Bendable and Transparent Barium Titanate Capacitors on Plastic Substrates for High Performance Flexible Ferroelectric Devices

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This article describes a fabrication procedure of high performance flexible ferroelectric materials supported on plastic substrates and the characterization of BaTiO3 thin films on flexible substrates. Ferroelectric BaTiO3 thin film was deposited using radio-frequency magnetron sputtering on a Pt/Ti/SiO2/(100) Si substrate and annealed at 700°C for crystallization. The metal-insulator (BaTiO3)-metal structure was successfully transferred onto flexible substrates by the standard microfabrication and soft lithographic printing methods after removing the underlying sacrificial TiO2 layer by buffered oxide etchant etching. The dielectric constant of the BaTiO3 thin films on the flexible substrate was comparable with that on a bulk Si substrate. No significant change in dielectric constant was observed upon bending with various radii and debending.

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Ferroelectric thin film materials, for example, ZnO,1,2 polymers [poly(vinylidene fluoride) and polypropylene],3,4 and perovskite-type oxides (e.g., BaTiO3, PbZrO3, SrTiO3, SrBi2Ta2O9, Ba0.5Sr0.5TiO3, Pb(Zr,Ti)O3, TiO2, SnO2, SrO, TiO2, and BiFeO3) are being studied with great interest for various applications, such as thin-film capacitors, piezoelectric microactuators, tunable microwave devices, nonvolatilable ferroelectric random access memories, and ferroelectric field effect transistors.3,4 Among these ferroelectric materials, BaTiO3 thin films have drawn considerable attention not only due to their excellent ferroelectric characteristics but also to their lead-free bio-eco-compatible material properties. Recently, research on printable, flexible, and stretchable technology has been quickly progressing,9-12 in particular, on flexible ferroelectric materials, BaTiO3 thin films have drawn considerable attention not only due to their excellent ferroelectric characteristics but also to their lead-free bio-eco-compatible material properties.

Experimental

Figure 1a shows the schematics of the fabrication steps, which consists of the following steps: (i) deposition of a BaTiO3 thin film on a Pt/Ti/SiO2/Si(100) substrate. The Si wafers (500 μm) were oxidized with a SiO2 (150 nm) layer. Pt (120 nm) and Ti (20 nm) layers of the bottom electrode were obtained by an E-beam evaporator. A 320 nm BaTiO3 thin film was deposited on a Pt/Ti/SiO2/Si substrate by rf magnetron sputtering at room temperature in an Ar atmosphere. Annealing at three different temperatures, 600, 700, and 800°C was carried out for the crystallization of the ferroelectric material. During the annealing process, Ti is oxidized to form a TiO2 layer between the Pt and SiO2 layers. (ii) Inductive coupled plasma–reactive ion etcher (ICP-RIE) etching of the metal-insulator-metal (MIM) structure. The Au/BaTiO3/Pt layers of the MIM structure were etched by chlorine gas based ICP-RIE etching using Al and plasma-enhanced chemical vapor deposited SiO2 mask (300 × 100 μm). The sacrificial TiO2 layer formed at the interface between the Pt and SiO2 layers was removed using a buffered oxide etchant (BOE) for 20 s. (iii) Transfer of MIM structure onto plastic substrate. The PDMS stamp, inked with MIM capacitors, was placed on a polyurethane (PU)-coated plastic substrate (Kapton film, 125 μm thick) and PU was cured by UV light.21 After peeling off the PDMS, the MIM capacitors were well settled on the plastic substrate. The final step of fabrication involved etching a portion of the Au/Cr/BaTiO3 layers (see supplementary material for fabrication details of flexible BaTiO3 capacitors, Fig. S1).25

The phases present in the thin films were characterized by X-ray diffractometer (XRD, Rigaku, D/MAX-IIIc, Tokyo, Japan) using Cu Kα radiation (λ = 0.15406 nm at 30 kV and 60 mA). Raman analysis (LabRAM HR UV/visible/near-IR, Horiba Jobin Yvon, France) was performed to provide a more comprehensive phase characterization of both bulk and flexible BaTiO3 thin films using a 514.5 nm Ar+ laser line as the excitation source. A scanning electron microscope (SEM, S-4800, Hitachi, Japan) was employed to observe the top and cross-sectional surfaces of the film. The dielectric properties of the BaTiO3 capacitors were measured by an Agilent (Hewlett-Packard) 4284A Precision LCR meter under 5 mV at 1 kHz.

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the Pt substrate. Mechanical polishing, unlike in previous investigations, the Si wafer can be reused for cost efficiency without chemical etching out of the TiO2 sacrificial layer by BOE etching. The SiO2 layer was not etched during the short period BOE etching. An apparent advantage of utilizing a TiO2 sacrificial layer is that the Si wafer can be reused for cost efficiency without chemical etching out of the TiO2 sacrificial layer by BOE etching. The SiO2 layer was not etched during the short period BOE etching (20 s), whereas the TiO2 layer was completely etched out. The fast interface etching of the TiO2 layer appears to delaminate the Pt and SiO2 layers. An apparent advantage of utilizing a TiO2 sacrificial layer is that the Si wafer can be reused for cost efficiency without chemical mechanical polishing, unlike in previous investigations. The indium tin oxide (ITO)-based BaTiO3 capacitors (indicated by a red dotted box) transferred onto the PDMS were transparent, as shown in Fig. 1d, and a magnified view is in the inset. Figure 1e is a photograph of a plastic substrate with MIM capacitors wrapped around an aluminum rod 9 mm in diameter, and an optical image of printed MIM structures on a PU-coated plastic substrate was magnified in the bottom inset. The upper inset shows the SEM image of BaTiO3 top surface on oxidized Si substrates.

Results and Discussion

Figure 1b and c shows cross-sectional SEM images of the MIM structure (Au/BaTiO3/Pt) on a SiO2/Si substrate, which were taken before and after BOE etching, respectively. The SEM image in the inset of Fig. 1b shows a dense and smooth surface of a typical BaTiO3 thin film on a Si substrate with no cracks or large pores. As shown in Fig. 1c, the Pt and SiO2 layers were separated as a result of etching out of the TiO2 sacrificial layer by BOE etching. The SiO2 layer was not etched during the short period BOE etching (20 s), whereas the TiO2 layer was completely etched out. The fast interface etching of the TiO2 layer appears to delaminate the Pt and SiO2 layers. An apparent advantage of utilizing a TiO2 sacrificial layer is that the Si wafer can be reused for cost efficiency without chemical mechanical polishing, unlike in previous investigations. The indium tin oxide (ITO)-based BaTiO3 capacitors (indicated by a red dotted box) transferred onto the PDMS were transparent, as shown in Fig. 1d, and a magnified view is in the inset. Figure 1e is a photograph of a plastic substrate with MIM capacitors (corresponding to Fig. 1a-iv) wrapped around an aluminum rod 9 mm in diameter, and an optical image of printed MIM structures on a PU-coated plastic substrate was magnified in the bottom inset. The upper inset shows the MIM structures on the PDMS stamp (corresponding to Fig. 1a-iii) before the capacitors were transferred on the plastic substrate.

Figure 2a shows the XRD patterns of the BaTiO3 thin films on Pt/Ti/SiO2/Si substrate after annealing at different temperatures. The inset shows the X-ray rocking curve of the BaTiO3 thin films on Si substrate annealed at 700°C for 1 h. The full width at half-maximum of the BaTiO3 thin films on Si substrate annealed at 700°C for 1 h is 0.35°, indicating a good crystallinity of the film. Figure 2b shows the Raman spectra of the BaTiO3 thin films on Si substrate (black, blue, and green lines) after annealing at different temperatures and that of the BaTiO3 thin film transferred on a plastic substrate after annealing at 700°C for 1 h (red line). [Before Raman characterization of the BaTiO3 thin film on plastic substrate, the top electrodes (Au/Cr) on the BaTiO3 thin film were removed.] The spectra of about 305 and 720 cm⁻¹ were attributed to the A1 and E (longitudinal optical) modes, specific to a tetragonal phase of BaTiO3. The XRD and Raman shift results indicate that the BaTiO3 thin films on both bulk and flexible substrates have good crystallinity with a ferroelectric tetragonal phase, however, the degree of BaTiO3 crystallinity was changed after the BOE (containing HF) etching.

The dielectric properties of the films on Si and plastic substrates were measured. Without annealing, the dielectric constant was low (εr < 20), possibly because of the lack of tetragonal phase formation. Figure 3a shows the room-temperature dielectric constant (solid lines) and loss tangent (dotted lines) of high temperature
Conclusion

We have developed a fabrication technique for ferroelectric, in particular, BaTiO$_3$ capacitor films on plastic substrates using microfabrication and soft lithography methods. To transfer the BaTiO$_3$ capacitor onto a plastic substrate, a metal oxide (TiO$_2$) sacrificial layer was introduced between the Si substrate and the MIM structure. The MIM structures on flexible substrates had dielectric constants comparable to that of BaTiO$_3$ thin film on a Si substrate and high mechanical stability upon harsh bending. The integration of flexible microstructured-ferroelectric materials utilizing the present technique may also provide innovative opportunities for designing flexible oxide-based-piezoelectric materials for sensing devices or energy harvesting systems.

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24. See supplementary material available at doi:10.1149/1.3407622 (EESLFEF-6-13-012007) for additional information.