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IN SITU MASS SPECTROSCOPY OF RECOILED ION STUDIES OF DEGRADATION PROCESSES IN $SrBi_2Ta_2O_9$ THIN FILMS DURING HYDROGEN GAS ANNEALING*

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DISCLAIMER

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ABSTRACT

It is known that the forming gas (N_2-H_2 mixture) annealing process required for microcircuit fabrication results in an unacceptable electrical degradation of $SrBi_2Ta_2O_9$ (SBT) ferroelectric capacitors due mainly to the interaction of H_2 with the ferroelectric layer of the capacitor. We have found a strong relationship between changes in the surface composition of the ferroelectric layer and the electrical properties of SBT capacitors as a result of hydrogen annealing. Mass spectroscopy of recoiled ions (MSRI) analysis revealed a strong reduction in the Bi signal as a function of exposure to hydrogen at high temperatures (~500 °C). The Bi signal reduction correlates with Bi depletion in the SBT surface region. Subsequent annealing in oxygen at temperatures in the range of 700-800 °C resulted in the recovery of the MSRI Bi signal, corresponding to the replenishment of Bi in the previously Bi-depleted surface region. XRD analysis (probing the whole SBT film thickness) showed little difference in the XRD spectra of the SBT films before and after hydrogen and oxygen-recovery annealing. The combined results of the MSRI and XRD analyses can be interpreted as an indication that the degradation of the electrical properties of the SBT capacitors, after hydrogen annealing, is mainly due to the degradation of the near surface region of the SBT layer.

INTRODUCTION

$SrBi_2Ta_2O_9$ (SBT) perovskite materials are being investigated as promising candidates for application to non-volatile ferroelectric random access memories (NVFRAM), because of high fatigue resistance with Pt electrodes [1]. Low density NVFRAMs are currently being incorporated in commercial "smart cards" [2]. However, intensive research is under way to overcome several challenges for the development of high density NVFRAMs. One of the challenges is the sensitivity of SBT to hydrogen gas.

The final step in micro-chip fabrication generally involves a forming gas (H_2-N_2 mixture) annealing to passivate the device and eliminate defects from the transistor interfaces. In the case of NVFRAM fabrication, the forming gas annealing step follows the ferroelectric capacitor fabrication, which results in this capacitor being exposed to the H_2-N_2 mixed forming gas at relatively high temperatures (400-500 °C). The hydrogen-based annealing process is known to result in an unacceptable degradation of ferroelectric capacitors integrated in CMOS devices [3-5]. In addition, the capacitor level dielectric (CLD) layer deposition typically involves the use of a hydrogen-containing silicon source such as TEOS (tetraethyl orthosilicate) for plasma enhanced chemical vapor deposition (PECVD). The contact etch process also requires a hydrogen-containing etching gas such as CHF_3.

Recent work has shown that forming gas annealing can seriously degrade the electrical properties of ferroelectric capacitors [3-5]., resulting in strong reduction of polarization and increase of leakage current. However, published work on this critical subject has been limited, resulting in a lack of understanding of the underlying process responsible for the observed

electrical degradation of the capacitors. We investigated compositional changes on the surface of SBT films during hydrogen annealing using in-situ MSRI. Since oxygen annealing at 800 °C was reported to restore the degraded SBT capacitors after a CLD deposition and contact etch process [3], the surface composition and electrical properties of the hydrogen annealed SBT films and capacitors after oxygen recovery annealing were studied also. The data indicate that the hydrogen annealing-induced degradation of the capacitors and oxygen annealing-induced recovery are largely due to surface compositional changes of the SBT layer.

EXPERIMENT

We have developed a mass spectroscopy of recoiled ions (MSRI) [6,7] technique, which permits compositional and structural analysis of the top surface layer of solids or thin films in backfill sputtering and reactive gas environments, using a differentially pumped ion source and detector. MSRI is a highly surface sensitive, non-destructive analytical tool with a depth resolution extending to the two top monolayers of solid surfaces. MSRI involves a time-of-flight scheme to detect atoms ejected from the surface under analysis after they are impacted by ~10 keV ions (e.g., Ar^+) in a single collision event. The peaks in the time-of-flight MSRI spectrum correspond to specific masses of the atoms ejected from the surface. The non-destructive character of MSRI is achieved by pulsing the incident beam to obtain a full spectrum with a total ion dose on the sample of about 10^{12} ions/cm^2, which is orders of magnitude smaller than the average atomic density of a solid surface (~10^{15} atoms/cm^2). Details of MSRI can be found elsewhere [6,7].

SBT films were synthesized by sol-gel processing on Pt(150nm)/TiO_2(40nm)/SiO_2/Si substrates [8]. One half of the sample area was coated with patterned circular top electrodes to define the capacitor structure for electrical characterization. The other half was uncovered to perform MSRI and complementary X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) analysis. The SBT capacitors were annealed in different hydrogen background pressures at 500 °C for 10 minutes to simulate the forming gas annealing process used in microchip fabrication. The electrical polarization of Pt/SBT/Pt capacitors was measured using a RT 6000s system (Radiant Technology). The leakage current was measured using a Keithley electrometer with a voltage step of 0.1V and delay time of 10 seconds. XRD, SEM, and AFM analyses were used to investigate the structural, morphological, and microstructural changes in the SBT layers of capacitors after hydrogen and oxygen recovery annealing.

RESULTS AND DISCUSSION

Electrical polarization ($2P_r$) and leakage current were measured to investigate the sensitivity of SBT capacitors to hydrogen environments. Fig. 1(a) shows the hysteresis loop of a Pt/SBT/Pt capacitor before hydrogen annealing. The electrical polarization values of the SBT capacitor decreased after hydrogen annealing at 500 °C as the pressure of hydrogen increased. After 30 mTorr hydrogen annealing at 500 °C, the hysteresis loop of the SBT capacitors showed the characteristic shape of a leaky loop (Fig. 1(b)), which renders ferroelectric capacitors useless for NVFRAM applications. Approximately ten orders of magnitude increase in the leakage current, from ~ 5 x 10^{-8} A/cm^2 to ~ 15 A/cm^2, was observed for SBT capacitors after hydrogen annealing at 500 °C for 10 minutes in 30 mTorr of hydrogen.

Conventional analytical methods, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used in conjunction with the new MSRI analysis in order to understand the mechanism responsible for hydrogen induced degradation of SBT capacitors. XRD analyses performed on SBT films before and after hydrogen gas annealing revealed no major changes in the bulk film crystallinity [Fig. 2(a) and (b)], nor any noticeable second phase formation. SEM and AFM imaging of the SBT film surface before and after annealing revealed no significant differences in the surface morphology nor in the grain structure of the films, as shown in Fig. 3 and Fig. 4.

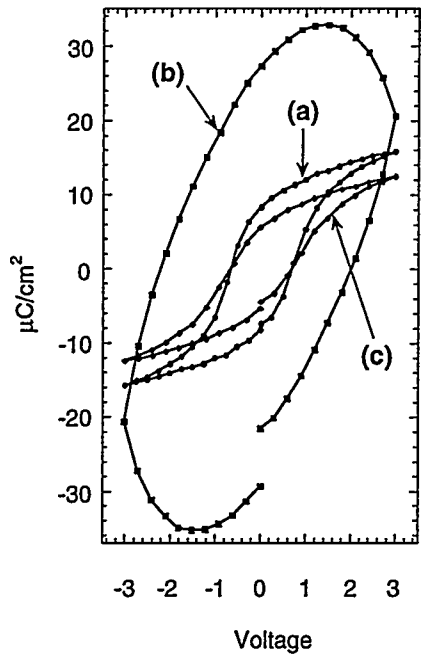


Figure 1. Hysteresis loops of Pt/SBT/Pt capacitors (a) before hydrogen annealing, (b) after hydrogen annealing at 500 °C under $P(H_2)$ = 30 mTorr, and (c) after an oxygen recovery annealing at 700 °C.

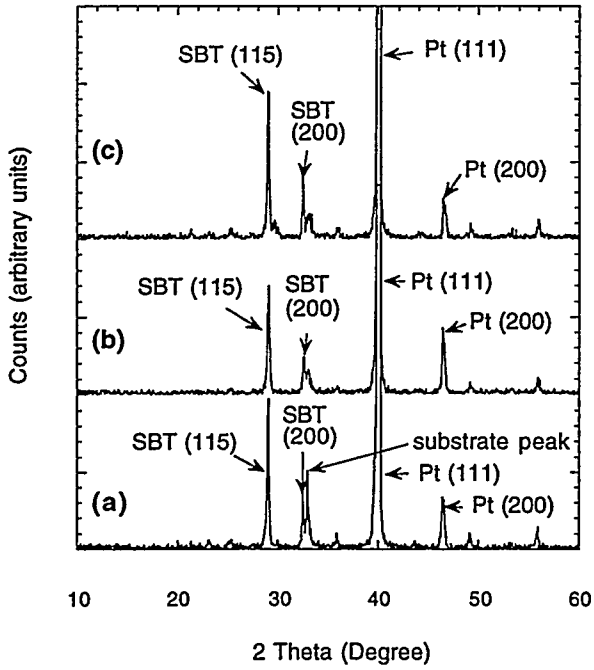
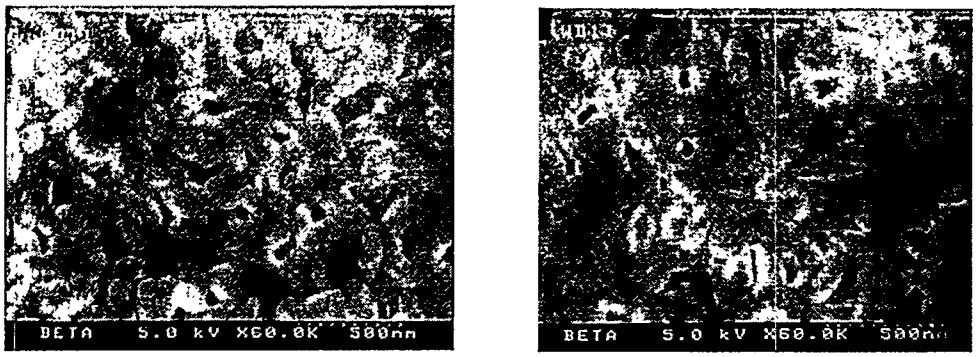
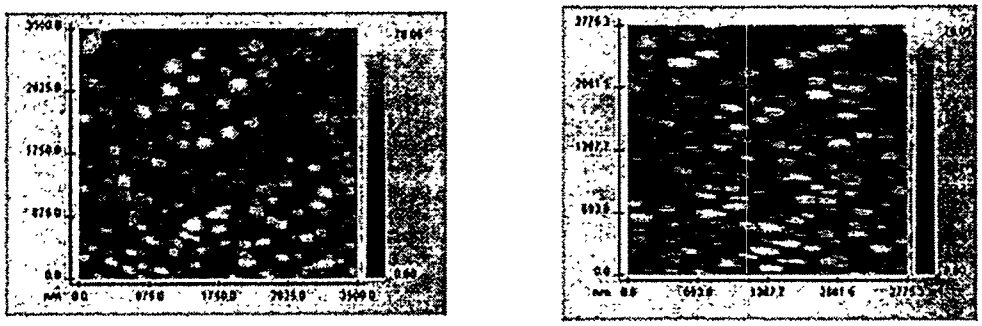


Figure 2. XRD spectra for SBT films (a) before hydrogen gas annealing, (b) after hydrogen gas annealing at 500 °C under $P(H_2)$ = 30 mTorr, and (c) after oxygen recovery annealing at 700 °C.



(a) (b)

Figure 3. SEM spectra for SBT films (a) before hydrogen gas annealing, (b) after hydrogen gas annealing at 500 °C under $P(H_2)$ = 30 mTorr.



(a) RMS=13nm **(b) RMS=12.5nm**

Figure 4. AFM images for SBT films (a) before hydrogen gas annealing, (b) after hydrogen gas annealing at 500 °C under $P(H_2)$ = 30 mTorr.

MSRI analysis of the SBT films before and after hydrogen annealing at 500 °C in different hydrogen background pressure revealed substantial compositional changes at the surface of the film. A substantial loss of Bi from the surface of the SBT films was observed after annealing in 30 mTorr of hydrogen, while Ta, Sr, and oxygen signals increased as a function of increasing hydrogen pressure (Fig. 5).

The question to be answered here is: what is the possible mechanism for hydrogen-induced degradation of Pt/SBT/Pt capacitors? Molecular hydrogen can be adsorbed on the Pt surface by dissociative adsorption during hydrogen annealing [9,10]. Subsequently, hydrogen atoms can diffuse either through the top Pt electrodes, or around the edges of the patterned top electrode. Hydrogen diffusion through a 2000Å thick Pt layer into a SBT film was observed using SIMS depth profiling [4]. Hydrogen may react with SBT, resulting in the oxide reduction. The reduced oxide layer can contribute to the observed electrical degradation of the Pt/SBT/Pt capacitors.

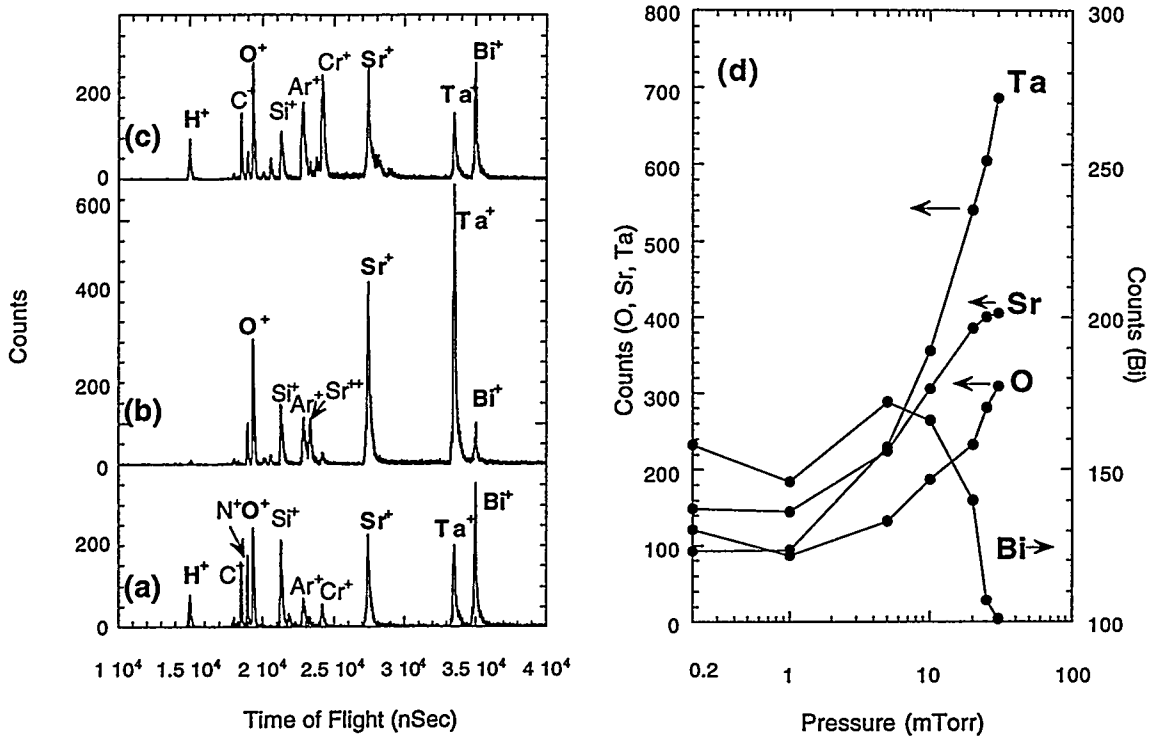


Figure 5. MSRI spectra of a SBT film (a) before hydrogen annealing at 25 °C in vacuum, (b) after hydrogen annealing at 500 °C in $P(H_2)$ = 30 mTorr for 10 minutes, and (c) after oxygen recovery annealing at 700 °C. (d) MSRI signal intensities for SBT film during hydrogen annealing at 500 °C under various hydrogen pressures. All MSRI counts were measured under $P(H_2)$ = 0.2 mTorr for normalization.

The hydrogen annealed SBT films and capacitors were subsequently annealed in oxygen at temperatures in the range 600-800 °C in a conventional furnace. Fig. 1(c) shows the recovery of the hysteresis loop of the hydrogen annealed SBT capacitor after oxygen annealing at 700 °C. Although a good hysteresis loop is recovered, the polarization is somewhat lower than that characteristic of the virgin capacitor [Fig. 1(a)]. It was not possible to recover the original polarization level of the virgin SBT capacitor, even after 800 °C oxygen annealing. XRD analyses of the SBT layers before and after the oxygen recovery anneal show no major changes in the crystalline structure of the bulk of the film [Figs. 2 (b) and 2(c)].

The MSRI spectrum of Fig. 5 (c) shows the restoration of the Bi signal after the SBT film oxygen annealing, which indicates that Bi was replenished on the surface, most probably via diffusion of Bi from the bulk of the SBT film. The recovery of the Bi MSRI signal correlates with the recovery of the hysteresis loop of the SBT capacitor [Fig. 1(c)]. However, the original value of P_r is not obtained after the oxygen recovery annealing. This may be due to the fact that although Bi is replenished at the surface of the SBT layer, there should be a slight deficiency of Bi throughout the sample, since the Bi recovery at the surface is due to diffusion from the bulk.

The data presented above indicated that there is a strong relationship between the surface composition changes and the electrical properties of SBT films and capacitors after hydrogen and oxygen annealing. It can be inferred that the compositional changes of SBT films during hydrogen annealing (specifically, loss of Bi) may lead to a substantial alteration of the SBT structure at the surface and/or a near surface region, resulting in a non-ferroelectric layer at the SBT/Pt interface. In order to determine whether a very thin non-ferroelectric layer at the SBT/Pt interface can significantly affect the electrical properties of the SBT capacitor, we intentionally introduced a thin amorphous (non-ferroelectric) SBT layer between the SBT film and the top electrode layer, and measured the electrical properties of the SBT capacitors. Even a 3 nm thick amorphous (non-ferroelectric) SBT layer deposited on a 180 nm ferroelectric SBT layer reduced the 2 P_r value of the SBT capacitors by 50%. The SBT capacitor with an amorphous SBT layer thicker than 10 nm exhibited a complete loss of polarization. Therefore, this study clearly implies that a very thin non-ferroelectric SBT layer, produced during hydrogen annealing, can result in a substantial degradation of the SBT capacitor electrical polarization. Further work is necessary to characterize the nature of the hydrogen-induced altered layer.

CONCLUSIONS

We have demonstrated that there is a strong relationship between compositional changes in the near surface region of SBT layers and the electrical properties of Pt/SBT/Pt capacitors after hydrogen and oxygen recovery annealing, respectively. The analysis of the SBT layer using the complimentary MSRI, XRD, SEM, and AFM analytical techniques suggest that the hydrogen-induced degradation in the electrical properties of SBT capacitors is mainly due to the loss of Bi in the near surface region of the SBT layer. It can be inferred that the compositional changes of SBT films during hydrogen annealing result in a substantial alteration of the SBT film structure near the surface. Both the MSRI analysis and the electrical characterization of SBT capacitors after oxygen annealing, reveal a correlation between replenishment of Bi in the near surface region via diffusion from the SBT film bulk and recovery of the capacitor polarization. Further work, particularly high resolution TEM studies currently underway in our laboratory, will be necessary to clarify the hydrogen-induced SBT degradation mechanism proposed in this paper.

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