JOURNAL OF MATERIALS SCIENCE **38** (2003) 1295–1300

Electrical properties of ferroelectric SBT thin films prepared using photosensitive sol-gel solution

TAE-HO PARK, KI-HO YANG, DONG-KYUN KANG
Department of Materials Science and Engineering, Korea University, Seoul 136-701, Korea
E-mail: pth@particology.com
TAE-YOUNG LIM
Korea Institute of Ceramic Engineering and Technology (KICET)
KEUN-HO AUH
Department of Ceramic Engineering, Hanyang University, Seoul 133-791, Korea
BYONG-HO KIM
Department of Materials Science and Engineering, Korea University, Seoul 136-701, Korea

Self-patterning of thin films using photosensitive sol-gel solution has advantages such as simple manufacturing process compared to photoresist/dry etching process. In this study, ferroelectric $Sr_{0.9}Bi_{2.1}Ta_2O_9$ thin films have been prepared by spin coating method using photosensitive sol-gel solution. Strontium ethoxide, tetramethylheptanedionato bismuth and tantalum ethoxide were used as starting materials. As UV exposure time to the SBT thin film increases, the intensity of UV absorption peak of metal beta-diketonate decreases due to degradation of solubility resulted from Metal-Oxygen-Metal (M–O–M) bond formation. The solubility difference by UV irradiation on SBT thin film allows to obtain a fine patterning of thin film. The ferroelectric properties of the UV irradiated SBT thin films are superior to those of the non-UV irradiated film.

1. Introduction

Ferroelectric Random Access Memory (FRAM) is considered to be a new potent memory for high-performance memory device due to its ideal properties, such as random access, high-density integration, fast read and write operation, long endurance, excellent retention and non-volatility with practically unlimited usage [1, 2]. FRAM uses thin films of ferroelectric oxide for capacitors, instead of silicon-oxide films which have been utilized for DRAM (Dynamic Random Access Memory), and can be adopted to electronic devices such as non-volatile memory devices due to non-volatile property of ferroelectric oxide thin films [3]. In other words, FRAM has not only the features of DRAM such as fast read and write operation, low voltage operation, but also non-volatility where the information during the operation of electronic devices is kept stored in the memory even after power of devices is turned off [4]. PZT (Lead Zirconium Titanate) has been mainly developed as a capacitor of FRAM. However, if metal electrode, especially Pt, is applied to PZT, it poses fatal fatigue problems in FRAM capacitors [4].

Various types of oxide electrodes instead of Pt have been investigated to improve fatigue phenomena [5]. Meanwhile, SBT (Strontium Bismuth Tantalate) which has layer Perovskite structure, is a material suitable to high integration due to its excellent fatigue resistance, low leakage current and insensitivity to film thickness [6]. Micro-patterning of ferroelectric thin films is one

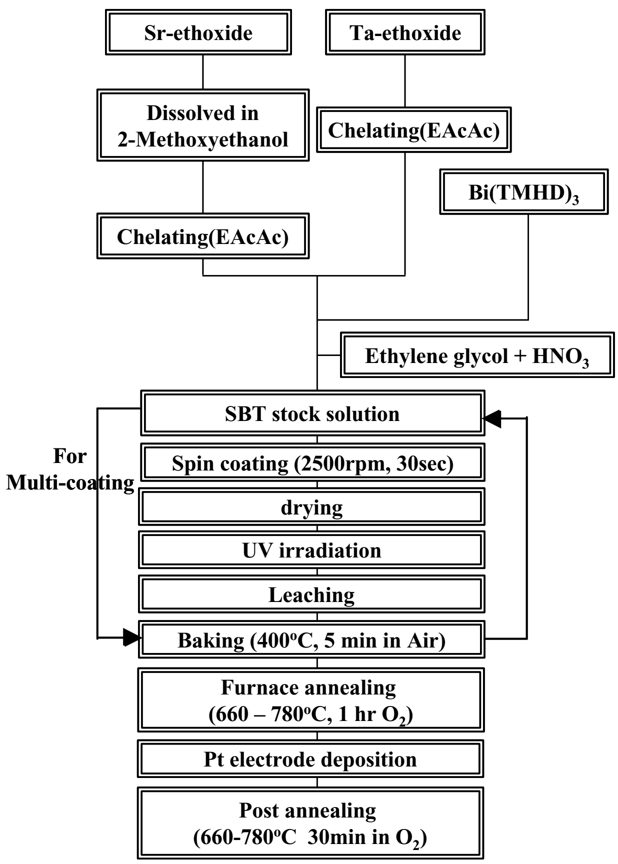

Figure 1 Preparation procedure of SBT thin films.

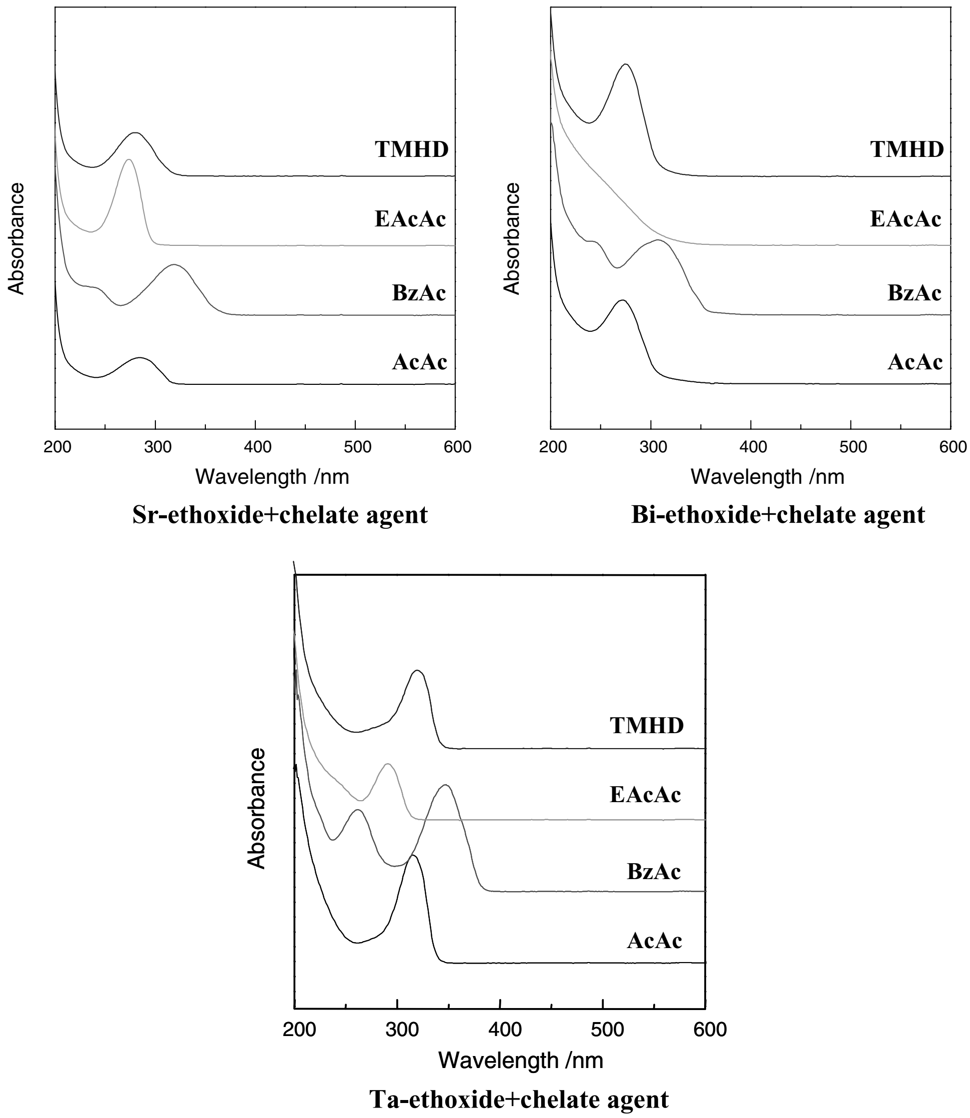

Figure 2 UV/VIS spectra of chelated metal alkoxides.

of the main issues in the manufacturing of ferroelectric micro-devices. Ion milling/reactive ion etching is currently the most widely applied technique for fine patterning of the ferroelectric films. However, such processes tend to degrade the capacitor performance. Metal alkoxides which chelate with β-diketonate ligands exhibit absorption bands in the UV region which are the characteristics of the π-π^* transition in the chelate ring of beta-diketonate ligands. The irradiation of the gel films with UV light corresponding to these bands dissociates the chelate rings, and simultaneously decreases the solubility of these gel films by M—O—M bond formation in organic solvent such as alcohol [7]. Solubility difference by UV irradiation allows to achieve a fine patterning.

In this study, preparation of SBT thin films through the self-patterning process using photosensitive sol-gel solution and ferroelectric properties of the patterned SBT thin films were studied.

2. Experimental procedures

2.1. Preparation of sol-gel solution and film formation

Sr, Bi, Ta-ethoxides were chelated by several β-diketone ligands in order to choose chelating agent

TABLE I Summary of λ_{max} in UV absorption peaks

Sr-ethoxide + TMHD	280 nm	Bi-ethoxide + TMHD	274 nm	Ta-ethoxide + TMHD	319 nm
Sr-ethoxide + EAcAc	274 nm	Bi-ethoxide + EAcAc	•	Ta-ethoxide + EAcAc	291 nm
Sr-ethoxide + BzAc	319 nm	Bi-ethoxide + BzAc	306 nm	Ta-ethoxide + BzAc	348 nm
Sr-ethoxide + AcAc	280 nm	Bi-ethoxide + AcAc	271 nm	Ta-ethoxide + AcAc	314 nm

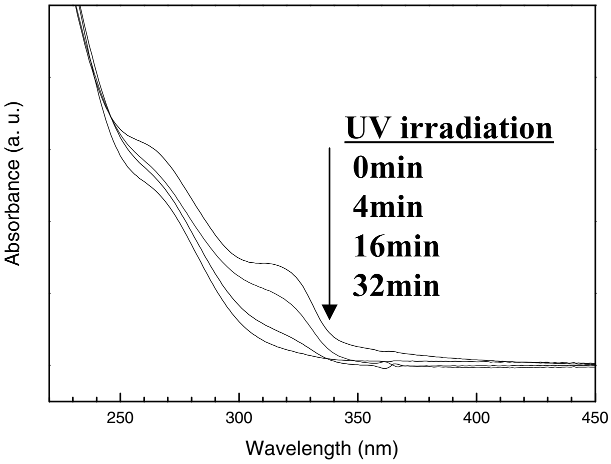

Figure 3 Change in opticalabsorption spectra with UV-irradiation for the SBT thin film.

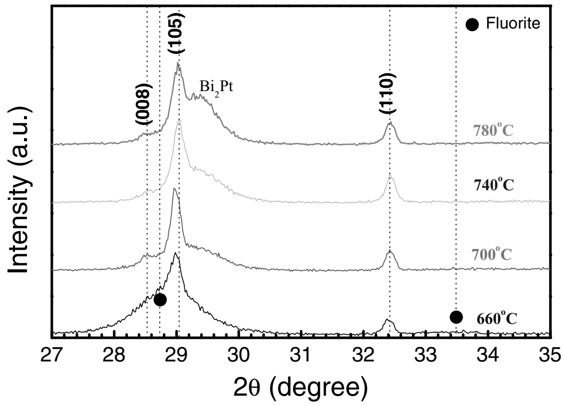

Figure 5 XRD patterns of $Sr_{0.9}Bi_{2.1}Ta_2O_9$ thin films with various temperature (No-UV).

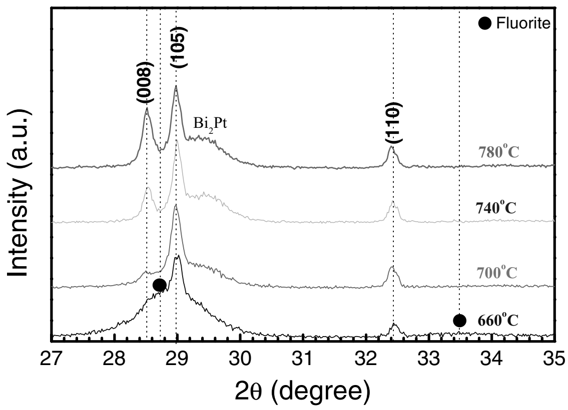

Figure 6 XRD patterns of $Sr_{0.9}Bi_{2.1}Ta_2O_9$ thin films with various temperature (UV).

having absorption peaks at similar wavelength in UV region. Chelating agents such as EacAc (Ethylacetoacetate), BzAc(Benzylacetate) and TMHD (Tetramethyl heptanedione) have been used for the experiment. Sr-EAcAc, $Bi(TMHD)_3$ and Ta-EAcAc were chosen as starting materials to prepare SBT solution using a sol-gel method. 2-methoxyethanol was selected as a solvent. After chelating, the metal alkoxides were mixed and stirred thoroughly. HNO_3 was added 0.05 g as catalyst for fast hydrolysis. To control coating properties of the thin film, ethylene glycol was added 0.1 g. The substrate used for patterning was $Pt/TiO_X/SiO_2/Si$ which was coated with Pt of 2000 Å and TiO_X of 400 Å. Comparing the ferroelectric properties of UV irradiated films and of non-UV irradiated films, the effect of UV irradiation on ferroelectric properties was identified. The substrates were coated with the above solution using a spin-coating method. The resultant gel films were leached by leachant, after being baked at around 400°C for 5 min. By repeating this process several times, SBT thin films coated with 2000 Å thickness were prepared. And then the films were annealed at 660, 700, 740, 780°C for 1 h. The samples were post-annealed at 660–780°C for 30 min in O_2 atmosphere. Fig. 1 is a schematic diagram for preparation of SBT Thin Films. The crystalline phases after heat treatment at different temperatures were identified by an X-ray diffractometer (MAC Science. Co. Ltd, M03XHF[22]). The micro-structure was observed from SEM(JEOL, JSM-6700F) photograph. The electrical properties such as polarization-electrical field (P-E) characteristics were measured using RT-66A (Radient Technologies).

TABLE II Summury of hysteresis loops

	UV–irradiation				No UV–irradiation			
Furnace annealing temp (°C)	660	700	740	780	660	700	740	780
Ps/Pr at 3V.	0.28	0.30	0.48	0.53	–	0.39	0.44	0.4
2Pr ($\mu C/cm^2$) at 3 V.	1.70	3.91	5.40	6.36	–	3.77	5.15	5.98

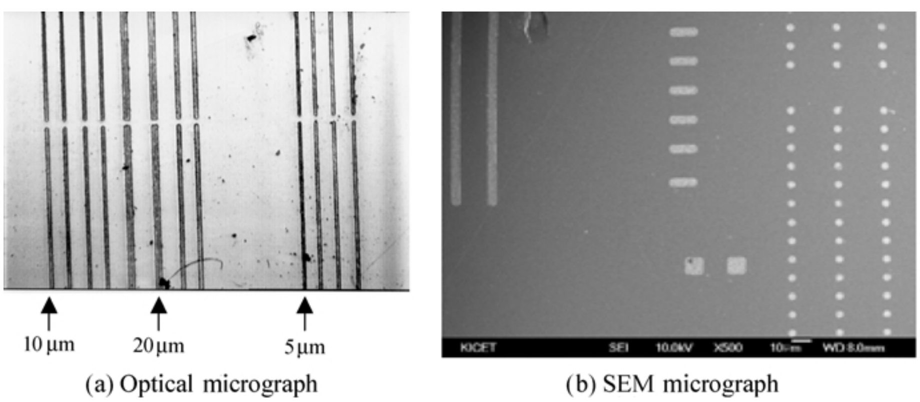

Figure 4 Opitical and SEM micrograph of the patterned SBT film on a $Pt/TiO_X/Si$ substrate.

3. Results and discussion

3.1. Optical properties of SBT gel films and effects of UV-irradiation

UV absorption spectra of metal-alkoxides chelated with various β-diketones are shown in Fig. 2 and tabulated in Table I. From these results, EacAc-chelated Sr-ethoxide, TMHD-chelated $Bi(TMHD)_3$, EacAc-chelated Ta-ethoxide were adopted as starting materials based on the fact that they show absorption band at similar wavelength, and stock solution was prepared by mixing of these materials. Using the solution, SBT thin film was coated on substrate using a spin-coater in an ambient atmosphere. And then, the UV-light was irradiated on the gel films with irradiation time. The spectrum of the SBT gel film with irradiation time is presented in Fig. 3.

The intensity of absorption band at 325 nm decreases with increasing irradiation time and the band almost disappears after 16 min irradiation, which implies that the irradiation on the gel film substantially dissociates the chelate rings remaining in SBT gel film. The UV-irradiation to the SBT film leads to the formation of more M—O—M bond and causes a degradation of solubility of the SBT gel films in alcohols or acidic aqueous solutions. The irradiated part of the gel film was remained after the leaching process, while the unirradiated part was leached out. The change in solubility of the gel film with UV-irradiation can be applied to the fine-patterning process. The gel film irradiated with UV-light through a mask was leached in a 2-methoxyethoxide solution, heat-treated at 400°C. Optical and SEM micrograph of the patterned SBT film on a $Pt/TiO_X/Si$ substrate are shown in Fig. 4.

The finest pattern in the figure is approximately 3 μm. It is expected that the finer pattern may be obtained if collimated UV-light is used. Figs 5 and 6 show X-ray diffraction patterns of the UV irradiated SBT films and non-UV irradiated SBT films subjected to the heat-treatment at various temperatures for 1 hr. For the film heat-treated at 660°C, the perovskite phase is observable, however, the pyroclore phase is still present. When the films are heat-treated at 700°C or higher temperature, the perovskite phase becomes dominant with improving crystallinity as the treatment temperature is increased. In Figs 5 and 6, it is observed that crystallinity temperature of UV-irradiated SBT films is lower than that of no-UV irradiated SBT films. From this observation, the patterned SBT gel films were heat-treated at 740°C for the crystallization.

3.2. Ferroelectric properties of patterned SBT films

UV irradiated films and non-UV irradiated films were fabricated to examine the effects of UV irradiation on P-E hysteresis loops of SBT films. SEM micrographs and hysteresis loops of non-UV irradiated SBT films with various furnace-annealing temperatures for 1 h are

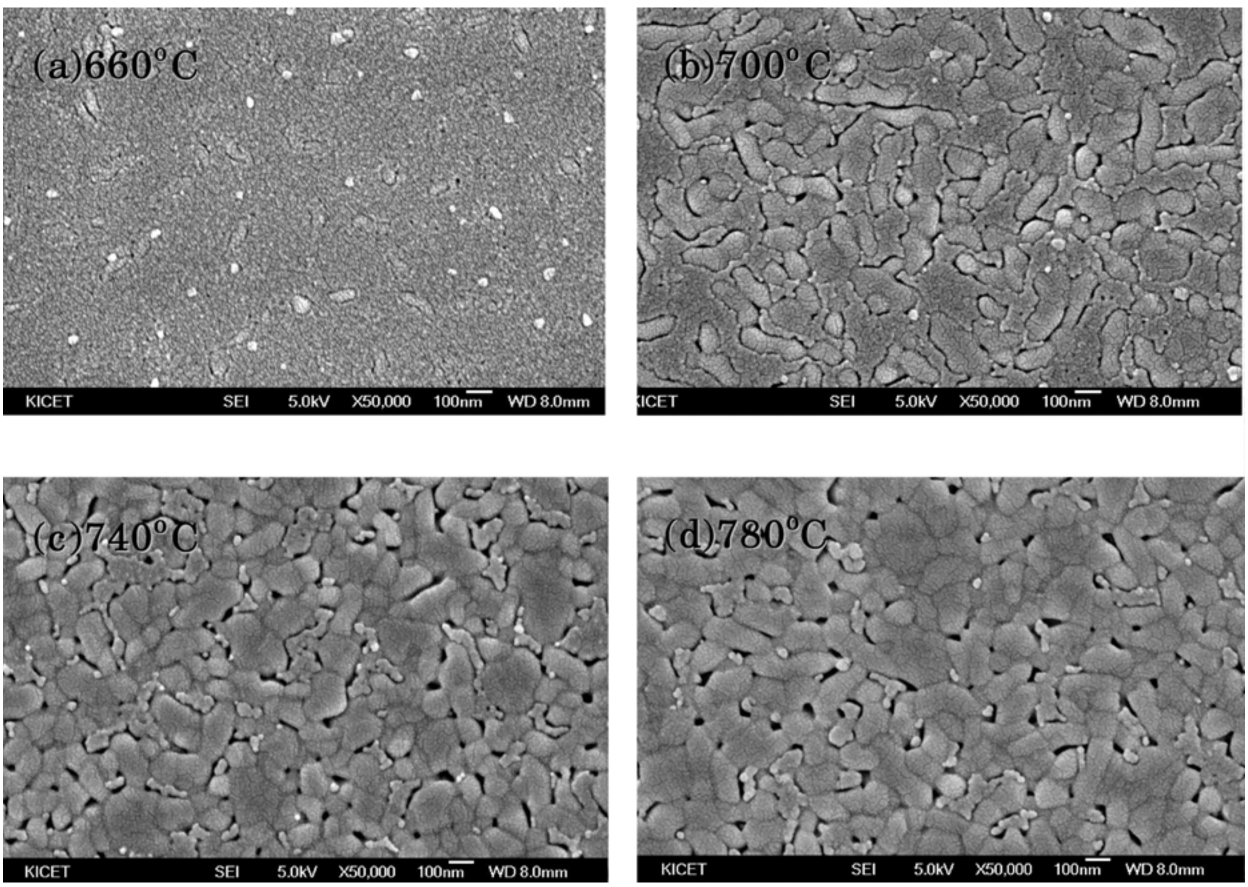

Figure 7 SEM micrographs of $Sr_{0.9}Bi_{2.1}Ta_2O_9$ thin films with various furnace annealing temperatures for 1 hr (No-UV irradiation).

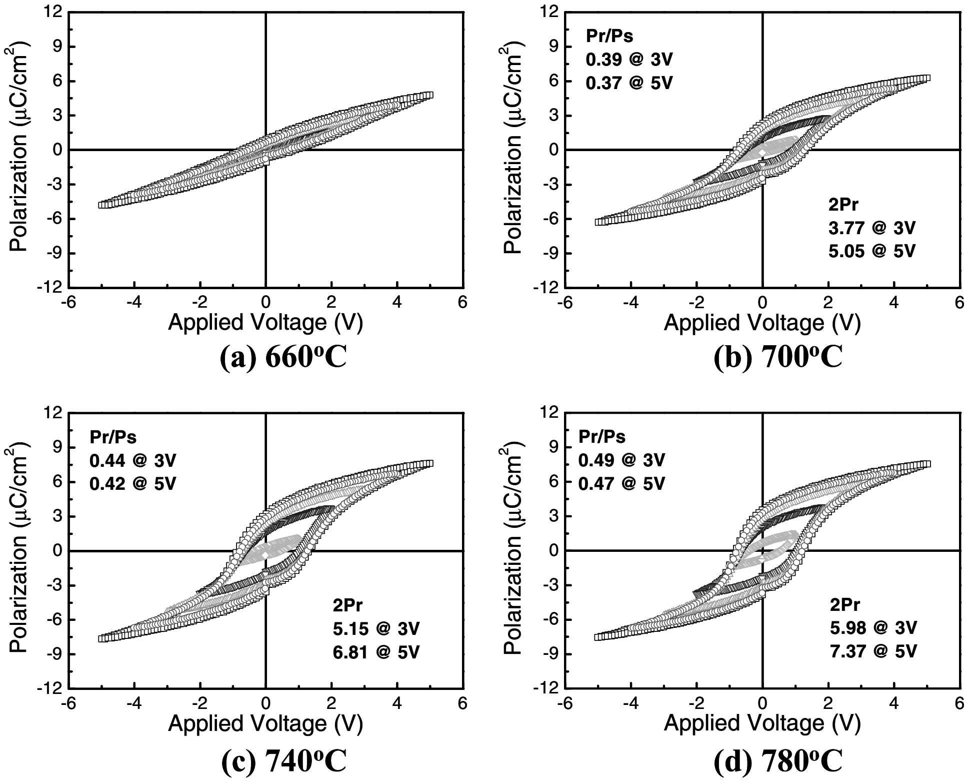

Figure 8 Hysteresis loops (No-UV irradiation).

exhibited in Figs 7 and 8. From the SEM data, it can be deduced that crystalline phases started to grow at 700°C. For the heat-treated SBT films at 700°C, Pr/Ps and 2Pr with the applied voltage of 3 V were 0.39 and 3.77 μC/cm^2, respectively. Similarly at 740°C, the values were 0.44 and 5.15 μC/cm^2, respectively.

SEM micrographs and hysteresis loops of UV irradiated SBT films are shown in Figs 9 and 10. Crystalline

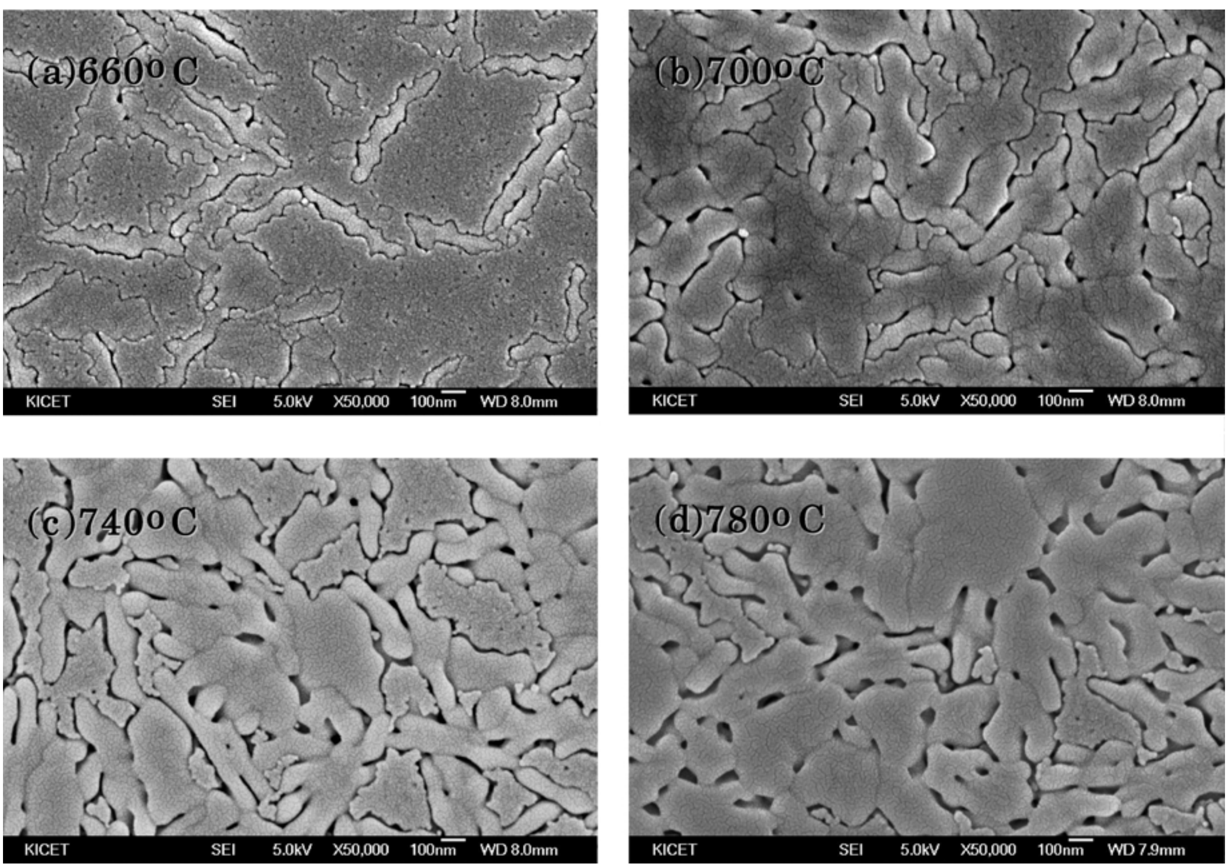

Figure 9 SEM micrographs of $Sr_{0.9}Bi_{2.1}Ta_2O_9$ thin films with various furnace annealing temperatures for 1 hr (UV-irradiation for 30 min).

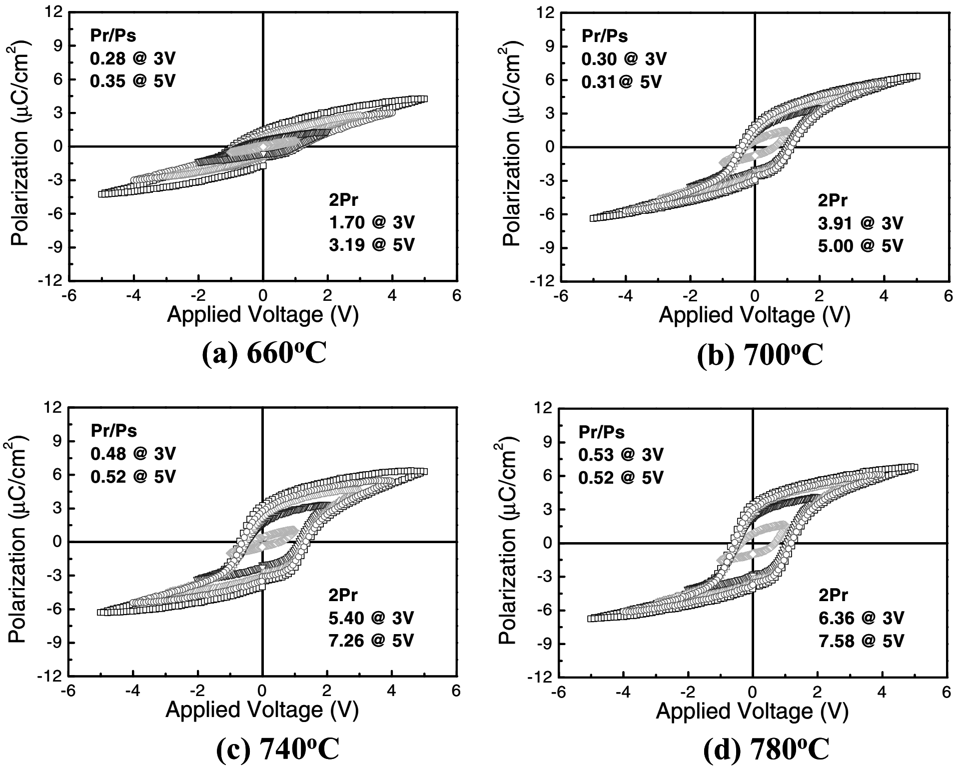

Figure 10 Hysteresis loops (UV irradiation).

phases start to grow at 660°C. For the heat-treated SBT films at 700°C, Pr/Ps and 2Pr were 0.30 and 3.91 μC/cm^2, respectively. It can be seen that the values of UV irradiated SBT films are improved compared to those of non-UV irradiated SBT films. And the values of Pr/Ps and 2Pr at 740°C, 780°C were 0.48, 5.40 μC /cm^2 and 0.53, 6.36 μC/cm^2, respectively. The ferroelectric properties of these samples were superior to those of non-UV irradiated SBT films as crystalline phases of UV irradiated SBT films was larger than those of non-UV irradiated SBT films.

4. Conclusions

β-diketone ligands have been used for preparing photosensitive sol-gel solution of SBT. A fine-patterned SBT film was successfully formed from a photosensitive sol-gel solution by means of UV irradiation. The finest pattern was approximately 3 μm. And the ferroelectric properties the UV irradiated SBT thin films were superior to those of the non-UV irradiated films.

Acknowledgement

The authors would like to thank Korea Science and Engineering Foundation for financial support in this study (2000-1-30100-014-3).

References

1. D. J. TAYLOR, R. E. JONES, Y. T. LII, P. ZURCHER, P. Y. CHU and S. J. GILLESPIE, *Mat. Res. Soc. Symp. Proc.* **433** (1996) 97.
2. Y. XU, in "Ferroelectric Materials and Their Applications" (North Holland, 1991) p. 206.
3. A. I. KINGON, S. K. STREIFFER, C. BASCERI and S. R. SUMMERFELT, *MRS Bulletin, Electroceramic Thin Films* Part II (1996) 46.
4. M. SUZUKI, *J. Cera. Soc. Jpn.* **103** (1995) 1099.
5. H. FUJISAWA, S. HYODO, K. JITSUI, M. SHIMIZU, H. NIU, H. OKINO and T. SHIOSAKI, *Integrated Ferroelectrics* **21** (1997) 107.
6. C. A. PAZ DE ARAUJO, J. D. CUCHIARO, L. D. MCMILLAN, M. C. SCOTT and J. F. SCOTT, *Nature* **374** (1995) 627.
7. N. TOHGE and Y. TAKAMA, Films Using Photosensitive Gel Films Derived from Chemically *J. Mater. Sci.* **10** (1999) 273 .

Received 5 February
and accepted 31 October 2002