All-Inorganic Flexible Ba$_{0.67}$Sr$_{0.33}$TiO$_3$ Thin Films with Excellent Dielectric Properties over a Wide Range of Frequencies

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ABSTRACT: With rapid advances in flexible electronics and communication devices, flexible dielectric capacitors exhibiting high permittivity, low loss, and large electric-field tunability over a wide frequency range have attracted increasing attention. Here, a large-scale Ba$_{0.67}$Sr$_{0.33}$TiO$_3$ (BST) dielectric thin film sandwiched between SrRuO$_3$ (SRO) bottom electrode and Pt top electrode is fabricated on a flexible mica substrate. The mica/SRO/BST/Pt capacitor exhibits a dielectric constant ($\varepsilon_r'$) of more than 1200, a loss tangent [tan(δ)] as low as 0.16, and a tunability of 67% at low frequencies around 10 kHz. Simultaneously, the capacitor can retain an $\varepsilon_r'$ of 540 and a tan(δ) of 0.07 at microwave frequencies, e.g., 18.6 GHz. Moreover, even when the capacitor is bent to a small radius of 5 mm or undergoes 12 000 bending cycles (at 5 mm radius), almost no deterioration in $\varepsilon_r'$, tan(δ), and tunability is observed. The excellent dielectricity and mechanical flexibility and durability endow the mica/SRO/BST/Pt capacitor with huge potential for flexible electronic and microwave applications.

KEYWORDS: flexible capacitor, (Ba,Sr)TiO$_3$, mica, dielectricity, microwave frequencies

1. INTRODUCTION

The new era of Internet of things promises a widespread use of flexible electronic devices, such as paperlike displays, bendable smartphones, and electronic skins. Notably, almost all of these flexible devices need the integration of a key component, namely, dielectric capacitors, to function properly. Therefore, flexible, lightweight, and scalable dielectric capacitors have been subjected to extensive research over the past few years. So far, a variety of flexible capacitors based on polymers, inorganic/polymer nanocomposites, and inorganic/flexible substrate heterostructures have been well developed, and their low-frequency (frequency below 1 MHz) dielectric properties, particularly energy density and charge/discharge efficiency, were generally concerned. However, the dielectric properties in the microwave region (frequency on the order of gigahertz) remain almost unexplored for these flexible capacitors. Indeed, the capacitors exhibiting tunable dielectric constant at microwave frequencies can find wide applications in the field of communication, such as waveguide phase shifters, frequency agile filters, and tunable oscillators. Hence, developing flexible capacitors with good dielectric properties over a wide frequency range (extending to the microwave region) is quite appealing.

While polymer-based capacitors are flexible enough, they typically exhibit limited thermal and operational stabilities, as well as poor compatibility with conventional inorganic electronic circuits. These drawbacks may be circumvented in all-inorganic flexible capacitors, which consist of the stack of inorganic dielectric layers on flexible substrates. For the inorganic dielectric layers, barium strontium titanate (Ba$_{x}$Sr$_{1-x}$TiO$_3$; BST) appears to be the best choice because it is among the lead-free materials with the highest dielectric constant ($\varepsilon_r'$) at room temperature.$^{21}$ More specifically, the BST possesses a distribution of $\varepsilon_r'$ ranging from several hundred to more than one thousand depending on the Ba/Sr ratio. The maximum $\varepsilon_r'$ at room temperature is achieved when the molar fraction of Ba approaches 0.7 because BST at this composition has a Curie temperature around room temperature.$^{21}$ At the Curie temperature, the transition between ferroelectric and paraelectric phases occurs, giving rise to a very high dielectric constant. Besides, the BST also has low dielectric loss [tan(δ)], high breakdown voltage, and large electric-field tunability of $\varepsilon_r'$, which makes BST a promising
candidate dielectric for dynamic random access memory and tunable microwave devices.22–24

However, the integration of BST on flexible substrates is still challenging because the growth of high-quality BST thin films typically requires high temperatures (>600 °C), which limits the selection of flexible substrates. Commercially available flexible polymer substrates, e.g., polyimide (PI),25 polyester [poly(ethylene terephthalate)],26 poly(dimethylsiloxane),27 and polyethylene naphthalate (PEN),28 have relatively low melting temperatures (T_m < 350 °C). Some inorganic substrates can be flexible when made ultrathin, e.g., ultrathin glass and silicon (~50 μm), but they are fragile and expensive.29,30 Alternatively, one may first grow thin films on rigid substrates and then transfer the free-standing films onto flexible substrates.15,31 However, this “grow-transfer” technique involves a tedious multistep process, and it can hardly produce large-scale films. Recently, mica has emerged as a popular flexible substrate for the van der Waals growth of two-dimensional materials and oxide thin films.32 Mica has mechanical flexibility, chemical inertness, high thermal stability (T_M > 700 °C), and high transparency. Additionally, the mica owns a layered structure, enabling it to be exfoliated down to ~10 μm with an atomically smooth cleavage surface and enhanced flexibility. Therefore, mica has been widely used as a flexible substrate for the development of all-inorganic flexible electronics with novel functionalities. For example, Jiang et al.33 developed flexible ferroelectric memories consisting of lead zirconium titanate (PZT) thin films on mica substrates, which exhibited a large polarization of 60 μC/cm^2 and almost no polarization degradation after being bent to 2.5 mm radius for 1000 cycles. In addition, Yang et al.13 prepared flexible mica/SrRuO_3 (SRO)/BaTi_0.95Co_0.05O_3 (BTCO)/Au resistive switching memories with an ON/OFF ratio of more than 50, which could withstand a bending radius down to 1.4 mm and 10,000 bending cycles. Because BST has a similar perovskite structure as PZT and BTCO, it is therefore expected that the high-quality BST films with desired dielectric properties [high ε_r’, low tan(δ), and large tunability] can be well integrated with the flexible mica substrates.

In this work, polycrystalline BST dielectric thin films sandwiched between SRO bottom electrodes and Pt top electrodes have been successfully fabricated on mica substrates (Figure 1a). The composition of Ba/Sr = 0.67/0.33 is chosen for BST because this composition is near the optimal one, which shows the highest room-temperature ε_r’, as introduced earlier. The mica/SRO/BST/Pt capacitors exhibit excellent dielectric properties in both low-frequency and microwave regions [ε_r’ = 1200 and tan(δ) = 0.16 @ 10 kHz, and ε_r’ = 540 and tan(δ) = 0.07 @ 18.6 GHz], and their dielectric performances show almost no deterioration after being bent to a small radius of 5 mm or repeatedly bending for 12,000 cycles (at 5 mm radius). The mechanisms for the performance degradation are also investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Fabrication of Thin Films. A flexible mica substrate of 15 × 15 mm^2 in area and ~10 μm in thickness was prepared by stripping a thin layer from a thick fluorophlogopite mica plate [KMg_3(AlSi_3O_10)-F_2] (Changchun Taiyuan Co.) in clean water with the aid of a polyimide tape. Then, SRO/BST/Pt heterostructures were sequentially grown on the mica substrate using pulsed laser deposition (PLD) (Shenyang Kecheng Vacuum Tech Co.) with a KrF excimer laser (λ = 248 nm) operated at a laser energy of 90 mJ and a
Figure 2. (a) Typical polarization–electric field (P–E) hysteresis loops of the mica/SRO/BST/Pt capacitor (frequency: 10 kHz) with different applied voltages. PFM (b) amplitude and (c) phase images of the BST film after box-in-box writing, where the outer box (2 × 2 μm²) was written by −8 V, whereas the inner box (1 × 1 μm²) was written by +8 V. (d) PFM amplitude and phase hysteresis loops.

repetition rate of 5 Hz. Both SRO and BST films were grown at 680 °C and under 15 Pa oxygen pressure. After it, the SRO/BST films were cooled to room temperature at a rate of 5 °C/min under 10⁴ Pa oxygen pressure. Then, Pt top electrodes with a diameter of 200 μm were grown on the SRO/BST films at room temperature and in high vacuum (10⁻⁴ Pa) through a shadow mask.

2.2. Characterizations. The transmission spectra were recorded using UV–vis spectroscopy (UV1800PC). The crystal structures were characterized by X-ray diffraction (XRD) (Bruker D8). The characteristics of surface morphology and piezoresponse force microscopy (PFM) were performed using a commercial atomic force microscope (AFM) (Cypher Asylum Research). The cross section of the sample was characterized by transmission electron microscopy (TEM) (Tecnai G2-F20). The TEM sample was prepared following the steps: cutting, grinding, polishing, and ion milling. The crystalline qualities of the BST and SRO were unambiguously confirmed by transmission electron microscopy (TEM) (Tecnai G2-F20). The direct current (DC) current–voltage (I–V) characteristics were measured with a source meter (Keithley 6430). The dielectric properties in the frequency range of 500–10⁶ Hz were measured using an inductance–capacitance–resistance meter (Agilent E4980A) with an alternating current (AC) voltage of 0.1 V. The microwave dielectric measurements were made with a network analyzer (Agilent N5244A) in a shielded resonant cavity (see Figure S1 and ref 34 for details). The tests under bending were performed when the flexible capacitor was taped on homemade semicircular iron molds with different radii. The repeated bending cycles were applied by a homemade uniaxial stretching machine.

3. RESULTS AND DISCUSSION

Figure 1a shows the photograph of an actual mica/SRO/BST/Pt flexible capacitor with a lateral size of 15 × 15 mm², where the mica substrate has been peeled off to ~10 μm thick. The capacitor is capable of being bent to millimeter-scale radii, demonstrating the good mechanical flexibility. In addition, the mica/SRO/BST film is seen to be semitransparent by eyes, whereas the mica substrate and the mica/BST film are quite transparent (Figure 1b).

The transmittances of both the mica substrate and mica/BST film are above 50% in the wavelength range of 400–900 nm. By contrast, the transmittance of the mica/SRO/BST film drops to below 20% in the same wavelength range. These results suggest that the BST layer itself exhibits good transparency, and it may be used in flexible screens if it is able to be grown on a transparent electrode like indium-tin oxide.

Figure 1c displays the XRD θ–2θ scan patterns (2θ = 20–50°) of a mica/SRO/BST bilayer film together with two control samples, i.e., a mica/SRO film and a mica substrate. The characteristic (00l) peaks from the mica substrate can be easily identified. Besides, the (00l), (110), and (111) peaks from BST and SRO are also observed, suggesting the polycrystalline nature of BST and SRO films. While the (001) and (110) peaks from BST and SRO may overlap, the presence of the (111) peak only in the BST film unambiguously confirms that a perovskite phase of BST (either ferroelectric or paraelectric or a mixture of both) exists. The average lattice constants of BST are estimated to be a = 3.95 Å and c = 3.96 Å, consistent with those reported previously.35,36

Figure 1d shows a typical topography image for a 3 × 3 μm² area of the mica/SRO/BST film. The film surface exhibits a granular feature, and it is relatively flat with a roughness of ~3.9 nm. As can be seen in the cross-sectional TEM image (Figure 1e), the BST layer is tightly adhered to the SRO layer, and their interface is sharp. In addition, the BST layer exhibits densely packed columnar grains, which are ~300 nm in height and ~50 nm in diameter. These results demonstrate the good crystalline qualities of the BST and SRO films grown on the mica substrate.

For BST at the composition of Ba/Sr = 0.67/0.33, the ferroelectric and paraelectric phases may coexist. The ferroelectric properties of the BST film grown on the mica substrate were therefore studied via the P–E hysteresis loop measurement and PFM. Figure 2a shows typical P–E hysteresis loops measured at 10 kHz with different applied voltages for the mica/SRO/BST/Pt capacitor. The loops are quite slim with
noticeable nonlinearity. As the applied voltage increases, the loop nonlinearity increases, indicating the gradual saturation of BST’s polarization. At the applied voltage of 6 V, a small remanent polarization ($P_r$) of $\sim 2 \mu C/cm^2$ and a coercive field ($E_c$) of $\sim 20$ kV/cm can be observed. Similar loops with comparable $P_r$ and $E_c$ values were observed for the BST films grown on rigid substrates, which indeed suggests the mixed ferroelectric–paraelectric behavior.\(^7\text{,}^{38}\) Figure 2b,c presents the PFM amplitude and phase images of the mica/SRO/BST film after a box-in-box writing. The outer $2 \times 2$ $\mu m^2$ region was first written with a tip bias of $-8$ V, followed by another tip bias of $+8$ V applied to the inner $1 \times 1$ $\mu m^2$. As seen in the phase image (Figure 2c), only a partial of the $-8$ V-written region shows white color, whereas the as-grown and $+8$ V-written regions exhibit mainly brown color. This phase contrast indicates that there are some switchable domains existing in the BST film. However, due to the coexistence of the paraelectric phase, a full switching of domains cannot be realized in the $-8$ V-written region. Additionally, as seen in Figure 2d, the PFM phase loop shows a sharp $\sim 180^\circ$ switching, whereas the amplitude loop shows a butterfly-like shape. These PFM results demonstrate that the BST film grown on the mica substrate contains a ferroelectric phase and thus it can exhibit ferroelectric switching behavior. Now, let us focus on the dielectric properties of the flexible mica/SRO/BST/Pt capacitor. Figure 3b,c shows the typical $\varepsilon'_r$ and $\tan(\delta)$ as a function of frequency in the bending states with different radii. The bending radii are indicated in (c), and “flat-1”, “flat-2”, and “flat-3” denote the initial flat state, second flat state after being bent to $R = 5$ mm, and third flat state after being bent to $R = 2$ mm. The inset in (b) illustrates that a smaller bending radius corresponds to a larger extent of bending.\(^39\text{,}^{40}\) In the initial flat state, the $\varepsilon'_r$ decreases monotonously with frequency (Figure 3b), consistent with the fact that fewer dipoles are able to follow the AC field with higher frequencies. At the frequency of 10 kHz, the $\varepsilon'_r$ can reach up to $\sim 1210$, whereas the $\tan(\delta)$ is as low as $\sim 0.16$ (Figure 3b,c). These dielectric properties are as good as those of BST and other dielectric films grown on rigid substrates,\(^38\text{,}^{41}\) which can be attributed to the good quality of our BST film. The growth of a high-quality BST film on the mica substrate is enabled by the SRO buffer layer, which is flat and highly conductive (Figure S2). If the SRO buffer layer is replaced with the Pt buffer layer, the BST film exhibits much poorer electrical properties (Figure S3).

After the measurement in the initial flat state, the capacitor was sequentially bent to the radii ($R$) of 20, 15, 10, and 5 mm in the flex-out bending mode, and the corresponding dielectric spectra were recorded. As shown in Figure 3b,c, the $\varepsilon'_r$ and $\tan(\delta)$ in these bending states remain almost unchanged compared with those in the initial flat state. After the bending with $R = 5$ mm, the capacitor was flattened again and the $\varepsilon'_r$ and $\tan(\delta)$ could be fully recovered. These results demonstrate the good mechanical flexibility of our mica/SRO/BST/Pt capacitor. However, when the capacitor was further bent to $R = 2$ mm, the spectrum of $\varepsilon'_r$ shifts downward, whereas that of $\tan(\delta)$ shifts upward (purple lines in Figure 3b,c). More specifically, at the frequency of 10 kHz, the $\varepsilon'_r$ drops to $\sim 930$ and the $\tan(\delta)$ increases to $\sim 0.47$. The degradation of dielectric properties seems to be persistent because the $\varepsilon'_r$ and $\tan(\delta)$ cannot be recovered after re-flattening the capacitor (orange lines in Figure 3b,c). Therefore, it is deduced that the BST film undergoes permanent damage after being bent to $R = 2$ mm.

Besides the $\varepsilon'_r$ and $\tan(\delta)$ spectra, the characteristics of $\varepsilon'_r$ (@ 10 kHz) versus applied electric field ($E$) were also measured for the flexible BST capacitor in the flat and bending states. As shown in Figure 3d, in the initial flat state, the $\varepsilon'_r$ at $E \approx 0$ exhibits a maximum value of $\sim 1210$, but it decreases nonlinearly to $\sim 420$ as $E$ increases to 133 kV/cm. The decrease of $\varepsilon'_r$ with increasing $E$ is due to the polarization gradually getting saturated at high electric fields, typical for nonlinear dielectrics like BST. In addition, the observation of two $\varepsilon'_r$ maxima located very close to $E = 0$ implies the mixed ferroelectric–paraelectric behavior in the BST film, consistent with the results of $P$–$E$ loops.\(^42\text{,}^{43}\) The ratio of electric-field-induced change in $\varepsilon'_r$ can be defined as a tunability

$$\text{tunability (\%)} = \frac{\varepsilon'_r'(0) - \varepsilon'_r'(E)}{\varepsilon'_r'(0)}$$

where $\varepsilon'_r'(0)$ and $\varepsilon'_r'(E)$ are the $\varepsilon'_r$ values at zero-DC field and $E$ (here, $E = 133$ kV/cm), respectively. The tunability of our mica/SRO/BST/Pt capacitor is calculated to be $\sim 67\%$, which is comparable to those achieved in BST and other dielectric films grown on rigid substrates.\(^44\text{,}^{45}\)

Figure 3d also illustrates that the $\varepsilon'_r$–$E$ characteristics almost do not change even when the capacitor is bent to $R = 5$ mm. However, when a further bending with $R = 2$ mm is performed, the $\varepsilon'_r$–$E$ curve exhibits a noticeable downward shift and the value of $\varepsilon'_r'(0) - \varepsilon'_r'(E)$ decreases. These changes are persisted after re-flattening the capacitor, indicating that the capacitor undergoes permanent degradations of both zero-DC field dielectric properties and tunable dielectric performance after being bent to $R = 2$ mm.

To demonstrate that the flexible mica/SRO/BST/Pt capacitor is sufficiently reliable to fulfill the requirement of flexible electronic applications, the capacitor was bent ($R = 5$ mm)
mm)/flattened repeatedly, and its dielectric properties were measured after various bending cycles. Figure 4a displays the schematic diagram of an automatic apparatus, which was used to perform the multiple bends for our flexible capacitor. As shown in Figure 4b−d, the $\varepsilon_r'$ and tan(δ) spectra as well as the $\varepsilon_r'$−$E$ characteristics remain roughly identical after being bent for 12 000 cycles, suggesting that the dielectric properties of the flexible BST capacitor are immune to up to 12 000 bending cycles. As the bending cycle increases to 16 000, the dielectric properties degrade slightly, and the degradation becomes more significant after another 4000 bending cycles. Nevertheless, an $\varepsilon_r'$ of $\sim$940, a tan(δ) of $\sim$1.75, and a tunability of $\sim$63% can be retained after the total bending cycles of 20 000.

For our flexible mica/SRO/BST/Pt capacitor, good mechanical flexibility and durability are observed not only in the flex-out bending mode but also in the flex-in bending mode. As shown in Figures S4 and S5, flex-in bending with R = 5 mm or bending repeatedly for 12 000 cycles does not degrade the dielectric performance. However, further decreasing R or increasing bending cycles leads to the degradation. These results are similar to those obtained in the flex-out bending mode, suggesting that the degradation of dielectric performance in the mica/SRO/BST/Pt capacitor depends on the magnitude of strain (or accumulated strains) rather than the type of strain (tensile or compressive).

Figure 5a depicts a schematic setup for measuring microwave dielectric properties, which mainly consists of a shielded resonant cavity and a network analyzer. The $\varepsilon_r'$ and tan(δ) at 18.6 GHz of the mica/SRO/BST/Pt capacitor after various bending cycles are shown in Figure 5b. In the initial flat state, the $\varepsilon_r'$ and tan(δ) are $\sim$540 and $\sim$0.07, respectively. Such a value of $\varepsilon_r'$ at a microwave frequency is indeed quite high, comparable to those obtained in rigid BST capacitors.46,47 Moreover, the $\varepsilon_r'$ almost does not change after the capacitor is bent for 10 000 cycles (@ R = 5 mm), but it decreases to $\sim$460 after 20 000 bending cycles. Nevertheless, the tan(δ) remains below 0.1 even after 20 000 bending cycles. Therefore, similar to those at low frequencies, the dielectric properties at microwave frequencies of our mica/SRO/BST/Pt capacitor are also very stable against mechanical bending.

To show the up-to-date research progress in flexible capacitors, the comprehensive dielectric and mechanical performances of some representative mica- and polymer-based capacitors are compared, as shown in Table 1. Notably, our mica/SRO/BST/Pt capacitor emerges as the first flexible capacitor ever reported, which can exhibit an $\varepsilon_r'$ higher than 500 and simultaneously a tan(δ) lower than 0.1 at a microwave frequency. In addition, the mica/SRO/BST/Pt capacitor can also exhibit an $\varepsilon_r'$ of more than 1200 and a tan(δ) of below 0.2 at low frequencies (e.g., 10 kHz), which are comparable to or even superior to those of other capacitors. Moreover, the tunability of $\sim$67% achieved in our mica/SRO/BST/Pt capacitor is the highest among all of the capacitors listed in Table 1. Last but not the least, the mica/SRO/BST/Pt capacitor be bent to R = 5 mm and endure 12 000 bending cycles (@ R = 5 mm), which are among the best mechanical properties of the reported capacitors. In a word, our mica/SRO/BST/Pt capacitors have excellent dielectricity in a wide frequency range as well as good mechanical flexibility and durability.

Below, we proceed to analyze the degradation mechanism of the mica/SRO/BST/Pt capacitor in the flex-out bending tests (because the results of flex-out and flex-in bending tests are similar, only the former are analyzed in detail to reveal the mechanism). Two capacitors, the one after being bent to R = 2 mm (denoted “cap-1”) and the other after undertaking 20 000 bending cycles at R = 5 mm (denoted “cap-2”), were systematically compared with their respective initial flat states, in terms of morphology, impedance, and DC conductivity. First, the AFM topography images of cap-1 and cap-2 after the
bending tests show the presence of microcracks (Figure S6). The microcracks often act as leakage paths,55,56 which may be the origin for the increase in dielectric loss.

Next, the complex impedance data of cap-1 and cap-2 were analyzed to gain deeper insights into the degradation of dielectric properties, using the Nyquist plot of the imaginary component of impedance \((Z)\) versus real component of impedance \((Z')\). Typically, the Nyquist plot would be composed of two semicircles, each semicircle representing a distinct process whose time constant is sufficiently separated from the other. The semicircle at higher frequencies represents the bulk (grains) contribution, whereas at lower frequencies represents grain boundary and film/electrode interface contributions.57 As shown in Figure 6, only one semicircular arc is observed in each Nyquist plot for cap-1 and cap-2 in the initial flat state and after bending. This semicircular arc can be assigned to the BST bulk, allowing for the fact that the BST bulk contributes mainly to the dielectric response in the frequency range of \(500-\)\((1 \times 10^{5})\) Hz.58 Therefore, the mica/SRO/BST/Pt capacitor may be modeled using an equivalent circuit, which combines a series resistance \((R_s)\) and an RC circuit consisting of a constant phase element (CPE) and a parallel resistance \((R_p)\). The \(R_s\) represents the contact resistance between the BST film and the electrode. The RC circuit represents the BST bulk, where the leakage contribution is reflected by \(R_p\) and the nonideal Debye-like dielectric behavior is described by CPE.59 The impedance of a CPE is defined by

\[
Z_{\text{CPE}}(\omega) = [A(j\omega)^n]^{-1}
\]

where \(A\) is the pseudocapacitance and \(n\) is a quantity between 0 and 1 describing the deviation from an ideal capacitor. For \(n = 1\), the CPE becomes an ideal capacitor with capacitance equaling \(A\), whereas, for \(n = 0\), the CPE represents an ideal resistor with resistance equaling \(1/A\).

As shown in Figure 6, the complex impedance data of both cap-1 and cap-2 can be well fitted using the equivalent circuit model. The fitting parameters are summarized in Table 2. For cap-1, the values of CPE-related parameters \((A\) and \(n)) remain almost unchanged after being bent to \(R = 2 \text{ mm}\), whereas the \(R_p\) decreases dramatically from \(1.1 \times 10^{7}\) to \(2.9 \times 10^{5}\) \(\Omega\) and the \(R_s\) increases from \(1.1 \times 10^{3}\) to \(7.0 \times 10^{7}\) \(\Omega\). The small changes in CPE-related parameters suggest that the BST bulk is nearly unaffected by the bending. The decrease in \(R_p\) is well correlated with the microcracks formed after a large extent of bending, which increases the leakage current. The enhancement in \(R_s\) may be due to the film/electrode contact becoming poor owing to the bending. Likewise, for cap-2, the variation of CPE-related parameters, \(R_p\) and \(R_s\), is similar to those for cap-1 (Table 2). It is therefore deduced that the cyclical bending leads to similar degradation behavior as the large extent of bending, i.e., the formation of microcracks increasing the leakage current and the deterioration of film/electrode contact.

The enhanced leakage current due to microcracks is responsible not only for the degradation of zero-DC field dielectric properties (as discussed above) but also for the degradation of tunable dielectric performance. It is known that the tunable dielectric constant results from the polarization increasing nonlinearly with the electric field. For the capacitor after bending, the enhanced leakage current can reduce the effective field used for inducing the polarization. Therefore, the dielectric constant variation \([\varepsilon_r'(0) - \varepsilon_r'(E)]\) is smaller in the capacitors after bending than in those before bending (Figures 3d and 4d).

| Table 1. Comparison of Dielectric Properties between our Flexible BST Capacitor and Other Flexible and Rigid Capacitors |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | mica/BST        | mica/PZT        | mica/BLT        | mica/BZT        | PVDF/BCZT       | silicon/PZT     | Ag/nanopaper    | LaAlO₃/BST     |
| \(\varepsilon_r'\) | 1200            | 540             | 1950            | 460             | 500             | 80              | 90              | 540            | 700            | 1660           | 1057           |
| \(\theta_{f} (\text{Hz})\) | 10k             | 18.6G           | 1k              | 1M              | 10k             | 10k             | 10k             | 10k            | 1.1G           | 10k            | 10G            |
| \(\tan(\delta)\) | 0.16            | 0.07            | 0.005           | 0.25            | 0.05            | 0.25            | 0.05            | 0.172          | 1.1G           | 10k            | 10G            |
| \(\theta_{f} (\text{Hz})\) | 10k             | 18.6G           | 10k             | 10k             | 1.1G           | 10k            | 10G            |
| tunability (%)\(^a\) | 67              | 11              | 43              | 42              | 18              | 56              |
| \(R_m\) (mm)    | 5               | 2.2             | 2.5             | 1.4             | 4               | 5               | 5               |
| \(N_{bending}\) | 12000           | 10000           | 1000            | 10000           | 1000            | 1000            | 1000            |
| \(\varnothing\) R (mm) | 5 mm            | 2.2 mm          | 5 mm            | 1.4 mm          | 4.5 mm          | 5 mm            |
| reference       | this work       | ref 48          | ref 33          | ref 49          | ref 50          | ref 51          | ref 52          | ref 53         |

\(^a\)This is a reference rigid capacitor. \(^b\)A benchmark for the evaluation of tunability was adopted: only the values of \(\varepsilon_r'(0)\) and \(\varepsilon_r'(E = 133 \text{ kV/cm})\) were used in eq.1 to calculate the tunability for all of the capacitors.

Debye-like dielectric behavior is described by CPE.59 The impedance of a CPE is defined by

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| Table 2. Parameters Obtained after Fitting the Complex Impedance Data Using the Equivalent Circuit Model |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| state           | \(R_s\)         | \(R_p\)         | \(A\)           | \(n\)           |
| cap-1 initial   | 1.1 \times 10^3 | 1.1 \times 10^3 | 3.7 \times 10^{-10} | 0.94          |
| R = 2 mm        | 7.0 \times 10^3 | 2.9 \times 10^3 | 3.7 \times 10^{-10} | 0.92          |
| cap-2 initial   | 6.9 \times 10^3 | 5.8 \times 10^3 | 3.0 \times 10^{-10} | 0.96          |
| 20 000 cycles   | 3.0 \times 10^3 | 3.1 \times 10^3 | 3.2 \times 10^{-10} | 0.94          |
Figure 7. Typical current–voltage (I–V) characteristics of (a) cap-1 and (d) cap-2. Replots of I–V characteristics (voltage range: 0 to −3 V) for (b) cap-1 and (e) cap-2 in log–log scale. Replots of I–V characteristics (voltage range: −3 to −6 V) for (c) cap-1 and (f) cap-2 as Ln(I/V^2) vs 1/V. The dotted lines are the fitting lines.

To further understand the enhanced leakage current arising from microcracks, the DC current–voltage (I–V) characteristics were measured for cap-1 and cap-2. As shown in Figure 7a, the leakage current in cap-1 increases significantly, from ~149.8 μA (@ 6 V) in the initial flat state to ~873.7 μA (@ 6 V) after the bending with R = 2 mm. Similar enhancement in leakage current is observed in cap-2, which undertakes 20,000 bending cycles (Figure 7d).

The conduction mechanisms at low and intermediate voltages (|V| < 3 V) were first analyzed. The I–V characteristics in this voltage range are replotted in the log–log scale for both cap-1 and cap-2, as shown in Figures 7b,e and S7a,c. The log(I)–log(V) curves show three characteristic linear regions, in accordance with a space-charge-limited current (SCLC) model. Region (i) at |V| < ~0.4 V exhibits a slope of ~1, indicating typical Ohmic conduction behavior

\[ J = \frac{qn_e \mu V}{d} \]  

where \( J \) is the leakage current density, \( q \) is the charge of an electron, \( n_e \) is the electron density, \( \mu \) is the mobility of the electrons (0.001 cm^2/(Vs)) for BST, \( V \) is the applied voltage, and \( d \) is the sample thickness. The \( n_e \) of cap-1 in the initial state is calculated to be \( 5.6 \times 10^{14} \) cm\(^{-3} \), which increases to 2.2 \( \times 10^{15} \) cm\(^{-3} \) in the bending state with \( R = 2 \) mm. For cap-2, the \( n_e \) increases from \( 1.1 \times 10^{14} \) cm\(^{-3} \) in the initial state to \( 2.1 \times 10^{15} \) cm\(^{-3} \) after 20,000 bending cycles. The increase in \( n_e \) may be caused by the defects in the microcracks contributing more free electrons.

In region (ii) at ~0.4 V < |V| < ~2 V, the number of injected electrons is greater than that of thermally stimulated free electrons, thus leading to the SCLC behavior with a slope of ~2. The current density from SCLC follows the modified Child’s law, which can be expressed as

\[ J = \frac{9}{8} \varepsilon_0 e \mu \frac{V^2}{d^3} \]  

where \( \varepsilon_0 \) is the permittivity of free space and \( \theta \) is the ratio of free-to-trapped electrons.

As the applied voltage enters region (iii) (~2 V < |V| < 3 V), the log(I)–log(V) slope abruptly increases to much greater than 2, indicating a trap-filling process. The voltage where the slope increases abruptly is called the trap-filled limit voltage (V\(_{\text{TFL}}\)), which can be used to calculate the trap density (\( N_t \))

\[ N_t = \frac{9}{8q} e \varepsilon_0 \frac{V_{\text{TFL}}}{d^2} \]  

where an average value of \( V_{\text{TFL}} \) is taken if the \( V_{\text{TFL}} \) values in positive and negative voltage regions are different. For cap-1, the average \( N_t \) value increases from \( 3.9 \times 10^{17} \) cm\(^{-3} \) in the initial flat state to \( 4.4 \times 10^{17} \) cm\(^{-3} \) after being bent to \( R = 2 \) mm. Similarly, the cap-2 also exhibits an increase in average \( N_t \) value, from \( 4.0 \times 10^{17} \) cm\(^{-3} \) in the initial flat state to \( 4.4 \times 10^{17} \) cm\(^{-3} \) after 20,000 bending cycles. The increase in \( N_t \) can also be attributed to the formation of microcracks after bending because the dangling bonds in microcracks may create a large number of trap states.

At high voltages (|V| > 3 V), the Fowler–Nordheim (FN) tunneling often occurs, manifesting itself as the tunneling of electrons through the triangular-shaped interface potential barrier (\( \Phi_i \)) into the conduction band of the dielectric. The current for the FN tunneling is given by

\[ I = B E^2 \exp \left( -\frac{8\pi \sqrt{2m_{\text{eff}} \Phi_i^{1/2}}}{3h\varepsilon_0 E} \right) \]  

where \( B \) is a constant, \( E \) is the electric field (i.e., \( V/d \)), \( m_{\text{eff}} \) is the effective electron mass, and \( h \) is the Planck constant. According to eq 6, a linear relationship between Ln(I/V^2) and 1/V exists for the FN tunneling. To check it, we have plotted the I–V curves of cap-1 and cap-2 in the voltage range of 3 V < |V| < 6 V as Ln(I/V^2) versus 1/V, as presented in Figures 7c,f and S7b,d. The Ln(I/V^2)–1/V curves exhibit good linearity at high voltages, indicating that the FN tunneling is the dominant conduction mechanism. Through the fittings, the \( \Phi_i \) values of both cap-1 and cap-2 are found to decrease after bending, which may be attributed to the microcracks that can lower the local potential barrier for electron tunneling.

From the above analyses, it is inferred that suppressing the formation of microcracks is critical to address the bending-
induced degradation of dielectric properties. A viable approach may be reducing the thickness of the mica substrate. This is because as the mica thickness becomes smaller, the bending-induced strain on the BST film is reduced (note: the strain can be estimated with \(d_{sib}/2R\), where \(d_{sib}\) and \(R\) are the mica thickness and bending radius, respectively, and the thicknesses of BST and SRO layers are neglected because they are too small compared with \(d_{sib}\)). The reduced strain may give rise to a smaller amount of microcracks formed during the bending.

4. CONCLUSIONS

In summary, large-scale and high-quality SRO/BST/Pt capacitors were fabricated on flexible mica substrates through PLD. The polycrystalline BST film shows an average grain size of \(\sim 50\) nm, a roughness of \(\sim 3.9\) nm, and a high transparency of \(\sim 50\%\) in the 400–900 nm wavelength range. The BST film also exhibits ferroelectricity with a small polarization of \(\sim 2\mu C/cm^2\). Then, we focused on the investigation of the dielectric properties of the flexible mica/SRO/BST/Pt capacitor in both low-frequency and microwave regions. The capacitor exhibits an 

\[\varepsilon_r', \tan(\delta)\]

as low as \(\sim 0.16\), and a tunability of \(67\%\) at low frequencies (e.g., 10 kHz). Meanwhile, a high \(\varepsilon_r'\) of \(\sim 540\) and a low \(\tan(\delta)\) of \(\sim 0.07\) are retained at microwave frequencies (e.g., 18.6 GHz). More importantly, the capacitor can endure a small bending radius of 5 mm and 12 000 bending cycles (@ \(R = 5\) mm) with almost no decays in \(\varepsilon_r', \tan(\delta)\), and tunability. Further decreasing the bending radius or increasing bending cycles leads to the dielectric performance degradation, which may be caused by the formation of microcracks increasing the leakage current. Nevertheless, the dielectricity of the BST bulk (grains) is sufficiently robust against the bending. Given the excellent dielectric and mechanical properties, the flexible mica/SRO/BST/Pt capacitor is promising for wide applications in flexible electronic and microwave devices.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b08712.

Details of the method for measuring microwave dielectric properties, morphology, and electrical conductivity of the SRO film; characterizations of the BST film grown on the Pt-buffered mica substrate; dielectric properties in the flex-in bending mode; observation of microcracks using AFM; and fittings of \(I−V\) characteristics in the positive voltage region (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(56) Qin, W. F.; Xiong, J.; Zhu, J.; Tang, J. L.; Jie, W. J.; Wei, X. H.; Zhang, Y.; Li, Y. R. High Tunability Ba0.9Sr0.1TiO3 Thin Films Fabricated on Pt−Si Substrates with La0.5Sr0.5CoO3 Buffer Layer. J. Mater. Sci.: Mater. Electron. 2007, 19, 429−433.


