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THERMO-SENSITIVE $Ba_{0.64}Sr_{0.36}TiO_3$ THIN FILM CAPACITORS FOR DIELECTRIC TYPE UNCOOLED INFRARED SENSORS

Liang Dong, Ruifeng Yue, Litian Liu, Xiaoning Wang, Jianshe Liu, and Tianling Ren

Institute of Microelectronics
Tsinghua University
Beijing 100084, China
Email: dongliang99@mails.tsinghua.edu.cn

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Abstract

$Ba_{0.64}Sr_{0.36}TiO_3$ (BST) thin films are prepared on Pt/Ti/SiO_2/Si_3N_4/SiO_2/Si substrates by a sol-gel method. Thermo-sensitive BST thin film capacitors with a Metal-Ferroelectrics-Metal (M-F(BST)-M) structure are fabricated as the active elements of dielectric type uncooled infrared sensors. XRD are employed to analyze the crystallographic structures of the films. AFM observations reveal a smooth and dense surface of the films with an average grain size of about 35 nm. Rapid temperature annealing (RTA) process is a very efficient way to improve crystallization quality. The preferable annealing temperature is 800℃ for 1 min. The butterfly shaped C-V curves of the capacitors indicate the films have a ferroelectric nature. The dielectric constant and dielectric loss of the films at 100 kHz are 450 and 0.038, respectively. At 25℃, where the thermo-sensitive capacitors work, the temperature coefficient of dielectric constant (TCD) is about 5.9 %/℃. These results indicate that the capacitors with sol-gel derived BST thin films are promising to develop dielectric type uncooled infrared sensors.

Keywords: BST thin films, IR sensors, Dielectric, Sol-gel method

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1. Introduction

These years have witnessed the development of Si-based uncooled infrared (IR) sensors for thermal imaging applications [1,2]. In contrast to conventional photo IR sensors, uncooled IR sensors can be operated at room temperature with comparable performance and low cost. A dielectric type IR sensor using ferroelectric thin films is one of the prospective candidates for uncooled IR detections, because there is no need of thermal stabilizer due to the current consumption as well as IR chopper compared to resistive and pyroelectric types [3,4]. It is well known that some ferroelectrics have large temperature coefficient of dielectric constants (TCD) around their Curie temperatures (T_c), such as $Ba_{1-x}Sr_xTiO_3$ and $PbSc_{1-x}Ta_xO_3$. In dielectric type uncooled IR sensors, thermo-sensitive ferroelectric thin film capacitors are used as the active elements. The dielectric constant change against temperature is detected through the capacitance change which corresponds to the IR radiation [5].

We are now devoting to developing a Si-based dielectric type uncooled IR sensor integrating with MOS readout circuits, as shown in Fig.1. The MOS part is first formed except Al connections. The thermo-sensitive $Ba_{0.64}Sr_{0.36}TiO_3$ (BST) thin film capacitor, i.e., the active element, is fabricated onto a leg-supported microbridge by using selective porous silicon (PS) micromachining [6]. It is essentially important for BST film capacitors that the following three factors should be of critical concern. A T_c of about 20℃ is preferable in point of room temperature work. A large TCD can assure high sensitivities since it is in direct proportion to the responsivity. And considering high density IR focal plane array sensors, the high value in dielectric constant with low dielectric loss is important for small size active elements.

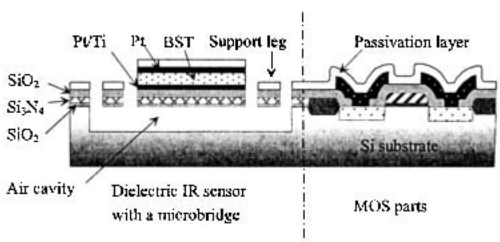

Fig.1. Schematic structure of BST dielectric type uncooled IR sensors

A variety of methods have been developed to deposit BST thin films, including sputtering [7], metal organic chemical vapor deposition (MOCVD) [8], pulsed laser ablation deposition (PLD) [9], and sol-gel [10]. Among them the sol-gel method is fairly simpler and offers some advantages such as stoichiometry control, homogeneity and low cost. In this paper, we investigate the microstructure of the sol-gel prepared $Ba_{0.64}Sr_{0.36}TiO_3$ thin films and the dielectric properties of thermo-sensitive capacitors, with the aims of suitable T_c, high dielectric constant and large TCD at room temperature.

2. Experiment

The precursor solution with a concentration of 0.4 mol/L is prepared by dissolving the barium acetate ($Ba(C_2H_3O_2)_2$), strontium acetate ($Sr(C_2H_3O_2)_2 \cdot 1/2H_2O$) and titanium isopropoxide ($Ti(C_3H_7O)_4$) in acetic acid (CH_3COOH) and ethylene glycol ($HOCH_2CH_2OH$) with appropriate stoichiometrics[11]. The solution is heated to promote the condensation reaction between acetic acid and ethylene glycol.

In order to be compatible with our dielectric infrared sensor structure, the BST thin films are deposited onto Pt (150 nm)/Ti (30 nm)/SiO_2 (500 nm)/Si_3N_4 (200 nm)/SiO_2 (100 nm)/Si substrates by spin coating. Each layer of the wet film is given a heat treatment at 100℃ for 5 min to remove H_2O, and then pyrolysed at 550℃ for 15 min. This step is repeated several times to obtain the desired thickness. The thin films are finally annealed in the O_2 ambient at different temperatures for 1 min by rapid thermal annealing (RTA) technique.

The prepared BST thin films are characterized for microstructure and morphology using X-ray diffraction (XRD) and atomic force microscopy (AFM).

The metal-ferroelectrics-metal (M-F(BST)-M) capacitors are constructed for the electrical and dielectric measurement. The upper electrodes of Pt (150 nm) are deposited by RF sputtering and patterned using lift-off method. The BST thin films are patterned by a photolithography process and subsequently dry etched. The dry etching process is carried out using reactive ion etching (RIE). $CHClFCF_3$ is used as the reactive gas with a flow of 10 sccm at a pressure of 3.2 Pa.

The C-V characteristic of BST thin films are performed on the capacitors using an HP 4061A semiconductor parameter analyzer.

Dielectric measurements are performed using an HP 4192A LF impedance meter at different temperatures ranging from 0℃ to 50℃ under 1 V at a frequency range of 10 Hz-10 MHz.

The capacitor samples below are with a $Ba_{0.64}Sr_{0.36}TiO_3$ thin film thickness of 300 nm and an upper electrode area of 100 μm ×100 μm without special descriptions.

3. Results and discussion

The crystallographic structure of BST thin films have been investigated by XRD analysis. Fig.2 shows the XRD patterns of BST thin films on a $Pt/Ti/SiO_2/Si_3N_4/SiO_2/Si$ substrate annealed at 700,750 and 800℃. Films annealed at 700℃ exhibit amorphous characteristic with a broad BaO_x peak. Films annealed at 750℃ appear to form perovskite structure with (110) peak dominating pattern. A perfect perovskite BST can be achieved at 800℃ anneal. As the temperature increased, the diffraction peaks are observed to be stronger and sharper, indicating the growth of grain and improvement of crystalline structure. It should be pointed out the films show some additional peaks near 30° besides the perovskite peaks. These peaks become distinct at 750℃ and disappear up further annealing to 800℃, which are considered to be of a SrO_2 or a $(Ba,Sr)_2Ti_2O_5CO_3$ phase [12].

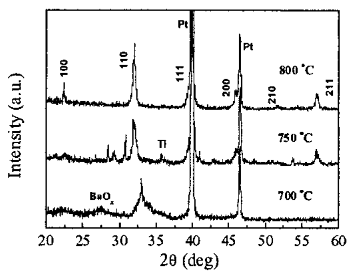

Fig.2. XRD patterns of the BST films annealed at various temperatures

The observation of surface morphology by AFM shows the dependence of grain growth on annealing temperature. The average grain sizes of the films annealed at 700,750 and 800℃ are approximate 8, 23 and

35 nm, respectively. Fig.3 shows the AFM images of BST thin films annealed at 800℃ in the scan area of 1 μm ×1 μm. It can be seen that the surface of the film is smooth, dense and uniform without any cracking, indicating the sol-gel derived BST thin film has a well-defined microstructure. As references, the conventional annealing process has also been performed. Our experiments have shown that RTA process can limit the defects and prevent crack to some extent. It probably should be contributed to the short-time thermal process, resulting in a reduction of interfacial reaction between BST and Pt/Ti film as well as a reduction of experiencing substantial shrinkage and internal stress. The experimental results show that the RTA process is a very efficient way to improve crystallization quality of BST thin films. The preferable annealing temperature is 800℃ for 1 min.

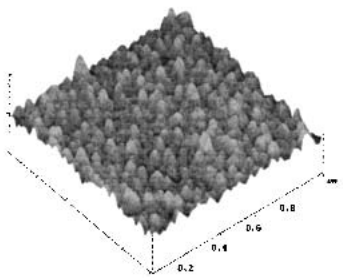

Fig.3. AFM image of the BST films annealed at 800℃ for 1 min

Fig.4 shows the C-V characteristic (at 100 kHz and 20℃) of the M-F(BST)-M capacitors with the BST films annealed at 800℃. Two peaks characterizing spontaneous polarization switching are clearly seen. The butterfly-shaped C-V curves indicate that the films have a ferroelectric nature. The absolute capacitance changes from 98 to 173 pF with the applied voltage in the -5 to 5 V range, which is considerable large and will make it easier to readout the capacitance change in application of dielectric type IR sensors. The capacitance value of different position varies by less than 2%, indicating a good degree of homogeneity in the thickness prepared by spin coating method. It is interesting to point out that the two curves in Fig.4 are not so symmetric. This distortion is probably concerned with the differences of the sputtering conditions and heat-treatments between those of the upper and bottom electrodes.

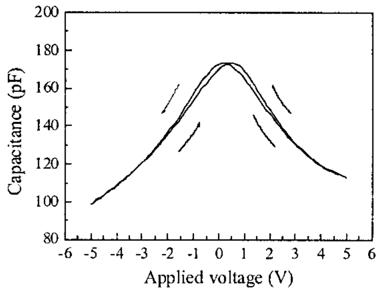

Fig.4. C-V characteristic of the M-F(BST)-M capacitor at room temperature

Fig.5 shows the dielectric constant (ϵ) and dielectric loss (tan δ) (at 25℃) as a function of frequency for the BST films annealed at 800℃. There is a tendency for the dielectric constant to decrease and the dielectric loss to increase at frequency above 1 MHz, which has also been reported for the films prepared by other methods[13]. However, at 1-100 kHz (which IR sensors work at) the former is relatively consistent and the later can maintain a relatively low value. At 100 kHz, the dielectric constant and dielectric loss are 450 and 0.038, respectively.

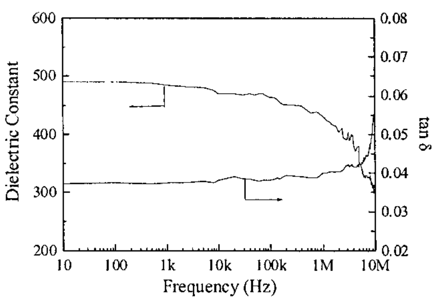

Fig.5. Dielectric constant and loss tangent of the BST films as a function of frequency

Fig.6 shows the temperature dependences of dielectric constant and dielectric loss (at 100 kHz) for the BST films annealed at 800℃. It is observed that the films have a distinct dielectric peak near 20℃ with a relatively broad temperature width, exhibiting characteristic feature of diffuse phase transition. Thus, T_c is considered to be about 20℃. The loss tangent is below 0.07 and increases with temperature. The dielectric constant against temperature is about 26/℃ at 25℃, where the absolute capacitance is 143 pF with the capacitor area of 100 μm ×100 μm. A TCD of about 5.9%/℃ is achieved at 25℃, which is comparable to that of PLD prepared BST films [9]. Therefore, it is possible that the M-F(BST)-F capacitor can work at room temperature (25℃) as the active elements of dielectric type IR sensors.

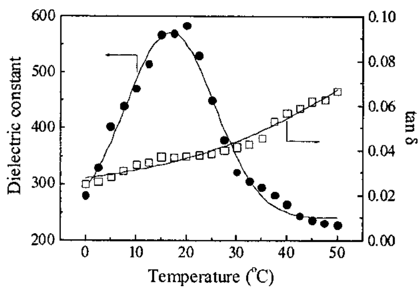

Fig.6. Temperature dependences of dielectric constant and loss tangent of the BST films

It is interesting to point out that after 10 times repetition of thermal cycling tests the dielectric constant and dielectric loss versus temperature curves are almost unchanged, keeping almost the same TCD. This indicates that the M-F(BST)-M capacitors are reproducible during the temperature change, which is considerable important for the dielectric type IR sensors.

4. Conclusion

High quality $Ba_{0.64}Sr_{0.36}TiO_3$ thin films have been successfully prepared by an improved sol-gel method with RTA processes. Thermo-sensitive BST ferroelectric thin film capacitors with a M-F(BST)-M structure have been fabricated as the active elements of dielectric type uncooled IR sensors. The perfect perovskite BST thin films with an average grain size of 35 nm can be achieved after annealed at 800℃ for 1 min. The experimental results show that the RTA process is a very efficient way to improve crystallization quality of the BST thin films. The existence of butterfly shaped C-V curves demonstrates the films have a ferroelectric nature. The dielectric constant is relatively consistent and the dielectric loss can maintain a relatively low value at 1- 100 kHz, and at 100 kHz, the former is 450 and the later is 0.038. The TCD is about 5.9%/℃ at 25℃, which is reproducible after thermal cycling tests. The thermo-sensitive M-F(BST)-F capacitors as the active elements should be a promising candidate for dielectric type uncooled IR sensors.

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