Paper

Application of Ferroelectric BST Thin Film Prepared by MOD for Uncooled Infrared Sensor of Dielectric Bolometer Mode

Non-Member Hong Zhu (Osaka Prefecture SEIS Project, Osaka University)
Member Minoru Noda (Osaka Prefecture SEIS Project, Osaka University)
Non-member Tomonori Mukaigawa (Osaka Prefecture SEIS Project, Hochiki Co.)
Non-member Huaping Xu (Osaka Prefecture SEIS Project, STA Fellow)
Non-member Kazuhiko Hashimoto (Osaka Prefecture SEIS Project, Matsushita Electric Ind. Co., Ltd.)
Member Masanori Okuyama (Osaka Prefecture SEIS Project, Osaka University)

Metal Organic Decomposition (MOD) has been applied to prepare Barium Strontium Titanate ($Ba_{1-x}Sr_xTiO_3$) ferroelectric thin film on micromachined Si wafer with an aim to fabricate dielectric bolometer(DB) type infrared image sensor. The detector pixel circuit is a capacitor-capacitor serially connected circuit, with one capacitor of BST film on Si membrane structure and the other on Si bulk structure. When exposed to IR radiation, the capacitance of the IR detecting capacitor on membrane structure changed as a result of the change in dielectric constant against temperature of BST ferroelectric film. Temperature Coefficient of Dielectric constant (TCD) of the MOD made BST (x=0.25,Ba/Sr=75/25) thin film is about 1%/K. Uniform and reproducible capacitance behavior in the BST ferroelectric thin film capacitor on micromachined Si substrate has been confirmed. Chopperless operation has been attained and IR responses of the fabricated sensor also have been obtained with R_v of 0.4 kV/W and D^* of $1x10^8$ $cmHz^{1/2}/W$, respectively.

Keywords: dielectric bolometer, infrared sensor, ferroelectric thin film, $Ba_{1-x}Sr_xTiO_3$(BST), metal organic decomposition(MOD)

1. Introduction

Recently, much attention has been focused on infrared Uncooled Focal Plane Arrays (UFPAs) because thermal image can be obtained easily without cooling the sensing pixels and its great potential exists in the commercial market[1-3]. UFPAs based on resistive bolometer mode have been developed intensively and are becoming commercially available in market[4,5]. There have been reported, on the other hand, some better results of sensitivities such as R_v, D^*, and NETD for the both sensors of pyroelectric (PE) and dielectric bolometer (DB) using ferroelectric material[6-9] compared to those using the resistive bolometers. Also reported that the temperature coefficient of dielectric constant (TCD) in the DB-mode sensor[10] is larger than that of resistance of around 2 %/K[4,5]. So the DB-mode sensors are expected to be applied for fabrication of highly sensitive UFPAs. Another merit in the DB-mode is that a chopperless operation is available, unlike in PE-mode. This is very advantageous to the increasing integration levels in UFPA because a chopping system is not needed. In the DB operation due to field-induced pyroelectric effect, the dielectric constant change against temperature is detected after infrared absorption through the capacitance change in the ferroelectric thin film such as $Ba_{1-x}Sr_xTiO_3$ (BST) and $Pb(Sc_{1/2}Ta_{1/2})O_3$.

We have done some research works on a new type of DB mode IR sensor and have developed both the pixel and readout circuit, thermally insulated multilayered structures for detector pixel, BST thin film deposition, the monolithic integration of ferroelectric thin film, and the thermally insulated detector pixel with the MOSFET process[11,12]. Of all the process, the most important is how to deposit a good ferroelectric thin film as the sensitivity of the sensor is directly linked with the property of the BST thin film. In our previous work, all the BST thin film is made by Pulsed Laser Deposition (PLD) method. PLD deposition has some merits such as good control of thin film composition (stoichiometric transfer), low temperature deposition and good ferroelectric property of the film. But it is difficult to make large area BST film by PLD due to the small plasma plume excited by the laser, and also the uniformity of the PLD made BST film is not as good as expected. MOD has its advantages, such as homogeneity, easy stoichiometry control and the ability to cover complex pattern over several-inch-size large area substrate. What is more, the MOD process is compatible with a Si-monolithic sensor fabrication process, when replacing conventional Al wiring to some heat-resistant metal such as Pt, on which a good BST film grows.

In this paper we report the ferroelectric properties of BST film prepared by MOD and performance of the fabricated IR sensor with the detector pixel using the MOD BST film.

2. Detector Pixel and Membrane Structure

The detector pixel circuit is a capacitor-capacitor serially connected circuit, followed by a MOSFET source follower output buffer[10,11]. The capacitance of the BST film above the thermally insulated membrane structure (the IR sensing capacitor) changes due to the temperature increase in the BST film upon the IR radiation, while the temperature of the BST film above the bulk Si substrate (the reference capacitor) remains unchanged and therefore its capacitance remains unchanged. When a couple of pulses are applied to the circuit, the change in the capacitance is detected as a voltage change, and this change is amplified by some followed circuits.

In fabricating IR sensor, thermally insulated structure is highly needed in order to get a large temperature increase in the detector pixel upon IR irradiation. Crack and deformation were easy to occur in the membrane structure in our early research stage, which seemed to be originated from stress unbalance in the structure. By considering and calculating the internal stress of each layer, a stress-balanced structure has been designed and fabricated by a multi-layered structure [11,12].

3. Preparation and Electrical Properties of BST Thin Film by MOD

0.06M MOD solutions with Ba/Sr ratio of 75/25 had been used to prepare BST film. A typical process to make BST film is to spin-coat the solution on a bulk Si wafer at 4000 rpm, 20 seconds at first; then the film is baked on hot plate at 150°C for 10 minutes to remove the solvent; and then the film is given a pyrolysis heat treatment in a furnace at 470°C for 30 minutes to remove the residual organics and promote chemical reaction. All the 3 processes were repeated several times until the desired thickness of the film is achieved. Finally, the film with certain thickness is annealed in the furnace at 800°C for 60 minutes to make the thin film become crystallized. Usually a 10 layers BST film is deposited with a thickness about 400 nm. Figure 1 shows the XRD patterns of BST films spin-coated at 4000rpm and annealed 1 hour at 600, 700 and 800°C, respectively. BST film annealed at 600°C shows a broad BaO_x peak, but does not show any perovskite BST (101) and (110) peaks, which shows that the BST crystalline is not formed at 600°C. Films annealed at 700°C and 800°C show perovskite BST (101) and (110) peaks dominating pattern, which shows the film becomes crystallized at these temperatures. The film annealed at 800°C seems to have a large and better crystalline than that annealed at 700°C, as its (101) and (110) peaks have higher intensities and are sharper than those of (101) and (110) peaks annealed at 700°C. From the XRD result, it is found that the anneal temperature of the BST film should be higher at least than about 700°C.

Ferroelectric BST ceramics with perovskite structure possess a large TCD around their Curie temperature (T_C) and the T_C can be easily changed from 0°C to 70°C by adjusting the ratio of Ba/Sr. This characteristic shows the transition of the BST from ferroelectric phase into paraelectric phase. A good BST thin film with a large TCD

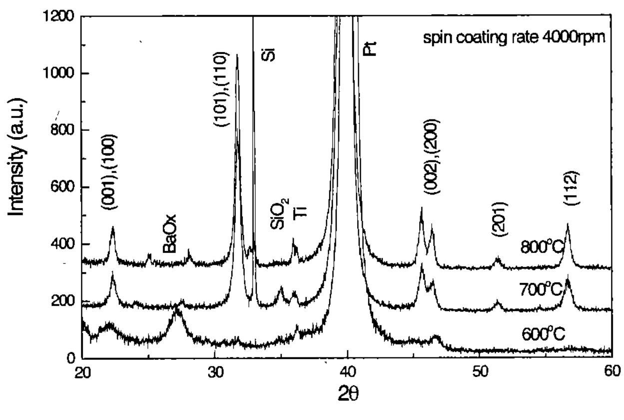


Figure 1. XRD patterns of BST films spin-coated at 4000 rpm annealed 1 hour at different temperatures.

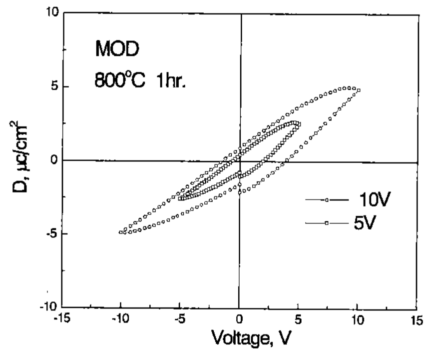


Figure 2. Hysteresis loops of BST film spin-coated on $Pt/Ti/SiO_2/Si_3N_4$ membrane at 4000 rpm and annealed for 1 hour, 800°C.

is highly expected so as to fabricate an IR sensor with a high sensitivity. Figure 2 shows the hysteresis loops of BST film spin-coated on micromachined chip at 4000 rpm, 10 layers, and annealed at 800°C for 1 hour. The film with about 400 nm thickness on membrane structure can only withstand 10V bias. However the BST thin film deposited on common $Pt/Ti/SiO_2/Si$ substrate can withstand 20V bias. This shows that the later etching process in the sensor fabrication after the ferroelectric film deposition has some effects on the electrical property of the BST film. Figure 3 shows the temperature dependence of the dielectric constant of the BST film spin-coated at 4000 rpm and annealed at 800°C for 1 hour on a micromachined chip. The dielectric constant was measured at 1 kHz and 1V (peak voltage) condition. The curve is very stable after rounds of thermal test. The dielectric constant of the film increased as the temperature increased. The TCD is about 1%/K, which is lower than that of the BST ceramics of about 3%/K. This is probably due to the grain size effect. The grain size of the BST film deposited at this condition was about 0.08 μm, far from the grain size of the bulk ceramics of about 1 to 2 μm.

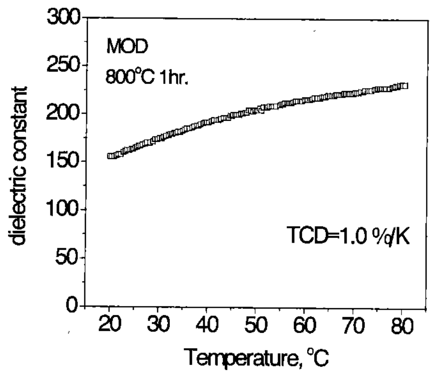


Figure 3. Dielectric constant of the BST film on $Pt/Ti/SiO_2/Si_3N_4/SiO_2$ membrane spin-coated at 4000 rpm, annealed for 1 hour at 800°C versus temperature.

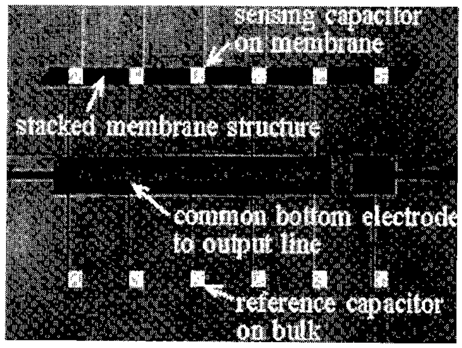


Figure 4. Layout of the detector pixel.

As TCD is very important to the sensitivity of IR sensor, more efforts should be taken to increase the TCD of the MOD BST film.

4. Uniformity and IR Response of Detector Pixel

Next the BST film was prepared on a thermally insulated structure for the DB mode sensor. Figure 4 is the photograph of 1x5 pixel array with another single pixel, in which the sensitive capacitors are fabricated on diagram membrane structure. After the final backside Reactive Ion Etching (RIE) of the Si with 50 μm thickness left under the membrane structure, the BST film is directly upon $SiO_2/Si_3N_4/SiO_2$ triple layer membrane structure. The Si below the sensing capacitor has all been etched out, and the $SiO_2/Si_3N_4/SiO_2$ triple layer looks transparent on the photograph compared with the reference capacitor on the Si bulk material.

The uniformity of the BST film made by MOD is very good. Figure 5 shows the D-E hysteresis loops of BST films on different electrodes deposited on micromachined chip. It is estimated that the difference between the dielectric constants of the BST film measured on different electrodes is within 5%. The good uniformity of BST film prepared by MOD is very important to sensor fabrication both in the aspect of increasing pixel density and also in the aspect of mass production. Compared with PLD, the MOD has the merit of good uniformity even in several-inch-size wafer and also the process is very compatible with the monolithic process of the Si micromachining sensor fabrication process. But the demerit of MOD is the high temperature and long time annealing, which might damage some properties of IC structure. We are now doing more experiments on how to make a good BST thin film by MOD at low temperature

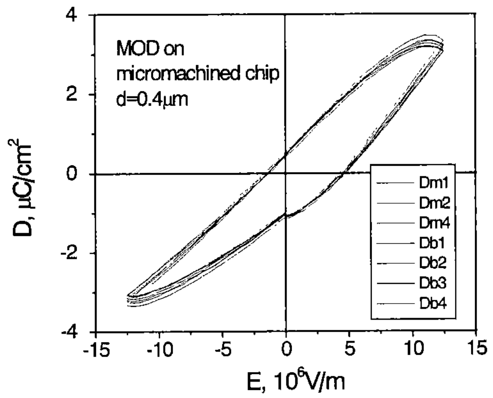


Figure 5. D-E hysteresis loops of the BST film on micromachined chip spin-coated at 4000 rpm annealed for 1 hour at 800°C measured on different electrodes.

(such as 650°C, which is the maximum allowable temperature for application to W/TiN plug structure used in recent ferroelectric capacitors in ferroelectric memory devices), long time annealing condition or high temperature (such as 750°C) short time (rapid thermal annealing) condition so as not to damage the IC elements.

IR response was measured by applying supply voltage of 1V at 1 kHz to the sample. Figure 6 shows an example of IR response of a detector pixel of MOD BST film when exposed to a black-body IR source with power density 20 mW/cm^2, using an IR filter in front of the pixel. A chopper was used only for making clear the output voltage difference in order to calculate the responsivity of the IR sensor; while in practical use this bolometer-type detector operates without a chopper. The output of IR response in Fig. 6 is defined as the voltage difference between exposed and not exposed to the IR radiation, which means the output is about 70 mV, where the size of the detector pixel is 200x200 µm^2. In addition, the output is ideally zero without

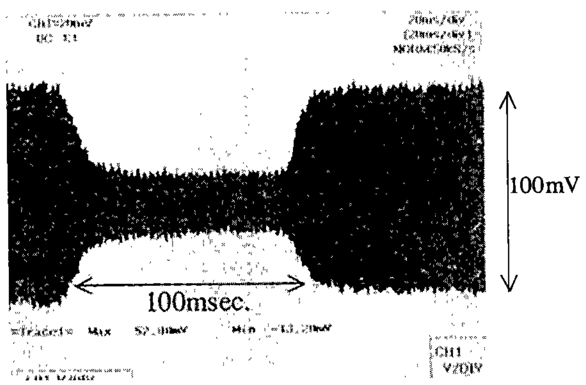


Figure 6. IR response of a detector pixel when exposed to IR source with power density of 20 mW/cm^2.

IR radiation, so the output appeared in Fig.6 originates from unbalance between the detecting and reference capacitance in the pixel, means offset voltage. Other pixels and measurement system were used to measure thermal noise voltage(V_n), where V_n was about 100 nV. It should be noted that further improvement is needed to stabilize V_n among samples. When V_n is assumed to be 100 nV, the calculated thermal responsivity R_v was 0.4 kV/W and the specific detectivity D^* was 1x10^8 cmHz$^{1/2}$/W. During the IR test, on the other hand, the offset of the IR signal is very small with a shift speed about 0.5-1 mV/10min, which indicates the electrical property of MOD BST thin film is very stable.

5. Conclusion

BST thin film prepared by MOD has been used in the detector pixel in dielectric bolometer type infrared sensor. The BST film was spin-coated on a bulk Si wafer at 4000 rpm, and annealed at 700 to 800°C. The TCD of the as deposited MOD BST film is about 1%/K. It is especially noted that the uniformity and reproducibility of the detector pixel were greatly improved by the developed MOD film. The IR response of a fabricated detector pixel that can be operated without a chopper has been confirmed with the voltage responsivity R_v and the specific detectivity D^* of 0.4kV/W and 1x10^8 cmHz$^{1/2}$/W, respectively.

Acknowledgments

The authors would like to thank all members of SEIS group and all fellow researchers in Okuyama Lab, Osaka University for their valuable advice and beneficial help. The support of Osaka Prefecture for this work also is greatly appreciated.

(Manuscript received April 28, 2000, rivised Sep. 4, 2000)

References

[1] R.S. Balcerak, *SPIE, Infrared Technology and Applications XXV*, **3498**, 110-118 (1999).

[2] C. Hanson, H. Beratan, R. Owen, M. Corbin and S. Mckenny, *SPIE, Infrared Detectors: State of the Art*, **1735**, 17-26 (1992).

[3] R. Watton, *Integrated Ferroelectrics*, **4,** 175-186 (1994).

[4] W. Radford, D. Murphy, A. Finch, K. Hay, A.Kennedy, M. Ray, A. Sayed, J. Wyles, R. Wyles, J. Varesi, E.Moody and

F. Cheung, *SPIE, Infrared Technology and Applications XXV*, **3498,** 119-130 (1999).

[5] J. Brady, T. Schimert, D. Ratcliff, R. Gooch, B.Ritchey, P. McCardel, K. Rachels, S. Ropson, M. Wand, M. Weinstein and J.Wynn, *SPIE, Infrared Technology and Applications XXV*, **3498,** 161-167 (1999).

[6] R. Owen, J. Belcher, H. Beratan, and S. Frank, *SPIE, Infrared Detectors and Focal Plane Arrays IV*, **2746,** 101-112 (1996).

[7] Y. Takada, M. Ikari, S. Kirihara, K. Uchizawa, and R. Taniguchi, *the 16th Sensor Sym. Kawasaki, Japan,* 231-234 (1998).

[8] R. Watton and P. Manning, *SPIE, Infrared Technology and Applications XXIV*, **3436,** 541-554 (1998).

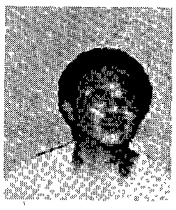
[9] J. F. Belcher, C. M. Hanson, H. R. Beratan, K. R. Udayakumar, and K. L. Soch, *SPIE, Infrared Technology and Applications XXIV*, **3436**, 611-622 (1998).

[10] M. Noda, K. Hashimoto, R. Kubo, H. Tanaka, T. Mukaigawa, H. Xu and M. Okuyama, *Sensors and Actuators A*, **77,** 39-44 (1999).

[11] M. Noda, T. Mukaigawa, K. Hashimoto, T. Kiyomoto, H. Xu, R. Kubo, H. Tanaka, T. Usuki and M. Okuyama, *SPIE, Infrared Technology and Applications XXV*, **3498,** 565-573 (1999).

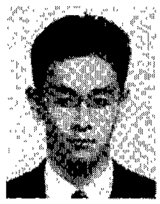
[12] H. Xu, T. Mukaigawa, K. Hashimoto, R. Kubo, T. Kiyomoto, H. Zhu, M. Noda and M. Okuyama, *Transducers '99 Sendai, Japan*, 398-401 (1999).

Hong Zhu (Non-member) received a B.S. degree in material science and engineering, University of Science and Technology, Beijing in 1990, and Ph.D degree in semicondutor, Ion Beam Lab, Shanghai Institute of Metallurgy, Chinese Academy of Sciences in 1995. From 1998 to 2000, worked in Okuyama lab, Graduate School of Engineering Science, Osaka University as a visiting scientist and joined in the SEIS research project. Now his research area are deposition of ferroelectric thin film, fabrication of IR image sensor, and ion implantation.

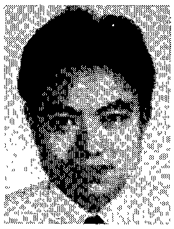


Minoru Noda (Member) received a B.S., M.S. and Dr.E. degree in electrical engineering from Osaka University in 1981, 1983 and 1993, respectively. He has been an associate professor of Osaka University since 1997, and is currently working in the field of applications of ferroelectric thin films to integrated circuits especially to infrared image sensor IC's and to electron devices such as MFIS(Metal-Ferroelectric-Insulator-Semiconductor) non-volatile memory device. Japan Society of Applied Physics, Institute of Electrical Engineers of Japan, The Institute of Electronics, Information and Communication Engineers and Society of Sensing Technology of Japan member.

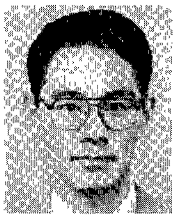
Tomonori Mukaigawa (Non-member) received a B.S. and M.S. degrees in material science from Science University of Tokyo in 1993 and 1995, respectively. Currently, he is working on research of thermal analysis in micromachined structures, and development of micromachined infrared sensor in Hochiki Co.



Huaping Xu (Non-member) received the B.S. and M.S. degrees in solid-state physics and materials engineering from Shanghai University of Science and Technology, and the Ph.D. degree in semiconductor device physics from Shanghai Institute of Metallurgy, Chinese Academy of Sciences (SIMCAS) in 1997. He joined the Super-Eye-Image-Sensor (SEIS) Development Group at Technology Research Institute of Osaka Prefecture (TRI) as a JSPS Postdoctoral Fellow and STA Research Fellow in 1997 and 1999, consecutively. The research work he involved is to develop ferroelectric thin-film microbolometers. Japan Society of Applied Physics member.



Kazuhiko Hashimoto (Non-member) received a B.S. degree in polymer science from Osaka University in 1985, and is presently a senior engineer in Human Environment System Development Center at Matsushita Electric Industrial Co., Ltd. He has worked on development of pyroelectric array infrared detector, ferroelectric material for dielectric bolometer sensor and sensing system. Japan Society of Applied Physics member.



Masanori Okuyama (Member) received a B.S. and Dr.E. degree in electrical engineering from Osaka University in 1968 and in 1972, respectively. He has been a professor at Osaka University from 1991. His current interests are preparation and characterization of ferroelectric thin films and their electronic devices including memory devices, sensors and actuators, characterization of SiO2/Si junction and Si surface and low-temperature preparation of dielectric thin films using photon and soft-X-ray. Japan Society of Applied Physics, Institute of Electrical Engineers of Japan, Institute of Electrical and Electronics Engineers, Society of Sensing Technology of Japan, Japan Society of Infrared Science and Technology, Surface Science Society of Japan, Japanese Society for Synchrotron Radiation Research, Physical Society of Japan and Institute of Systems, Control and Information member.