Journal of the European Ceramic Society 21 (2001) 2731–2734
www.elsevier.com/locate/jeurceramsoc

Synthesis and properties of dielectric $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ thin films

Yi-Chun Chen[a,*], Hsiu-Fung Cheng[a], You-Ming Tsau[a], Petr Kužel[b], Jan Petzelt[b], I-Nan Lin[c]

[a]*Department of Physics, National Taiwan Normal University, Taipei 117, Taiwan, ROC*
[b]*Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic*
[c]*Materials Science Center, National Tsing-Hua University, Hsinchu 300, Taiwan, ROC*

Abstract

Crystalline, $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, BiZN thin films can be easily obtained when the films were in-situ deposited at high enough substrate temperature 450–600 °C (30 min). The optical parameters ($N=n+ik$) measured and analyzed by optical transmission spectroscopy are insensitive to the deposition parameters, provided that the films are crystalline. The dielectric properties converted from optical parameters are $\varepsilon'=4.75$ and $Q=325$. The dielectric constant of BiZN thin films in THz frequency regime, $(\varepsilon')_{f\cdot THz}=32$, is markedly smaller than the ε' value of BiZN bulk materials in microwave regime, and the quality factor of the thin films is less than 20% of the bulk materials. However, the dielectric constant of the thin films in THz region is still markedly larger than that derived from optical transmission spectroscopy in optical region.

Keywords: Dielectric properties; Microwave ceramics; Pulsed laser deposition; Thin films

1. Introduction

Among the microwave dielectrics, $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ series materials exhibit marvelous properties such as high dielectric constant, low dielectric loss and adjustable temperature coefficient of resonance frequency and, most of all, need lower temperatures for sintering. Microwave dielectric thin films possess overwhelming advantages over bulk materials in several aspects, including (1) lower operation voltage, (2) faster response and nonlinear relationship in dielectric properties,[1,2] which increases the tunability of the devices. Therefore, applications of these thin films as planar capacitors, coplanar waveguide, tunable phase shifter, tunable mixers and tunable filters have been extensively investigated.[1,3–5]

Pulsed laser deposition (PLD) technique,[6] as compared with other thin film deposition techniques, such as RF-sputtering, sol-gel, metal-organic chemical vapor deposition (MOCVD) processes, can synthesize the multicomponent materials at rapid rate with precise control in composition. The PLD technique is thus adopted in this research for synthesizing $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ microwave dielectric thin films. The effects of deposition parameters on material's characteristic and dielectric behavior in optical frequency range were investigated. Moreover, THz-TDS technique[7–9] is used to study the dielectric properties of thin films in terahertz regime.

* Corresponding author. Tel.: +886-2-2933-107; fax: +886-2-2932-6408.
E-mail address: s41409@cc.ntnu.edu.tw (Y.-C. Chen).

2. Experimental procedure

The Bi_2O_3, ZnO and Nb_2O_5 of the compositions as 80.8 mol% $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (BiZN) and 19.2 mol% $Zn_1Nb_2O_6$ (ZN), BiZN–ZN, were mixed, pelletized and then, directly sintered at 1080–1120 °C for 4 h. The BiZN thin films were prepared by pulsed laser deposition (PLD) technique, using a pulsed XeCl excimer laser ($\lambda=308$ nm, Lambda Physik) with an energy density of 3 J/cm^2. The films were deposited at 400–600 °C in 0.1 mbar oxygen pressure (P_{O_2}), followed by 10 min of annealing at the depositing temperature under 1 atm P_{O_2}. MgO [100] substrates were used for growing the thin films.

The phase constituent and microstructure of the sintered materials (targets) and thin films were examined using X-ray diffractometer (Rigaku, Dmax/IIB). The microwave dielectric properties of the bulk ceramic materials were measured by a cavity method using H. P. 8722 network analyzer. The optical dielectric properties of the thin film materials were evaluated using optic transmission spectra measured by spectrophotometer (Hitachi, U-3410). In terahertz spectroscopy, a large aperture photoconducting antenna is used as the THz

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00353-3

transmitter and an electro-optic sampling technique is used for the detection of the THz pulses. The experimental setup can measure the loss and dispersion properties of materials up to 1.0 THz range.

3. Results and discussion

When the mixture of Bi_2O_3, ZnO and Nb_2O_5, in a proportion corresponding to nominal compositions: 80.8 mol% $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ and 19.2 mol% $Zn_3Nb_2O_8$ were pelletized and sintered directly, the materials contain only $Bi_2ZnNb_2O_9$ (cubic BiZN) and $Zn_3Nb_2O_8$ phases. The characteristics of the materials are optimized for 1100 °C (4 h) sintered samples, which possess high density (~7.0 g/cm^3), large dielectric constant ($K \cong 67$), high quality factor ($Q \times f \cong 80{,}000$ GHz) and small temperature coefficient of resonance frequency ($\tau_f \cong -10$ ppm/°C).

$Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (BiZN) thin films prepared by pulsed laser deposition process are readily crystallized for a substrate temperature higher than 450 °C (Fig. 1). Secondary phase appears for the films grown at a substrate temperature higher than 550 °C, which is presumably induced by Zn-loss phenomenon. The dielectric response of the BiZN thin films was evaluated using optical transmission spectroscopic (OTS) technique, since direct measurement on dielectric properties of the films in microwave frequency regime is very difficult. Fig. 2a illustrates the variations of the OTS spectra for BiZN thin films with deposition temperature. The optical parameters, including refractive index (n) and absorption coefficient (κ) can be derived from the maximum transmittance (T_{max}) and minimum transmittance (T_{min}) of the OTS spectra using theory in optics,[10] that is,

$$n = [N + (N^2 - n_0^2 n_1^2)^{\frac{1}{2}}]^{\frac{1}{2}}, \tag{1}$$

where

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0 \cdot n_1 \frac{T_{max} - T_{min}}{T_{max} T_{min}} \tag{2}$$

and n_0 and n_1 are the refractive indices of air and MgO, respectively. Moreover, the κ value is

$$e^{-\kappa d} = \frac{C_1\left[1 - \left(\frac{T_{max}}{T_{min}}\right)^{\frac{1}{2}}\right]}{C_2\left[1 + \left(\frac{T_{max}}{T_{min}}\right)^{\frac{1}{2}}\right]} \tag{3}$$

where $C_1 = (n + n_0)(n_1 + n)$ and $C_2 = (n - n_0)(n_1 - n)$; d is film thickness. After calculation, Fig. 2a leads to the results, i.e. the refraction index (n) varies in between $n = 2.0$ and 2.4, which is insensitive to the deposition temperature and time used for growing the films. By contrast, the absorption coefficient κ varies in between $\kappa = 1.0 \times 10^{-4}$ and 2.4×10^{-4} nm^{-1}, which is more sensitive to the crystallinity of the films. The dielectric constant

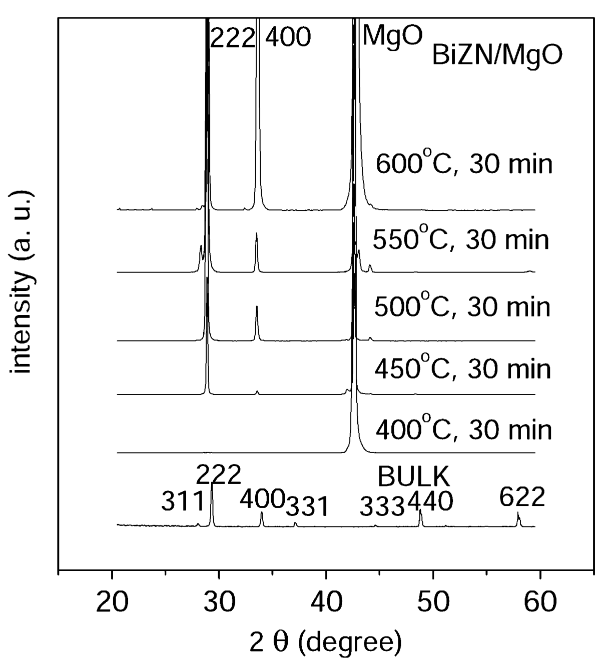

Fig. 1. X-ray diffraction patterns of BiZN/MgO thin films deposited at 400–600 °C for 30 min.

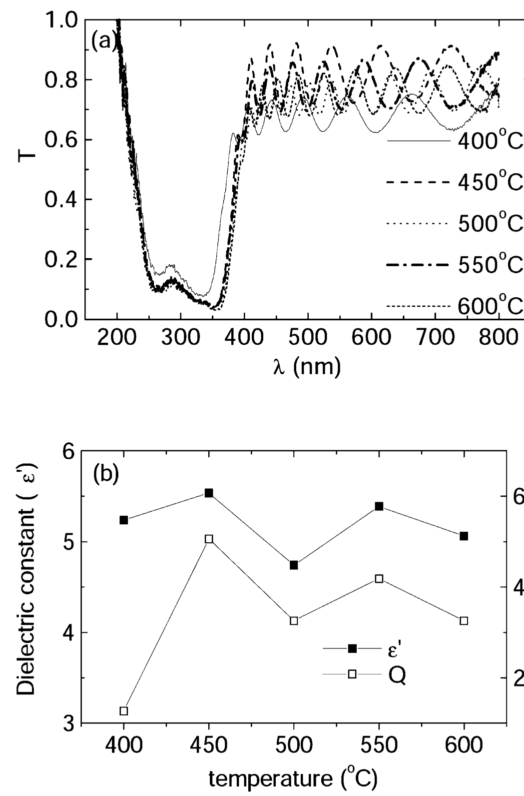

Fig. 2. (a) Optical transmission spectra and (b) dielectric properties, ε' and quality factor, Q values, for $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ thin films deposited on MgO at 400–600 °C for 30 min.

(real and imaginary parts ε', ε'') and quality factor ($1/Q = \tan\delta = \varepsilon''/\varepsilon'$) of the films can be calculated using the simplified relationships:

$$\varepsilon' = n^2 - k^2 \quad (4)$$

$$\varepsilon'' = 2nk \quad (5)$$

where $k = \lambda\kappa/4\pi$ is the extinction coefficient. Fig. 2b indicates that the average dielectric constant (ε') thus obtained is about $\varepsilon' = 4.75$ and the average quality factor is around $Q = 325$. The dielectric constant for the BiZN films in the optical region is markedly smaller than that of the BiZN ceramics in the microwave region ($(K)_c = 67$ at 10 GHz).

Comparison on the dielectric properties of the thin films in various frequency regions is not practical when the measuring frequency regions involve different mechanisms. Therefore, terahertz transmission spectroscopy (TTS) is thus utilized. Typical time domain terahertz (THz) waveforms through the MgO substrates and those through BiZN/MgO samples are illustrted in Fig. 3. After Fourier transformation, the complex transmission function $t(\omega)$ in angular frequency (ω) response of the materials can be computed from the ratio of electric fields E for the two terahertz (THz) waveforms:

$$t(\omega) = \frac{E(\omega)_{\text{samples}}}{E(\omega)_{\text{empty}}} \frac{4N\exp[i\omega(N-1)d/c]}{(N+1)^2} \times \sum_{a=0}^{m} \left[\left(\frac{N-1}{N+1} \right) \exp(i\omega Nd/c) \right]^{2a} \quad (6)$$

where $N = n + ik$ is the complex optical parameters of the materials, $2m$ is the number of internal reflections in the sample, c is the light speed in free space and d is the thickness of the samples.

The dielectric properties of the BiZN thin films can be evaluated using Eqs. (4) and (5), after the $t(\omega)$ were solved numerically. The dielectric constant (ε') of the BiZN thin films, $(\varepsilon')_{f:\text{THz}} \cong 32$–$40$ is significantly larger than the ε' value in the optical regime, $(\varepsilon')_{\text{op}} \cong 4.75$, but is markedly smaller than the ε' value of BiZN bulk materials in microwave regime. Moreover, the quality factor calculated for the BiZN thin films is $(Q \times f)_{f:\text{THz}} \cong 1.02$ THz = 1020 GHz at 0.8 THz, which is again pronouncedly smaller than that of bulk material in microwave regime. Such a phenomenon mainly results from the difference in polarization mechanism. The ionic polarization mechanism, which predominates in the microwave frequency region, ceases to operate in the optical frequency region and the materials respond to the electric field only through the electron polarization mechanism. The dielectric constant of the materials in the optical regime is thus markedly smaller than that in the microwave regime. Moreover, zero phonon softening phenomenon, which occurs at a frequency in between the two regimes, will, apparently, further suppress the dielectric response of the materials.

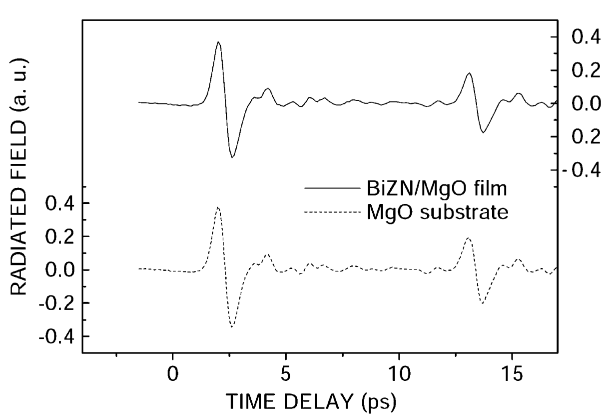

Fig. 3. Typical time domain THz waveforms, through substrate and sample for BiZN/MgO thin film.

4. Conclusions

BiZN bulk ceramic materials were prepared by mixed oxide process and BiZN thin films were prepared by pulsed laser deposition (PLD) process. The dielectric properties converted from optical parameters are $\varepsilon' = 4.75$ and $Q = 325$. Direct measurement on the dielectric response of BiZN thin films using THz spectroscopy indicates that in THz frequency regime, the dielectric constant and quality factor for the BiZN thin films are pronouncedly smaller than those in microwave regime, but the dielectric constant is still larger than those in optical regime.

Acknowledgements

Financial support of National Science Council, R.O.C. through the projects NSC-89-2112-M-003-037 and NSC-90-2112-M-003-028 is gratefully acknowledged by the authors.

References

1. Hoerman, B. H., Ford, G. M., Kaufmann, L. D. and Wessels, B. W., Dielectric properties of epitaxial $BaTiO_3$ thin films. *Appl. Phys. Lett.*, 1998, **73**, 2248–2250.
2. Li, H.-C., Si, W., West, A. D. and Xi, X. X., Near single crystal-level dielectric loss and nonlinearity in pulsed laser deposited $SrTiO_3$ thin films. *Appl. Phys. Lett.*, 1998, **72**, 190–192.
3. Wang, X., Helmersson, U. F., Olafsson, S., Rudner, S., Wernlund, L. and Spartak, G., Growth and field dependent dielectric properties of epitaxial $Na_{0.5}K_{0.5}O_3$ thin films. *Appl. Phys. Lett.*, 1998, **73**, 927–929.
4. Wang, C. C., Linke, R. A., Nolte, D. D., Melloch, M. R. and Trivedi, S., Signal strength enhancement and bandwidth tuning in moving space charge field photodetecors using alternating bias field. *Appl. Phys. Lett.*, 1998, **72**, 100–102.

5. Carlsson, E. and Gevorgian, S., Effect of enhanced current crowing in a CPW with a thin ferroelectric film. *Electronics Lett.*, 1997, **33**, 145–146.
6. Watts, B. E., Leccabue, F., Bocelli, G., Calestani, G., Valderon, F., De Melo, O., Gonzalez, P. P., Vidal, L. and Carrillo, D., On the preparation of PZT thin films by laser ablation deposition. *Mater. Lett.*, 1991, **11**(5), 183–186.
7. Van Exter, M. and Grischkowsky, D., Carrier dynamics of electrons and holes in moderately doped silicon. *Phys. Rev. B*, 1990, **41**, 12140–12149.
8. Cai, Y., Brener, I., Lopata, J., Wynn, J., Pfeiffer, L., Stark, J. B., Wu, Q., Zhang, X. C. and Federici, J. F., Coherent terahertz radiation detection: direct comparison between free-space electro-optic sampling and antenna detection. *Appl. Phys. Lett.*, 1998, **73**, 444–446.
9. Park, S.-G., Melloch, M. R. and Weiner, A. M., Comparison of terahertz waveforms measured by electro-optic and photoconductive sampling. *Appl. Phys. Lett.*, 1998, **73**, 3184–3186.
10. Cheng, H. F., Chen, Y. C. and Lin, I. N., Frequency response of microwave dielectric $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ thin films laser deposited on indium-tin oxide coated glass. *J. Appl. Phys.*, 2000, **87**, 479–483.