(Na, Bi)TiO_3 based lead-free ferroelectric thin films on Si substrate for pyroelectric infrared sensors

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Abstract. In this study, we report ferroelectric and pyroelectric properties of $(Na_{0.5}Bi_{0.5})TiO_3$-$BaTiO_3$ (NBT-BT) thin films on Si substrates using chemical solution deposition for the first time. The NBT-BT thin films deposited on Pt/Ti/SiO_2/Si substrates have exhibited a typical hysteresis loop with remnant polarization of 5 μC/cm^2 and coercive field of 80 kV/cm. Furthermore NBT-BT films showed pyroelectricity with pyroelectric coefficient of 0.6×10^{-8} C/cm^2K. Monolithic-integration of Si electronics and lead-free ferroelectric NBT thin films has been archived using SiN passivation layer. It was previously believed that LSI processes could not incorporate any sodium-containing material which would cause characteristic degradation, such as threshold voltage shift. In this work, no threshold voltage shift in MOS characteristics was observed using this SiN layer. The SiN layer not only blocked diffusion from NBT chemistry, but also from crystallized NBT films during NBT formation process.

1. Introduction

In recent years, ferroelectric thin films have become important because of their numerous useful and attractive applications, such as ferroelectric random access memories (FeRAMs), micro actuators, piezoelectric micromachined ultrasonic transducers and pyroelectric infrared (IR) sensors. To realize such devices, thin film fabrication of ferroelectric materials and the integration of ferroelectric thin films on Si substrates are required. Previously, we reported highly sensitive pyroelectric IR image sensor arrays using epitaxial Pb(Zr,Ti)O_3 (PZT) thin films deposited on epitaxial γ-Al_2O_3(100)/Si(100) substrates [1]. PZT thin films are, today, widely used due to their good ferroelectric properties and high compatibility with LSI processes. However, lead-based ferroelectric materials, such as PZT, are not environmentally friendly because of their lead toxicity. Therefore lead-free ferroelectric materials with excellent properties are needed. $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) and NBT based solid systems, such as $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ (NBT-BT) [2,3] and $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$ (NBT-KBT) [4-6] , are promising lead-free materials due to their excellent ferroelectric properties. NBT has a perovskite-type structure, as typified by PZT, and several studies have reported a relatively large remnant polarization (Pr) of 38 μC/cm^2 at room temperature, high curie temperature (Tc) of 320 °C [7] and pyroelectric coefficient (p) of 2.5×10^{-8} C/cm^2K [8]. However, it is difficult to introduce NBT into an

LSI process because NBT contains sodium which causes degraded characteristics of Si devices, such as threshold voltage shifts.

Usually, Si circuitry is passivated by a SiO_2 film. The Diffusion coefficient of sodium in SiO_2 is about 10^{-6} cm^2/s. This is an extremely higher value than for other impurities in Si devices, such as Arsenic (As), Antimony (Sb) and Boron (B). According to rough calculations, sodium could pass through SiO_2 films about 10 μm in thickness. Therefore sodium can easily reach circuitry, passing through the SiO_2 passivation layer during thermal processes such as NBT deposition. Several studies have reported that SiN films were able to block diffusion of alkali ions including sodium. [9]

In this study, first NBT based thin films were deposited on the SiO_2/Si substrates by chemical solution deposition (CSD), and crystallographic orientations, ferroelectric properties and pyroelectric properties were investigated. Then, we investigated the feasibility of employing a SiN passivation layer in the integration processes of NBT films with Si electronics to create Si based lead-free ferroelectric devices. SiN is a conventional passivation material in LSI processes to block mobile ions, such as sodium and potassium.

2. Experimental

2.1. NBT-based ferroelectric thin film

50-nm-thick SiO_2 films were formed on p-Si(100) substrates by thermal oxidation. Pt/Ti stacked layer were deposited by sputtering on the SiO_2/Si substrate for bottom electrodes. NBT-BT films were prepared as NBT-based thin films. The precursor solution was prepared using sodium nitrate, bismuth nitrate, titanium isopropoxide, and barium acetate as starting materials.

The preparation procedure of precursor solution for NBT-BT is schematically described in figure.1. NBT-BT precursor solution with a nominal composition of 94 mol% of NBT and 6 mol% of BT was synthesized.

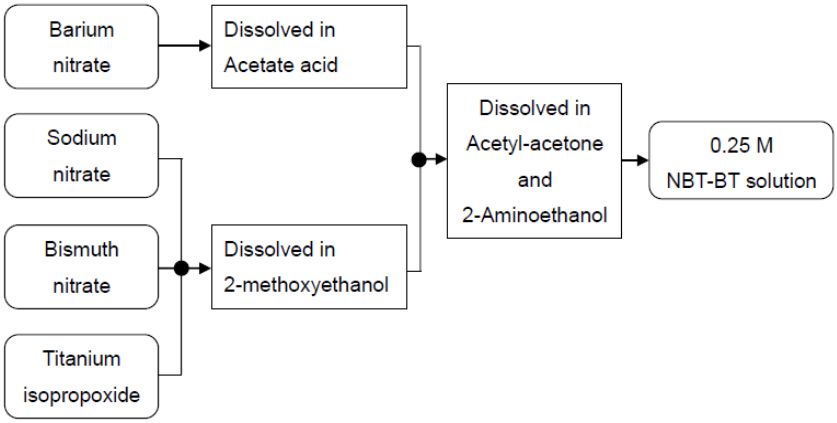

Figure 1. Preparation flow of the NBT-BT precursor solution.

The precursor solution was spin-coated on Pt/Ti/SiO_2/Si substrates at 3500 rpm for 30 s. The drying condition was 150 °C for 5 min, and the pre-fired condition was 450 °C for 5 min in air with a hotplate. The final annealing condition was 650 °C for 5 min in oxygen atmosphere with rapid thermal annealing system. The coating process was repeated three times to obtain the about 120 nm thick NBT-BT films.

The crystallographic orientations of NBT-BT films were analyzed by XRD. The ferroelectric properties were measured using a standardized ferroelectric test system (Toyo Corp. FCE) with Pt/NBT-BT/Pt capacitors by making circular Pt top electrodes 500 μm in diameter using RF magnetron sputtering through a shadow mask. The pyroelectric properties were measured using a Keithley 6517 electrometer and a fine temperature control system (Toyo Corp. FCEOPT/PY1).

2.2. Sodium blocking test

To confirm the sodium ion blocking by SiN films, a simple MOS capacitor has been used. Figure 2 shows the sample preparation processes. First, 50-nm-thick SiO_2 films were formed on p-Si(100) substrates by thermal oxidation to act as oxide of an MOS capacitor. SiN films were deposited on the oxidized substrate by plasma enhanced chemical vapor deposition (PECVD) as the alkali ion blocking layer. Thicknesses of the SiN film were 100 nm or 200 nm. 150-nm-thick NBT films were coated on the SiN layer by a same method described above. After crystallization of the NBT films, the NBT and SiN films were removed by BHF solution and hot phosphoric acid, respectively. An indium electrode was formed on the back of the substrates. Capacitance-Voltage (C-V) characteristics of the MOS capacitors were measured at a frequency of 1 kHz using mercury probe system (CVmap92A, Four Dimensions, Inc) and an impedance analyser (4285A, Agilent).

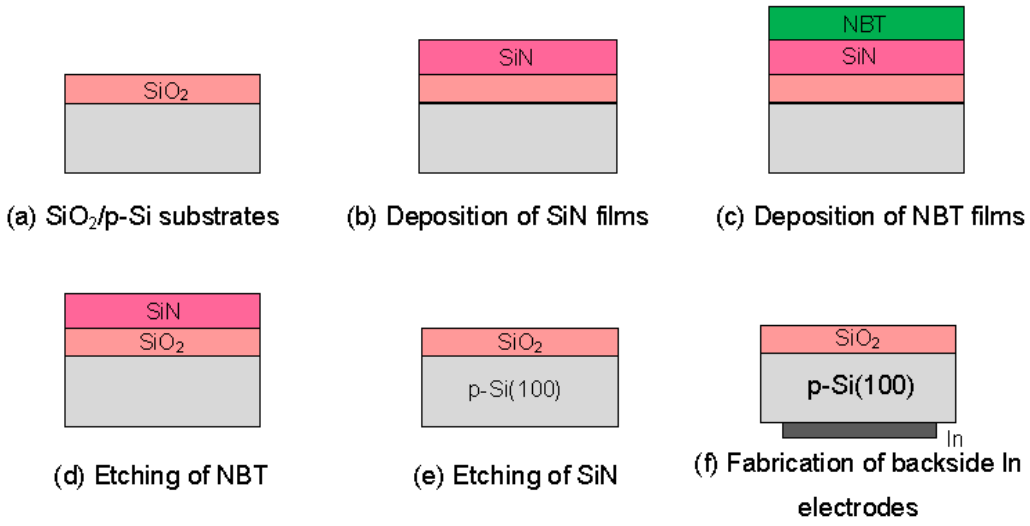

Figure 2. Fabrication processes of MOS capacitor for sodium blocking test.

2.3. Integration of pyroelectric infrared sensor using NBT based thin films and Si electronics

An integrated pyroelectric sensor, comprising NBT thin films, N-MOSFETs and N-Junction FETs (N-JFETs), was fabricated on an epitaxial γ-Al_2O_3 (100)/Si(100) substrate. The fabrication process flow is described below. (a) Epitaxial γ-Al_2O_3 films, 50 nm in thickness, were deposited on Si(100) substrates by metal organic CVD [10]. A partial area of γ-Al_2O_3 films was etched to create an LSI fabrication area. (b) N-MOSFETs and N-JFETs were fabricated by standard LSI process on the LSI fabrication area. (c) Passivation SiN/SiO_2 layers were deposited by PECVD. The passivation layer on the Al_2O_3 film was removed to form a sensor structure. (d) The Pt/Ti/TiN layer was formed by RF sputtering. 150-nm-thick NBT films were coated by CSD described above. 100-nm-thick SRO films were deposited by RF sputtering. (e) The SRO/NBT/Pt/Ti/TiN structures were patterned by a conventional photolithography technique and dry etching processes. (f) A 500-nm-thick SiN film as an inter-layer dielectric was deposited by PECVD and the Al-Si wiring was formed by DC sputtering. V_{GS}-I_D characteristics of the N-MOSFETs and the N-JFETs were measured with a semiconductor parameter analyser (4155B, Agilent).

3. Results and Discussion

3.1. NBT-based ferroelectric thin film

Figure.3 shows the XRD pattern of NBT-BT thin films deposited on Pt/Ti/SiO_2/Si(100) substrates with various annealing temperature. Only the peaks from NBT-BT were observed at annealing temperature of 650 °C.

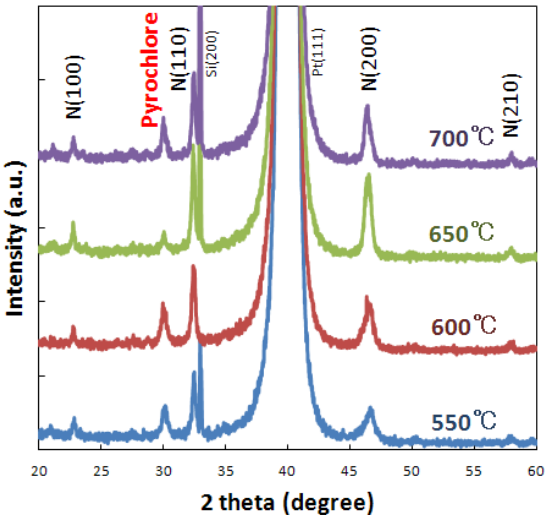

Figure 3. XRD patterns of NBT-BT films on Pt/Ti/SiO_2/Si substrate annealing at various temperature.

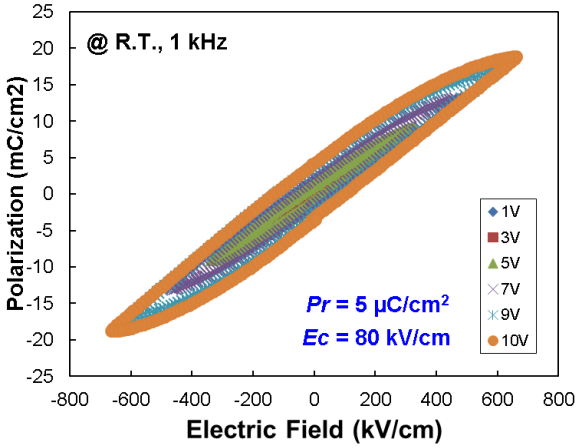

Figure 4. Typical ferroelectric hysteresis loop of NBT-BT films on Pt/Ti/SiO_2/Si substrate with various sweeping voltage

Figure.4 shows ferroelectric properties measured at a frequency of 1 kHz for the Pt/NBT-BT/Pt capacitor structure. The obtained NBT films on Pt/Ti bottom electrode showed a hysteresis loop with remnant polarization (*Pr*) of 5 μC/cm^2 and coercive filed (*Ec*) of 80 kV/cm at sweeping voltage of ±10 V. These values are in good agreement with the reported value deposited on Pt/Ti/SiO_2/Si substrates by sol-gel method [11].

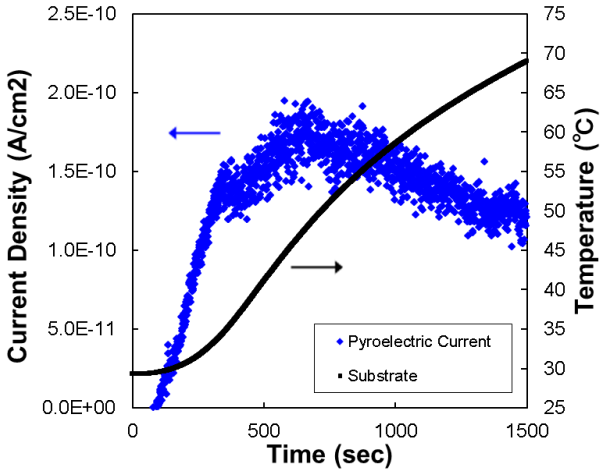

Figure 5. Pyroelectric current of the NBT-BT thin film.

Figure.5 shows the pyroelectric current of NBT films. A pyroelectric coefficient was defined as the following Eq. (1).

$$I_p = pA\frac{dT}{dt} \tag{1}$$

where *I*p is the pyroelectric current, *p* is the pyroelectric coefficient, *A* is the area of the top electrode and d*T*/d*t* is the temperature gradient of NBT-BT films. A pyroelectric coefficient was calculated using the Eq. (1). The average pyroelectric coefficient of NBT-BT films is 0.6×10^{-8} C/cm^{2}K. This is the first time report of pyroelecricity of the NBT-BT thin film on Si substrates.

3.2. Sodium Blocking

Figures 6 (a) and (b) show the CV characteristics of MOS capacitors using various thicknesses of SiN passivation layer and as-formed MOS capacitors (SiN films and NBT films were not deposited). Without a SiN passivation layer, CV characteristics exhibited an anomalous capacitance value and hysteresis, as indicated by arrows shown in Fig. 6(a). It is suggested that mobile ions contaminate the SiO_2 film during NBT film deposition. On the other hand, Fig. 6(b) shows that no hysteresis is observed in MOS capacitors using a SiN passivation layer. Compared with the as-formed MOS capacitor, small threshold voltage shifts of 0.1 V in the positive direction were observed in an NBT formed MOS capacitor. This is not diffusion of sodium ions. If positive sodium ions exist in the SiO_2, the flat band voltage shifts in the negative direction. These results indicate sodium diffusion during deposition of NBT films could be prevented by the SiN passivation layer.

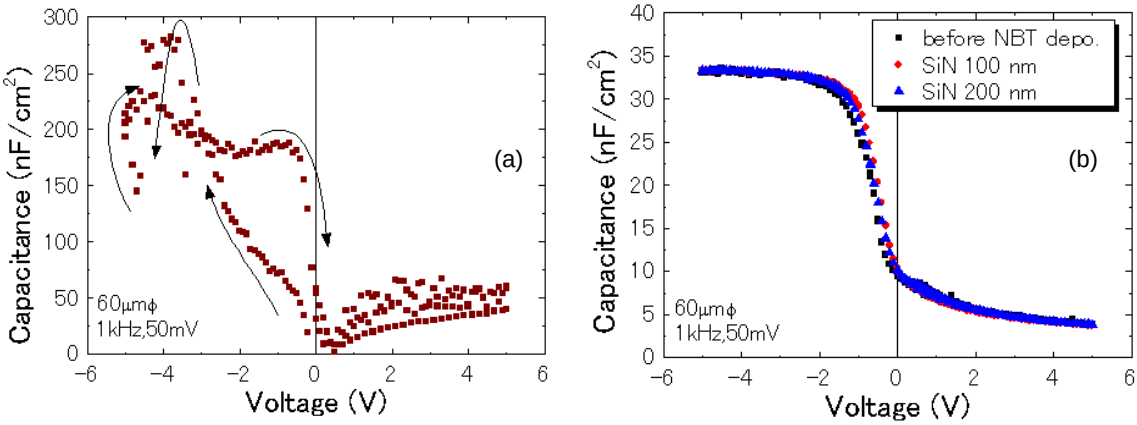

Figure 6. C-V characteristics of MOS capacitors after NBT thin film deposition. (a) without a SiN layer and (b) with a SiN layer under the NBT film.

3.3. Integration of pyroelectric infrared sensor using NBT based thin films and Si electronics

The V_{GS}-I_D characteristics of the circuitry on the fabricated device are shown in Fig. 7. Both the N-MOSFET and the N-JFET operated properly, without threshold voltage shifts. This result also shows that the SiN passivation layer blocked sodium diffusion during the NBT deposition and patterning processes.

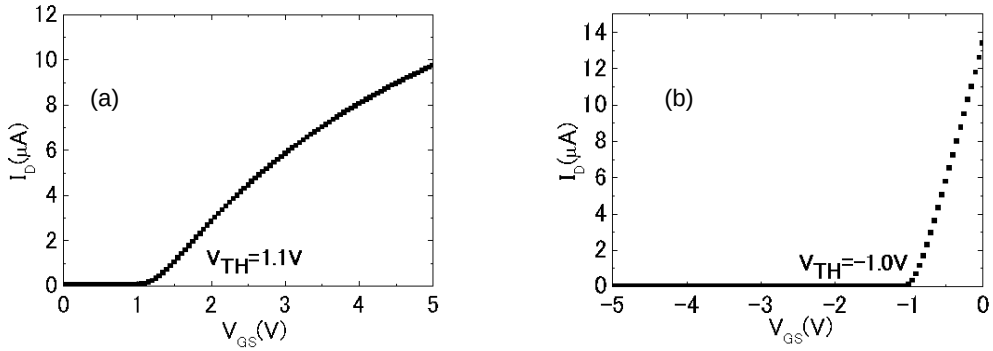

Figure 7. Typical V_{GS}-I_{DS} characteristics of (a) an NMOSFET and (b) an N-JFET. Both FETs operated well.

4. Conclusion

First, NBT-BT thin films have been deposited onto Pt/Ti/SiO_2/Si substrates by CSD. NBT-BT films showed a typical hysteresis loop with remnant polarization of 5 μC/cm^2 and a coercive field of 80 kV/cm. Pyroelectricity was obtained with pyroelectric coefficient of 0.6×10^{-8} C/cm^2K

Then, we demonstrated that a SiN film could be used as a passivation layer between Si electronics and an NBT layer to prevent diffusion of sodium ions or atoms into the Si electronics region. No threshold voltage shift in MOS C-V characteristics was observed when using a SiN passivation layer. The SiN layer not only blocked diffusion from the NBT solution, but also from crystallized NBT films during the NBT formation process. Also we have achieved monolithic integration of MOSFETs and lead-free ferroelectric material, which includes potassium, on Si substrates. These results can be applied to future integrated sensors using lead-free ferroelectric materials.

References

[1] Akai D, Kawazu N, Sugai T, Sawada K and Ishida M 2009 *Proceedings of SPIE* **7419** 741905
[2] Takenaka T, Maruyama K and Sakata K 1991 *Jpn. J. Appl. Phys.* **30** 2236.
[3] Chu B J, Chen D R, Li G R and Yin Q R 2002 *J. Eur. Ceram. Soc.* **22** 2115
[4] Sasaki A, Chiba T, Mamiya Y and Otsuki E 1999 *Jpn. J. Appl. Phys.* **38** 5564.
[5] Wang T B, Wang L E, Lu Y K and Zhou D P 1998 *J. Chin. Ceram.* **14** 14.
[6] Li Y, Chen W, Zhou J, Xu Q, Sun H, Liao M 2005 *Ceram. Int.* **31** 139
[7] Smolensky G A, Isupov V A, Agranovskaya A I and Krainik N N 1961 *Soc. Phys. Solid State* **2** 2651
[8] Hagiyev M S, Ismaizade L H and Abiyev A K 1984 *Ferroelectrics* **56** 215
[9] Sze S M 1981 *Physics of semiconductor devices 2nd ed* (New York: Wiley)
[10] Ishida M, Katakabe I and Nakamura T 1988 *Appl. Phys. Lett.* **52** 1326
[11] Yu T, Kwok K W and Chan H L W 2007 *Thin Solid Films* **515** 3563