



## Effects of Long-Time DC Bias on D<sub>2</sub>O- and D<sub>2</sub>/N<sub>2</sub>-Annealed BST Thin Films

R.-V. WANG, R.J. BECKER & P.C. MCINTYRE

*Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA*

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**Abstract.** Effects of long time dc bias on both D<sub>2</sub>O- and D<sub>2</sub>-annealed BST thin films were investigated by secondary ion mass spectrometry (SIMS) analysis and electrical measurements before and after bias stressing. Bias conditions were sufficient to cause the degradation of (1) subsequently-measured current density-voltage characteristics and (2) a significant positive shift of the capacitance-voltage curve along the voltage axis. This latter effect may be attributed to the asymmetric space charge distribution in the BST thin film after bias stressing or, possibly, to changes in the interface state density. No significant deuterium motion was observed in D<sub>2</sub>O-annealed capacitors biased at an elevated temperature or in D<sub>2</sub>/N<sub>2</sub>-annealed capacitors biased at room temperature in high electric fields ( $\sim 3.5 \times 10^7$  V/m) for more than 8 hours. The small values of the D<sub>i</sub> mobility which were inferred from the SIMS results are consistent with recent data on the kinetics of deuterium incorporation in and removal from similar BST thin films.

**Keywords:** resistance degradation, BST, deuterium doping, defects

High dielectric constant thin films of (Ba, Sr) TiO<sub>3</sub> (BST) have attracted considerable attention due to their potential application in on-chip capacitors, such as those used in dynamic random access memory (DRAM). A schematic current density-time ( $J-t$ ) behavior of a metal/high- $\kappa$  dielectric (BST)/metal capacitor is shown in Fig. 1 [1]. The current density-time behavior usually exhibits a decaying relaxation current at an early stage and then reaches a steady-state leakage current density. After a long period of time, the capacitor may experience an increase in leakage current, which is the so-called dc resistance degradation. Resistance degradation is usually accompanied by the deterioration of electrical properties and may limit the reliability of integrated BST capacitors in on-chip applications.

Resistance degradation has been widely studied in the bulk ceramics, such as SrTiO<sub>3</sub> and BaTiO<sub>3</sub>. Electrocoloration and thermally-stimulated current measurements show evidence of the migration and accumulation of oxygen vacancies at the interface of dielectrics and metal electrodes under dc bias stress [2–4]. Besides

oxygen vacancies, hydrogen interstitials are another possible mobile ionic charge carrier in ferroelectric thin films. Hydrogen interstitials act as shallow donor defects in perovskite-structure titanate. Studies on both bulk BaTiO<sub>3</sub> and SrTiO<sub>3</sub> ceramics and single crystals indicate that interstitial H and D defects are highly soluble and have a small activation enthalpy for migration ( $\sim 1$  eV) [5, 6].

Resistance degradation is also observed in BST thin films, but there are qualitative differences between the field- and electrode-dependence of resistance degradation observed in bulk ceramic capacitors and in thin films [7]. At this moment, the extent to which the ionic defect redistribution contributes to resistance degradation in BST thin films is unclear. In this study, we focus on the effects of long-time dc bias on deuterium/hydrogen interstitial motion in D<sub>2</sub>O-annealed and D<sub>2</sub>/N<sub>2</sub>-annealed Pt/BST/Pt thin film capacitors.

Barium strontium titanate thin films of 50 nm thickness with a 1:1 Ba:Sr ratio and approximately 1 at% Ti excess were grown on a Pt bottom electrode at a nominal substrate temperature of 640°C [8]. The Pt

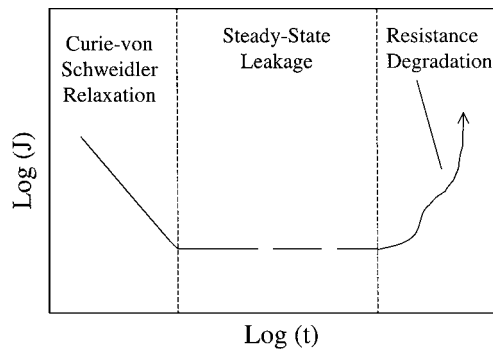


Fig. 1. Schematic  $J-t$  behavior of the metal-BST-metal system (after C. Basceri, et al.) [1].

bottom electrodes were deposited by e-beam evaporation at 300°C. Platinum top electrodes were deposited by e-beam evaporation through a shadow mask at room temperature. After top electrode deposition, the samples were annealed in O<sub>2</sub> at 550°C for 30 minutes prior to any further experiments. Instead of hydrogen, deuterium doping was used to avoid the interference during depth-profiling analysis from the hydrogen present in as-deposited MOCVD-grown BST films [9, 10]. Deuterium was introduced into BST thin films by two different methods: annealing in an N<sub>2</sub> atmosphere saturated with D<sub>2</sub>O vapor and annealing in a deuterium forming gas (5% D<sub>2</sub> + 95% N<sub>2</sub>). Secondary ion mass spectrometry (SIMS) was used to analyze the deuterium and hydrogen distribution of the reference and degraded samples. A SIMS calibration standard was prepared by D<sup>+</sup> and H<sup>+</sup> ion implantation for quantitative analysis of deuterium and hydrogen concentrations. QuadSIMS depth profiling was performed on a PHI-6600 quadrupole mass spectrometer (Charles Evans and Associates, Sunnyvale, CA). In long-time bias experiments, the current was measured as a function of time using a Keithley 6512 electrometer. Both reference and degraded D<sub>2</sub>O annealed capacitors were also characterized using electrical measurements. Current-voltage measurements were carried out using the Keithley 6512 electrometer with a 1-sec delay time and 0.1 V step. Capacitance-voltage measurements were performed using a HP 4284A LCR meter with a 5 s delay time and 0.1 V step at ac frequency 100 KHz and amplitude 100 mV.

After being annealed in D<sub>2</sub>O ambient at 300°C for 30 minutes, a Pt/BST/Pt capacitor was biased at +1.7 V on the top electrode at 84°C for 8 hours. This temperature was chosen because it is similar to maximum

operating temperatures quoted in reliability specifications for semiconductors, and because of concern that higher bias stressing temperatures would result in loss of deuterium from the BST capacitors. The reported mechanism for incorporating deuterium into perovskite titanates by D<sub>2</sub>O annealing can be expressed by the following defect reaction:  $D_2O + O_o^x + V_o^{\bullet\bullet} \rightarrow 2(D_i^{\bullet}-O_o^x)$ , where Kroger-Vink defect notation is used to denote charge and site-occupancy of the defects [6]. Based on this mechanism, an oxygen vacancy is removed, and an ionized interstitial deuterium is created and bound to an oxygen ion. Such a process results, therefore, in no net change of the integrated space charge present in the films. The  $J-t$  and post-bias stressing  $J-V$  characteristics of D<sub>2</sub>O-annealed Pt/BST/Pt capacitors were not significantly different from those of identical capacitors that were processed without deuterium exposure [11]. Figure 2 shows the  $J-t$  behavior of the capacitor during biasing. The first data point was taken after 30 seconds under bias. As shown in Fig. 2, the current initially increases with time, reaching its maximum value at 5 minute. After reaching the maximum value, the current gradually decreases with time. This type of  $J-t$  characteristic is consistent with space charge limited (SCL) currents [12], and suggests that a large reservoir of charges forms at the injecting electrode during biasing. This reservoir of charges may result from the creation or accumulation of ionic defects, such as oxygen vacancies, hydrogen, or deuterium interstitials at the interface, or the redistribution of electronic charge within the dielectric.

Electrical measurements were performed on the D<sub>2</sub>O annealed capacitors before and after the degradation experiments. As shown in Fig. 2, an increase in current typical of resistance degradation was not observed under constant applied voltage over a 8-hour period. However, the data in Fig. 3(a) measured by step  $J-V$  tests indicates that electrical degradation of this capacitor did occur. The leakage current increases for both positive and negative polarity. The conduction mechanism at low temperatures is different from that at high temperatures. At low temperatures such as 300 K, the low voltage “knee” in measured  $J-V$  curves is strongly affected by the magnitude of the Schottky barrier, and SCL-like currents are only observed at higher voltages. Therefore, our results suggest that the barrier height may be lowered on both polarities as a result of dc bias stressing. As shown in Fig. 3(b), the  $C-V$  curves of the degraded capacitor shift in the positive direction and the maximum permittivity also decreases.

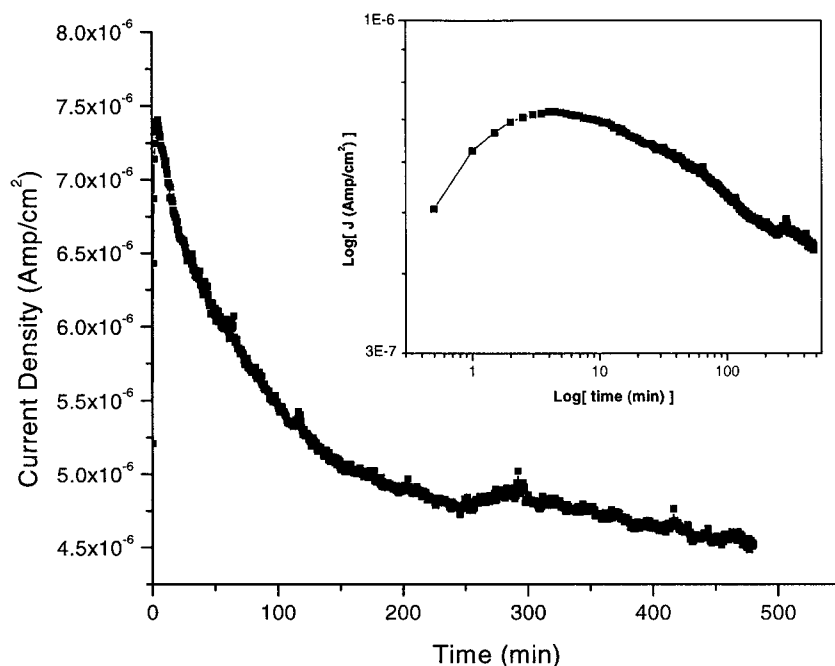


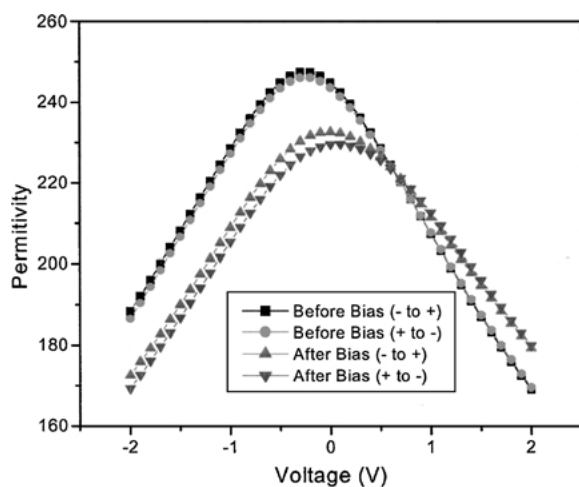
Fig. 2.  $J$ - $t$  behavior of D<sub>2</sub>O-annealed BST capacitor in the following bias condition: +1.7 V at the top electrode at 84°C for 8 hours.

The SIMS analysis method was used to investigate D/H redistribution in D<sub>2</sub>O-annealed BST thin films under dc biasing. The deuterium and hydrogen distributions across the D<sub>2</sub>O-annealed capacitor before and after degradation are shown in Fig. 4. No changes in the deuterium depth profiles were observed within the experimental detection limits; however, a prominent hydrogen peak appeared at the BST bottom electrode interface after long time dc bias.

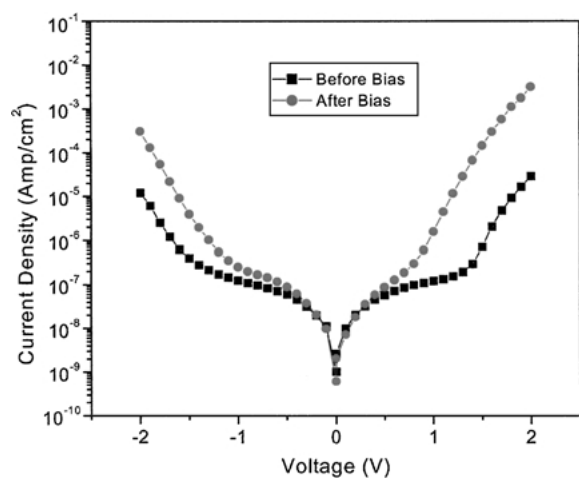
In addition to annealing in a saturated D<sub>2</sub>O ambient, deuterium was introduced into BST thin films by annealing in D<sub>2</sub>/N<sub>2</sub> forming gas. In this case, the incorporation of charged deuterium interstitials is believed to occur as follows:  $D_{2(g)} \rightarrow 2D_i^+ + 2e^-$ , consistent with the shallow-donor character of deuterium interstitials [13]. During the annealing process, a reduction reaction may also occur under the low oxygen partial pressure produced by D<sub>2</sub>/N<sub>2</sub> annealing, and oxygen vacancies may be created. The typical  $J$ - $V$  characteristics of capacitors that did not undergo bias stressing were seriously degraded as a result D<sub>2</sub>/N<sub>2</sub> annealing [9]. To avoid possible dielectric breakdown during dc bias, an oxygen recovery annealing at 200°C for 30 min was performed after D<sub>2</sub>/N<sub>2</sub> annealing but prior to dc bias stressing. Previous work has shown that this recovery anneal reduces

the concentration of deuterium defects in the film from  $\sim 10^{20} \text{ cm}^{-3}$  to (a still easily-detectable)  $\sim 10^{19} \text{ cm}^{-3}$ , and simultaneously greatly improves the leakage resistance [9]. The D<sub>2</sub>/N<sub>2</sub> annealed capacitors were then biased at either +1.75 V for 24 hours or -1.7 V for 20 hours at room temperature. Figure 5 shows the deuterium and hydrogen profiles before and after degradation experiments for both capacitors biased at opposite polarities. Similar to the D<sub>2</sub>O case, no significant bias-induced change of the deuterium profiles was observed and the concentration of hydrogen increased at the interface between the BST and Pt bottom electrode. The spread in nominal deuterium concentrations shown in Fig. 5 is consistent with capacitor-to-capacitor variations typically observed in these recovery-annealed, D<sub>2</sub>-exposed specimens.

In previous studies of the kinetics of incorporation and removal during deuterium annealing [10], it was shown that the diffusivity of  $D_i^+$  extracted from the data analysis of the BST thin films was several orders of magnitude smaller at 300°C than the expected deuterium/hydrogen interstitial diffusivity obtained from data on bulk titanate ceramics and single crystals [5]. A summary of the  $D_i^+$  diffusivities and corresponding mobilities in bulk titanate ceramics and BST thin films



(a)



(b)

Fig. 3. (a) Permittivity vs. voltage for the  $D_2O$ -annealed capacitor before and after being biased at +1.7 V at  $84^\circ C$  for 8 hours; (- to +) means that this CV measurement started at a negative voltage (-2 V) and increased the applied voltage on the top electrode with respect to the bottom electrode; (b) Leakage current density vs. voltage for the  $D_2O$ -annealed capacitor before and after being biased at +1.7 V at  $84^\circ C$  for 8 hours.

similar to the ones studied in this work is presented in Table 1. According to the mobility values for  $D_i^+$  defects in these BST thin films, observation of any significant deuterium migration under our experimental dc bias conditions would be unlikely. This is consistent with the deuterium SIMS profiles after bias stressing shown in Figs. 4 and 5.

As-grown MOCVD BST films have a substantial hydrogen concentration, which may be incorpo-

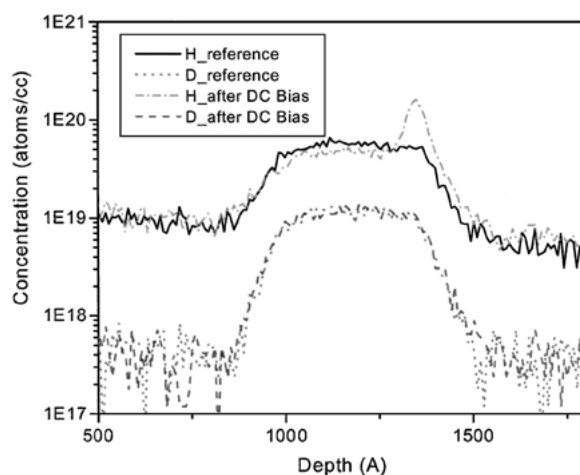


Fig. 4. SIMS depth profiles of deuterium and hydrogen across the  $D_2O$ -annealed capacitor biased at +1.7 V at  $84^\circ C$  for 8 hours and the reference  $D_2O$ -annealed capacitor.

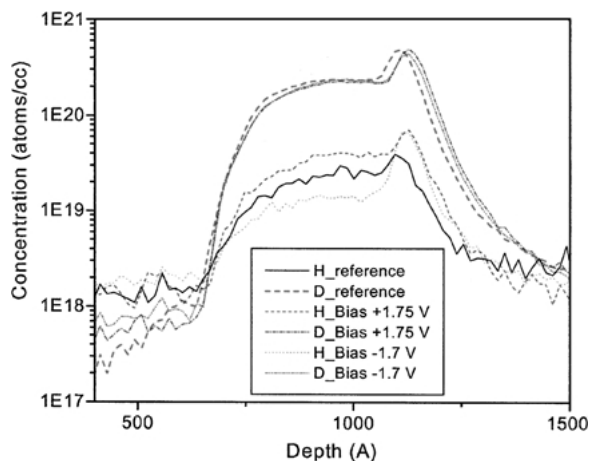


Fig. 5. SIMS depth profiles of deuterium and hydrogen across the  $D_2$ -annealed capacitor biased at different polarities for a long period of time; +/- refers to the polarity of the voltage applied on the top electrode.

rated during film deposition. Frequently, we have observed that a portion of the hydrogen present at the BST/bottom electrode interface after deposition is significantly more mobile than that in the "bulk" of the BST thin films, and it is removed from the films during subsequent treatments even at moderate temperatures. Therefore, the hydrogen present in the "bulk" of the films appears to result primarily from the MOCVD process and maybe present in the form of  $H_2O$  or hydrogen bonded to incorporated carbon. Since we do not observe any evidence of  $D_i^+$  motion, it is hard to

Table 1. A summary of diffusivity and mobility values at room temperature and 84°C for D<sub>i</sub><sup>+</sup> in SrTiO<sub>3</sub> single crystals and BST thin films, extrapolated from data in references 5, 6 and 10.

	Diffusivity @ RT (cm <sup>2</sup> /s)	Mobility @ RT (cm <sup>2</sup> /V·s)	Diffusivity @ 84°C (cm <sup>2</sup> /s)	Mobility @ 84°C (cm <sup>2</sup> /V·s)
Undoped SrTiO <sub>3</sub> crystals	$3.56 \times 10^{-19}$	$1.38 \times 10^{-17}$	$5.62 \times 10^{-16}$	$1.83 \times 10^{-14}$
SrTiO <sub>3</sub> crystals doped with 0.1 at% Mn (acceptor dopants)	$6.73 \times 10^{-19}$	$2.60 \times 10^{-17}$	$7.7 \times 10^{-16}$	$2.5 \times 10^{-14}$
BST thin films (D(300°C) $\sim 10^{-15}$ cm <sup>2</sup> /s) Assume the activation energy $\sim 1$ eV	$10^{-23}$	$4 \times 10^{-22}$	$5 \times 10^{-21}$	$1.62 \times 10^{-19}$

rationalize how the significant hydrogen accumulation seen in Figs. 4 and 5 could occur only by migration of charged interstitials within the BST grains. The hydrogen peak may result from some chemical reaction during the biasing process.

The electrical character of the hydrogen that appears at the BST/Pt bottom electrode interface under bias can be assessed by examining the measured *C-V* shifts shown in Fig. 3(b). For capacitors with a metal/dielectric/metal structure, formation of an asymmetric space charge distribution would cause a *C-V* shift, while a symmetric space charge distribution would not. If the hydrogen at the bottom electrode interface were ionized, the electrical field resulting from these positively-charged defect near the bottom electrode would shift the *C-V* curve in the positive direction. The “total effective electric field” across the film due to the hydrogen peak at the bottom electrode can be roughly estimated by considering a sheet of positive charges ( $1.6 \times 10^{26} \text{ m}^{-3} \times 50 \text{ \AA} \cong 8 \times 10^{17} \text{ m}^{-2}$ ) at the bottom interface, assuming that the hydrogen is completely ionized. To maintain global charge neutrality across the capacitor, there are “effective” negative charges near the top electrode interface. By applying Gauss’s law, the required effective electric field across the film would be about  $6.6 \times 10^7 \text{ V/m}$ , and the resulting *C-V* shift on 500 Å films can be as large as  $\sim 3 \text{ V}$ . Therefore, although a large amount of hydrogen is present at the bottom interface after the bias stressing experiments, *C-V* results suggest that most of it is not electrically active.

Another possible cause of the observed *C-V* shift in the positive direction is the redistribution of non-hydrogenic charges within the “bulk” of the film. To avoid the undesirable electrical characteristics resulting from Ti deficiency, it is common to add excess Ti during the BST film deposition process. The BST thin films in this study were deposited with  $\sim 1\%$  excess Ti.

Because the formation of Ti interstitials is unlikely in close-packed perovskite structures, excess Ti present in the grains may be structurally-accommodated by formation of oxygen vacancies and A-site (Ba or Sr) cation vacancies [14]. Therefore, in addition to electronic charge carriers, possible charged species include  $V_A''$ ,  $D_i^+$ ,  $V_o^{\bullet\bullet}$  and  $H_i^+$ . Under long time bias stress, the as-deposited charge distribution across the film may be rearranged. Because  $D_i^+/H_i^+$  motion is not observed, such redistribution may be achieved by the segregation of charged oxygen vacancies, or by trapping and de-trapping processes involving electronic carriers. As a result, the appearance of an asymmetric space charge distribution in the film during biasing may contribute to the observed *C-V* shift to the positive polarity.

On the other hand, a chemical reaction at the electrode interfaces during long time dc bias may alter the interface state density. Metal oxide films are susceptible to reaction with atmospheric species such as water vapor and carbon dioxide, as well as with introduced impurities such as hydrogen and deuterium (in the present experiments). Electrical bias stressing may encourage such interface reactions and results suggestive of such behavior involving hydrogen were obtained in this study. As previously reported, the potential barrier at the Pt/BST interface may be significantly altered by changes in the interface state density [9]. Changes in the electrical potential at the interfaces may contribute to the observed *C-V* shifts, and a chemical reaction-induced lowering of barrier heights may result in degradation of *J-V* behavior.

In summary, motion of deuterium defects introduced into BST thin films by D<sub>2</sub>O/N<sub>2</sub> and D<sub>2</sub>/N<sub>2</sub> was not observed under dc bias stressing conditions at 25°C–84°C that cause a post-stressing, polarity-independent lowering of the apparent Schottky barrier for Pt/BST/Pt capacitors. These results suggest a very small mobility for D<sub>i</sub><sup>+</sup> defects, which is consistent with

recent deuterium diffusion measurements in these BST thin films, but is inconsistent with the reported  $D_i$  diffusivity obtained in measurements at higher temperatures from bulk metal titanate crystals. Motion of charged deuterium (or hydrogen) defects is, therefore, unlikely to contribute to dc resistance degradation of BST thin films at typical operating temperatures in semiconductor devices.

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