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Interface-related decrease of the permittivity in $PbZr_xTi_{1-x}O_3$ thin films

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In ferroelectric thin films, a decrease of the permittivity is observed obeying a logarithmic time dependence. In the literature, a similar effect has been reported for ferroelectric single crystals and ceramics, which is referred to as ferroelectric aging, and different models have been proposed to explain this phenomenon. In this letter, ferroelectric aging of $PbZr_xTi_{1-x}O_3$ thin films is studied as a function of dopant types and concentrations as well as the temperature. The results clearly show that the traditional models for the aging mechanism of ferroelectric single crystals and ceramics are not applicable. Based on these results, a mechanism is proposed which explains the decrease of the dielectric constant in ferroelectric thin films by the growth of a thin surface layer with suppressed ferroelectric properties in the course of aging. © *2002 American Institute of Physics.*
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Ferroelectric thin films of complex oxides such as $PbZr_xTi_{1-x}O_3$ (PZT) and $SrBi_2Ta_2O_9$ (SBT) are promising candidates for the use in nonvolatile memory applications.[1,2] For their use in nonvolatile memory applications the large signal behavior, i.e., the $P-V$ hysteresis loop, is of great interest. Many publications in the literature have pointed out that the large signal behavior is subjected to aging, which manifests itself as a voltage shift ($V_{c,\mathrm{shift}}$) of the $P-V$ hysteresis loop[3] (Fig. 1). In this letter, the small signal behavior, i.e., the variation of the dielectric constant with time, is addressed. It will be shown that in ferroelectric thin films also the dielectric constant deteriorates with time. In the course of aging the dielectric constant slowly decreases, obeying a logarithmic time law (Fig. 1). This aging effect does not directly influence the memory operation since for this memory operation the large signal ($P-V$) behavior is exploited. However, the small signal aging effect might give additional information which might be useful to understand the large signal aging effect. A similar aging effect of the permittivity ε is observed in ferroelectric bulk material (single crystals and ceramics). In ferroelectric bulk materials this effect has been intensively studied since the 1950s and several physical mechanisms have been suggested to explain this effect (e.g., Ref. 4, and the citations therein). In the literature, generally two different mechanisms have been discussed to explain the decrease of the dielectric constant in ferroelectric bulk material, stress-related models and domain-wall-related models. In the following, the validity of these models for ferroelectric thin films will be studied in the light of the experimental results obtained in this study.

According to the piezoelectric equation ($D=\varepsilon_0 E_{\mathrm{appl}} + P + dT$, where D is the dielectric displacement, E_{appl} the applied electric field, P the polarization, d the piezoelectric constant, and T the stress) the measured dielectric constant $[\varepsilon_{\mathrm{eff}}=D/(\varepsilon_0 E_{\mathrm{appl}})]$ is coupled to the stress in ferroelectric materials. The stress in ferroelectric ceramics is believed to increase the dielectric constant due to the piezoelectric coupling if the stress is *in the direction* of the applied field. According to the stress-related models,[5,6] the stress in the material is reduced in the course of aging and, hence, leads to a decrease of the dielectric constant. In thin films, however, stress is expected to cause a decrease of the dielectric constant compared to the stress-free value since the stress is in the plane due to thermal expansion mismatch between substrate and thin film.[7] Hence, the stress in thin films is in contrast to ceramics perpendicular to the applied field and thus should lead to a reduction of the dielectric constant. Thus, a reduction of the stress in plane upon time would lead to an increase of ε. However, the opposite is observed. Therefore, the stress *relief* approach seems not to be appropriate to explain the small signal aging in thin films. However, in principle, a modification of the stress situation in thin films might be reasonable to explain the variation of the dielectric constant with time. To understand the reduction of ε an *increase* of the stress in plane would be necessary.

The domain-wall-related models in ferroelectric bulk ceramics[8–11] and in PZT thin films[12] interpret the decrease of ε with a reduction of the domain-wall contributions to the dielectric constant. The domain walls are stabilized in their position and, hence, less movable by the external field. Robels and Arlt explained the domain-wall stabilization by the orientation of defect dipoles similarly to the defect dipole alignment model for the evolution of the internal bias.[11] The oriented defect dipoles clamp the domain walls in their current position and, hence, lead to a reduction of the domain-wall mobility, which then results in a reduction of the domain-wall contributions to the dielectric constant. In this work, acceptor- and donor-doped PZT films were prepared in order to investigate the validity of the domain-wall stabilization due to the defect dipole alignment. Details about the sample preparation can be found elsewhere.[13] The aging of the dielectric constant has been measured unless otherwise stated at room temperature after quenching the thin film from

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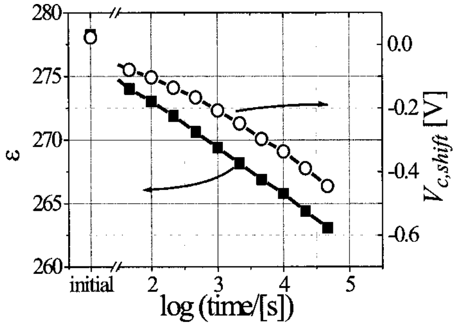

FIG. 1. Decrease of the dielectric constant (filled symbols) and the evolution of the voltage shift of the $P-V$ hysteresis loop (open symbols) under $+3$ V bias on the same PZT film (PZT 30:70, 200 nm, room temperature).

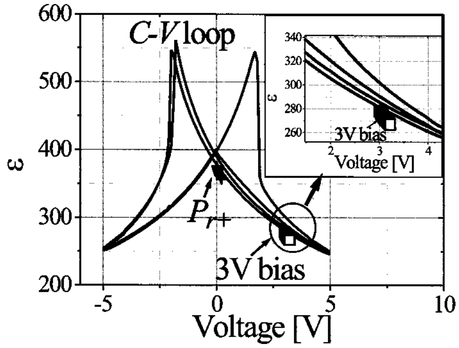

FIG. 3. $C-V$ measurement of a PZT film. The decrease of ε is plotted vs the voltage shift $V_{c,\mathrm{shift}}$ (both data taken from Fig. 1). [PZT 30:70, 200 nm, room temperature for P_{r+} and $P(3\text{ V})$ established.]

500 °C to room temperature using a standard HP4284 bridge. According to the defect chemistry model,[14,15] acceptor doping is expected to increase the concentration of alignable defect dipoles, whereas donor doping leads to the opposite. According to the defect dipole model, a different aging rate should be observed depending on the dopant type and concentration, which was experimentally confirmed for PZT ceramics.[11] However, aging of the dielectric constant in PZT films is essentially independent of the dopant additions (Fig. 2). For both the Fe-acceptor as well as Nb-donor doping, the decrease of the dielectric constant with time seems to be independent of the dopant additions. This independence of doping indicates that domain-wall stabilization caused by defect dipole alignment cannot explain the small signal aging in ferroelectric thin films. Additionally, in thin films the dielectric constant even ages when an additional bias is applied in the direction of the polarization (Fig. 1). However, the domain-wall density is significantly reduced upon applying a bias parallel to the polarization since ideally it should approach a single-domain state when the bias exceeds a specific saturation voltage. Figure 1 depicts the aging of ε when at the same time a bias of 3 V is applied. In that case the ferroelectric film is almost saturated, resulting in a very small number of domain walls present in the ferroelectric. But still, it can clearly be seen in Fig. 1 that even though the ferroelectric film is nearly in a single-domain state, the dielectric constant decreases. Based on the experimental results presented above, the domain-wall stabilization models seem to be unlikely to explain the decrease of the dielectric constant in ferroelectric thin films.

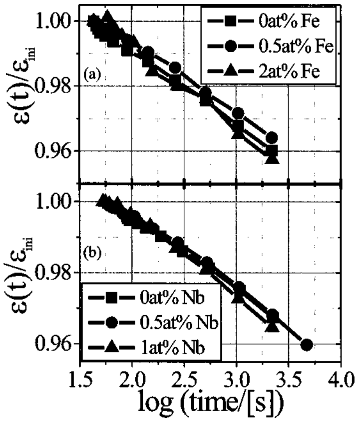

FIG. 2. Aging of the dielectric constant for differently Nb- and Fe-doped PZT films (PZT 30:70, 150 nm, room temperature).

In this work, experimental data referring to the decrease of ε have been presented for different established polarization states. For example, in Fig. 2 small signal aging is shown for P_{r+} established and no additional bias applied $[P(0\text{ V})=P_{r+}]$. On the other hand, Fig. 1 illustrates the decrease of ε for a polarization state established when an additional bias of 3 V is applied in the direction of the polarization $[P(3\text{ V})>P_{r+}]$. It is well known that for both polarization states, additionally to the decrease of ε, also an evolution of the voltage shift of the hysteresis loop ($V_{c,\mathrm{shift}}$) is observed (see Fig. 1). In Fig. 1 the evolution of the voltage shift is illustrated measured under identical conditions on the same film as the small signal aging shown in Fig. 1. Since the decrease of ε goes hand in hand with the evolution of the voltage shift $V_{c,\mathrm{shift}}$ these two effects might be correlated.

It is known that the dielectric constant in ferroelectrics is itself a function of the applied bias. Hence, the decrease of ε could also be caused by the evolution of the internal bias. In Fig. 3 a $C-V$ measurement is shown for a PZT thin film. It can clearly be seen that upon increasing the bias ε decreases. In the course of aging of a poled ferroelectric capacitor the dielectric constant decreases while at the same time an internal bias is evolving. Therefore, the evolution of the internal bias could explain, via the bias dependence of ε, the decrease of the dielectric constant. To investigate this assumption, the aging of the dielectric constant as well as the evolution of the voltage shift have been measured on the same ferroelectric capacitor while identical conditions have been established [condition (i): poled to P_{r+} and (ii): $+3$ V bias, see Fig. 1]. In order to investigate whether the evolution of the voltage shift can explain the decrease of the dielectric constant the measured values of $\varepsilon(t_i)$ have been plotted versus the values of the voltage shift $V_{c,\mathrm{shift}}(t_i)$ (with reversed sign) measured at the same time, t_i $[\varepsilon(t_i)$ vs $-V_{c,\mathrm{shift}}(t_i)$, $i=1, 2, 3,\ldots]$. Note that the sign of $V_{c,\mathrm{shift}}(t_i)$ has to be reversed in this plot since a positive internal bias leads to a negative voltage shift of the hysteresis loop.

The $\varepsilon(t_i)$ vs $-V_{c,\mathrm{shift}}(t_i)$ plot is shown in Fig. 3 for both conditions. In the enlargement in Fig. 3 it can be seen that the internal bias can indeed explain a part of the decrease of ε. However, the correlation between the two measured aging effects seems to be significantly more pronounced than anticipated from the $C-V$ measurement. Therefore, it is con-

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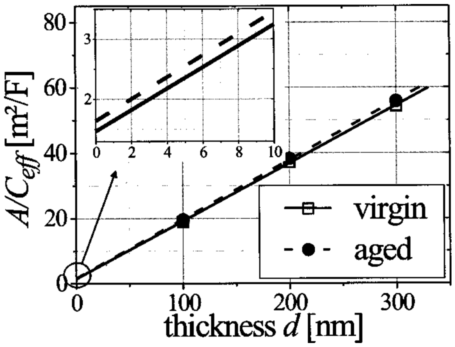

FIG. 4. Reciprocal capacitance vs film thickness d in the virgin and in the aged state (PZT 30:70, room temperature).

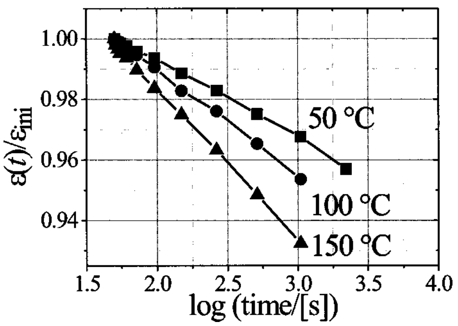

FIG. 5. Aging of the dielectric constant at different temperatures. The decrease of ε is more pronounced for higher temperatures (PZT 30:70, 200 nm).

cluded that the evolution of the internal bias alone cannot explain the decrease of the dielectric constant, it rather contributes a minor part to the decrease of ε. Therefore, an additional mechanism must be involved to explain the small signal aging in ferroelectric thin films consistently.

In ferroelectric thin films many indications have been reported about the existence of a thin surface layer between the electrodes and the ferroelectric film.[16–19] Hence, the dielectric constant, which is usually evaluated, is not the dielectric constant of the ferroelectric layer alone. It rather describes an effective dielectric constant resulting from two capacitors in series, the interface capacitance C_{if} in series with the ferroelectric capacitance C_{fe}. Thus, the measured, effective dielectric constant $\varepsilon_{\mathrm{eff}}$ obeys

$$\frac{d}{\varepsilon_{\mathrm{eff}}}=\frac{d-\delta}{\varepsilon_{\mathrm{fe}}}+\frac{\delta}{\varepsilon_{\mathrm{if}}}, \tag{1}$$

where $\varepsilon_{\mathrm{fe}}$ and $\varepsilon_{\mathrm{if}}$ are the dielectric constants of the ferroelectric and the interfacial layer, respectively. The total film thickness is d and the extension of the surface layer is δ.

Up to now, the interfacial capacitance has been neglected in the interpretation of the small signal aging effect in thin films. However, a modification of the interface capacitance in the course of aging seems to be the dominating reason for the decrease of the effective dielectric constant $\varepsilon_{\mathrm{eff}}$. If the interfacial capacitance C_{if} decreases in the course of aging, possibly due to an increase of the extension δ of the surface layer or due to a decrease of the permittivity $\varepsilon_{\mathrm{if}}$ it would result in a decrease of the effective $\varepsilon_{\mathrm{eff}}$.

Indeed, determining the interfacial capacitance of aged capacitors of a PZT thickness series indicates a decrease of the C_{if} in the course of aging (Fig. 4). In Fig. 4 the virgin interface capacitance has been determined at room temperature right after a thermal de-aging treatment (heating above T_c), revealing a value of $C_{\mathrm{if}}=680\ \mathrm{fF}/\mu\mathrm{m}^2$. In the aged state (after 1000 s aging at room temperature) the interfacial capacitance C_{if} has been decreased by approximately 10% to $609\ \mathrm{fF}/\mu\mathrm{m}^2$. Hence, in ferroelectric thin films the decrease of the dielectric constant upon time might be caused by a slight increase of the extension of the interfacial layer after the film is cooled below the transition temperature. This effect could explain the observed decrease of C_{if} in the course of aging as well as the decrease of $\varepsilon_{\mathrm{eff}}$ according to Eq. (1). Bratkovsky and Levanyuk recently proposed a similar effect to be the main origin of fatigue in ferroelectric thin films.[19] They attribute the decrease of the switchable polarization observed during fatigue to the growth of a passive layer with damaged ferroelectric properties at the surface similar to the surface layer discussed in this work.

Investigating the decrease of the dielectric constant at different temperatures, one observes that the decrease of ε is more pronounced at higher temperatures (Fig. 5). This temperature dependence displayed in Fig. 5 indicates that the growth of the passive layer is more pronounced at higher temperatures.

To summarize, the experimental data presented in this letter suggest that the small signal aging in ferroelectric thin films might be of a different origin compared to ferroelectric bulk materials. Similarly to the evolution of the voltage shift of the $P-V$ hysteresis loop, a thin surface layer might be responsible for the significant part to the decrease of ε. There is experimental evidence that the interfacial capacitance is being decreased in the course of aging, which might be explained by a temperature-activated increase of the extension of the surface layer. With the diminishment of the interfacial capacitance the decrease of the dielectric constant can be understood.

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