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Loss mechanisms in fine-grained ferroelectric ceramic thin films for ULSI memories (DRAMs)

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Abstract

Ferroelectric thin films can now be prepared by a variety of techniques to have dielectric constants of 800, loss tangents of 0.01, and leakage currents as small as 1 nA cm^{-2}, which means that a capacitance of 120 fF μm^{-2} can be achieved at 60 nm thickness (30 fF $cell^{-1}$ in a 0.25 μm^2 256 Mbit DRAM). It is significant that these properties are maintained up to 2 or 3 GHz, permitting operation of memories at very high clock rates (greater than 100 MHz). High-frequency roll-off of dielectric constants and loss tangents for barium strontium titanate fine-grained ceramics are compared with those for lead zirconate–titanate and discussed in terms of grain size and processing. The low loss tangents for very fine-grained material (40–100 nm) are surprising in view of earlier work on strontium titanate. Our data support the Neumann–Hofmann theory [*Ferroelectrics, 134* (1992) 201] of surface-layer dominated loss.

1. Introduction

Attenuation and loss mechanisms are important practical problems in the design and optimization of ferroelectric thin-film devices [1]. Dielectric loss tangents increase from 0.001–0.01 at 1 MHz to *ca.* 0.2 at 1–5 GHz, preventing the use of many films in microwave devices, such as phased array radar systems [2]. For the high internal clock rates ($\geq$100 MHz) envisioned for the next generation of ULSI (ultra large scale integrated) DRAMs (dynamic random access memories), this frequency-dependent loss is also a serious handicap.

Loss mechanisms, both ultrasonic and dielectric, are poorly understood in ferroelectric thin films such as lead zirconate–titanate (PZT) or barium strontium titanate (BST). Perhaps the best experimental papers on the subject are in ref. 3, where for pure strontium titanate the dependence of dielectric loss upon grain size, temperature and impurity concentration was carefully determined. From such studies, the conventional wisdom has evolved that loss is principally determined by grain size, with very fine-grained ceramics being generally more lossy than large crystallites. The tan δ values in single-crystal strontium titanate are *ca.* 10^{-3} at room temperature and can be 10^{-4} or less at cryogenic temperatures. Electrical "Q" values of $\geq$20 000 are readily achievable in many ferroelectric ceramics at microwave frequencies [4]. Theoretical reviews of microscopic loss mechanisms were published recently by Gurevich and Tagentsev [4], and a qualitatively different surface-layer loss model by Neumann and Hofmann [4]. For barium strontium titanate, Varadan *et al.* [2] report δ as low as 0.006 at 17 GHz. It is known from earlier work [2] by Sharpe and Brockus and by Powles and Jackson that *ca.* 1% Fe or Mn reduces dielectric loss. Sol-gel spin-on deposition generally yields less lossy material than does sputtering. The microscopic mechanisms behind these two empirical observations are not well understood.

Unfortunately, electrical measurements are complicated by the electrode used and, in particular, the electrode–dielectric interface. The role of space charge at such interfaces and its effect on frequency-dependent loss mechanisms have been studied for 30 years [5–8]. Separate from this interface problem is the role of space charge accumulation at grain boundaries [9, 10] and consequent aging and fatigue mechanism; continuous defect entrapment occurs, particularly of oxygen vacancies [11–13], resulting in an activation energy lowering with time for [7] Frenkel–Poole bound-to-free electron transitions (detrapping). However, the microstructures of grains are qualitatively different in PZT (columnar, perpendicular to electrodes) and BST (roughly spherical polyhedral). Therefore, no generic description of space-charge related loss mechanisms is possible that encompasses all materials of interest for DRAM applications. Microdomains of ferroelectric

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phases within a paraelectric matrix may be important in some cases [14–17], as are 90°-domain wall mobilities and related stresses [18–20].

It would be desirable to separate clearly electrode (or space charge) mechanisms from other microscopic loss processes in these ferroelectric thin films. Internal friction and ultrasonic techniques would be welcome and highly complementary to existing data.

2. Experimental details

Ferroelectric films for DRAMs can be produced via a variety of deposition techniques: sputtering, laser ablation, sol-gel spin-on are all popular research methods for PZT. BST is superior to PZT with respect to leakage current and high-frequency loss (tan δ is typically 0.015 to 0.017) and is best deposited by metal-organic deposition or liquid-source chemical vapor deposition [21], although good work has also been done with sputtered BST [22].

When we compare our tan δ *vs.* frequency data for 40–100 nm diameter BST films with earlier data on PZT and strontium titanate, it is clear that grain size is not the dominant parameter. Domain structure, intergrain amorphous regions, and other microstructural details are apparently more important and probably depend subtly upon processing parameters. Table 1 shows loss tangents at 1 kHz for barium strontium titanate with different electrodes, oxygen ambient during anneal, or annealing temperature. The leakage currents for these specimens varied from 20 to 800 nA cm^{-2} and were uncorrelated with tan δ values. We interpret these data as showing that the dominant dielectric losses in our materials are not intrinsic. Annealing temperature and ambient gas are the most critical parameters. Doping is also very important; additions of 1% Fe, Mn, or Y reduce losses. Domain wall motion, piezoelectric resonances and intrinsic phonon losses are apparently unimportant. Most important is thickness; the very low loss BST in Table 1 from ref. 2 were samples 1000 μm thick; they had tan δ values as low as 0.002. BST specimens 0.25 μm thick usually have losses of about 0.015–0.017, roughly an order of magnitude larger. This change depends upon thickness very much as in the TGS (triglycine sulfate) data of Neumann and Hofmann, who find tan $\delta=0.001$ at thicknesses of 10 μm or greater and 0.10 for the thinnest films. The theoretical dependence upon film thickness d predicted by these authors is:

$$\tan\delta(d)=[\tan\delta_s+\tan\delta_b+y]/[1+y] \quad (1)$$

where

$$y=[\epsilon_s d_b(1+\tan^2\delta_s)]/[\epsilon_b d_s(1+\tan^2\delta_b)] \quad (2)$$

the subscripts s and b designate surface and bulk (of the film); and

$$d_s+d_b=d \text{ (total film thickness)} \quad (3)$$

Fitting the parameters in eqn. (1) requires sufficient data to extract six quantities: the thickness, dielectric constant and loss tangent of the surface layers and the interior (bulk) of the film. At present, insufficient data exist for BST to evaluate unambiguously these parameters and thereby test the theory. For TGS, Neumann and Hofmann find surface layer thickness of 20 nm, a surface layer dielectric constant of about 4, and a surface layer loss tangent of about 0.1. Similar numerical values fit the existing BST data, as shown in Fig. 1, but more experimental data are required to test the theoretical prediction in eqn. (1) above.

The exact frequency of the dielectric roll-off is an equally important parameter in modelling these phenomena. We can adjust it experimentally [22–24] in

TABLE 1. Dielectric losses in barium strontium titanate thin films: $Ba_{1-x}Sr_xTiO_3$

Ba-ratio x	Electrode	Anneal temperature (°C)	Ambient	tan δ (1 kHz)
0.70	Pt/Ti	650	O_2	0.04
0.70	Pt/Ti	650	O_3	0.06
0.70	Pt/Cr	650	O_2	0.07
0.70	Au/Cr	650	O_3	leaky
0.70	W	650	O_2	leaky
0.70	Au/Cr	650	O_2	0.05
0.70	Pt/Ti	600	O_2	0.46
0.00	Pt/Ti	600	O_2	0.03
0.00	Pt/Ti	650	O_2	0.015
0.50[a]	none	1400	–	0.05
		(sintered)	–	0.002
0.24[a]	none	1400		

[a]Varadan *et al.* [2]; values of tan $\delta=0.005$ have also been reported by F.J. Elmer and S.J. Jang, *Army Science Conference Proceedings* (1988) p. 283, and by C.B. Sharpe and C.G. Brockus, *University of Michigan Research Institute report 2732-4-4* (1959).

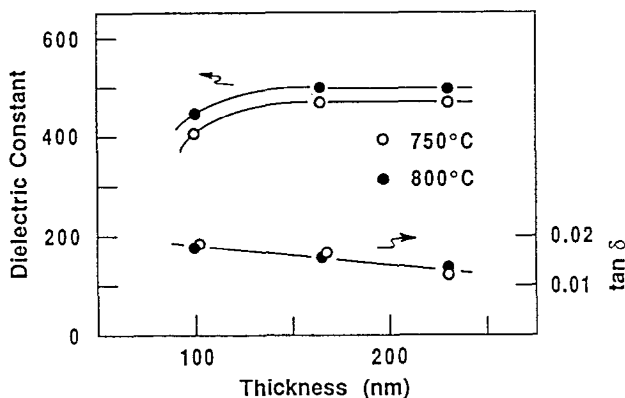

Fig. 1. Dielectric constant and loss tangent *vs.* film thickness for barium strontium titanate (70% Ba) sol-gel films at two different annealing temperatures.

our BST films from *ca.* 100 MHz to *ca.* 5 GHz. It is not limited by extrinsic impurity concentrations (which are nominally identical in most of our specimens), but apparently by parameters such as oxygen vacancy concentration, barrier heights at grain boundaries, and other microstructural details. The inference from Table 1 is that low temperature (600 °C) anneals worsen losses as does annealing in ozone (rather than oxygen). In each case this is apt to affect the surface layer of the film.

3. Inferences from switching times

Recently Hase and Shiosaki [25] have found that small-area ferroelectric thin-film capacitors have faster switching times than do large-area devices. This is contrary to the predictions of most nucleation models [26] but has very recently been reconciled by Ishibashi [26]. In this section, we briefly make some numerical estimates relating to this observation and further relate the inferences therefrom to the question of why our very fine-grained films have extremely low dielectric losses.

From our earlier study [11], we extracted a domain nucleation rate for 40 nm ferroelectric oxide films of $J=1.5\times10^{22}$ s^{-1} m^{-2}, and an average domain wall speed of $v=440$ m s^{-1}. We use these numbers below in an estimate of parameters for barium strontium titanate films in the ferroelectric phase (Ba-rich) and the superparaelectric phase (in which ferroelectricity can be induced by applied electric fields).

Ishibashi's model has two cases: Case II (switching kinetics dominated by pre-existing nuclei), and Case I (nucleation only after electric field is applied and at a constant rate). He predicts size effects become important in case I only if the inequality

$$8JL^3/v<1 \quad (4)$$

holds, where L is the size of the film. However, we note here a point not considered before [26]: if domain walls are limited by grain boundaries, L is the radius of a grain (20–50 nm in our films) and the switching time will be quite independent of capacitor cell size (*ca.* 100 μm on each side); whereas if the domain walls pass smoothly through the grain boundaries during switching, L is the length of the capacitor cell. Using our values of J and v above, we find that switching speeds will decrease (from eqn. (1)) noticeably for L somewhat less than a micron. This is in reasonable agreement with experiment. Note that at present most test devices are 100 μm on a side, whereas ULSI DRAM cells will be *ca.* 1 μm.

Case II has a different inequality of importance:

$$4NL^2<1 \quad (5)$$

where N is the number of latent nuclei. This is expected to be the dominant criterion in most real oxide films [26]. Our earlier estimate for that was [11] $4NL^2\sim3$, if L is taken as the grain radius. Therefore, the inequality in eqn. (5) is perhaps never satisfied in our films. Making L equal the capacitor cell size (larger than one grain) only worsens the ability to satisfy eqn. (5), independent of whether domain walls traverse grain boundaries or not.

The suggested inference is that the size effects on switching speed observed by Hase and Shiosaki make sense within Ishibashi's nucleation model only if the continuous nucleation description is invoked (Case I), and then only if it is further assumed that domain walls move through grain boundaries in BST. However, this sequence of assumptions helps explain the mystery of why fine-grained ceramic BST has such low losses. There is negligible pinning of domain walls (we assume that the BST is in the ferroelectric phase or at a minimum, that it has microphases that are ferroelectric) by grain boundaries, and hence dielectric losses approximate that of single crystals.

4. Conclusions

Ultra fine-grained (40 nm) ceramic thin films have remarkably low loss tangents (0.015) which remain low into the gigahertz regime. This permits their use for bypass capacitors in microwave devices [2] and in computer memories with high clock rates; Beall *et al.* [2] report 14 GHz voltage-tunable microstrip resonators with $SrTiO_3$ sputtered films on $YBa_2Cu_3O_{7-x}$ with Q of 670 (limited by external loading) at 14 GHz. However, it is contrary to the conventional wisdom regarding grain size and lacks a quantitative understanding. Our inference, based upon Shiosaki's switching time size

dependence [25] and Ishibashi's nucleation model [26], is that domain walls pass through grain boundaries in these very fine-grained devices, until defect (oxygen-vacancy) entrapment prohibits that [27]. Existing dielectric loss data would benefit from detailed internal friction and ultrasonic attenuation studies. All of our data support the surface-layer loss mechanisms proposed by Neumann and Hofmann as dominant in BST ceramic thin films.

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