

PbZr_xTi_{1-x}O₃ Ferroelectric Thin-Film Capacitors for Flexible Nonvolatile Memory Applications

Jonghyun Rho, Sang Jin Kim, Wook Heo, Nae-Eung Lee, Hwan-Soo Lee, and Jong-Hyun Ahn

Abstract—This letter reports the fabrication of PbZr_xTi_{1-x}O₃ (PZT) thin-film capacitors on flexible plastic substrates. The PZT film was formed on a wafer using a sol-gel method and transferred to a thin plastic substrate using an elastomeric stamp. The PZT film on the plastic substrate showed a well-saturated hysteresis loop with a P_r of $\sim 20 \mu\text{C}/\text{cm}^2$ and a V_c of $\sim 1.1 \text{ V}$ at a supplied voltage of 3 V, which are similar to those observed for PZT films on rigid wafers, as well as stable operation under an 8-mm bending radius. These characteristics suggest promising applications in flexible electronic systems.

Index Terms—Ferroelectric, flexible electronics, nonvolatile memory, PZT.

I. INTRODUCTION

FLEXIBLE electronics have attracted considerable attention over the last decade owing to their range of applications, such as smart cards, biomedical sensors, and foldable antennas [1]–[3]. To realize these applications, the development of flexible nonvolatile memory devices for data storage or radio-frequency transponders is required [4], [5]. Most flexible nonvolatile memories reported to date have demonstrated organic materials, including small molecules and polymer organics, because of their good mechanical bendability [6]–[9]. However, the low degree of crystallinity associated with these classes of materials results in relatively low performance of the as-fabricated devices. On the other hand, recent effort to address this issue explores the direct formation of high-quality inorganic materials onto plastic substrates through a sol-gel process to construct flexible memory with high performance [10]. However, the types of materials that are suitable for this process are limited.

This letter reports a promising approach to transfer PZT thin films formed on rigid substrates through a conventional

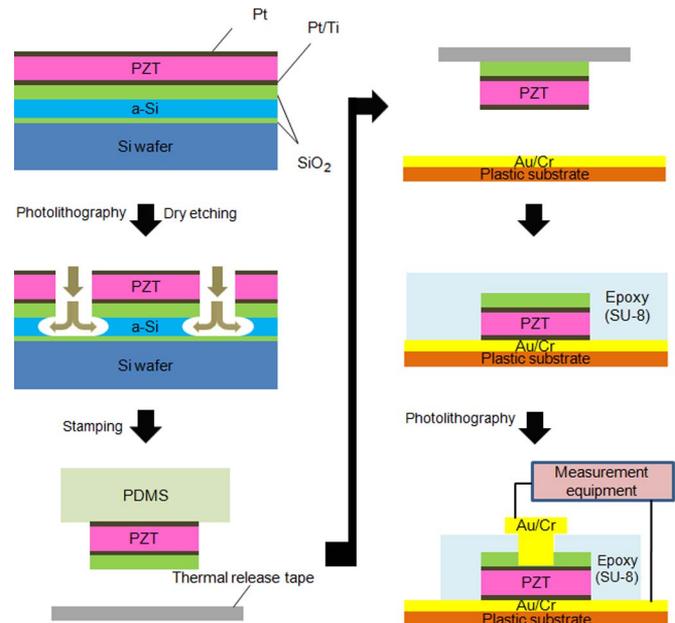


Fig. 1. Schematic illustration of the fabrication steps of flexible PZT capacitors. A PZT active layer was formed on the bottom electrodes using the sol-gel method. After depositing the top electrode and removing the sacrificial layer, the Pt/PZT/Pt/Ti/SiO₂ thin film ribbons were transfer-printed onto a plastic substrate coated with a Au film. Finally, the ribbons were coated with an encapsulation layer of epoxy.

high-temperature sol-gel method onto flexible plastics. The devices constructed with the printed materials showed excellent electrical and mechanical properties and are expected to be important for flexible electronic systems.

II. EXPERIMENTAL SETUP

Fig. 1 shows a schematic diagram of the fabrication steps for flexible PZT capacitors. The process begins with the deposition of the Pt/Ti bottom electrodes (thickness $\sim 80/20 \text{ nm}$) on a rigid SiO₂ ($\sim 300 \text{ nm}$)/a-Si ($\sim 400 \text{ nm}$)/SiO₂ ($\sim 100 \text{ nm}$)/Si wafer. SiO₂ layers and a-Si were deposited as a buffer and a sacrificial layer, respectively. Subsequently, a PZT active layer ($\sim 360 \text{ nm}$) was formed on the bottom electrodes using a sol-gel method. The film was annealed at 650 °C for 30 min to improve the electrical and mechanical properties [11]. A Pt ($\sim 100 \text{ nm}$) layer as a top electrode was then deposited on the PZT film [12]. After the film deposition process, Pt/PZT/Pt/Ti/SiO₂/a-Si ribbons with the desired size ($100 \mu\text{m} \times 400 \mu\text{m}$) were patterned using a photolithographic method. Each ribbon has two anchors ($15 \mu\text{m}$ in width). Inductively coupled plasma reactive ion etching (etch gas: Ar; Cl₂; and CHF₃) through a patterned layer

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J. Rho, W. Heo, N.-E. Lee, and J.-H. Ahn are with the School of Advanced Materials Science and Engineering and the Center for Human Interface Nanotechnology, SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, Korea (e-mail: ahnj@skku.edu).

S. J. Kim and H.-S. Lee are with the Advanced Materials Laboratory, Samsung Electro-Mechanics, Suwon 443-743, Korea (e-mail: hwansoo725.lee@samsung.com).

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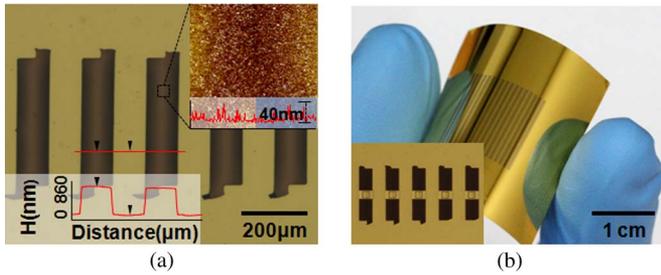


Fig. 2. (a) Optical image of the PZT ribbons printed onto a polyimide substrate coated with Au. The inset shows the surface profiles of ± 20 nm. (b) Large-area image of the PZT capacitors built on a polyimide substrate. The inset presents a magnified image of the PZT capacitors with the top electrodes.

of photoresist was performed to remove certain regions of the Pt/PZT/Pt/Ti/SiO₂/*a*-Si layers to isolate the active device ribbons. The thin ribbons can be lifted from the wafer using a polydimethylsiloxane (PDMS) elastomeric stamp after removing the underlying *a*-Si sacrificial layer with additional NF₃ remote plasma or XeF₄ dry etching [13]–[17]. The lifted ribbons were transferred on the sticky surface of the thermal release tape and then attached on a target plastic substrate coated with 100-nm-thick Au film. After heating to 100 °C for 10 min, the surface of the thermal release tape lost an adhesive force and, as a result, released the PZT ribbons on the plastic substrate. The Pt back side of the PZT ribbon can form a conductive connection with the Au film due to the transfer printing process without an adhesive layer [16], [17]. Finally, the ribbons were coated with an encapsulation layer of epoxy (~ 1.2 μm) to protect them from the applied strain and to prevent delaminating them.

III. RESULTS AND DISCUSSION

Fig. 2(a) shows an optical image of the PZT ribbons with a length and a width of 400 and 100 μm , respectively, printed onto a polyimide substrate coated with Au. This indicates that the ribbons are well aligned without destroying the orientation and cracking of the ribbons. The insets show the top surface images and height of the ribbons on a substrate. The line-cut through the AFM image shows the surface profiles of ± 20 nm, indicating that the ribbons are bonded flatly to the substrate. Fig. 2(b) shows a photograph of the flexible plastic substrate that houses the PZT capacitors made from the transferred PZT ribbons. The inset shows a magnified image of the PZT ribbons with the top electrodes. The substrate can be bent to a radius of curvature of 8 mm without delamination or cracking of the ribbons, as observed by optical microscopy.

Fig. 3(a) shows the results of the C - V measurement of the PZT capacitors measured on a bulk wafer, a PDMS stamp, and a plastic substrate after transfer. The capacitance and voltage shift of the PZT capacitor transferred to the PDMS and the plastic substrate were 2.76 $\mu\text{F}/\text{cm}^2$ and 1.6 V, and 2.70 $\mu\text{F}/\text{cm}^2$ and 1.6 V, respectively. The PZT capacitor with the same geometry of the device on the bulk wafer showed a capacitance and a voltage shift of 2.90 $\mu\text{F}/\text{cm}^2$ and 0.6 V, respectively. The etching and transfer processes using the PDMS stamp appear to mainly lead to a 7% decrease in capacitance and a 166% increase in voltage shift. We believe that this was attributed

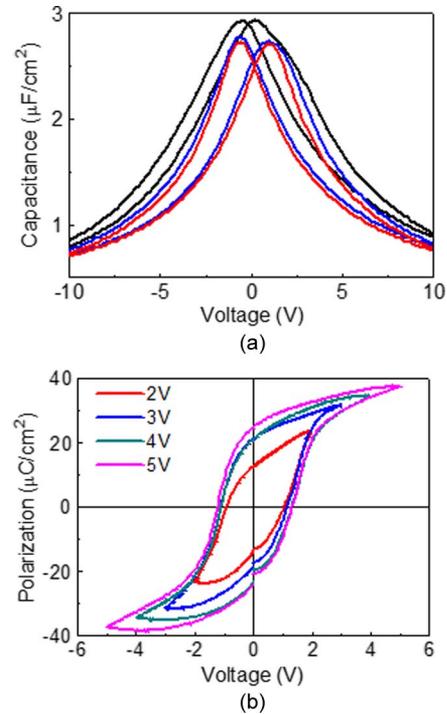


Fig. 3. (a) Results of the C - V measurement of the PZT capacitors. The capacitance was measured on a bulk wafer, a PDMS, and a plastic substrate (black: on bulk wafer; blue: on PDMS; red: on plastic substrate). The transfer process appears to lead to $\sim 7\%$ decrease in capacitance and $\sim 166\%$ increase in voltage shift. (b) Polarization hysteresis loop of the PZT capacitors on a plastic substrate under different applied voltages.

mainly to degradation of the PZT/Pt interface induced by undercutting of the PZT layer during the isotropic dry etching process and mechanical stress during the lift-up process using a stamp, which might be improved by more careful process optimization. Fig. 3(b) shows the polarization hysteresis loop of the PZT capacitor on a plastic substrate for different applied voltages. The remnant polarization (P_r) increased from ~ 17 $\mu\text{C}/\text{cm}^2$ at 2 V to 25 $\mu\text{C}/\text{cm}^2$ at 5 V, which is comparable to the reported values [18]–[20].

Good mechanical flexibility is essential for applications to flexible electronics. The flexibility was evaluated by performing front- and backward bending tests. Fig. 4(a) and (b) shows the hysteresis loops of the PZT capacitors for various bending radii (R_c) at an applied voltage of 3 V and the change in P_r values as a function of bending radius, respectively. For bending radii up to 8 mm that correspond to a strain value of 0.11%, very stable responses in the measured P_r and V_c were observed [21].

The small differences between these values suggest that the PZT capacitors are not damaged by the bending cycles. This shows that the PZT thin film capacitor may have good electrical properties even under mechanical strain.

IV. CONCLUSION

In conclusion, this letter has reported a method for fabricating high-performance PZT capacitors on plastic substrates. Dry etching and transfer printing procedures enable the integration of organized arrays of PZT ribbons into flexible formats on plastic sheets. The PZT capacitors formed in this manner

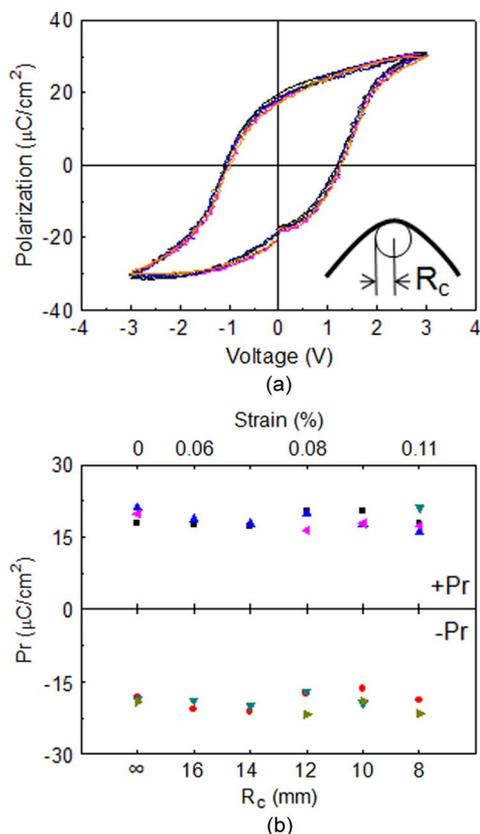


Fig. 4. (a) Hysteresis loops of the PZT capacitors for various bending radii (R_c) at an applied voltage of 3 V (orange: $R_c = 8$ mm; navy: 10 mm; dark yellow: 12 mm; magenta: 14 mm; blue: 16 mm; black: ∞). (b) Change in Pr values at different bending radii.

showed good electrical and mechanical properties. These results suggest that printable PZT capacitors can provide interesting opportunities for the development of flexible nonvolatile memory devices that are suitable for use in high-performance electronic systems.

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