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The structural and electric behavior of $SrBi_2Ta_2O_9$ ferroelectric thin films with H^+ implantation

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Abstract

The structural and electrical characteristics of H^+-implanted $SrBi_2Ta_2O_9$ (SBT) ferroelectric thin films were investigated by X-ray diffraction analysis and electrical measurements. 25 keV H^+ with doses ranging from $1 \times 10^{14}/cm^2$ to $3 \times 10^{15}/cm^2$ 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 H^+-implanted SBT films compared with unimplanted films. Ferroelectric properties measurements indicate that both remnant polarization and the coercive electric field of H^+-implanted SBT films decrease with increasing the implantation dose. The disappearance of ferroelectricity was found in the H^+-implanted SBT films up to a dose of $3 \times 10^{15}/cm^2$. The leakage current-voltage (I–V) and capacitance-voltage (C–V) characteristics of the H^+-implanted SBT films were also discussed before and after a recovery process. © 1999 Elsevier Science B.V.

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1. Introduction

Recently, $SrBi_2Ta_2O_9$ (SBT) and other ferroelectric thin films have received great attention for future applications on memories because of their high-speed operation, radiation hardness, low operating voltage and the high level of integration using a simple structure [1-4]. Mega-bit-scale nonvolatile memories have been prepared using ferroelectric thin films such as lead zirconate titanate (PZT) and strontium bismuth tantalate (SBT). However, there still remain several problems concerning the incorporation of the ferroelectric thin films with the conventional microelectronic devices fabrication [5,6]. One important problem is the effect of hydrogen on the electrical properties of the ferroelectric thin films in the process of fabricating integrated ferroelectric devices, such as nonvolatile ferroelectric memories [7-9]. "Forming gas" annealing (annealing in a hydrogen containing ambient) is observed to degrade the ferroelectric capacitors: the disappearance of ferroelectricity and the increase of leakage current. The cause of degradation is not well understood.

Ion implantation, as a conventional microelectronic process, has been extensively used in the fabrication of microelectronic and optoelectronic devices, and as a method to alter the properties of oxide materials without constraints imposed by thermal equilibrium.

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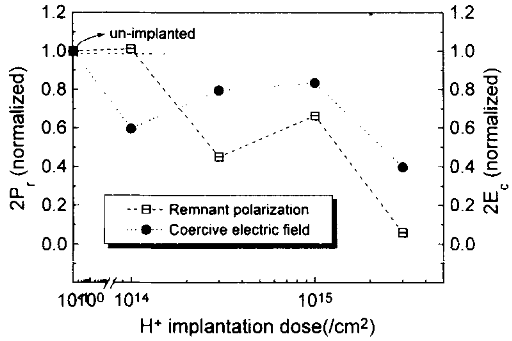

Fig. 1. Hydrogen dose dependence of $2P_r$ and $2E_c$ for H^+-implanted SBT thin films.

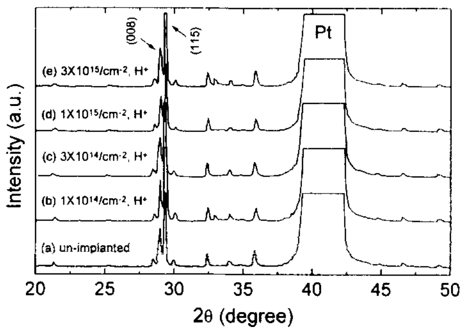

Fig. 2. The X-ray diffraction patterns of SBT thin films implanted with different hydrogen doses.

It can be used to control the structural and electrical properties of ferroelectric films without removing material [10,11]. Basic investigations of ion implantation effects on ferroelectric thin films are thus important for developing integrated ferroelectric devices technology. However, up to now, few attempts have been made to implement ion implantation technology in ferroelectric thin films and devices.

In this paper, the effects of H^+ implantation on the structural and electrical properties of $SrBi_2Ta_2O_9$ (SBT) ferroelectric thin films will be investigated.

2. The experiments

The SBT ferroelectric films used in this study were prepared on platinum coated silicon substrates by using a simple solution deposition process, which was a similar route as reported by Amanuma et al. [12]. SBT thin films were crystallized with an oxygen annealing process at 850 °C for 1 hour. The obtained SBT film thickness was about 400 nm. After crystallization at elevated temperature, the 25 keV H^+ 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). The platinum top electrodes with diameter of 0.5 mm were vaporized on the films to form Pt/SBT/Pt capacitors by an ultra-high vacuum electron beam vaporization system (UMS 500 P, made by Balzers). To recover the implantation-ion induced damage, we also performed an annealing process at a temperature of 500 °C for 15 min.

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 circuit, capacitance–voltage (C–V) characteristics using an HP4280A tester, and leakage current–voltage (I–V) characteristics of the Pt/SBT/Pt capacitors using a Semiconductor Parameter Analyzer (Hewlett-Packard 4156A).

3. Results and discussion

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

Fig. 2 shows the X-ray diffraction (XRD) patterns of SBT thin films implanted with different doses of H^+. The patterns were observed using CuKα radiation. The 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.

The effects of H^+ implantation at various doses on the leakage current–voltage characteristics are shown in Fig. 3. The obvious increase of leakage current density in the H^+-implanted SBT ferroelectric thin films

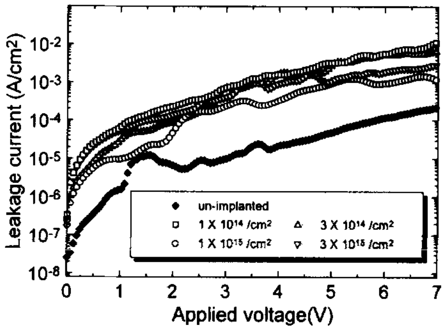

Fig. 3. The leakage-current–voltage (I–V) characteristics of H^+-implanted SBT thin films with various implantation doses.

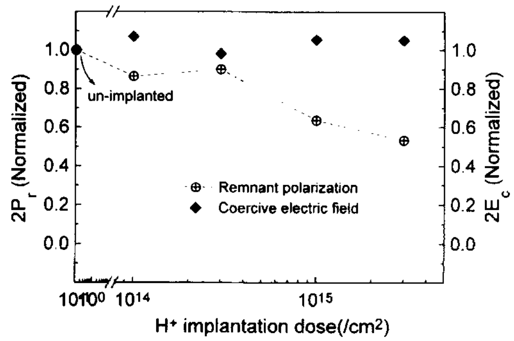

Fig. 4. Hydrogen dose dependence of $2P_r$ and $2E_c$ for H^+-implanted SBT thin films after a post annealing process at 500 °C for 15 min.

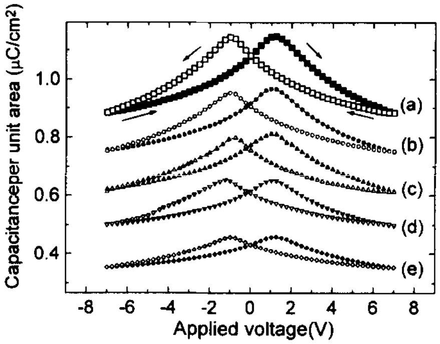

Fig. 5. Capacitance–voltage (C–V) characteristics on SBT films with various doses of H^+ implantation (a) unimplanted, (b) $1 \times 10^{14}/cm^2$, (c) $3 \times 10^{14}/cm^2$, (d) $1 \times 10^{15}/cm^2$, (e) $3 \times 10^{14}/cm^2$. The C–V measurements were started with a −7 V dc bias, stepped up with an increment of 0.25 V until +7 V was reached and then stepped similarly back down to −7 V at a frequency of 1 MHz.

was observed. The leakage current density of the H^+-implanted films at a dose ranging from $1 \times 10^{14}/cm^2$ to $3 \times 10^{15}/cm^2$ is approximately one order of magnitude larger than that value of the un-H^+-implanted SBT films at the applied voltage ranging from 0 to +7 V.

It has been reported that "forming gas" annealing may cause severe degradation of ferroelectric thin films: the disappearance of ferroelectricity and the increase of leakage current [7,13]. Similar results were found in the H^+-implanted SBT films. These suggested that the degradation of ferroelectric and electrical properties of H^+-implanted films would be due to the similar reason of "forming gas" annealing. Hydrogen implanted in ferroelectric SBT thin films substitutes at regular atom sites of the SBT films. Since ferroelectricity of oxide materials is strongly concerned with composition, composition variation would directly result in degradation of ferroelectricity.

In order to decrease or prevent the effect of hydrogen on SBT ferroelectric thin films, the H^+-implanted SBT films were treated with a conventional annealing process, which was usually used to recover the degradation of ferroelectric properties induced by "forming gas" annealing though it was not very efficient.

Fig. 4 shows the dependence of $2P_r$ and $2E_c$ on various H^+ implantation doses for the implanted SBT films after annealing at 500 °C for 15 min. The obvious degradation of remnant polarization was still found though the coercive field was recovered. The good recovery of coercive field was also observed from the capacitance–voltage (C–V) measurements of H^+-implanted SBT films after a post annealing process, as shown in Fig. 5. However, a small capacitance of the implanted films after post annealing was found, compared with the unimplanted SBT films. It also shows a general lowering of the capacitance with increasing H^+ implantation dose. In addition, the leakage current measurements indicated a large leakage current in the H^+-implanted SBT films after a post annealing process.

These results revealed that the conventional annealing process at 500 °C could not recover the degradation of the ferroelectric and electrical properties for the H^+-implanted SBT thin films. A similar result was found in the recovery processing of "forming gas"-induced damage in the ferroelectric thin films with an annealing process. It would be due to the presence of a large number of implantation-ion-induced charges in the H^+-implanted SBT films, which resulted in the spatial variation of electric field through the depth of the films. The implantation-ion-induced local-field variation should couple with the electrical properties through the depth of capacitors. Further studies should be performed to elucidate this.

4. Conclusions

The crystalline structure and electrical properties of ferroelectric SBT thin films have been investigated as a function of H^+ implantation at room temperature. The severe degradation of ferroelectricity and increasing of leakage current were found in the H^+-implanted SBT films with a dose ranging from $1 \times 10^{14}/cm^2$ to $3 \times 10^{15}/cm^2$, while the crystal structure was almost unchanged. After a recovery annealing process at 500 °C for 15 min, the large leakage current density and the obvious degradation of electrical properties, as well as the decreasing of the capacitance with increasing H^+ implantation dose were still observed in the H^+-implanted SBT ferroelectric thin films due to the presence of implantation-ion charges in the SBT films. A new recovery method is investigated, which might also be used to recover the "forming gas" induced degradation of ferroelectric thin films in the processing of integrated ferroelectric devices, such as nonvolatile memories.

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