

# Electrode dependence of hydrogen-induced degradation in ferroelectric $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films

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Forming gas annealing causes changes in the remanent polarization ( $P_r$ ), coercive field ( $E_c$ ), and leakage current ( $I$ ) in both PZT [ $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ] and SBT ( $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ) samples with a variety of top electrode materials (Pt, Au, Ag, Cu, Ni, and  $\text{In}_2\text{O}_3$ ), and the degree of degradation depends strongly on the top electrode material. These results may be explained by a model that is based on the catalytic activities of the top electrode to dissociate hydrogen molecules into hydrogen atoms, with the latter subsequently migrating into PZT or SBT films to cause oxygen deficiency and its associated property degradation. This model can be expanded to explain the recovery phenomenon resulting from oxygen annealing, which also depends on the catalytic activity of the top electrode to produce atomic oxygen from molecular oxygen. © 1997 American Institute of Physics. [S0003-6951(97)01835-4]

Since the submission of our abstract in September of 1996 and the subsequent presentation of the corresponding paper at the 9th International Symposium on Integrated Ferroelectrics<sup>1</sup> in March of 1997, there have been many inquiries about our results on the top electrode dependence of hydrogen-induced degradation of ferroelectric  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  and  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  thin films, and the catalytic-reactions model that we proposed also received a lot of attention. Therefore, we decided to use this letter as a efficient means of disseminating the essential information in a timely fashion.

It has become well known that postmetal annealing (PMA) in a hydrogen-containing ambient (e.g., forming gas) may cause severe degradation of ferroelectric thin films.<sup>2-4</sup> To gain some understanding of the possible mechanisms involved, we made a systematic study of the effects of forming gas annealing on  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) and  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) films having six different top electrode materials over a temperature range of 116–464 °C, and found that the results depend very strongly on the top electrode material. In particular, the trend suggested that the electrode dependence was directly linked to the degree of catalytic activity of the electrode in dissociating molecular hydrogen into atomic hydrogen.<sup>5</sup>

All of the samples used in this study were fabricated on Pt/ $\text{SiO}_2$ /Si bottom electrodes. The PZT films were deposited by the jet-vapor technique<sup>6</sup> while the SBT films were deposited by the MOD spin-on technique.<sup>7</sup> After crystallization at elevated temperatures, various top electrodes, including Pt, Au, Ag, Ni, Cu, and  $\text{In}_2\text{O}_3$ , were deposited by physical vapor deposition. The polarization as a function of electric field ( $P$ – $E$ ) and current as a function of voltage ( $I$ – $V$ ) were measured before and after forming gas (5%  $\text{H}_2$ +95%  $\text{N}_2$ ) annealing in a conventional annealing furnace with a quartz tube. A standard Sawyer–Tower circuit was used for the  $P$ – $E$  measurement, and an HP4145 parameter analyzer was used for the  $I$ – $V$  measurement. The annealing temperature ranged from 116 to 464 °C, and the annealing results that

will be reported in this letter were all obtained after an isochronal anneal for 5 min at each temperature.

An oxygen anneal (450 °C in  $\text{O}_2$  for 30 min) was performed on some samples following the forming gas anneal to find out if the oxygen annealing step could undo some of the changes caused by the forming gas anneal.

Figure 1 shows the forming gas annealing results for a set of PZT samples with five different top electrodes. One can see that the degradation in the remanent polarization ( $2Pr$ ) is most severe for the sample with a Pt electrode, and least severe for the one with an indium oxide electrode. The other electrodes are in between the two.

SBT samples also show similar top electrode dependence, as shown in Fig. 2 where four different top electrodes were included. Again, the Pt electrode shows the most severe degradation. In fact, it was shorted after 230 °C of annealing, and completely lost its polarization. The sample with Au seems to have suffered the least degradation. Note that the data for the two group-IB metals (Au and Ag) tend to exhibit a similar trend between the two, while the two group-VIII metals (Pt and Ni) seem to suffer more severe degradation.

In addition to the  $2Pr$  degradation, the forming gas anneal also caused significant changes in the coercive field

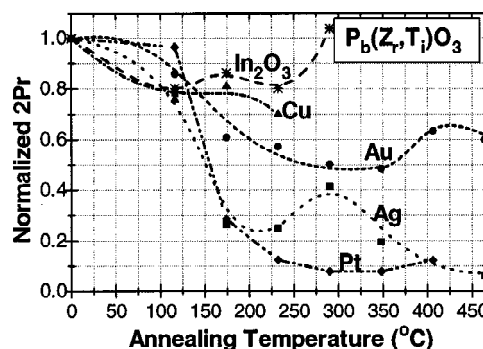


FIG. 1. Remanent polarization, normalized with respect to the original value, as a function of isochronal (5 min) forming gas annealing temperature for a set of PZT samples with five different electrode materials.

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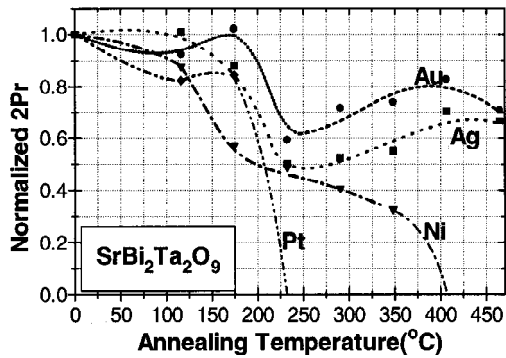


FIG. 2. Remanent polarization, normalized with respect to the original value, as a function of isochronal (5 min) forming gas annealing temperature for a set of SBT samples with four different electrode materials.

( $2Ec$ ) and leakage current ( $I$ ). One interesting feature that we observed is that, in most samples, the annealing curves for  $2Pr$  and for  $2Ec$  track each other very well, shown in Fig. 3(a) as an example. This strongly suggests that the changes in  $2Pr$  and in  $2Ec$  may come from the same mechanism. In some samples the leakage current also correlated with  $2Ec$ , as shown in Fig. 3(b) for a SBT sample after forming gas annealing, in which the leakage current was measured at  $-1$  V. The correlation between the leakage current and the coercive field is much weaker in some samples than in others, and the exact cause for that is not yet clear.

Note that the annealing curves in Figs. 1–3 do not all show a monotonically downward trend, and there exist local up-and-down swings on many curves, suggesting that there are at least two competing mechanisms, one of which tends to decrease the  $2Pr$  whereas the other tends to increase the  $2Pr$ . While it would be interesting to find out both of these mechanisms, the focus of this work is on the degradation part only.

Although there is little doubt that hydrogen is somehow involved in the degradation mechanism,<sup>1–4</sup> the modest temperature ( $\sim 100$  °C) and the relatively short time required to

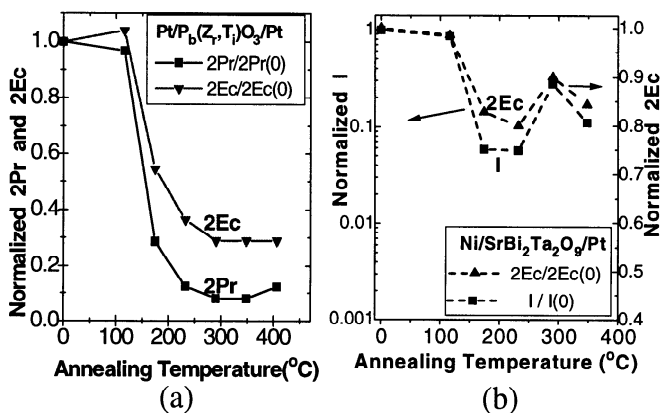


FIG. 3. (a) The forming gas induced changes in coercive field ( $2Ec$ ) and remanent polarization ( $2Pr$ ) track each other very well in this PZT sample with a Pt top electrode. Both quantities are normalized with respect to their original values. (b) The forming gas induced changes in coercive field ( $2Ec$ ) and leakage current (measured at  $-1$  V) track each other very well in this SBT sample with a Ni top electrode. Both quantities are normalized with respect to their original values.

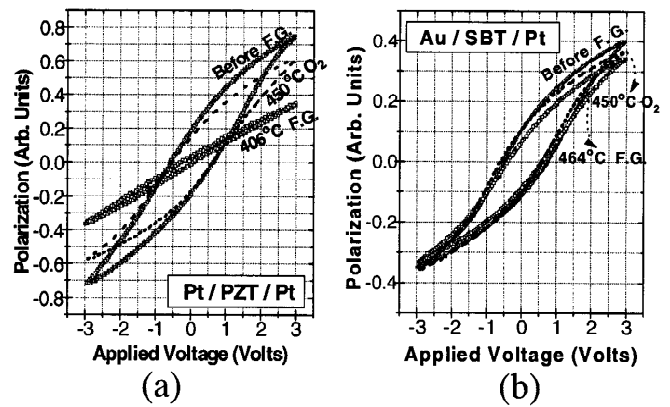


FIG. 4. Hysteresis loops for (a) a PZT sample with a Pt top electrode and (b) a SBT sample with a Au top electrode, respectively, showing that oxygen annealing can largely recover the degraded loop previously damaged by the forming gas annealing.

observe significant degradation suggest that atomic hydrogen may play an important role, as it is believed that a much higher temperature and/or time are needed if only molecular hydrogen is involved for similar perovskite-type oxides.<sup>8</sup> To explain the top electrode dependence, we propose the following model.<sup>1</sup> First, hydrogen molecules are chemisorbed at the electrode surface or at the electrode/ferroelectric interface during forming gas annealing (e.g.,  $H_2 + 2M \rightarrow 2H - M$ ). At elevated temperatures, hydrogen atoms are released from the chemisorbed sites (e.g.,  $2H - M \rightarrow 2H + 2M$  or  $2H - M \rightarrow H + M + H - M$ ). These hydrogen atoms can diffuse into the ferroelectric and react with the oxide to cause reduction of the oxide. The end result is that the ferroelectric becomes oxygen deficient, and the properties degrade. The reason that different top electrodes cause different degrees of degradation is due to their different chemical reactivities, that is, some top electrodes act as strong catalysts to dissociate hydrogen molecules during forming gas annealing, and those are the ones that cause the most severe degradation. It is well known that Pt is a strong catalyst, especially when it is supported on certain oxides (particularly transition-metal oxides),<sup>9,10</sup> which is consistent with our experimental observation. The group-VIII (Pt and Ni) and group-IB (Au and Ag) metals are expected to give rise to different catalytic activities,<sup>11</sup> which may account for the difference between these two groups observed in Fig. 2.

Since the catalytic activity of a given electrode is also a strong function of its support material,<sup>9,12</sup> one would expect that the degree of degradation would be different between PZT and SBT even with the same top electrode, which is also consistent with the experimental results.

Figure 4 shows that the degradation caused by the forming gas anneal can be largely recovered by an oxygen anneal treatment at  $450$  °C for 30 min, for both a PZT sample with a Pt top electrode [Fig. 4(a)] and a SBT sample with a Au top electrode [Fig. 4(b)]. It is interesting to note that even shorted samples (caused by the previous forming gas anneal) can be recovered by the oxygen anneal, as we frequently observed on samples with a Pt top electrode (data not shown here).

In the context of our model, the recovery of the ferro-

electric properties by oxygen anneal should not be too surprising, as the primary reason for the degraded properties, the oxygen deficiency, is presumably removed by the oxygen annealing. Although a systematic study of the electrode dependence of the recovery phenomenon remains to be conducted, our preliminary observation has indicated that the recovery is also more enhanced for samples that have top electrodes which act as strong catalysts for dissociating molecular oxygen to atomic oxygen.

In summary, we have observed that the degradation caused by forming gas annealing depends strongly on the top electrode material for both PZT and SBT films. Of the many electrode materials that we have investigated, Pt is among the worst in terms of the forming gas annealing effects. The forming-gas annealing-induced changes in  $2Pr$ ,  $2Ec$ , and  $I-V$  seem to be strongly correlated in many samples, suggesting that they may arise from the same degradation mechanism. We believe that the top electrode dependence that we observed is consistent with the model where atomic hydrogen is the reactive species that causes the degradation, and that the amount of atomic hydrogen generated depends on the catalytic activities of the top electrode to dissociate

molecular hydrogen during forming gas annealing. Although in this study we only investigated six top electrodes (Pt, Au, Ag, Cu, Ni, and  $In_2O_3$ ), we believe our proposed model is generally applicable to other electrode materials as well.

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