Electrical Characteristics of Ferroelectric PZT Thin Films for DRAM Applications

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Abstract—Ferroelectric lead zirconate titanate (PZT) films with as much as 2.5 times the storage capacity of the best-reported silicon oxide/nitride/oxide (ONO) stacked dielectrics have been fabricated. A 2000-Å PbZr0.52Ti0.48O3 film with an effective SiO2 thickness of 10 Å is demonstrated. Because of the extremely high dielectric constant (εr ≥ 1000), even larger storage capacities can be obtained by scaling the ferroelectric film thickness whereas the thickness of ONO films is limited by direct tunneling through the film. Electrical conduction in the PZT films studied here is ohmic at electric fields below 250 kV/cm and follows an exponential field dependence at higher fields. This type of behavior is shown to be consistent with a simple model for electronic hopping through the film. Leakage current as low as 9 × 10−14 A/cm² at 2.5 V for a 4000-Å film is obtained with the addition of lanthanum and iron to compensate for lead and oxygen vacancies in the film. Further improvement in both leakage current and time-dependent dielectric breakdown characteristics are necessary to ensure reliable DRAM operation.

I. INTRODUCTION

A S DYNAMIC random access memory (DRAM) density continues to increase, the required storage capacitance per unit area poses a serious challenge to trench and stacked-capacitor cell technologies based on SiO2/Si1-xNₓ. In order to meet the charge storage requirements, high dielectric constant materials such as tantalum pentoxide [1]-[5] (εr ~ 20-25) and yttrium oxide [6] (εr ~ 12–16) have been proposed as alternatives to silicon dioxide and oxide/nitride/oxide (ONO) stacked structures. While the relative permittivity of these materials is three to six times that of SiO2, their net gain in charge storage density is only a factor of two at best because of the highest leakage current and lower dielectric breakdown strength. Recently, an effective area increase of as much as 2.5 has been reported by depositing ONO films on rugged polysilicon [7]. The equivalent SiO2 thickness for such a film has been demonstrated to be as low as 25 Å. ONO on rugged polysilicon provides as much gain in storage capacity as can be obtained from state-of-the-art tantalum oxide films. However, neither ONO nor tantalum oxide can be scaled any further since the thickness of the film is already limited by direct tunneling. The charge storage capacity can be increased further by using higher dielectric constant materials such as ferroelectric lead zirconate titanate PbZr1-xTixO3 (εr ≥ 1000). The purpose of this study is to evaluate PZT thin films as a potentially attractive candidate for the storage capacitor dielectric in future DRAM technologies. The polarization, electrical conduction, and time-dependent dielectric breakdown characteristics of PZT are presented and compared with other proposed dielectric structures.

II. POLARIZATION CHARACTERISTICS

Polycrystalline PZT films (x = 0.5) were prepared by sol-gel deposition [8] and subsequent annealing at 650°C in an O2 ambient. Platinum was used for both top and bottom electrodes. The polarization characteristics of these films are determined from large-signal quasi-static capacitance–voltage (voltage ramp rate = 1 V/s) and high-frequency small-signal capacitance–voltage measurements (1-MHz, 10-mV rms signal). All characteristics are obtained at room temperature. The resultant films exhibit ferroelectric behavior with a coercive field of 25 kV/cm and a remanent polarization of 150 μC/μm² (15 μC/cm²) at 5 V for a 4000-Å film as shown in Fig. 1(a). It is clearly apparent from the quasi-static C-V curves (Fig. 1(b)), which are determined directly from the displacement current as the ferroelectric film is switched under a linear voltage ramp at 1 V/s, that there is no distinct switching threshold for domain switching. Domain reversal occurs over a wide range of applied fields. In this sense, the coercive field as determined from the intercept of the hysteresis loop offers little insight into the actual switching process and is of questionable value as a figure of merit in comparing different films or for monitoring the behavior of a specific film.

Nonvolatile ferroelectric memory cells experience fatigue, a gradual loss of detectable polarization during continuous polarization cycling, and are vulnerable to retention failure caused by dielectric aging [9]. In order to avoid fatigue, a ferroelectric DRAM [10] must be oper-
ated in such a way that the polarization of the ferroelectric film is not reversed, i.e., the ferroelectric capacitor is always biased in one polarity\(^1\) (see Fig. 2). In addition, long-term data retention is no longer required for DRAM operation. In this case, the available polarization can be better determined from unipolar small-signal capacitance–voltage measurements rather than hysteresis curves such as those shown in Fig. 1.

The polarization obtained from the small-signal capacitance consists primarily of ionic and electronic polarizability, i.e., the elastic contribution to polarizability rather than the inelastic component attributed to ferroelectric domain switching. The polarizability due to domain-wall displacement is believed to be small since virtually no small-signal frequency dispersion is observed in these films between 1 kHz and 1 MHz [11]. However, the polarizability of domain-wall ions may still represent a significant contribution to the total small-signal capacitance [12]. Furthermore, the small hysteresis loop (solid lines in Fig. 3(a)) indicates that the effect of changes in the ferroelectric domain structure on the small-signal capacitance is negligible. This hysteresis is expected, asuming that the polarizability is a function of the orientation of the domains and that there is a change in the population of 90° (i.e., a-axis-oriented with a axis normal to the applied field) domains during the switching process. This hypothesis is not unlikely since it is known that in single-crystal BaTiO\(_3\), the dielectric constant of an

\(^1\)In contrast, in conventional DRAM's, the storage capacitor can be biased in either polarity depending on the logic state. This method of operation reduces the maximum field across the capacitor dielectric and improves the reliability without any loss in charge storage density. Biasing a ferroelectric capacitor in only one polarity is not as detrimental to the reliability as in a conventional DRAM since the ferroelectric film thickness is much greater than that of a conventional capacitor dielectric and the corresponding electric field is much lower for the ferroelectric film.
Fig. 4. The large-signal capacitance degrades during constant-voltage stress although the degradation mechanism shows little field enhancement as the stress field increases. Similar degradation is also observed during pulse dc stress. The small-signal capacitance shows virtually no degradation and can therefore be used as the lower limit for the charge storage capacity available during DRAM operation. For all stress conditions, the polarization of this 4000-Å film was determined from capacitance-voltage characteristics measured between 0 and 5 V.

Fig. 5. The small-signal polarizability scales linearly with thickness. For a 2.5-V voltage swing, the 2000-Å PZT film has the same charge storage capacity as a 10-Å SiO₂ film.

The polarization calculated from the quasi-static (large-signal) capacitance has an additional contribution from the switching of nonremanent domains as demonstrated by the hysteresis in the capacitance characteristics in Fig. 3(b). A gradual loss of this contribution is observed after both dc bias and unipolar cycling [14] as shown in Fig. 4. A realistic estimate of the polarization available for DRAM operation must take this degradation into account. Even if this additional contribution is completely lost, the small-signal capacitance, which exhibits relatively little degradation, is still available and is used to determine the lower limit for polarization available for DRAM applications.

This limit demonstrates the scaling potential of ferroelectric memory: For DRAM operation, the 4000-Å film is in the worst case equivalent to a 16-Å silicon dioxide film subjected to a 2.5-V voltage swing (55 fC/μm²). The 2000-Å film has a worst case (i.e., small-signal capacitance limit) polarization of 90 fC/μm² equivalent to a 10-Å silicon dioxide film with a 2.5-V voltage swing (see Fig. 5). A DRAM cell typically requires 100 fC of stored charge (equivalent to a 1.1-μm² 2000-Å thick PZT capacitor) to prevent soft errors. Typical charge storage capacities for conventional SiO₂/Si₃N₄/SiO₂ (ONO) dielectrics are equivalent to a 50-Å SiO₂ film [15]. The highest charge storage capacities reported for ONO on a rugged polysilicon electrode [7] and Ta₂O₅ [15] dielectrics correspond to a 25-Å SiO₂ film. In contrast, equivalent SiO₂ thickness of less than 5 Å have already been obtained for 425-Å sol-gel PZT thin films [16]. Also note that in the case of ONO and Ta₂O₅, the thickness of the dielectric film has reached the fundamental limit set by direct tunneling through the film. However, at the present time PZT film scaling is tracking the progress in ferroelectric thin-film deposition technology.

III. ELECTRICAL CONDUCTION

The leakage current characteristics exhibit ohmic behavior at low fields and exponential behavior at moderately high fields as shown in Fig. 6 [17]. An expression of the form

\[ J \propto \sinh BE \]  

where \( J \) is the current density, \( E \) is the applied electric field, and \( B \) is a constant, provides a good fit to the data. A field dependence of this type has been derived for ionic or electronic hopping assuming single-particle transport [18]. In this case, \( J \) is expressed as

\[ J = A \exp \left( \frac{-E_o}{kT} \right) \sinh \left( \frac{BE}{kT} \right) \]  

where \( A \) is a constant (equal to 10 A/cm² for the data in Fig. 6) and \( E_o \) (equal to 0.35 eV) is the activation energy. The coefficient \( B \) is proportional to the particle charge \( Ze \), and the hopping distance \( \lambda : B = Ze\lambda / 2 \). Assuming a singly-charged species (\( Z = 1 \)) and \( B = 0.057 \: eV \: cm / MV \) (from Fig. 6(b)), the hopping distance is determined to be approximately 11 Å. Since the total charge flowing through the ferroelectric film before dielectric breakdown \( Q_{bd} \) is typically much greater than the number of ions available in the film (i.e., \( Q_{bd} >> 1 \: mC/cm² \)), the conduction must be dominated by electronic rather than ionic hopping. Also note that in this simple model, the effect of grain boundaries has been neglected and needs to be included to model the conduction properties more accurately [19].

In the low-field regime where DRAM operation is expected, (2) reduces to the relation [20]

\[ J = A \frac{BE}{kT} \exp \left( \frac{-E_o}{kT} \right) \]  

The low-field resistivity and activation energy determined from Fig. 6(a) are \( 3.5 \times 10^{10} \Omega \: cm \) and 0.33 eV in agreement with the \( A, B, \) and \( E_o \) determined using (2) and Fig. 6(b). Because of this low activation energy, p-n junction leakage dominates the DRAM refresh time at high temperatures (see Fig. 7).

In order to compare PZT with other proposed DRAM dielectrics, the leakage current density \( J \) is plotted as a function of the equivalent silicon dioxide field \( E_{eff} \) needed to obtain the same capacitor charge storage density \( Q = 3.96e_0E_{eff} \) (see Fig. 8). \( Q/J \) is the capacitor discharge time constant. Because of its extremely large polarizability, at
high effective fields, PZT exhibits superior leakage characteristics compared to other proposed dielectric structures. However, the magnitude of the leakage current is too large to meet the refresh times required for high-density DRAM's. Similar to bulk PZT ceramics, adding the proper impurities suppresses the conductivity arising from oxygen and lead vacancies and can further increase the resistivity of PZT films [23]. For example, the resistivity of a lanthanum-iron-modified PbZr$_x$Ti$_{1-x}$O$_3$ film is more than an order of magnitude greater than that of an unmodified film: the leakage current at 2.5 V drops from $10^{-6}$ to $9 \times 10^{-8}$ A/cm$^2$. This improvement meets the refresh time specification illustrated in Fig. 8. Since the data shown are typical, not worst case, characteristics, further optimization is needed to reduce the leakage current to acceptable levels.

Note that even though the effective fields shown in Fig. 8 are extremely high, the actual operating fields for PZT thin films are in the desired range. For example, 2.5 V on a 4000-Å film corresponds to a field of 62.5 kV/cm but an effective SiO$_2$ field of 21 MV/cm due to the high dielectric constant of PZT ($\varepsilon_r \approx 1000$). This is not true for lower dielectric constant materials. Even SrTiO$_3$, which has the same perovskite structure as PZT but is paraelectric at room temperature, does not have a sufficiently high dielectric constant ($\varepsilon_r \approx 300$) and breakdown strength to provide a large enough storage capacity at typical operating voltages [24], [25]. The high breakdown strength and low leakage current of the SrTiO$_3$ film in Fig. 8 was obtained with the formation of a thin SiO$_2$ layer at the SrTiO$_3$/Si interface [24] but with a severe penalty in charge storage capacity: 2.5 V for this 1800-Å SrTiO$_3$ film corresponds to an effective SiO$_2$ field of only 3.4 MV/cm. In order to obtain a 21-MV/cm effective field (corresponding to 72 IC/µm$^2$), a 15-V DRAM operating voltage is required.

IV. TIME-DEPENDENT DIELECTRIC BREAKDOWN

The time-dependent dielectric breakdown (TDDB) behavior was studied to determine the reliability of PZT films for DRAM applications. At room temperature, the current density during constant-voltage stress decreases by several orders of magnitude before destructive breakdown (Fig. 9(a)). This behavior appears to follow a power-law relationship. However, at higher temperatures, saturation and turn-around are observed before breakdown (Fig. 9(b)). The decrease in current during constant-voltage stress is attributed to electronic charge trapping in the film. Note that in the case of a ferroelectric film, the high electric fields which exist at ferroelectric
Fig. 9. (a) The current density during room-temperature constant-voltage stress is a power-law function of the stress time. (b) At higher temperatures, saturation and turn-around are observed.

domain walls and at the metal–ferroelectric film interface are expected to facilitate electronic charge motion into and out of traps in the ferroelectric film. In fact, if a constant-voltage stress is interrupted, significant detrapping occurs even at room temperature (Fig. 10). This behavior is observed to a lesser extent in PZT films fabricated in a similar manner but with a composition chosen to be in the paraelectric rather than ferroelectric phase.

The time to breakdown $t_{BD}$ is plotted as a function of the current density in Fig. 11; approximate power-law relationships are obtained. The lifetime is proportional to $J^{-2.8}$ at 150°C and $J^{-2.6}$ at room temperature. The average activation energy between room temperature and 150°C is approximately 0.6 eV and increases at low fields. Lifetime projections are obtained by plotting the time to breakdown as a function of the stress voltage (Fig. 12). Lifetime extrapolation based on an exponential field dependence yields lifetimes shorter than a month at 3 V and 150°C. The electric field acceleration factor (defined as the slope of log $t_{BD}$ versus applied field) is approximately 4 decades per 1 MV/cm. This exploration scheme is justified assuming that the lifetime is a function of the total number of carriers passing through the film since according to (2) the conduction follows an exponential field dependence. However, if the breakdown mechanism is related to the energy of charge carriers such as in an impact ionization process, lifetime extrapolation should be permitted according to an inverse-field law as shown in Fig. 12. In this case, the expected lifetime may be as high as 100 years at 150°C and 3 V. In either case, the extrapolated lifetimes are unacceptably low and need to be improved significantly especially considering that defect-induced breakdown is not considered here and will reduce the lifetime even further. Therefore, even though for the same charge storage capacity, PZT films have much longer extrapolated lifetimes than other DRAM dielectrics [21], [26]–[28] for typical power supply voltages TDBD appears to be the single most limiting factor for the use of PZT films in DRAM's.

V. SUMMARY AND CONCLUSIONS

The viability of ferroelectric PZT films for DRAM applications is examined. 4000-Å PZT films with an effective SiO$_2$ thickness of 16 Å are prepared by sol-gel deposition. The films exhibit ohmic behavior at low fields (with a resistivity of $3.5 \times 10^{10}$ Ω · cm and an activation energy of 0.33 eV) and exponential field dependence at high fields. Electrical conduction is primarily attributed
to electronic hopping. At the same charge storage capacity, the leakage and time-dependent dielectric breakdown characteristics are superior to other dielectric systems. However, lifetime extrapolation to the desired charge storage capacity equivalent to 10 Å of SiO₂ with 2.5-V operation shows that time-dependent dielectric breakdown may be a very serious limitation for DRAM applications. Optimization of material properties of PZT films, especially the TDDB lifetime, is necessary for reliable DRAM operation.

REFERENCES


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William H. Shepherd, photograph and biography not available at the time of publication.