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Influence of strain on the dielectric relaxation of pyrochlore bismuth zinc niobate thin films

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Abstract

$\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$ (BZN) films were deposited by rf magnetron sputtering on different substrates to systematically vary the film stress due the thermal mismatch between BZN and the substrate. Substrates included Pt/SiO₂ covered silicon, vycor glass, magnesium oxide and sapphire. The BZN film microstructures (orientation, grain size and roughness) were similar on the different substrates. Measurements of the permittivity and dielectric loss tangent were carried out between 80 and 300 K at frequencies between 10 kHz and 10 MHz. Films that were under a moderate tensile stress showed a low temperature dielectric relaxation, associated with a dielectric loss peak and drop in permittivity, at ~ 100 K. In contrast, the dielectric relaxation was shifted to temperatures below 80 K in films on vycor that were under a large tensile stress. This shift reflected a lowering of the activation energy of the dielectric relaxation processes due to tensile stress. It is expected that films under large tensile stress require higher frequencies than bulk BZN to shift the dielectric relaxation to room temperature, which makes these films attractive for low-loss, high-frequency applications.

Recently, $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Nb}_{1.5}\text{O}_7$ (BZN) thin films with the cubic pyrochlore structure have attracted interest for integrated capacitor applications because of their relatively high permittivity (~ 170 - 220) [1-4] and dielectric loss tangents ($\tan \delta$) that were as low as 5×10^{-4} [1]. Furthermore, BZN thin films exhibit an electric field tunable dielectric constant [1-4]. At a maximum applied bias field of 2.4 MV/cm, the tunability is about 55 % at room temperature [1]. Films that combine a high tunability with low loss are attractive for tunable microwave device applications. However, bulk BZN shows a low temperature dielectric relaxation that is associated with a dielectric loss peak [5,6]. This loss peak shifts to higher temperatures at higher measurement frequencies, approaching room temperature in the microwave frequency region [5].

In BZN, Bi and Zn are randomly mixed on the A-site of the pyrochlore structure (space group $Fd\bar{3}m$, general formula $A_2B_2O_6O'$ where O' is the seventh oxygen bonded only to the A-site). Both the A-cations and O' ions are randomly displaced from their ideal positions in cubic pyrochlore [7]. The movement of these off-centered ions is thought to contribute to the relatively broad dielectric relaxation in BZN [8]. The dielectric relaxation is thermally activated, and has been described by an Arrhenius equation [2,8]

$$1/\tau \propto \exp(-E_a/kT) \quad (1)$$

where τ is the relaxation time, E_a is the activation energy associated with each relaxing species and k and T are the Boltzmann constant and temperature, respectively.

We have recently reported that BZN films deposited on Si and Al_2O_3 , respectively, showed different dielectric tunabilities [1]. In this letter, we investigated the

influence of film strain, due to the thermal mismatch with the substrate, on the dielectric properties.

Substrates for BZN growth included vycor glass, (001) Si, (0001) sapphire and (001) MgO, to systematically vary the film strain. Texture variations between the films that may also influence the dielectric properties were avoided by depositing a 60 nm SiO₂ layer by plasma-enhanced chemical vapor deposition at 250 °C on each substrate [9]. The SiO₂ layer was densified in 25 mTorr oxygen at 800 °C for 30 min. 100 nm Pt layer bottom electrodes were deposited by electron beam evaporation on 3 nm Ti adhesion layers. X-ray diffraction (XRD) showed that the Pt was (111) textured. Approximately 150 nm thick BZN films with composition Bi_{1.5}Zn_{1.05}Nb_{1.5}O_{7.0+x} [1] were deposited by rf sputter deposition simultaneously on the four substrates. The substrate temperature was 300 °C during deposition. The films were crystallized using a post-deposition anneal at 750 °C in air, as described elsewhere [1,10]. To confirm similar BZN microstructures on the four substrates, films were characterized by atomic force microscopy (AFM), cross-section transmission electron microscopy (TEM) and XRD. AFM and TEM showed no detectable differences in the grain sizes (110 –120 nm). The film roughness (RMS) was 6.5, 6.2, 6.5 and 5.4 nm on vycor, Si, Al₂O₃ and MgO, respectively. XRD θ -2 θ scans detected only the cubic pyrochlore phase. The intensity ratios of the film reflections were similar on all substrates, indicating similar film orientation (Fig. 1). On all substrates, the relative intensities of the (111)-type reflections were somewhat increased compared to those of random, polycrystalline BZN, indicating a slight preference for (111) orientations.

For dielectric measurements, planar capacitor structures with $50 \mu\text{m} \times 30 \mu\text{m}$ Pt top electrodes were fabricated, as described elsewhere [1,10]. Room temperature measurements were carried out with a 500 mV oscillating voltage using an impedance analyzer (Agilent 4294A) connected to an air coplanar probe (Cascade Microtech, Inc.). For measurements between 80 and 300 K, the impedance analyzer was attached to a probe station with a Joule-Thompson refrigerator (MMR). At room temperature, all films showed very low losses ($\tan \delta < 10^{-3}$), as reported previously [1]. Although films were deposited simultaneously, small variations in the film thickness ($< 10 \text{ nm}$) were possible. Therefore, to calculate the permittivity from the measured capacitance, film thicknesses were determined by AFM (the films were too rough and the grain sizes too large to determine statistically meaningful differences in the average film thickness in TEM).

Figure 2 shows the zero-bias permittivity and $\tan \delta$ measured at 1 MHz as a function of temperature for the BZN films on the four substrates. At room temperature, the permittivities on vycor, Si, sapphire and MgO were ~ 184 , 180, 177 and 170, respectively. The dielectric constants of all four films were electric field tunable. The tunability was $\sim 30\%$ at 1.2 MV/cm (on Si, MgO and Al_2O_3) and was defined as $(\kappa_{\text{max}} - \kappa_{\text{min}})/\kappa_{\text{max}}$, where κ_{min} is the minimum measured permittivity at the maximum applied field, and κ_{max} is the dielectric constant at zero bias. The tunability could be increased by increasing the bias field [1]. The breakdown strength ($\sim 0.8 \text{ MV/cm}$) of capacitor structures on vycor was too low to achieve a large tunability. This may be due to a poor quality of the bottom electrode due to the large tensile stresses in Pt on this substrate.

Figure 2 shows the low temperature dielectric relaxation, exhibiting a characteristic loss peak and drop in permittivity, of BZN on the four substrates. The maximum of the dielectric loss was at ~ 100 K on sapphire and Si. This is close to the temperature for bulk ceramics and for films on Pt coated Si reported in the literature [4,5]. Due to a shift of the loss peak to lower temperatures, the temperature of the maximum on MgO could not be determined. Furthermore, on vycor, only a very slight drop in permittivity and a small increase in loss could be detected above 80 K at 1 MHz.

Figure 3 shows the permittivity and loss as a function of temperature and measurement frequency (1 kHz – 10 MHz) for films on sapphire and on vycor, respectively. For BZN on sapphire (Fig. 3a), the temperature of the loss peak increased with frequency, similar to what is observed in bulk ceramics [4,5]. Similar behavior was observed for the films on Si and MgO. In contrast, the permittivity of the film on vycor (Fig. 3b) showed a shift in drop-off only at the highest measurement frequency (10 MHz). It is likely that the film on vycor also shows a dielectric relaxation at these measurement frequencies, but at temperatures below 80 K.

As discussed above, the microstructure and texture of the films on vycor, Si, MgO and Al_2O_3 were very similar. Thus, their different dielectric behavior must be due to differences in the film stress. Stresses in polycrystalline thin films are either intrinsic (growth stresses) or arise due to the difference in the thermal expansion between film and substrate. Since the films were deposited and annealed under identical conditions, the intrinsic stresses are likely the same on all substrates. The thermal strain, $\epsilon_{thermal}$, is given by

$$\epsilon_{thermal} = \int_{T_1}^{T_2} (\alpha_{film} - \alpha_{substrate}) dT \quad (2)$$

where α is the thermal expansion coefficient. The thermal expansion coefficients [11,12] and the estimated thermal strains are listed in Table I for the four substrates. The thermal expansion coefficient of BZN was assumed to be similar to that of pyrochlore $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Sb}_{1.5}\text{O}_7$ reported in literature [13]. More accurate measurements are currently underway [14]. T_1 was set to 750 °C, that is the recrystallization temperature of the films, and T_2 was 25 °C. The film on vycor is under a large biaxial tensile strain, whereas the film on MgO is under compressive strain.

The large shift of the dielectric relaxation on vycor to lower temperatures correspond to a reduction of the activation energy for the relaxation processes due to biaxial tensile strain (eqn. 1). BZN films are not ferroelectric [2] and thus no extrinsic contributions to the dielectric response under stress, such as reorientation of domains, are expected. Biaxial film strain changes the distances between ions and their local symmetry, thus changing the potential wells of the hopping ions and the correlation lengths between the dipoles. This may affect the films polarizability and dielectric relaxation in complex ways. For example, a decrease in correlation of dipolar motion should reduce the activation energy, change the slope of the permittivity vs. T curve and the height of the loss peak [15]. To further interpret the results, detailed investigations of the local atomic structure of BZN on the different substrates should be performed.

The observed shift of the loss peaks to lower temperatures by a biaxial strain may have practical advantages, in particular with respect to achieving low losses in the microwave region. For example, the loss peak will likely remain below room temperature for much higher operating frequencies than for bulk BZN. Dielectric measurements at temperatures below 80 K are underway in order to use eqn. (1) to

estimate the temperature of the loss peak at microwave frequencies for the different substrates.

With respect to the difference in the room temperature dielectric constants, larger tensile strains appeared to increase the films' permittivity, whereas compressive strains reduced the permittivity. Tensile film stresses reduce the permittivity of perovskite ferroelectric films in their paraelectric state, such as (Ba,Sr)TiO₃, due to $Q_{12} < 0$ [9,16]. The increase of the permittivity of a cubic, dielectric film under tensile stress would imply an unusual electrostrictive coefficient $Q_{12} > 0$ [16], unless extrinsic contributions, such as polar nanodomains, play a role. However, the observed differences in permittivity are small enough that errors (< 10 nm) in the measurement of the film thickness could also provide a likely explanation. Further studies, such as mechanical bending tests, are planned. No electrostrictive coefficients of pyrochlores have been reported in literature.

In summary, we have shown that biaxial stresses have a significant influence on the dielectric relaxation behavior of a non-ferroelectric thin film, cubic bismuth zinc niobate. Large tensile strains shift the dielectric relaxation to lower temperatures, extending the upper frequency bound for which these films may show low losses. Thus, dielectric properties of BZN films may be optimized by choice of a suitable substrate. Investigations are currently underway to determine losses in the microwave region and the tunability of films on vycor with improved the electrode stacks.

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Table I: Thermal expansion coefficients and estimated thermal strain [11-13].

Material	α (25/750 °C) $\times 10^{-6}/\text{K}$	$\epsilon_{\text{thermal}}$ (%)
BZN (estimated) ^(a)	7.92	--
Vycor	0.75 - 1	0.50 - 0.52
Si	2.618/4.4 ^(b)	~ 0.30
Sapphire	5.9/7.39	0.13
MgO	11.14/16.06	- 0.27

^(a) Assumed to be same as that of $\text{Bi}_{1.5}\text{Zn}_{1.0}\text{Sb}_{1.5}\text{O}_7$

^(b) Between 300 K to 1000 K

Figure Captions

Figure 1

XRD patterns of BZN films on the four different substrates. BZN film reflections are in bold with no subscript. The origin of the apparent doubling of the (400) film peak on MgO, vycor and Al₂O₃ could not be identified.

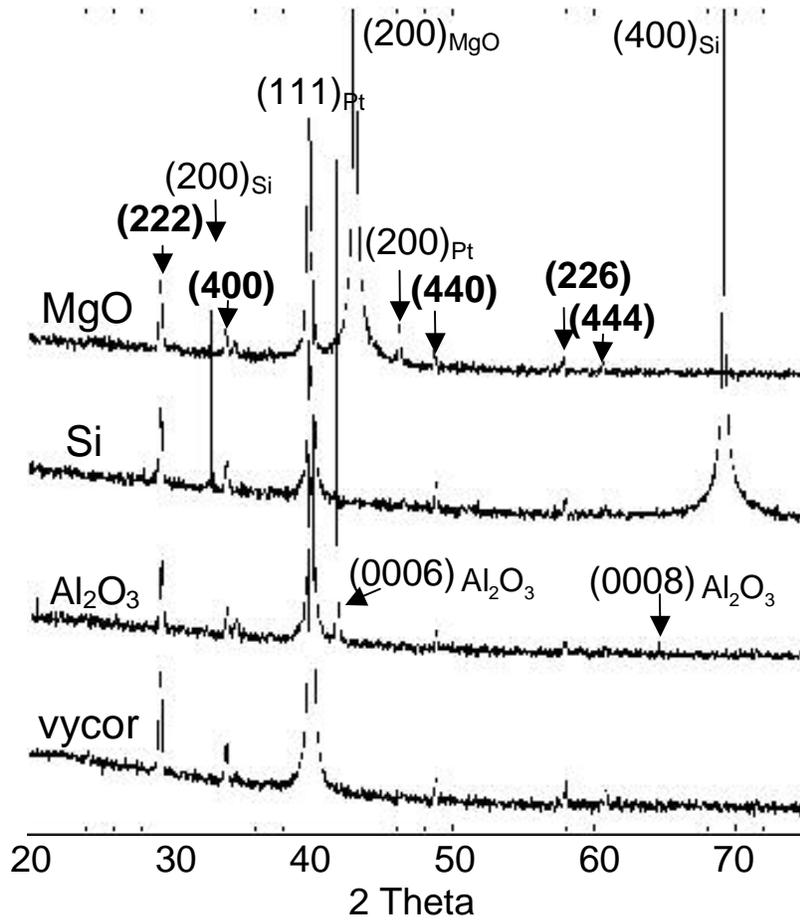
Figure 2

Permittivity and $\tan \delta$ as a function of temperature for BZN thin films on different substrates measured with 500 mV oscillation voltage at 1 MHz. The measured capacitance was independent of the measurement frequency between 10 kHz and 10 MHz, as reported previously [1].

Figure 3

Permittivity and loss as a function of temperature and frequency between 1 kHz and 10 MHz (permittivity) and 1 kHz and 1 MHz (loss) for (a) the film on Al₂O₃ and (b) the film on vycor. Above 1 MHz the losses increased due to conductor losses in the electrode [1] and are not shown.

Figure 1



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Figure 2

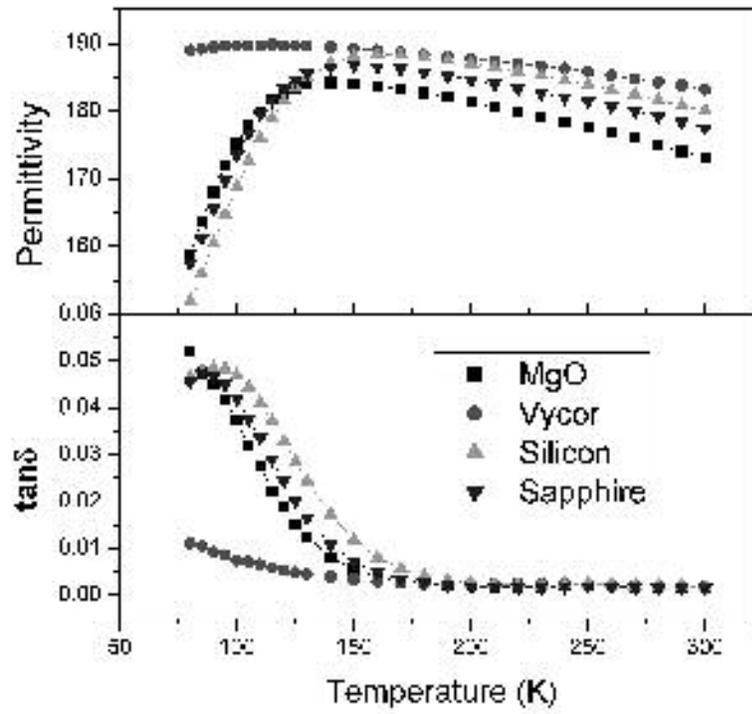


Figure 3

