Temperature effects on charge retention characteristics of integrated $SrBi_2(Ta,Nb)_2O_9$ capacitors

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Temperature effects on charge retention characteristics of integrated $SrBi_2(Ta,Nb)_2O_9$ thin film capacitors were examined in the temperature range of 27–150°C. The decay in remanent polarization at 27°C was linear in logarithmic time from 10^{-3} to 10^5 s with a decay rate of 0.24 $\mu C/cm^2$ per decade. The elevation of storage temperature resulted in an instantaneous decrease in remanent polarization, while the decay rate at elevated temperatures after the instantaneous decrease was as small as that at 27°C. The instantaneous decrease in remanent polarization caused by elevating the temperature was explained by the temperature dependence of spontaneous polarization in the vicinity of the second order transition temperature. The development of asymmetry in the hysteresis loop during high temperature storing indicates that the logarithmic time dependence of the decay in remanent polarization is due to redistribution of space charges rather than polarization reversal. © *1997 American Institute of Physics.* [S0003-6951(97)02143-8]

Nonvolatile ferroelectric memories using $SrBi_2Ta_2O_9$ (SBT), a material with a bismuth-layered perovskite structure, have stimulated much interest due to their extremely low polarization fatigue, a phenomenon induced by repetitive polarization switching.[1,2] In addition, polarization in bismuth-layered perovskite thin film capacitors can be switched and saturated at low voltages below 3 V. For the use of bismuth-layered perovskite thin film capacitors in nonvolatile memory applications, however, charge retention, typically required to be longer than 10 years under specified temperature stresses, still remains as a potential reliability concern. It is therefore of interest to study the thermal stability of remanent polarization in ferroelectric memory capacitors fabricated from bismuth-layered perovskites. In this letter, we investigate the charge retention characteristics of integrated $SrBi_2(Ta,Nb)_2O_9$ (SBTN) capacitors poled by an applied voltage of 3 V.

The SBTN films were prepared by metalorganic decomposition processing on Pt-deposited silicon wafers with integrated metal-oxide semiconductor (MOS) circuits for driving ferroelectric memories.[3] Film thickness after high temperature annealing in atmospheric oxygen was 240 nm. Following deposition of the top Pt electrode, capacitor arrays containing 110 elements were patterned. The top electrode size of each capacitor element was $5\times5\ \mu m^2$. We then carried out the interlayer dielectric deposition, metallization, and passivation processes necessary for ferroelectric memory fabrication. Finally, the test capacitor arrays were assembled in ceramic packages with wiring.

Figure 1 shows typical polarization versus voltage (P-V) loops of an SBTN capacitor that has been allowed to relax for about 5 s after poling, where P_s is the switched polarization for a capacitor in the up state, and P_{ns} is the nonswitched polarization for a capacitor in the down state both when a negative voltage pulse is applied. In a ferroelectric memory cell with two transistors and two capacitors $(2T/2C)$, a voltage difference on a bitline pair corresponding to the acquired charges P_s and P_{ns}, is amplified for the logic state discrimination.[4] The hysteresis loop, therefore, should have a certain difference between the switched polarization and the nonswitched polarization, defined as $P_{nv} = P_s - P_{ns}$, to generate a signal available to the sense amplifier.[5] In either memory cell configuration, P_{nv} must be greater than an incoming noise margin of the sense amplifier.

For the transient polarization decay measurement, we monitored the change in the output voltage from an operational amplifier with a linear capacitor C_s which integrates the switching current from the ferroelectric capacitor in a Sawyer–Tower circuit, yielding a voltage proportional to the amount of polarization charge in the ferroelectric capacitor by a factor of $1/C_s$. Since there was a limitation in duration of the transient polarization measurement, a pulse polarization measurement technique was used for the retention test exceeding 530 ms. The pulse sequence used is shown in Fig. 2. The voltage pulses are triangular waves of ± 3 V with a duration of 11 ms. The P-V measurements were made with a Radiant Technologies RT6000SI tester. Each capacitor array was tested only once in order to prevent history-dependent effects such as imprint.

Figure 3 shows P_{nv} versus retention time. The data set

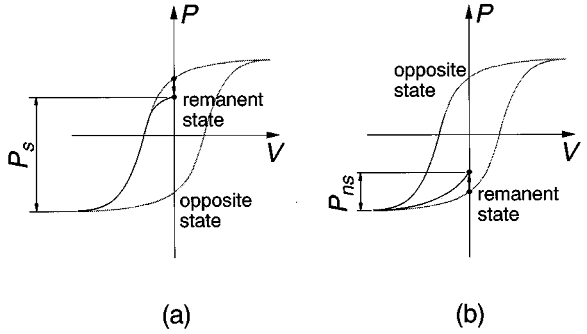

FIG. 1. Typical hysteresis loops, showing charge losses after the storage for a certain period of time. (P_s) Switched polarization acquired from a capacitor in the up state. (P_{ns}) Nonswitched polarization acquired from a capacitor in the down state.

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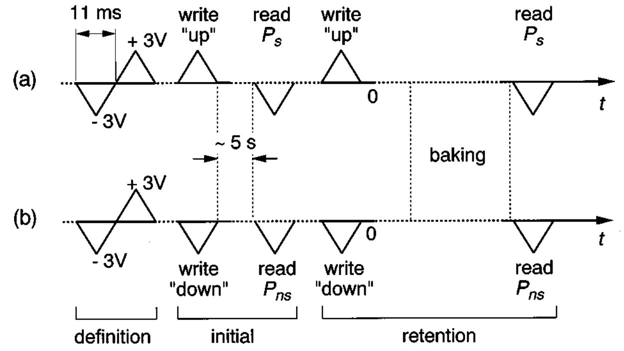

FIG. 2. Pulse trains used for the measurement of the retention property. For the retention measurement, a positive voltage pulse sets the polarization state of a capacitor array into (a) the up state and a negative voltage pulse sets it into (b) the down state. The amount of retained polarization after storing is determined with a negative voltage pulse for both states.

for the first 530 ms after poling was obtained from transient polarization measurements. The initial pulse polarization measurement was made at 10 s and the values of P_{nv} at 27°C were approximately 12 μC/cm^2. Subsequently, test capacitor arrays were stored at selected temperatures (27, 75, 125, and 150°C) for 2, 24, and 100 h. The values of P_{nv} after 27°C storages showed a good agreement with a straight fitting line extrapolated from data points in the transient regime. It is therefore reasonable to extend the fitting line to 100 h, and is assumed that the decay in P_{nv} is governed by a single mechanism in the short to long time regime (10^{-3}–10^5 s). The linear dependence of the decay curve on logarithmic time yields a decay rate of 0.24 μC/cm^2 per decade at 27°C. The logarithmic time dependence suggests that the polarization decay process is associated with a wide distribution over orders of magnitude in relaxation time, and is described by[6–9]

$$P(t)=P_0-m\log\left(\frac{t}{t_0}\right), \qquad (1)$$

where t is the time, t_0 is a characteristic time at which the linear behavior of $P(t)$ begins with respect to log t, P_0 is the polarization at $t=t_0$, and m is the decay rate.

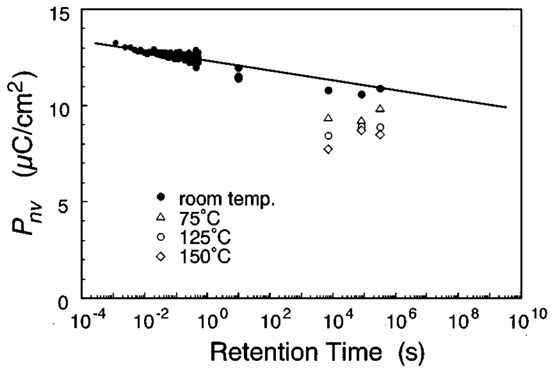

FIG. 3. Charge retention characteristics of SBTN capacitor arrays integrated in a nonvolatile memory test structure for storing temperatures of 27, 75, 125, and 150°C as functions of time, showing the change in nonvolatile component, $P_{nv}=P_s-P_{ns}$, where P_s and P_{ns} are the switched and nonswitched polarization, respectively.

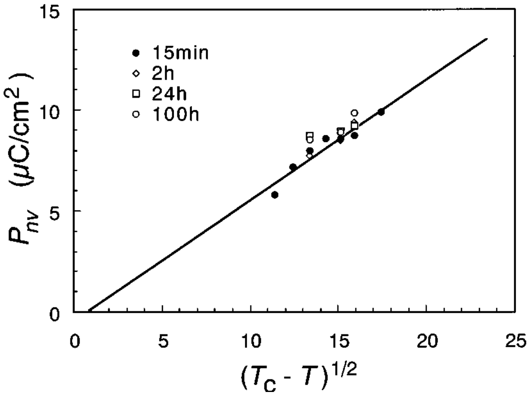

FIG. 4. Nonvolatile polarization component P_{nv} vs storage temperature T, where T_C is the Curie temperature. Polarization measurements were made at 27°C after storing at temperatures from 27 to 220°C for 15 mins.

At elevated storage temperatures, a 2 h storage resulted in a significant decrease in P_{nv} by up to 4 μC/cm^2, depending on storage temperature. However, measurements after the next 24 and 100 h storages showed no pronounced change in P_{nv} within the measurement reproducibility. Thus the primary decrease in P_{nv} at high temperatures is supposed to occur within a short time, as seen in SBT.[10] To evaluate the temperature effect on P_{nv}, poled samples were baked at temperatures of 27–220°C only for 15 min, whereas it is enough to allow relaxation of capacitors. Supposing the second order transition near the Curie temperature, T_c, the values of P_{nv} were plotted as a function of baking temperature, T, so as to obtain the relation between P_{nv} and $(T_c-T)^{1/2}$. As shown in Fig. 4 an extrapolation from this data set, symbolized by closed circles, indicates a collapse of P_{nv} at a temperature of 330°C, which is close to an experimentally determined value of the Curie temperature for SBTN films.[11] To account for the temperature effect in the high temperature storage test, values of P_{nv} in Fig. 3, whose measurements were made after 2–100 h storages, were overlaid on the same plot (Fig. 4). Then we found good agreement in the temperature dependence between the long-time storage values and the 15 min storage values. This fact indicates that the decrease in P_{nv} at high temperatures from its initial (10 s) value is primarily due to an instantaneous decrease in remanent polarization within 15 min and that the temperature dependence is quite similar to that of spontaneous polarization in the vicinity of the second order transition. The decrease in P_{nv} caused at high temperatures is explained by the loss of measurable charge in the capacitor electrodes coupled with polarization charge. Therefore P_{nv} at high temperatures is quenched to room temperature.

Small changes in P_{nv} from 2 to 24 and 100 h storages at high temperatures lead to a supposition that P_{nv} at high temperatures has a similar logarithmic time dependence to that at 27°C. When discussing the origin of the distributed relaxation time for the decay in remanent polarization, one can indicate two possible factors:

(1) distribution of coercive energy responsible for polarization reversal and
(2) distribution of the depth of traps responsible for space charge transport.

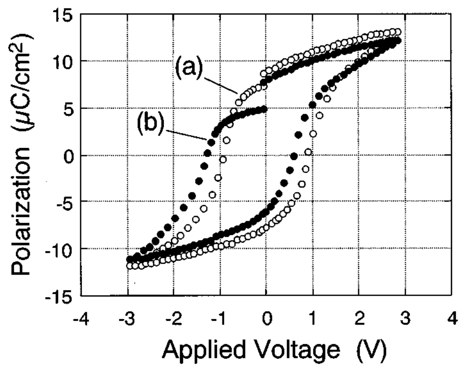

FIG. 5. P-V hysteresis curves of a SBTN capacitor array measured at 27°C (a) before and (b) after storing at 125°C for 120 h.

Although either process leads to the distributed relaxation time, there is a substantial difference between them. The thermal fluctuation process is reversible if the coercive energy distribution does not change with time. In contrast, the space charge redistribution process is irreversible, and as a result the final polarization state is more stable than the other. In ferroelectric materials, such memory effects are referred to as imprint, which can be described as the establishment of a preference in the poled direction.[12–14] This phenomenon was also observed in our SBTN samples. As shown in Fig. 5, for instance, there is a definite drift in the hysteresis loop as a result of a storage at 125°C for 120 h. Once imprint has occurred, the initial hysteresis loop is no longer restored even by polarization switching. This fact strongly indicates that the polarization decay process is accompanied by imprint caused by the space charge redistribution. This conclusion is consistent with a speculation that the decrease in polarization of SBT capacitors is independent of the reversal of domains.[15] The time required for emitting trapped charges into the conduction band may depend on the distributed trap depth in energy, resulting in a logarithmic time dependence of the change in remanent polarization. In addition, the distribution of the trap depth responsible for transport of emitted charges is probably limited in a shallow range because the dominant traps are metal cations such as Bi^{3+} ions for holes and Ta^{5+} ions for electrons.[16] It is therefore expected that the polarization decay rate exhibits a weak temperature dependence.

In summary, the temperature dependence of charge retention characteristics of integrated SBTN capacitors was studied. The primary decrease in remanent polarization during high temperature storing was attributed to an instantaneous decrease in remanent polarization in accordance with the behavior of spontaneous polarization in the vicinity of the second order transition temperature, while a small variation in remanent polarization is observed for additional storage times. The remanent polarization decay at 27°C showed good linearity to the logarithmic retention time over a wide range of $10^{-3}-10^{5}$ s. The logarithmic time dependence of the decay in remanent polarization was attributed to the distribution of trap depth responsible for the space charge redistribution because of the irreversible change in resultant hysteresis loops.

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