Piezoelectric BaTiO$_3$ Thin Film Nanogenerator on Plastic Substrates

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ABSTRACT The piezoelectric generation of perovskite BaTiO$_3$ thin films on a flexible substrate has been applied to convert mechanical energy to electrical energy for the first time. Ferroelectric BaTiO$_3$ thin films were deposited by radio frequency magnetron sputtering on a Pt/Ti/SiO$_2$/Si(100) substrate and poled under an electric field of 100 kV/cm. The metal–insulator–metal (BaTiO$_3$–metal)–metal-structured nanoribbons were successfully transferred onto a flexible substrate and connected by interdigitated electrodes. When periodically deformed by a bending stage, a flexible BaTiO$_3$ nanogenerator can generate an output voltage of up to 1.0 V. The fabricated nanogenerator produced an output current density of 0.19 $\mu$A/cm$^2$ and a power density of $\sim$7 mW/cm$^2$. The results show that a nanogenerator can be used to power flexible displays by means of mechanical agitations for future touchable display technologies.

KEYWORDS BaTiO$_3$, thin film, piezoelectric, flexible electronics, nanogenerator, energy harvesting

Energy harvesting technologies that convert existing sources of energies, such as thermal energy as well as vibrational and mechanical energy from the natural sources of wind, waves, or animal movements into electrical energy, is attracting immense interest in the scientific community. The fabrication of nanogenerators is particularly interesting because it can even scavenge the biomechanical energy from inside the human body, such as the heart beat, blood flow, muscle stretching, or eye blinking, and turn it into electricity to power implantable biodevices.

One way of harvesting electrical energy from the mechanical energy of ambient vibrations is to utilize the piezoelectric properties of ferroelectric materials. Piezoelectric harvesting has been proposed and investigated by many researchers. Chen et al. reported on the fabrication of a nanogenerator that involves the use of lead zirconate titanate (PbZr$_{x}$Ti$_{1-x}$O$_3$, PZT) nanofibers on a bulk Si substrate. The PZT nanofibers were connected to interdigitated electrodes (IDEs) and, when pressure was applied perpendicularly to the nanogenerator surface, the nanogenerator produced an outstanding output voltage. Wang and co-workers used piezoelectric ZnO nanowires to develop a multiple lateral-nanowire-array integrated nanogenerator (LING) and a high-output nanogenerator (HONG) on plastic substrates. They also demonstrated the feasibility of harvesting energy from the breath and heartbeat of animals. As of today, the nanogenerator has an output voltage of 2 V, and the power generated can be used to power a commercial light-emitting diode (LED). Recently, there have been attempts to transfer flexible perovskite materials and capacitors onto flexible substrates for the purpose of utilizing the high inherent piezo-properties of ferroelectric materials from bulk substrates. In those attempts, perovskite thin films (PZT and BaTiO$_3$) deposited on bulk substrates were annealed at high temperatures and transferred onto plastic substrates by the removal of the sacrificial layers (MgO and TiO$_2$).

This work reports on the first use of lead-free biocompatible BaTiO$_3$ in the fabrication and characterization of a nanogenerator on a flexible substrate. A perovskite ceramic BaTiO$_3$ thin film deposited on a Pt/Ti/SiO$_2$/Si(111) substrate by rf magnetron sputtering was annealed at 700 °C for crystallization and poled to enhance the high piezoelectric property. The BaTiO$_3$ thin film was then transferred onto a flexible substrate by means of standard microfabrication and soft lithographic printing techniques. To measure the positive and negative output voltage/current signals, we deposited the IDEs on flexible BaTiO$_3$.

Figure 1a shows a schematic of the fabrication steps. (i) Deposition of an amorphous BaTiO$_3$ thin film on a Pt/Ti/SiO$_2$/Si substrate. A 300 nm BaTiO$_3$ thin film was deposited on a Pt/Ti/SiO$_2$/Si substrate by rf magnetron sputtering at room temperature in an Ar atmosphere. The BaTiO$_3$ thin film was then annealed at 700 °C for 15 min in oxygen using the rapid thermal annealing (RTA) for the crystallization of the amorphous film. (ii) Inductive coupled plasma-reactive ion etcher (ICP-RIE) etching of metal–insulator–metal (MIM) structures (Au/BaTiO$_3$/Pt layers). The MIM structure was etched by chlorine gas based ICP-RIE etching using an Al plasma enhanced chemical vapor deposited-SiO$_2$ (PEO) mask made with a narrow bridge pattern (300 $\mu$m × 50 $\mu$m).
Anisotropic wet etching with 5% tetramethylammonium hydroxide (TMAH, 80 °C for 18 min) removed the underlying Si layer and separated the MIM structure ribbons from the mother substrates. (iii) Transfer of the MIM structures onto a plastic substrate. For the transfer, we placed a PDMS stamp (Sylgard 184, Dow Corning) in uniform contact with the top surface of the free-standing MIM structures. Upon quick removal from the Si wafer, the narrow bridge-shaped MIM structures were transferred onto the PDMS. An elastomer slab, inked with MIM structures, was then placed on a polyurethane (PU)-coated plastic substrate (Kapton film, 100 µm in thickness). The PU was optically cured by a ultraviolet (UV) light. MIM structures were well settled on a plastic substrate when the PDMS was peeled away. (iv) Fabrication of self-powered flexible devices. The diluted UV sensitive epoxy (SU8) was spin-coated on top of BaTiO3/PU/plastic substrates and the metal contact area was then opened with a standard photolithography process. MIM structures in nanogenerator were connected with IDEs (Au) and poled at 150 °C by applying an electric field of 200 kV/cm for about 15 h (see Supporting Information for details on the fabrication of a flexible BaTiO3 nanogenerator on plastic substrates, Figure S1).

Figure 1b shows a cross-sectional scanning electron microscopy (SEM) image of a MIM structure (Au/BaTiO3/Pt layers). The X-ray photoelectron spectroscopy (XPS, Al Kα source) spectrum of the annealed BaTiO3 film in the inset consists mainly of Ba, Ti, and O peaks with a minor C peak; the latter might be due to the C contamination of the sample during its exposure in air. Figure 1c shows an SEM image of MIM structures obtained at the intermediate stage of partial anisotropic etching of the underlying Si layer using TMAH etchant. The inset is a magnified cross-sectional view of the MIM structures. Note the mechanical flexibility of the ~550 nm thick MIM structures. The photograph in Figure 1d (corresponding to Figure 1a-ii) shows MIM structures (of about 1 cm²) that were successfully transferred from a bulk Si wafer to a PDMS stamp without forming any cracks. The upper inset in Figure 1d shows a photograph of a twisted PDMS stamp that contains MIM structures; the bottom inset shows a magnified top view of the MIM structures on the PDMS stamp. Figure 1e (corresponding to Figure 1a-iv) displays a photograph and a magnified optical image of a flexible BaTiO3 nanogenerator device with a fill factor of about 16.4%. The inset shows that the top and bottom electrodes of the MIM structures were connected to the IDEs. Copper (Cu) wires attached to the metal pads by silver (Ag) paste were used to measure the output voltage and current.

We characterized the crystalline structure of the BaTiO3 thin films by X-ray diffraction (XRD) and Raman spectroscopy and measured the piezoelectric response by means of a piezoresponse force microscope (PFM). The XRD and Raman shift results indicate that the annealed BaTiO3 thin films on both bulk and flexible substrates have good crystallinity with a ferroelectric tetragonal phase (see Supporting Information for XRD and Raman analysis results of BaTiO3 thin films, Figure S2). As schematically shown in Figure 2a, the PFM technique was used to measure the piezoelectric constant, d33 (the induced polarization per unit stress applied in an out-of-plane direction), of the BaTiO3 thin films on Si substrates. Figure 2b presents the PFM results (in a plot of the piezoelectric response amplitude versus the applied AC bias voltage) for poled and unoed BaTiO3 thin films on Si substrates. As shown in the inset, the amplitudes of the piezoelectric response have a hysteresis loop over the applied voltage range. The piezoelectric coefficient (d33) is determined by the slope of the curve (piezoelectric response/applied voltage range).
voltage). Without poling, the effective piezoelectric coefficient, $d_{33}$, of the BaTiO$_3$ thin film on a Pt/Ti/SiO$_2$/Si substrate was 40 pm/V. After the poling at 140 °C under an electric field of 100 kV/cm for about 15 h, $d_{33}$ increased to 105 pm/V. The measured result of the poled BaTiO$_3$ thin film compares favorably with previously reported values for BaTiO$_3$ thin film on Si substrates (that is, $d_{33} = 30$–100 pm/V)$^{23,24}$ and verifies that our process was well optimized.

Figure 3a-i,ii shows schematics of the appearance and cross-sectional structure of the poled BaTiO$_3$ nanogenerator in its original state without bending. The piezoelectric material has dipoles that are aligned by poling under a high electric field. As depicted in the cross-sectional structure of the poled nanogenerator device in the original state of Figure 3a-ii, the dipoles in the BaTiO$_3$ thin film were arrayed in a longitudinal direction with the surface of the device. When the nanogenerator was bent (corresponding to Figure 3a-iii), charges were generated in each MIM structure due to the tensile stress induced by the deflection of the device (corresponding to Figure 3a-iv). The generated charges could then flow through the Au electrodes and build up an output voltage ($\Delta V$) between the IDEs. The measured output current (left, i) and voltage (right, ii) of the BaTiO$_3$ nanogenerator on a plastic substrate during periodic bending and unbending (b) when forward-connected (corresponding to the inset of Figure 3b-i) to the current meter and (c) when reverse-connected (corresponding to the inset of Figure 3c-i) to the current meter. The insets show optical images of nanogenerator in bent and unbent positions.
Figure 4 shows the calculated piezopotential distributions inside the BaTiO₃ thin film. We calculated the piezopotential distributions for a BaTiO₃ (500 nm)/PU (2 µm)/plastic substrate (t = 100 µm) with a bending radius of R (1 cm). A Young’s modulus of \( E = 67 \) GPa and a piezoelectric coefficient of \( d_{31} = 78 \) pC/N were used for the finite element analysis (FEA). The strain \( (\varepsilon) \) of the thin film is approximately equal to the strain \( (\varepsilon) \) of the outer surface of the plastic substrates due to thickness of the substrate is much larger than the thickness of the BaTiO₃ thin film.27 According to the eq 1, the calculated tensile strain of BaTiO₃ thin film is \( \approx 0.5% \).

\[
\varepsilon = \varepsilon_{s} = \frac{\Delta L}{L_0} = \frac{t}{2R}
\]

The calculated results demonstrate that the tensile stress is 0.54 GPa in the parallel direction. Although the lateral dimension (i.e., the length) of BaTiO₃ thin films on plastic substrate influences the mechanics (tensile stress and surface strain) and the failure mode (cracking, slipping, or delamination) of films,29 for simplicity, we have ignored these effects, which might be insignificant, in our FEA simulation. The color code of Figure 4 represents the output piezopotential. The inside of the BaTiO₃ thin film has a piezopotential difference of 0.53 V, which agrees well to our measured output voltage.

In summary, we fabricated a BaTiO₃ film based flexible nanogenerator. Annealed and poled ferroelectric BaTiO₃ thin films were successfully transferred to a plastic substrate by means of conventional microfabrication and soft lithographic techniques. The BaTiO₃ nanogenerator fabricated on a plastic substrate converted mechanical energy (bending) into electrical energy with an output voltage of up to \( \approx 1.0 \) V and a current signal of up to \( \approx 26 \) nA. The output current density was calculated to be \( \approx 0.19 \) mA/cm² and power density was calculated to be \( \approx 7 \) mW/cm². The calculations are based on the total area and volume of the MIM structures. The output voltage agrees well to the theoretically calculated piezopotential. Our nanogenerator technique of transferring ferroelectric thin films from a bulk substrate to a flexible substrate demonstrates the feasibility of fabricating thin film nanogenerators with other perovskite-type oxide materials (e.g., BiFeO₃ and PZT), which can exhibit higher piezoelectric performance than BaTiO₃ and expanding the progressive application for energy harvesting devices. They also provide progressive opportunities for implantable biological devices (e.g., self-powered wireless biosensors and robots) due to the biocompatible material properties of BaTiO₃ and have clear potential for use in electrical applications (e.g., artificial skin, LED, touchable piezoelectric displays, and piezotronics), which are driven by pressure induced external sources.

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Supporting Information Available. The detailed fabrication processes (Figure S1) of flexible BaTiO₃ nanogenerator, the XRD and Raman shift results of BaTiO₃ thin films (Figure S2), and the real time live views (Video S1) and the output signals (Figure S3) of experiment on power generation during periodical bending and unbending with a finger. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

Supporting Information for:

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1. Microfabrication and Soft lithography process

Figure S1 shows the schematics of the fabrication steps for the flexible BaTiO$_3$ nanogenerator. The first step started with the oxidation of Si wafers (620 μm) to form a 150 nm thick SiO$_2$ layer. Pt (130 nm) and Ti (20 nm) layers of a bottom electrode were fabricated by RF sputtering. A 300 nm thick amorphous BaTiO$_3$ film was deposited on a Pt/Ti/SiO$_2$/Si substrate by RF magnetron sputtering at room temperature for 2 h in an Ar atmosphere. BaTiO$_3$ thin film was annealed at 700 °C for 15min in oxygen by rapid thermal annealing (RTA) for the crystallizing the amorphous film. Cr (10 nm) / Au (100 nm) layers were deposited on the BaTiO$_3$ thin film to form a top electrode by RF sputtering [Fig. S1a]. A layer of 2.4 μm thick SiO$_2$ (PEO) was deposited by plasma enhanced chemical vapor deposition (PECVD, 400 mTorr, 20 SCCM 9.5% SiH$_4$, 10 SCCM N$_2$O, 300 °C, 20 W) and an aluminum (Al) thin film of a 600 nm thickness was obtained by RF sputtering. To make a mask for the subsequent inductive coupled plasma-reactive ion etcher (ICP-RIE) etching, the Al (wet etching for 10 min, AL-12 SK, CYANTEK Co.) and PEO (ICP-RIE etching, 25 mTorr, 50 SCCM CF$_4$, 150 W Power/40 W bias, 65 min) layers were patterned using the standard photolithography and etching technique [Fig. S1b]. Au/Cr/BaTiO$_3$/Pt/Ti layers of MIM structures were also etched by chlorine gas based ICP-RIE etching (25 mTorr, 5 SCCM Ar/100 SCCM Cl$_2$, 400 W power/200 W bias, 22 min) [Fig. S1c]. The residual PEO layers on MIM structures were etched out by fluorine gas based ICP-RIE etching (10 mTorr, 25 SCCM SF$_6$, 150 W power/40 W bias, 12 min). The underlying Si layer was anisotropically etched with 5% tetramethylammonium hydroxide (TMAH, 80 °C for 18 min) and the MIM structured ribbons (narrow bridge pattern of 300 μm x 50 μm) were separated from the Si substrate [Fig. S1d]. The MIM structures were contacted with a polydimethylsiloxane
(PDMS, Sylgard 184, Dow corning) stamp. Upon quick removal from the Si wafer, the narrow bridge shaped MIM structures were transferred onto the elastomer [Fig. S1e]. The PDMS stamp, inked with MIM structures, was then placed on a plastic substrate (Kapton film, 125 μm in thickness) which was coated with polyurethane (PU, Norland optical adhesive, No. 73). UV light was then used to cure the PU [Fig. S1f]. After peeling off the PDMS, the MIM structures were well settled on the plastic substrate. The residual PU on the plastic substrate was etched out by oxygen RIE etching (10 mTorr, 100 SCCM O₂, 200 W, 15 min) [Fig. S1g]. Au/Cr/BaTiO₃ layers of MIM structures patterned by the PR (Photoresist, AZ 5214) were partially etched by wet etching of Au/Cr metal layers (Au/Cr etchant, Transene Inc.) and BaTiO₃ layers (H₂O : HF : HCl = 97 : 1 : 2, 20 s) [Fig. S1h]. The patterned epoxy layer (SU8-5 photosresist) was formed by the standard photolithography techniques [Fig. S1i]. To connect the MIM structures, the interdigitated electrodes (Au/Cr) were deposited on the device [Fig. S1j]. Copper (Cu) wires were fixed on metal lines by a silver (Ag) paste [Fig. 1e in manuscript]. The final step of fabrication involved poling process at 150 °C by applying an electrical field of 200 kV/cm for about 15 h using a sourcemeter (Keithley 237 High-Voltage Source-Measure Unit) for the high performance piezoelectric material.
Figure S1.
2. XRD and Raman analysis results of BaTiO$_3$ thin film

The phases of BaTiO$_3$ thin films were characterized by X-ray diffraction (XRD, Rigaku, D/MAX-IIIC X-ray diffractometer, Tokyo, Japan) using CuKa radiation ($\lambda = 0.15406$ nm at 30 kV and 60 mA). Raman analysis (LabRAM HR UV/Vis/NIR, Horiba Jobin Yvon, France) was performed to provide a more comprehensive phase characterization of the BaTiO$_3$ thin films on both bulk and flexible substrates using a 514.5 nm Ar$^+$ laser line as the excitation source. Figure S2a shows the XRD analysis results of the BaTiO$_3$ thin films on a Pt/Ti/SiO$_2$/Si substrate annealed at 700 °C for 5, 15, and 30 min in an O$_2$ atmosphere. The as-deposited BaTiO$_3$ thin film on a Si substrate is amorphous, whereas the samples annealed at 700 °C are well crystallized. The inset shows the XRD rocking curve of the (111) and (200) peaks of the BaTiO$_3$ thin film annealed at 700 °C for 15 min. The full width at half maximum (FWHM) of (111) and (200) peaks are about 0.45 and 0.55, respectively, indicating a good crystallinity of the film.$^1$ Figure S2b shows the Raman shifts of the BaTiO$_3$ thin films on a Si substrate (black, blue, and green line) after annealing for different durations of time and that of the BaTiO$_3$ thin film transferred on a plastic substrate after annealing at 700 °C for 15 min (red line). (Before Raman characterization of the BaTiO$_3$ thin film on a plastic substrate, the top electrodes (Au/Cr) on the BaTiO$_3$ thin film were removed.) The spectra of about 305 and 720 cm$^{-1}$ were attributed to E (TO) and A$_1$ (LO) modes, respectively, specific to a tetragonal phase of BaTiO$_3$.$^{2-4}$ The XRD and Raman shift results indicate that the BaTiO$_3$ thin films on both bulk and flexible substrates have good crystallinity with a ferroelectric tetragonal phase.$^{1-4}$
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Figure S2.
3. The real time live views and the output signals of experiment on nanogenerator during repeated bending and unbending with a finger

Video S1. The real time live views of experiment on power generation during the periodical bending and unbending with a finger.

Video S1 (AVI)

Figure S3.
FIGURE CAPTIONS

Figure S1. Schematic illustration of the processes for fabricating of flexible BaTiO$_3$ nanogenerator. (a) Prepared MIM (Au/BaTiO$_3$/Pt) structures on Si substrate. (b) Narrow bridge mask with Al/PEO layers. (c) ICP-RIE etching of Au-BaTiO$_3$-Pt structure and (d) Removal of residual PEO using ICP-RIE and TMAH anisotropic etching of Si layer. (e) Transfer to PDMS stamp. (f) UV light exposure after contact of PDMS to PU coated-plastic substrates. (g) Peeling off PDMS and removing of residual PU using RIE. (h) PR pattern and partial removal of Au/Cr/BaTiO$_3$ layer for fabricating the BaTiO$_3$ nanogenerator devices on plastic substrates. (i) Epoxy layer (SU8-5 photoresist) coating. (j) Deposition of metal lines for connecting the MIM structures and measuring the piezoelectric properties.

Figure S2. (a) XRD patterns of BaTiO$_3$ thin films deposited on a Pt/Ti/SiO$_2$/Si substrate by RF sputtering and annealed at 700 °C for various durations of time (5, 15, and 30 min) in oxygen by RTA. The inset shows the X-ray rocking curve of BaTiO$_3$ (111) and (200) peaks. (b) Raman spectra of annealed BaTiO$_3$ thin film deposited on Si substrates (black, blue, and green line) and transferred on a plastic substrate (red line).

Figure S3. The measured output voltage (a) and current signal (b) of the BaTiO$_3$ nanogenerator on a plastic substrate under repeated bending and unbending with a finger.