ELSEVIER Nuclear Instruments and Methods in Physics Research B 147 (1999) 207–211

NIM B
Beam Interactions
with Materials & Atoms

Effect of H^+ and O^+ implantation on electrical properties of $SrBi_2Ta_2O_9$ ferroelectric thin films

Jianming Zeng [a,*], Chenglu Lin [a], Lirong Zheng [a], A. Pignolet [b], M. Alexe [b], E. Richter [c], D. Hesse [b]

[a] *State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, 865 Changing Road, 200050 Shanghai, People's Republic of China*
[b] *Max-Planck-Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany*
[c] *Institute of Ion Beam Physics and Materials Research, Research Center Rossendorf, D-01314 Dresden, Germany*

Abstract

The effect on the crystalline structure and ferroelectric properties of ion implantation in $SrBi_2Ta_2O_9$(SBT) ferroelectric thin films has been investigated. 25 keV H^+, 140 keV O^+ with doses from $1\times10^{14}/cm^2$ to $3\times10^{15}/cm^2$ were implanted into the Sol–Gel prepared SBT ferroelectric thin films. The X-ray diffraction patterns of SBT films show that no difference appears in the crystalline structure of as-H^+-implanted SBT films compared with as-grown films, H^+ and O^+ co-implanted SBT films show an obvious degradation of crystalline structure. Ferroelectric properties measurements indicate that both remnant polarization and coercive electric field of H^+ implanted SBT films decrease with increasing the implantation dose. The disappearance of ferroelectricity was found in the H^+, O^+ co-implanted SBT films at room temperature. The great recovery of hydrogen-induced degradation in SBT films was obtained with O^+ implantation using a heat-target-implantation technique. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 61.80.Jh; 68.55; Ln; 68.60.Bs
Keywords: Ferroelectric thin films; $SrBi_2Ta_2O_9$(SBT); Ion implantation

---

1. Introduction

Integration of ferroelectric thin films with the current semiconductor technologies opens a variety of possibilities to improve existing devices or to design new devices, such as nonvolatile ferroelectric random access memories, uncooled pyroelectric infrared sensors (or linear arrays), micro-mechanical actuators and various electro-optical devices [1–4]. However, problems still remain concerning integration, such as the stability of ferroelectric materials in the silicon process, interdiffusion of ferroelectric thin films, electrodes and silicon substrates, and so on. Ion implantation, as a conventional microelectronics process, has been extensively used in the fabri-

---

[*] Corresponding author. Tel.: 86-21-62511070; fax: 86-21-62513510; e-mail: jmzeng@kali.com.cn

PII: S0168-583X(98)00558-8

cation of microelectronic and optoelectronic devices, and as a method to alter the properties of oxide materials without constraints imposed by thermal equilibrium [5,6]. However, up to now, few attempts have been made to implement ion implantation technology into ferroelectric thin films and devices. In our previous papers [7,8], we reported ferroelectric and fatigue properties of PZT thin films implanted by O^+ ions. Recently, the Bi-layered $SrBi_2Ta_2O_9$ (SBT) ferroelectric thin films have attracted considerable attention because of their unique physical properties [9–11], characterized by fatigue-free, as well as high remnant polarization (P_r) and low coercive field (E_c). In the present paper, the effect on the crystalline structure and ferroelectric properties of H^+ and O^+ ion implantation in $SrBi_2Ta_2O_9$ ferroelectric thin films has been investigated.

2. Experimental

The samples used in this study were prepared on platinum coated silicon substrates by using a simple solution deposition process, which was a similar route reported in Amanuma's literature [10]. SBT thin films were crystallized with an oxygen annealing process at 850°C for 1 h. The obtained SBT film thickness was about 400 nm. After crystallization at elevated temperature, the platinum top electrodes with diameter of 0.5 mm were vaporized by an ultra-high vacuum electron beam vaporization system (UMS 500P, Made by Balzers).

The 25 keV H^+, 140 keV O^+ with doses ranging from $1\times10^{14}/cm^2$ to $3\times10^{15}/cm^2$ were implanted into the SBT ferroelectric thin films at room temperature (20°C) and a temperature of 450°C. The crystalline structures of the SBT films were investigated by the X-ray diffraction (XRD) analysis. Electrical properties of the SBT films were analyzed by measuring ferroelectric hysteresis loops, using a modified Sawyer–Tower circuits, and leakage current–voltage (*I–V*) characteristics of the Pt/SBT/Pt capacitors, using a HP4156A analyzer.

3. Results and discussion

Fig. 1 shows the dependence of $2P_r$ (the sum of positive remanent polarization, P_r and negative one) and $2E_c$ (the sum of positive coercive electric field, E_c, and negative one) on various H^+ implantation dose. The remarkable degradation of ferroelectricity for SBT thin films after H^+ implantation was observed. The $2Pr$ of SBT films with H^+ implantation for a dose of $3\times10^{14}/cm^2$ decreased to 2.4 μC/cm^2 from the initial value of 5.8 μC/cm^2. H^+-implantation of SBT films for a dose up to $3\times10^{15}/cm^2$ resulted in a obviously paraelectric characteristics.

The X-ray diffraction (XRD) analysis before and after H^+ implantation at room temperature showed that H^+ implantation for a dose up to $3\times10^{15}/cm^2$ resulted in almost unchanged XRD patterns for SBT thin films. Therefore, the degradation of ferroelectricity for H^+-implanted SBT films would not be caused by the lattice destruction.

It has been reported that post annealing in a hydrogen containing ambient may cause severe degradation of ferroelectric thin films [12,13]. The degradation of ferroelectricity of H^+-implanted SBT films would be due to the similar reason. Hydrogen implanted in ferroelectric SBT thin films substitutes at regular oxygen sites of the SBT films. Since ferroelectricity of oxide materials strongly concerned with oxygen content, oxygen deficiency

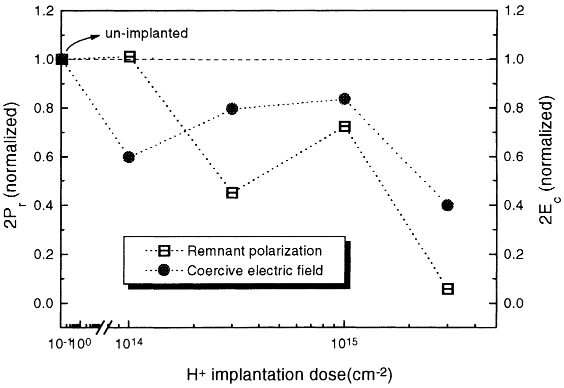

Fig. 1. Hydrogen dose dependence of $2P_r$ and $2E_c$ for H^+-implanted SBT thin films.

would directly result in degradation of ferroelectricity, and lead to destruction of crystal structure.

In order to decrease or prevent the effect of hydrogen on SBT ferroelectric thin films, oxygen implantation in the H^+-implanted SBT thin films has been investigated. Fig. 2 shows the X-ray diffraction patterns of the SBT thin films implanted by oxygen ions at room temperature with dose ranging from $1\times10^{14}/cm^2$ to $3\times10^{15}/cm^2$. The H^+ and O^+ co-implanted SBT films exhibit an obvious implantation damage with increasing the dose of oxygen. It is reasonable that the loss of ferroelectricity appeared in H^+ and O^+ co-implanted SBT films with a post annealing process at 500°C for 15 min, as shown in Fig. 3, and the leakage current–voltage measurement also indicated a great increasing leakage current in the implanted SBT thin films. These results revealed that the O^+implantation at room temperature could not recover the hydrogen-induced degradation of physical properties in the SBT thin films, due to the severely lattice destruction in SBT films resulted from the collisions with the implanted oxygen atoms.

The damage induced by ion implantation can result in point defects, clustered point defects, and, even, amorphization of the crystal structure. However, the implantation-induced damage of crystal structure shows a remarkable temperature dependence. The damage could be completely removed while the implantation temperature is higher than certain temperature.

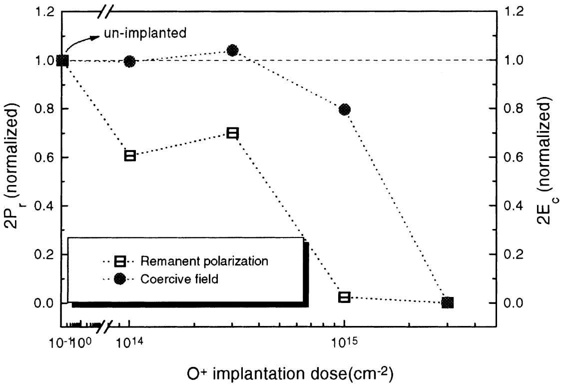

Fig. 3. Oxygen dose dependence of $2P_r$ and $2E_c$ for $1\times10^{15}/cm^2$-H^+-implanted SBT thin films with O^+-implantation at room temperature and a post annealing process at 500°C for 15 min.

The variations of the leakage current of the SBT films as function of the applied voltage are shown in Fig. 4. A leakage current density of less than 5×10^{-6} A/cm^2 at a applied voltage ranging from −5 V to +5 V was measured from the heat-target-implanted SBT films at 450°C for a oxygen dose of $1\times10^{15}/cm^2$. This leakage current is several orders of magnitude smaller than that of the value of room-temperature-implanted SBT films.

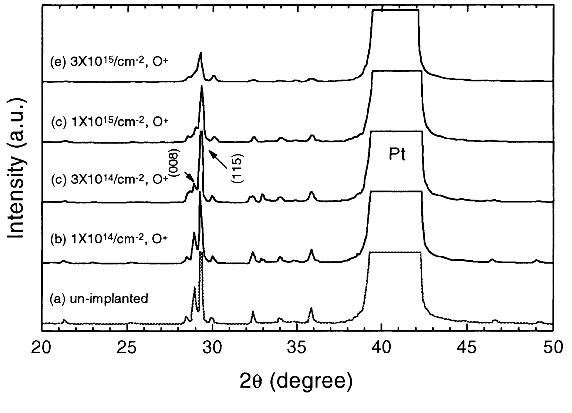

Fig. 2. The X-ray diffraction patterns of $1\times10^{15}/cm^2$-H^+-implanted SBT thin films before and after O^+ implantation at room temperature.

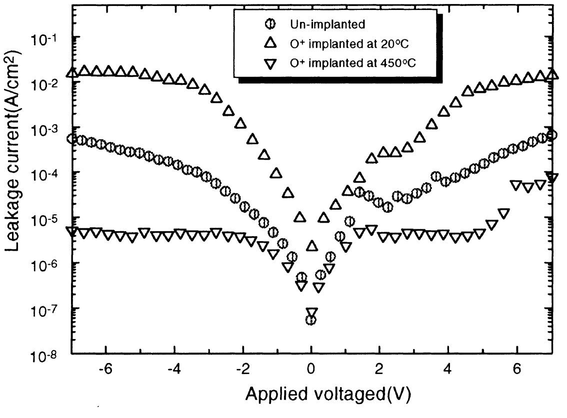

Fig. 4. The variations of the leakage current of the $1\times10^{14}/cm^2$-O^+-implanted films at room temperature (20°C) and 450°C as function of the applied voltage for $1\times10^{15}/cm^2$-H^+-implanted SBT thin films.

Meanwhile, the obvious recovery of ferroelectricity are observed in the hydrogen-induced SBT films with a oxygen implantation at an elevated temperature of 450°C, as shown in Fig. 5. The $2P_r$ of the SBT films with 1×10^{14}/cm^2-O$^+$-implantation at 450°C increased to 3.5 μC/cm^2 from the value of 2.0 μC/cm^2, though the somewhat degradation of ferroelectricity still exists.

Fig. 6 shows the X-ray diffraction of heat-target-O$^+$-implanted SBT films. The slightly degraded crystal structure still exists in SBT films with O$^+$ implantation at a elevated temperature of 450°C. This results indicated that the higher implanted temperature is necessary for recovering the influence of lattice destruction induced by processing of O$^+$ implantation into the SBT films. The complete recovery of hydrogen-induced degradation of ferroelectricity in SBT films would be achieved by oxygen implantation at an elevated temperature.

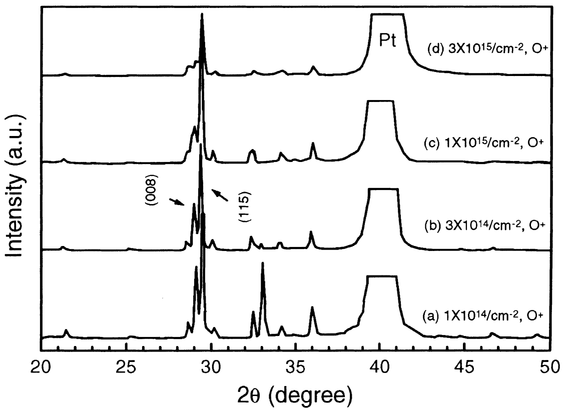

Fig. 6. The X-ray diffraction patterns of 1×10^{15}/cm^2-H$^+$-implanted SBT thin films after O$^+$ implantation at a temperature of 450°C.

4. Conclusions

Electrical properties and crystal structure were investigated about ferroelectric SBT thin films with H$^+$ and H$^+$, O$^+$ co-implantation at room temperature or an elevated temperature of 450°C. The ferroelectricity of H$^+$ implanted SBT films was severely degraded, while the crystal structure was almost unchanged. Ferroelectricity of hydrogen degraded films could not be recovered by using O$^+$ implantation at room temperature and with a

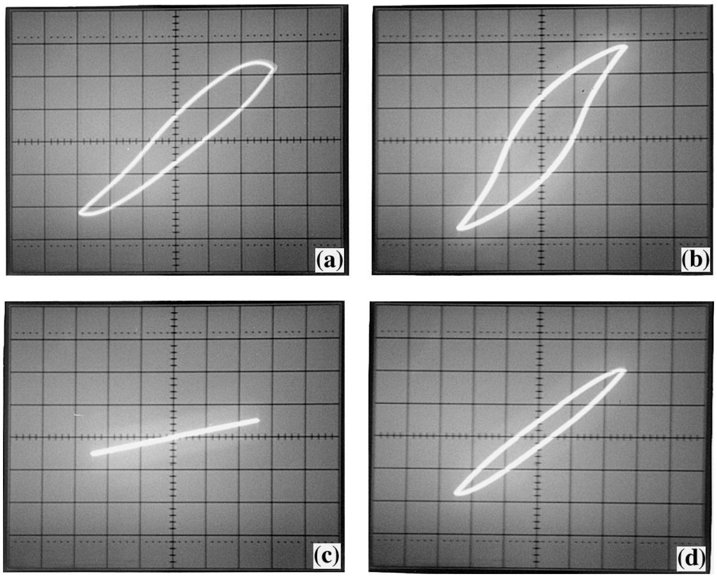

Fig. 5. The variations of the hysteresis loops of the 1×10^{15}/cm^2-H$^+$-implanted SBT films after O$^+$ implantation for a dose of: (a) 1×10^{14}/cm^2 at room temperature (20°C); (b) 1×10^{14}/cm^2 at 450°C; (c) 3×10^{15}/cm^2 at room temperature (20°C); (d) 3×10^{15}/cm^2 at 450°C (*Y* scale: 1.4 μC/cm^2/div, *X* scale: 62.5 kV/cm/div).

post annealing process, due to the existence of obvious lattice destruction resulted from O^+ implantation. On the contrary, the great recovery of hydrogen-induced degradation in SBT films was achieved with O^+ implantation at an elevated temperature of 450°C, though the slight degradation of ferroelectricity and crystal structure still existed. These results in the present study revealed that the heat-target-O^+-implantation technique would be a novel and potential process to recover the "forming gas"-induced degradation of ferroelectricity for ferroelectric thin films in the process of fabricating integrated ferroelectric devices, such as non-volatile ferroelectric memories.

Acknowledgements

The authors are grateful to Prof. Z.C. Wang, Z.X. Lin and J.Q. Zhong for their help in the present work. This work was supported by the National Advanced Materials Committee of China (NAMCC) and the National Natural Science Foundation of China, No. 69738020.

References

[1] J.F. Scott, C.A. Paz de Araujo, Science 246 (1989) 1440.
[2] S.L. Swartz, V.E. Wood, Condensed Matter News 1 (1992) 4.
[3] M.H. Francombe, S.V. Krishnaswamy, J. Vac. Sci. Technol. A8 (1990) 1382.
[4] C.A. Paz de Araujo, Ferroelectric News Lett. 2 (1994) 2.
[5] Y. Li, J. Appl. Phys. 69 (1990) 7915.
[6] C.E. Land, P.S. Peercy, Ferroelectrics 45 (1982) 25.
[7] L.R. Zheng, P.X. Yang, L.W. Wang, C.L. Lin, S.C. Zou, Nucl. Instr. and Meth. B 127/128 (1997) 621.
[8] L.R. Zheng, C.L. Lin, K.V. Rao, Abstracts of the Second European Meeting on Integrated Ferroelectrics, September 29-30, Jouy-en-Josas, France, 1997.
[9] C.A. Paz de Araujo, J.D. Cuchiaro, M.C. Scott, L.D. McMillan International Patent Publication No. WO 93/12542, 24 June 1993.
[10] K. Amanuma, T. Hase, Y. Miyasaka, Appl. Phys. Lett. 66 (1995) 221.
[11] A.L. Kholkin, K.G. Brooks, N. Setter, Appl. Phys. Lett. 71 (1997) 2044.
[12] S. Zafer, V. Kaushik, P. Caberge, P. Chu, R.E. Jones, R.L. Hance, J. Appl. Phys. 82 (1997) 4469.
[13] J.P. Han, T.P. Ma, Appl. Phys. Lett. 71 (1997) 1267.