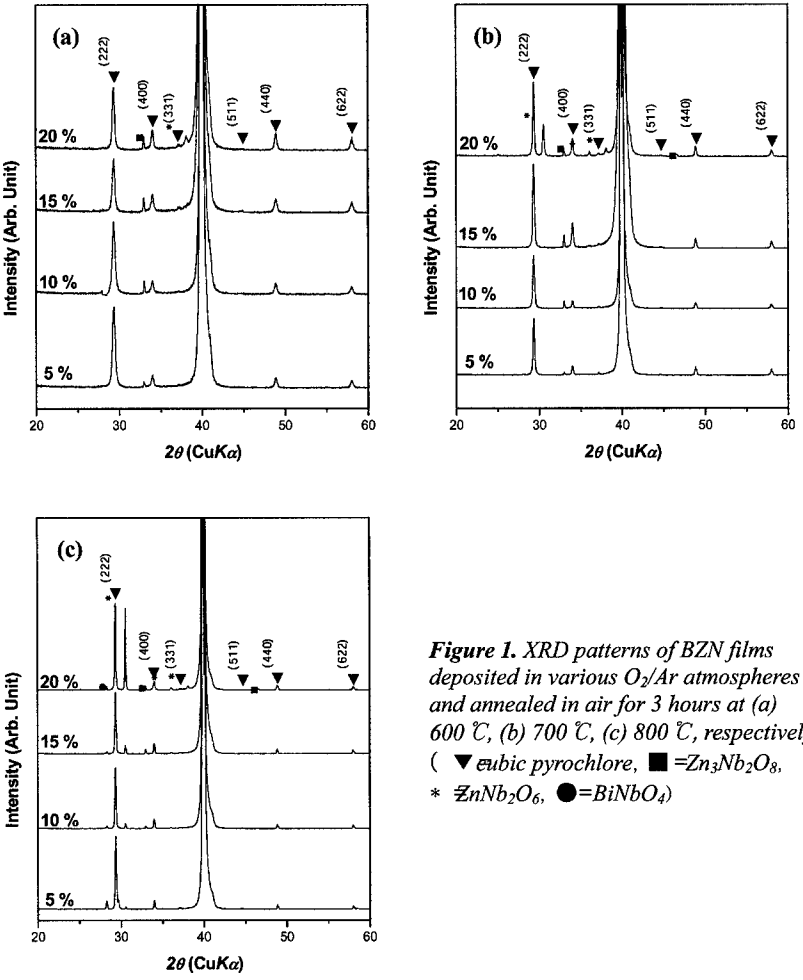

Figure 1. *XRD patterns of BZN films deposited in various O_2/Ar atmospheres and annealed in air for 3 hours at (a) 600 ℃, (b) 700 ℃, (c) 800 ℃, respectively. (▼=cubic pyrochlore, ■ =$Zn_3Nb_2O_8$, * =$ZnNb_2O_6$, ●=$BiNbO_4$)*

diameter after annealing at 600℃. The average grain sizes increased with annealing temperature. At temperature of 800℃, the grain size reached around 400nm. The surface grain size was not changed at the same annealing temperature even though oxygen content increased from 5% to 20%. These results show that oxygen contents, unlike annealing temperature, during sputter deposition had not so great effects on the microstructures of BZN thin film.

Figure 2. *FE-SEM surface morphology of BZN films deposited in 15% O_2 and annealed in air for 3 hours.*

Dielectric properties

The dielectric properties of sputtered BZN films as a function of O_2/Ar ratios and annealing temperature are shown in Fig. 3. The dielectric constants of films that were annealed at same temperature increased up to O_2/Ar of 15% and decreased again at that of 20%. Also, films annealed at 700℃ had high dielectric constants as compared with 600℃ and 800℃. The dielectric constant of the BZN films had a maximum value of 153 at O_2 of 15%, 700℃ annealing. All films exhibited very low dielectric losses ($0.0015 < \tan\delta < 0.0054$, measurement frequency = 1MHz). With increasing O_2 % and decreasing annealing temperature, the loss tangents continuously decreased.

The dc bias electric field dependence of the dielectric properties of the BZN films was investigated. Fig. 4 gives the voltage tunability of films with O_2/Ar ratios and annealing temperature. The tunability (%) is defined as $(C_0-C_v)/C_0$ where C_0 and C_v are the capacitance

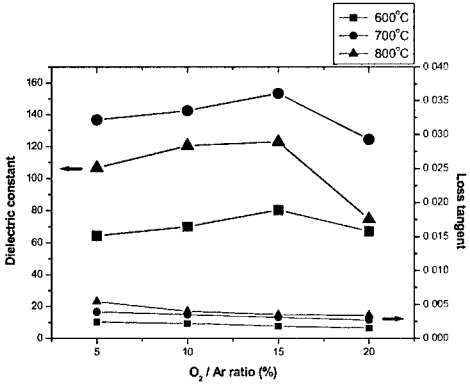

Figure 3. *Dielectric constant and loss tangent of BZN films annealed at different temperature as a function of O_2/Ar ratio (measurement frequency=1MHz).*

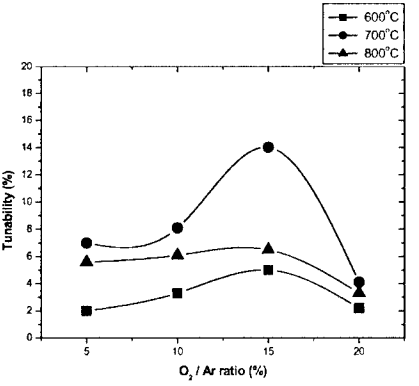

Figure 4. *Tunability of BZN films annealed at different temperature as a function of O_2/Ar ratio (measurement frequency=1MHz, maximum dc bias field=±40V).*

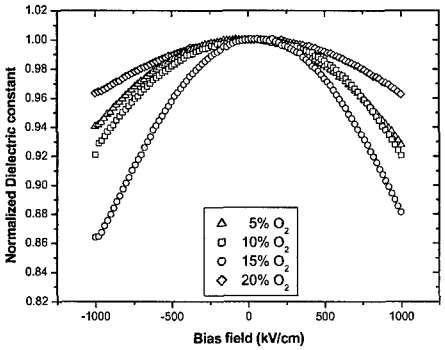

Figure 5. Normalized dielectric constant versus dc bias field plots for BZN films deposited in various O_2/Ar atmospheres and annealed in air for 3 hours at 700 ℃.

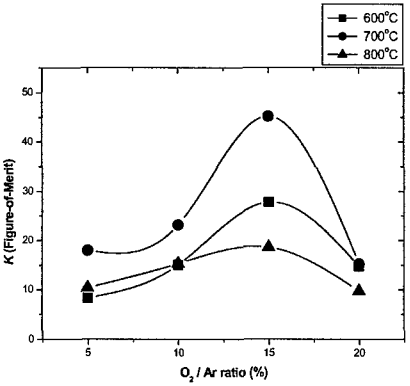

Figure 6. The Figure-of-Merit, K factors of BZN films annealed at different temperature as a function of O_2/Ar ratio.

values at zero and maximum dc voltage levels. For the BZN films deposited with 15% of oxygen and annealed at 700℃, the maximum tunability of 14% achieved under a bias 1,000kV/cm.

Fig. 5 shows normalized dielectric constant versus bias field plots for BZN films deposited with various O_2/Ar ratios and annealed at 700℃. The dielectric constant decreased with the bias field, while the loss tangent was constant (not shown in the figure). The curve was symmetric with respect to zero bias and had no hysteresis. There is no evidence of saturation in the tunability up to the maximum measurement field. For tuning applications, both tunability and tan δ must be considered when comparing the relative merits of different film compositions, process techniques and device configurations. So the figure of merit, the K-factor, defined as $K = (C_0-C_v) / (C_0 \tan \delta)$ where tan δ is measured without dc bias was measured. The K factors of BZN films are shown in Fig. 6. The films annealed at 700℃ possess high K values, but the films annealed at 800℃ possess lower K values than 600℃ due to the high loss.

Conclusively, it could be seen that the composition of reactive gas mixture and post-annealing treatment were very effective to control basic dielectric properties and tunability.

CONCLUSIONS

The BZN thin films were successfully prepared by the reactive RF magnetron sputtering. The BZN films showed the cubic pyrochlore structure. The sputtered cubic BZN thin films have the voltage tunability in spite of the containing secondary phases. It was found that O_2/Ar ratio during sputtering and annealing temperature was the primary critical factors on the dielectric constant and tunability. The maximum tunability of 14% at 1,000kV/cm was achieved from films post-annealed at 700℃ after deposition in a 15% O_2/Ar ratio mixture at pressure of 10mTorr and RF power of 150W.

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