Paper

Preparation of BST Ferroelectric Thin Film by Metal Organic Decomposition for Infrared Sensor

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

Barium Strontium Titanate ($Ba_{1-x}Sr_xTiO_3$) ferroelectric thin films have been prepared by Metal Organic Decomposition (MOD) on $Pt/Ti/SiO_2/Si$ and on micromachined $Pt/Ti/NSG/Si_3N_4/SiO_2/Si$ wafer with an aim to fabricate dielectric bolometer type infrared sensor. The XRD pattern and D-V hysteresis curve of the film have been measured in order to investigate the effects of the final annealing temperature and annealing time on the property of the film. The results show that the films annealed at 700 or 800°C all have good perovskite structure, while the film annealed at 800 °C has better ferroelectric loops. Films annealed at 800°C with different annealing time from 5 to 60 minutes show a similar perovskite structure, among which films annealed at 30 and 60 minutes condition have the better ferroelectric loops. Temperature Coefficient of Dielectric constant (TCD) of the MOD made BST thin film on micromachined substrate is about 1%/K. The uniformity of the BST film on micromachined Si wafer also has been confirmed to be well enough for operation of sensor array.

Keywords: ferroelectric thin film, BST, dielectric bolometer, infrared sensor, metal organic decomposition

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)]. 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 to 70 °C by adjusting the ratio of Ba/Sr. This characteristic shows the transition of the BST from ferroelectric phase into paraelectric phase.

Our research group has done some research works on a new type of dielectric bolometer mode IR sensor and has 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 [(4)]. Of all the process, the most important is how to deposit a good ferroelectric thin film as the sensitivity of the sensor is directly originated from 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 very compatible with the monolithic sensor fabrication process. In this paper we report the preparation and ferroelectric properties of BST film prepared by MOD under different temperatures (600-800 °C) and different time (5-60 min.) annealing condition for application to infrared sensor fabrication.

2. Preparation of BST Thin Film by MOD

MOD solutions of 0.06M (mol/liter) with ratio of Ba to Sr

75/25 have been used to prepare BST film. The deposition process and parameter is listed in Table I. A typical process to make BST film is to spin-coat the solution on the micromachined 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 silica tube furnace at 470 °C for 30 minutes in air 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 obtained. Finally, the film with certain thickness is annealed in the furnace in air at 800 °C for 60 minutes to make the thin film become crystallized. Usually a 10-layer BST film is deposited with a thickness about 400 nm. The bulk substrate material $Pt/Ti/SiO_2/Si$ is used to find the best condition to deposit BST film. The micromachined $Pt/Ti/NSG/Si_3N_4/SiO_2/Si$ chip is used to fabricate the sensor. The ferroelectric properties of the BST film are measured by means of RT6000 System made by Radiant Technologies Incorporation.

Table I. Process and parameters of MOD.

1. Spin coating	500 rpm 5 sec,
	2000~4000 rpm, 20 sec
2. Drying	150 ℃, 10 min.
3. Prebaking	470 ℃, 30 min.
4. Final annealing	600~1000 ℃, 5~60 min.

3. Structure and Ferroelectric Property of BST Thin Film

A good BST film should have a smooth surface and should have no macro or micro cracks. Good surface is very important to the later process in the sensor fabrication as the upper Pt/Ti electrode is directly deposited on the BST surface and also the upper electrode pattern is fabricated by lift–off process. What is more, cracks in BST film will have bad effects on the electrical property. The surfaces of the BST films deposited at different spin-coating rates and under different final annealing temperatures have been observed under optical microscope and all the samples are prepared on bulk material $Pt/Ti/SiO_2/Si$ substrate. It was found that the films spin coated at 2000 rpm all have macro-cracks even though they are annealed at different temperatures from 600, 700, 800 °C. This is because each layer of the film spin coated at 2000 rpm is very thick and this makes the final film have high internal stress during the final high temperature annealing process, which results in a film with macro-crack. The surface of the BST films spin coated at 3000 rpm and 4000 rpm are good and no macro-crack is observed. The film deposited at low spin coating rate tends to have crack on them, so the film should be deposited at a high spin coating rate. Between 3000 rpm and 4000 rpm spin coating rate, we prefer 4000rpm as it gives out a thinner thickness of each layer.

Figure 1 shows the X Ray Diffraction (XRD) patterns of BST films spin-coated at 4000rpm annealed for 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 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

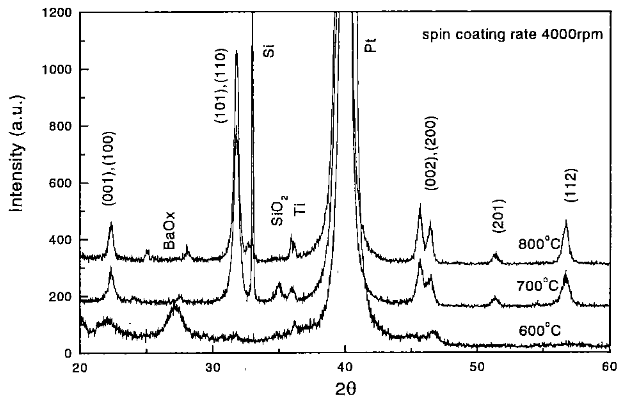


Figure 1. XRD patterns of BST films spin-coated at 4000 rpm annealed at different temperatures for 1 hour.

annealed at 700 °C, as its (101) and (110) peaks have a higher intensity and are sharper than those of (101) and (110) peaks annealed at 700 °C. From the XRD result, we can learn that the best condition to anneal the BST film is between 700 and 800 °C.

Figure 2 shows the XRD pattern of the films spin coated at 4000 rpm and annealed at 800 °C for 5, 10 and 30 minutes, respectively. The three films all have almost the same XRD pattern. In the case of the XRD pattern of the film annealed for 5 minutes, although its annealing time is only 5 minutes, the main peak of BST can be seen clearly, which means that the film has become crystallized. It seems that the annealing temperature is

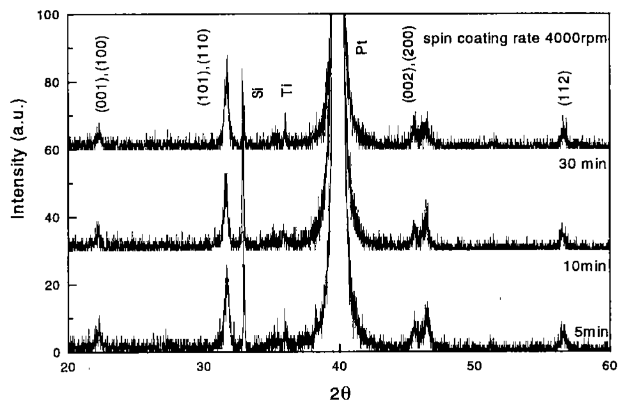


Figure 2. XRD patterns of BST films spin-coated at 4000 rpm annealed at 800 °C with different annealing time.

more important than annealing time. At a right temperature, a short time annealing is quite enough to make the film become crystallized.

Figure 3 shows the micrograph of BST film observed by

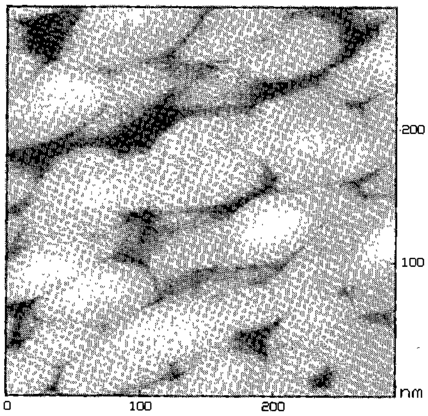


Figure 3. AFM image of the BST film spin coated at 4000 rpm annealed at 800 °C for 1 hour.

Atomic Force Microscope (AFM). The grain size of film spin-coated at 4000 rpm, annealed at 800 °C for 1 hour is not large, in the range from 50 to 80 nm. Observed from the three dimensional view, the surface of the film is very smooth.

Figure 4 shows the hysteresis loops of BST film spin-coated at 3000rpm annealed for 1 hour at different temperatures. The films annealed at 800 and 700 °C can withstand 20 V bias, while the film annealed at 600 °C can only withstand 5 V bias. The best loop among them is the one annealed at 800 °C, a slim sloop, while a fat loop when annealed 700 °C. The film annealed at 600 °C almost gives out a leak loop. Considering the XRD pattern of the films annealed at different temperatures in Fig. 1, we can understand why the film annealed at 600 °C does not have a good ferroelectric property. The BST crystalline almost has not formed when the film is annealed at 600 °C. The films annealed at 800 and 700 °C almost have the same XRD pattern, but their hysteresis loops are quite different from each other. This shows that the microstructure has great effects on the electrical property of the BST film. This microstructure is beyond the ability of XRD analysis and should be observed by Scanning Electronic Microscope (SEM) or AFM.

Figure 5 shows the hysteresis loops of BST film spin-coated at 4000rpm annealed at 800 °C with different annealing time. The four kinds of films all can withstand 20 V bias. The loops of the films annealed for 60 and 30 minutes are almost the same, a slim loop showing typical ferroelectric characteristics in both cases. The loops of the films annealed for 10 and 5 minutes are not as good as that annealed for 60 and 30 minutes, both giving out a fat loop. The loop of the film annealed for 10 minutes is better than that annealed 5 minutes. It seems that the ferroelectric property of

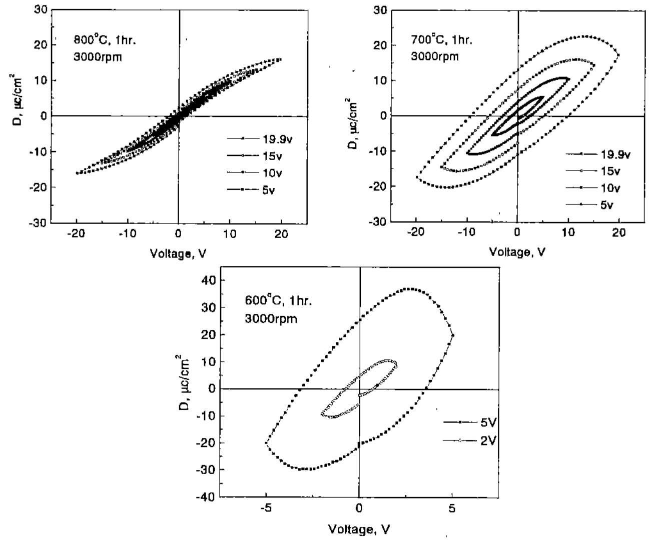


Figure 4. Hysteresis loops of BST film spin coated at 3000 rpm annealed for 1 hour with different annealing temperatures.

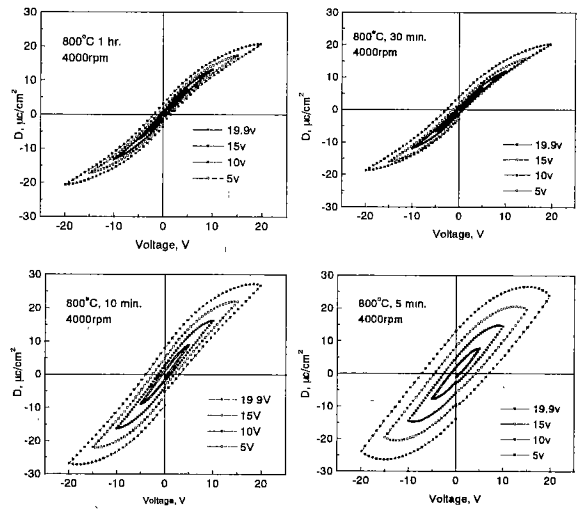


Figure 5. Hysteresis loops of BST film spin coated at 4000rpm annealed at 800°C temperature with different annealing time.

the film annealed for long time is better than that annealed for short time, which is probably because that long time annealing tends to result in a bigger grain size of the film. From the XRD pattern in Fig. 2, we can see that the films annealed for 30, 10 and 5 minutes almost have the same kind of XRD pattern, but their hysteresis loops are quite different from each other. The microstructure of the film has great effects on the ferroelectric property of BST film. Many papers have reported that the ferroelectric properties have great connection with the grain size of the film [5, 6]. BST film with large crystal size tends to have better ferroelectrical property. Considering that long time annealing tends to give out a BST film with large crystal size, we choose the 60 minutes annealing condition to anneal the sample.

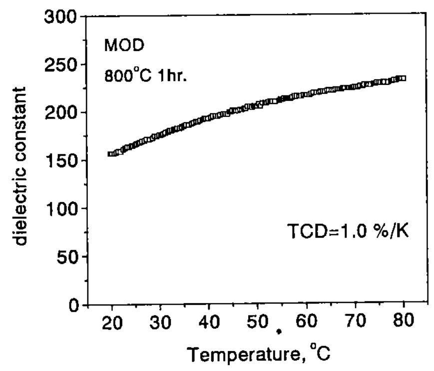


Figure 6. Dielectric constant versus temperature of the BST film on $Pt/Ti/NSG/Si_3N_4/SiO_2/Si$ substrate spin-coated at 4000 rpm annealed for 1 hour at 800 °C.

Figure 6 shows the temperature dependence of the dielectric constant of the BST film spin-coated at 4000 rpm annealed at 800°C for 1 hour on 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 Temperature Coefficient of Dielectric constant (TCD) is about 1%/K, which is lower than that of the BST ceramics with a TCD about 3%/K. This is probably because of the grain size effect [5,6]. The grain size of the BST film deposited at this condition is about 0.08 μm, far from the grain size of the bulk ceramics about 1~2 μm. 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.

The uniformity of the BST film made by MOD is very good. Figure 7 shows the D-V hysteresis loops of BST film deposited on micromachined chips measured on different electrodes. It is estimated that the difference between the dielectric constants of the BST film measured on different electrodes on the micromachined chips is within 5%. The good uniformity of BST film by MOD is very important in practical sensor fabrication process, as this will result in a uniform capacitor of the detector pixel [4]. MOD process is very applicable in preparing thin film for sensors as it can easily deposit on a large area substrate even on a 4-inche wafer and with good uniformity.

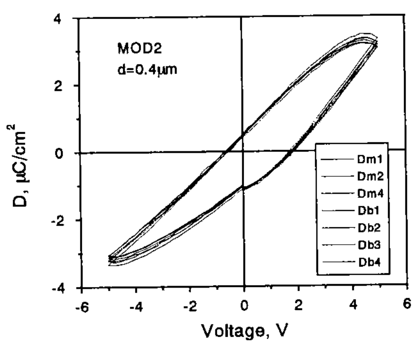


Figure 7. The D-V hysteresis loops of the BST film on micromachined chip spin coated at 4000 rpm annealed for 1 hour at 800 °C measured on different electrodes.

4. Conclusion

BST ferroelectric thin films have been prepared by MOD on $Pt/Ti/SiO_2/Si$ substrate under different annealing temperatures and annealing time and examined for application to infrared sensor. The BST film should be deposited at a high spin-coating rate like 4000 rpm to avoid macro crack in the film. The XRD pattern and ferroelectric loops measurements show that the films annealed 700 or 800 °C have become crystallized, while the film annealed at higher temperature has better ferroelectric property. BST Films annealed at 800°C for short time (such as 5 or 10 minutes) do not exhibit a good ferroelectric property, while films annealed for long time (such as 30 or 6 0 minutes) show a good property. The TCD of the as deposited MOD BST film on micromachined substrate is about 1%/K. The good uniformity of MOD made BST film and the possibility to deposit on a large area substrate make the MOD process very competitive in preparing thin film for sensor fabrication.

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

References

[1]C. Hanson, H. Beratan, R. Owen, M. Corbin and S. Mckenny, “Uncooled thermal imaging at Texas Instruments”, SPIE, Vol. 1735 Infrared Detectors: Sate of the Art, pp.17-26, 1992.

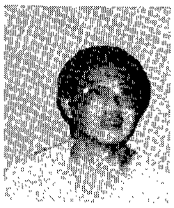
[2]R. Watton, “Ferroelectric materials and IR bolometers arrays: from hybrid arrays towards integration”, Integrated Ferroelectrics, 4, pp.175-186, 1994.

[3]M. Ueno, O. Kaneda, T. Ishikawa, K. Yamada, A. Yamada, M. Kimata and M. Nunoshita, “Monolithic uncooled infrared image sensor with 160X120 pixels”, SPIE, Vol. 2552 Infrared Technology XXI, pp.636-643, 1995.

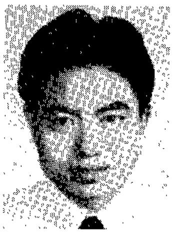
[4]M. Noda, K. Hashimoto, R. Kubo, H. Tanaka, T. Mukaigawa, H. Xu and M. Okuyama, “A new type of dielectric bolometer mode of detector pixel using ferroelectric thin film capacitors for infrared image sensor”, Sensors and Actuators A, 77, pp.39-44, 1999.

[5]G. Arlt, D. Hennings, and G. de With, “Dielectric properties of fines-grained barium titanate ceramics” J. Appl. Phys. 58, pp.1619-1625, 1985.

[6]H. F. Cheng, “Structural and Optical propetties of laser deposited ferroelectric $(Sr_{0.2}Ba_{0.8})TiO3$ thin films”, J. Appl. Phys. 79, pp.7965-7971, 1996.

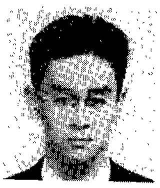


Hong Zhu (Non-member) received a B.S. degree in material science and engineering, University of Science and Technology, Beijing in 1990, and Ph.D degree in semicondutor, Ion Beam Lab, Shanghai Institute of Metallurgy, Chinese Academy of Sciences in 1995. From 1998 to 2000, worked in Okuyama lab, Graduate 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.

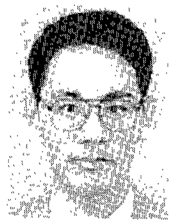


Huaping Xu (Non-member) received the B.S. and M.S. degrees in solid-state physics and materials engineering from Shanghai University of Science and Technology, and the Ph.D. degree in semiconductor device physics from Shanghai Institute of Metallurgy, Chinese Academy of Sciences (SIMCAS) in 1997. He 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.

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-Semicond uctor) 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.



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.