Effect of electric field on the dielectric properties of the Barium Strontium Titanate film

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Abstract: We investigated the tunability of the dielectric characterization of the Ferroelectric Barium Strontium Titanate ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$) thin film on the Strontium Titanate substrate by a dc bias electric field through the terahertz time-domain spectroscopy. The tunability of the real part of the permittivity reached up to 74.8% and the imaginary part of the permittivity reached up to 33.6% when the bias electric field up to 30 V. And the results are attributed to the soft mode hardening caused by the electric field.

Keywords: BaSrTiO_3 film; dielectric characterization; THz; electrically tunability

1. Introduction

Due to the excellent nonlinear optical properties, ferroelectric and electro-optical physical properties and comprehensive application in various areas, ferroelectric materials have been drawn great attention both in scientific research and technology development[1]. The ferroelectric perovskite oxide materials Barium Strontium Titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$) has attracted great interests for several decades due to its low loss and composition dependent Curie temperature (T_c)[2], which ranges from -163 to 120°C as x could varied from 0 to 1 continuously. Now $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ has been widely used in the design of electronic devices intended for controlling radiation in the optical and microwave frequency ranges [3], and used in the dynamic random access memories[4, 5] and the functional elements in devices [6,7].

However for the bulk BST material: the annealing temperature demands very high to obtain the good crystallinity; the size is too large and is not convenient to do device integration; and the dielectric constant is so big that demands a very complicated impedance matching circuit[2], all these characters hamper the bulk BST in the integrated applications. Thin BST film offers advantages over bulk BST for tunable applications. Large electric fields (0–400 kV/cm) can be achieved in thin film BST (224 nm) using low voltages[2]. For ferroelectric BST film, the tunable properties are most researched in the microwave region and in the terahertz range by the means of dc electric-field[8,9,10], or by the means of codoping and adjusting sintering temperature for attain the high modulation of $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ ceramics[2], or adopted the method of temperature control[2]. Due to the excellent optical performance, many properties of the film have been experimentally and theoretically studied[11]. And for the investigation of modulate properties of the thin film BST, many solutions have been proposed in

literature[8,12].

Recently, there are some observations of the BST film tunability have been reported [13,14,15], but most of these literatures focus on the temperature dependent photoelectric properties. It is necessary for the permittivity to be modulated over a range as wide as possible around room temperature for practical applications. In this manuscript, we report a study of the dielectric THz properties and the electrical-field-induced tunability of BST film at room temperature.

2. Experiment

The BST film samples were prepared from a stoichiometric $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ target on the single crystal STO(100) under the conditions listed in Table I. The substrates were ultrasonically cleaned with acetone and isopropanol prior to BST deposition. Films prepared at the condition of Ar/O₂ is 40/10. After the deposition, the film was immediately annealed for 10 minutes in a vacuum condition inside the quick anneal oven, and then cooled to room temperature by nitrogen. The structural analysis of the film has been performed by XRD (X-ray Diffraction) scan and shown in the Fig.1. Mainly STO(100) and STO(200) peaks are observed, which clearly shows that highly oriented the film prepared on STO (100) substrate. As could be seen that the film is cubic crystal. The calculated lattice constants is 3.965 nm, these values are very closed to those of bulk samples[16]. The surface roughness of the BST films analyzed by atomic force microscopy (AFM), and the results is shown in Fig.2. The root mean square (RMS) roughness of BST was 2.038 nm, indicating sufficiently smooth surfaces for dielectric measurements with THz-TDS and IDEs are realized. The dimensions of the studied substrates were 2 mm×2 mm×0.5 mm. We measured the thickness of the film of 25 nm (4% accuracy) by Step profiler.

Table I. Sputtering conditions for BST deposition.

conditions Specimen	Target diameter	Source to substrate distance	RF power	Sputtering gas	Substrate temperature	Gas pressure
BST film	3 inch	4 inch	140 W	Ar/O ₂	400 °C	50 mT

Fig. 1. XRD patterns for BST thin film on the substrate of STO. Diffraction peaks from a STO (100) substrate are marked in the figure.

Fig. 2. (color online) AFM images of the sample.

The gold electrodes were prepared by standard photolithography and ion beam etching of a 20 nm thick titanium/200 nm thick gold film deposited on top of the BST film. The interdigitated capacitor structure of 16 mm $\times$ 10 mm size was composed of 5 μ m wide gold lines separated by 15 μ m wide gaps, as shown in Fig.3.

Fig. 3. (color online) Scheme of the sample geometry.

We used a THz time domain spectrum (THz-TDS) system produced by the Zomega Terahertz Corporation of the US to measure the transmittance spectrum at room temperature. The fiber femtosecond laser beam was divided into two beams (named the pump beam and the probe beam, respectively) by a polarized beam splitter. The THz pulses transmitted through the sample were detected using a usual electro-optic sampling scheme with another 1 mm thick ZnTe (110) crystal and a pair of balanced Si photodiodes. The TDS probes the in-plane response of the sample. The measured frequency resolution is 10 GHz.

3. Results and discussion

The measurements were carried out in two steps[8]: firstly, measurement of a reference wave form $E_{ref}(\omega, V)$ with a bare substrate STO and the result was shown in Fig.4(a); secondly, measurement of a signal wave form $E_s(\omega, V)$ with different bias electric field with the thin film on a substrate as shown in Fig.4(b), where the V is the bias external field. The transmission is extracted from the ratio of the Fourier-transformed amplitude spectra of the signal and reference, defined as:

$$\tau(\omega, V) = \frac{E_s(\omega, V)}{E_{ref}(\omega, V)} \quad (1)$$

As can be seen, the signal waveforms transmitted through the BST film show little time delay with increasing bias field, as shows in Fig.4(b), the transmittance waveform shifts about 0.35 ps when the bias electric field up to 30 V, compared to the waveform without bias field. And that the transmitted

THz signal decreases with the increasing electric field.

Fig. 4. (color online) THz wave forms: (a) sample without electrodes; the data serve for the evaluation of the thin film properties without electric field and (b) sample with electrodes; 0 V is a reference wave form without field and 30 V is a difference signal waveform.

Both the real parts and imaginary parts of the dielectric constant of the BST thin film have been evaluated by numerically inverting the expression for $T(\omega)$ [17]:

$$T(\omega) = \frac{2N_f(N_s + 1) \exp[i\alpha(N_f - 1)d_f / c]}{(N_f + 1)(N_f + N_s) + (1 - N_f)(N_f - N_s) \exp[i\alpha N_f d_f / c]} \quad (2)$$

where, d_f is the film thickness, c is the speed of light and $N_s = \sqrt{\varepsilon(\omega)}$ is the complex optical refractive index of the substrate as a function of ω . The technique allows us to determine the dielectric response of the thin film in the range from 0.2 THz to 1.2 THz[17]: $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$.

Figure 5 shows the complex dielectric spectra of the BST film under different values of the bias electric field. The detectable frequency range is from 0.2 THz to 1.2 THz. It is clearly seen in Fig.5 that the electric-field-induced changes are significantly weaker when below 25 V. The both real parts ε' and the imaginary parts ε'' were demonstrated in Fig.5, which showed both the real part and the imag part of the permittivity decrease with an increasing bias electric field. As can be seen from Fig.5 (a), the value of the permittivity is about 6000, the values of the calculated are larger than the previous results [3], which is consistent with the other report [18], the calculated dielectric constant are inversely proportional to the thickness of the film.

Fig. 5.(color online) Measured frequency dependent dielectric spectra of BST thin film in the THz range (symbols) and their fits by a single damped harmonic oscillator model (lines). Frequency dependences of (a) the real part and (b) the imaginary part of the complex dielectric constant of BST film with different external electric fields at room temperature.

Fig. 6. The dielectric constant as a function of applied voltage for different frequencies.

Figure 6 shows the electric field tunability of the complex permittivity from 0.2 THz to 1.2 THz. From the figures, we could get the tunability of the dielectric constant for different bias field using the following equations:

$$tunability = \frac{|\varepsilon(V) - \varepsilon(0)|}{\varepsilon(0)} \times 100\% \quad (3)$$

According to the Fig.6, the measured real part decrease up to 74.8% at the highest fields at 0.2 THz and the imaginary part decrease up to 33.6% at the highest fields at 1.2 THz.

In order to quantitatively describe the degree of the tunability of the permittivity, we adopt the damped harmonic oscillator model to analyze the characters of the BST film. In Fig.5(a), we fitted the experimental data by a damped harmonic oscillator model, and the model was given by Eq. (4)[19, 20].

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{f}{\omega_0^2 - \omega^2 - i\omega\gamma} \quad (4)$$

where ω is the angular frequency of the incident terahertz wave, and ε_{∞} is a cumulative contribution to the permittivity caused by higher-frequency excitations such as hard phonons and electrons[21] and considered to be a constant. f is the oscillator strength, γ is the damping coefficient; and ω_0 is the external field dependent soft mode frequency[22].

From the Table II, the soft mode frequency ω_0 varies from 82.43 cm^{-1} to 82.96 cm^{-1} when the bias electric field from 0 V increased to 30 V, the parameters are in reasonable agreement with their values reported for the film[8], and it indicates soft-mode hardening. When the bias field is 30 V, the largest field induced change in the soft mode frequency reaches 0.53 cm^{-1} , which is $\sim 0.64\%$ of the frequency of the soft mode. In the whole experiment process, the soft mode is not heavily damped and the γ haven't changed much and it is about 20 cm^{-1} .

TABLE II. Summary of the evaluated characteristics of the thin-film structures.

Bias field	0V	5 V	10V	15 V	20V	25 V	30V
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f	1×10^7	1×10^7	9.9×10^6	9.9×10^6	1×10^7	1×10^7	9.9×10^6
ω_0	82.43	82.56	82.57	82.73	82.77	82.78	82.96
γ	19.25	19.99	20.75	22.79	21.20	22.47	23.42

To explain the electric-field-induced soft-mode characters, we adopt the model in Ref. [23]. The soft-mode frequency ω_0 then changes with the applied bias electric field. In the weak-field limit ($E < 20$ kV/cm) the field-induced soft-mode hardening is then expressed in the following way [24]:

$$\omega_0(E) = \omega_0(0) \sqrt{1 + 3\beta [\epsilon_{vac} f / \omega_0^2(0)]^3 E^2} \quad (5)$$

where β is the coefficient that characterizes the fourth-order anharmonicity of the soft-mode potential minimum[23] and ϵ_{vac} is the vacuum permittivity, we adopt the $\omega_0(0)$ value of the soft mode eigenfrequency at a given temperature and without electric bias. f is the strength as in the Table II. In our terahertz experiment with bias field, because the BST film and the STO substrate are both in the paraelectric phase, there is no spontaneous polarization. The system of interdigitated electrodes implies that the adjacent gaps between the electrode fingers are poled with opposite field. This means that the term of E in Eq.(5) should be contributes to the electric-field-induced soft-mode hardening. The experimentally obtained electric-field dependencies of the soft mode in BST film was fit in Table II. It describe well the basic features: the variation of $\omega_0(E)$ with field tends to be linear even for low applied fields. Both these phenomena are explained by the bias field E .

By investigation from the formula (4) and Table II, we found out that the original of the permittivity of the film are decreasing with the harden of the soft mode, which are determined by the bias field increasing from the Eq.(5). Figure 7 displayed the modulation of the permittivity versus frequency at different values of the field. Such a variation in the dielectric spectrum could be used in the modulator in the terahertz range. We can also see great potential for applications of active barium strontium titanate film in the design and fabrication of active metamaterials for the terahertz regime.

Fig.7. (color online) Electric field induced modulation of the permittivity and losses of BST films for different values of the external electric field.

4. Conclusion

To summarize, the electric field-induced tunable dielectric properties of the BST film in the THz

frequency range are systemically discussed. The real and the imaginary part dielectric spectrum of thin film irradiated by electric fields exhibit a tenability up to 74.8% and 33.6% at the voltage of 30 V. This tunability of the real part is attributed to the hardening of the soft mode. Using such electrically controllable thin films would considerably provide the methods in oxides potential applications for tunable device applications in multifunctional responses.

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