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PREPARATION AND PROPERTIES OF SOL-GEL DERIVED PZT THIN FILMS FOR DECOUPLING CAPACITOR APPLICATIONS

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Abstract The use of ceramic thin films as decoupling capacitors offers the possibility of capacitor integration within the integrated circuit (IC) package, and potentially, directly onto the IC itself. Since these configurations minimize series inductance, higher operational speeds are possible. In the present study we have investigated the dielectric and leakage characteristics of sol-gel PZT films. For compositions near the morphotropic phase boundary, dielectric constants of 1000, and loss tangents of about 0.02, were observed. The current - voltage behavior of the capacitors was characterized by a non-linear response, and significant asymmetry in both the leakage and breakdown characteristics as a function of bias sign was observed. Breakdown fields for PZT 53/47 thin films were typically ~ 800 kV/cm at 25°C.

We have also studied the effects of La and Nb dopant additions and alternate firing strategies on film leakage characteristics. Donor doping at 2 - 5 mol % lowered leakage currents by a factor of 10^3 . For films prepared by a multilayering approach, firing each layer to crystallization resulted in leakage currents that were a factor of 10^2 lower than films prepared by the standard process.

INTRODUCTION

Lead zirconate titanate ($\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$; PZT) thin films are currently being investigated for a variety of electronic applications.¹⁻⁵ The applications which have received the most attention, DRAMs¹ and nonvolatile memories,² are also the applications which, potentially, place the most stringent demands on material properties. For example, in the development of PZT thin films for nonvolatile memory devices, considerable attention has been given to minimizing hysteresis loop fatigue, which accompanies polarization switching in these devices. For the successful development of ceramic thin films for use in these applications, fatigue, aging, and imprinting problems must all be solved. Interestingly, given these difficulties, it is surprising that the comparatively simpler use of PZT thin films as decoupling capacitors has received little attention in the published literature.⁶

Decoupling capacitors are so named because they serve to decouple the IC from the power supply; i.e., they reside close to the IC and serve as a local source, or sink, of charge.⁷ Currently, chip capacitors are most frequently used in this application. However, the ability to fabricate ceramic thin films may allow for a higher level of

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integration and packaging density than is presently possible with ceramic chip capacitors. For example, it should be feasible to use photolithography to integrate thin-film decoupling capacitors directly onto the IC. This approach can minimize inductance, leading to higher operational speeds.

For decoupling capacitor applications, the primary material requirements are high dielectric constant at high frequency, low dielectric loss, and high resistivity. Because of the known properties of bulk PZT ceramics,⁸⁻¹¹ PZT thin films would appear to be ideal candidates for development as thin-film decoupling capacitors. Furthermore, since decoupling capacitors operate in a nonswitching mode, material performance issues, such as fatigue and imprinting, are not important considerations.

In the present paper, we report on our studies of undoped and donor-doped (La and Nb) PZT thin films fabricated by sol-gel processing. We discuss properties of the films that are pertinent to the development of these materials as thin-film decoupling capacitors. Results are presented for the dielectric properties of the films, general characteristics of dielectric breakdown, and effects of La and Nb additions on leakage current and thin-film resistivity.

EXPERIMENTAL

Doped and undoped PZT thin films were fabricated by a solution deposition process that we have discussed previously.^{12,13} Briefly, 0.4 M solutions of PZT, PLZT and PNZT were prepared from carboxylate and alkoxide precursors, and acetic acid, methanol and water additions. For preparation of the PZT solutions, the appropriate amounts of the B-site precursors, zirconium butoxide-butanol and titanium isopropoxide were mixed and allowed to react for 5 minutes. Acetic acid, which chelates the metal alkoxides was then added. After 5 minutes, methanol was added, followed by addition of lead (IV) acetate. The solution was then heated to 85°C to dissolve the lead precursor, and solution preparation was completed with further additions of methanol, acetic acid and water. For the doped PZT films, lanthanum was incorporated as lanthanum acetate, which was added to the solution batch at the same time as the lead precursor, and niobium was incorporated as niobium ethoxide, which was added to the solution batch at the same time as the B-site alkoxides. For the solutions of the present study, 5 mol % excess lead was utilized.

Thin films were fabricated on Pt coated silicon substrates (Pt/Ti/SiO₂/Si) by spin-casting at 3000 rpm for 30 seconds. After deposition, solvent removal and organic pyrolysis were accomplished by heat treatment at ~ 300°C for 3 to 5 minutes on a hot

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plate. A multilayering approach was used to prepare thicker films. Typically four layers ($0.1\text{ }\mu\text{m}$ /layer after firing) were deposited prior to heat treatment for crystallization into the perovskite phase. Standard firing conditions for crystallization utilized heat treatment at either 650°C or 675°C for 30 minutes. To determine heat treatment effects on leakage characteristics, selected films were heated to crystallization temperatures after the deposition of each layer. Top Pt or RuO_2 electrodes, 1.0 - 2.0 mm in diameter, were deposited by sputtering using a shadow mask. The electrodes were annealed at 500°C for 10 minutes prior to electrical property testing. Electrode annealing resulted in improved dielectric breakdown.

Dielectric constants and loss tangents of the films were determined with an HP 4194 impedance analyzer operated at an oscillation level of $2 \times 10^{-2}\text{ V}$. Low oscillation levels were used to minimize domain switching contributions. The effects of applied bias on dielectric properties were also determined. Leakage currents were measured using a Keithley 286 source measurement unit interfaced through an IEEE bus to a personal computer. For temperature-dependent property measurements, a Signatone dc controlled power supply hot stage was employed. Results for electrical properties are reported for top and bottom electrode thicknesses of $\sim 0.3\text{ }\mu\text{m}$. We are presently using much thicker ($1.5\text{ }\mu\text{m}$) electrodes to minimize the effective series resistance of the capacitor devices.

RESULTS & DISCUSSION

Dielectric Properties

One important aspect of capacitor performance is the temperature dependence of the dielectric constant. In general, it is desirable that k' be relatively independent of temperature over the operational temperature range of interest. For most applications, the operational temperature range will lie between the limits of -55°C and 125°C . Shown in Fig. 1 is the temperature dependence, from 25°C to 125°C , of k' for a $0.8\text{ }\mu\text{m}$ PZT 53/47 thin film. Under zero applied bias, k' is strongly dependent on temperature, increasing from a value of ~ 1100 at 25°C , to a value of ~ 1525 at 125°C . This $\sim 40\%$ increase in k' places this material outside of the specification range for Z 5U capacitors. Other compositions displayed similar behavior. The dielectric loss of the films was typically between 0.015 and 0.030.

Since most decoupling capacitors are operated under an applied bias with a small oscillation level (e.g., $5.0 \pm 0.3\text{ V}$), the temperature dependence of the dielectric constant under applied bias is also of importance. The general effect of applied bias was

Fig. 1. Temperature dependence of the dielectric constant of a PZT 53/47 thin film at 0 V and 5 V bias.

to decrease the temperature dependence of k' . Also shown in Fig. 1 is the temperature dependence of the same thin film measured under an applied bias of 5 V (62.5 kV/cm). Under these conditions, dielectric constant only increases by $\sim 19\%$, from 800 to 950, with temperature increasing from 25°C to 125°C. From a design standpoint, this lower variation in dielectric constant is very desirable.

We have further investigated the effects of electric field on dielectric constant at 25°C and 85°C. Results are presented in Fig. 2 for a 0.8 μm PZT 53:47 thin film. With increasing bias, the dielectric constant first increases, then decreases. This behavior correlates well with the observed hysteresis loop properties of the films. The slight increase in k' with bias increasing from 0 to ~ 15 kV/cm is most likely due to domain switching. At fields above the switching threshold, the dielectric constant decreases with further increases in electric field, as expected. At both temperatures the effects of electric field on dielectric constant are pronounced. For example, at 25°C, the dielectric constant at 0 V bias is ~ 1100 . Under an applied bias of 5 V, k' has decreased to ~ 800 , and at 10 V bias, k' has decreased to ~ 550 . Similar effects of bias are observed at elevated temperature, although the absolute values for k' are greater. It is also evident from this figure that as bias level is increased the temperature dependence of the dielectric constant is minimized still further.

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Fig 2. Field dependence of the dielectric constant of a PZT 53/47 thin film at 25°C and 85°C.

Leakage Characteristics

In addition to characterizing temperature and electric field effects on dielectric properties, we have studied the leakage characteristics of the films, including the effects of donor-dopant additions and novel firing conditions on leakage behavior. The general current versus time ($I - t$) characteristics of the films were similar, irrespective of firing conditions or dopant additions. Typically, as voltage was applied to the thin-film capacitor, a high leakage current transient response was observed, followed by a slow decay to steady state.⁶ We believe that the decay in leakage current to steady state is related to electric field redistribution within the film. The time constant of the decay was affected by both the magnitude of the electric field and temperature, although in general, at least 30 minutes was required for the attainment of steady state current. More detailed explanations of this time dependent response have been presented by other authors.¹⁴

Typical leakage currents for our undoped PZT 50/50 thin films are between 1×10^{-6} and 2×10^{-6} A/cm² at an electric field of 65 kV/cm and a temperature of 125°C. While these are reasonable values for leakage, further improvements in leakage current densities are desirable. Because of previous reports on the effects of donor-dopant additions on the resistivity of PZT bulk ceramics,¹⁵ we studied the effects of La and Nb additions on the leakage characteristics of our PZT thin films. To simplify the

determination of the effects of dopant additions on leakage current, films were evaluated under one set of test conditions: 125°C with an applied electric field of 65 kV/cm. Under these conditions, leakage currents were measured 30 minutes after application of the electric field (i.e., essentially at steady state). Results are shown in Fig. 3 for the effects of La (A-site) and Nb (B-site) doping on PZT 50/50 thin-film leakage current. The two dopants yielded essentially equivalent results. Small dopant addition levels (< 0.5 mol %) resulted in only a minimal improvement in leakage current density. With higher doping levels, i.e., 2 mol % or above, significant improvements in leakage currents were noted. At a doping level of 5 mol %, leakage current was $\sim 2 \times 10^{-9}$ A/cm², i.e., an improvement in leakage by about a factor of 10^3 compared to the nominal, undoped PZT 50/50 thin film. Calculated resistivities of the more highly doped films are in the range of $1 - 2 \times 10^{13}$ Ω -cm.⁶

These results are of interest for two reasons. First, they demonstrate that improvements in leakage performance, similar to those observed for bulk ceramics, are possible with the incorporation of either A- or B-site dopants. Second, assuming that leakage behavior improves due to a charge compensation effect, the doping level necessary to obtain this performance improvement would seem to indicate that in addition to simple acceptor impurities, there exists in these films, a fairly high level of another acceptor species, most likely lead vacancies. This, at first, may seem like a surprising result due to the incorporation of excess lead precursor in the initial

Fig. 3 Effect of lanthanum and niobium doping on the leakage currents of doped 0.4 μ m PZT 50/50 thin films heat treated at 675°C for 30 minutes.

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solution batch. However, significant lead volatility at temperatures as low as 550°C has been reported previously by other investigators.¹⁶ Further, this hypothesis is also supported by recent studies of lanthanum-doped samples that contain a greater lead excess.¹⁷ For these samples, improvements in leakage behavior are indeed noted for lower donor-doping levels.

Other strategies for improvement of leakage characteristics may also be employed. A second approach that we have investigated is the use of a crystallization heat treatment step after the deposition of each layer. This procedure contrasts with our nominal heat treatment strategy of only firing to crystallization after every fourth layer. Typical results are presented in Fig. 4 for a standard 4 layer film, which is heat treated only once, after deposition and organic pyrolysis of the fourth layer; a film which was heat treated after the second and fourth layers; and a four layer film which was heat treated for crystallization after each layer. All crystallization heat treatments were carried out at 650°C for 30 minutes with a 15°C/minute ramp rate. As can be observed in Fig. 4, films that are fired after each layer display leakage currents which are almost a factor of 10^2 better than films prepared using the nominal firing conditions. Cross-sectional scanning electron microscopy observations indicate that this behavior is potentially due to the presence of an interlayer phase which is formed during the separate firing steps.

Fig. 4. Effect of heat treatment at 650°C on the leakage characteristics of PLZT 1/50/50 thin films. Four layer, single fire film = standard process. (100 kV/cm, 125°C)

Dielectric Breakdown

Another thin-film characteristic important for decoupling capacitors is reliability. We have recently started to characterize capacitor reliability by measuring breakdown strength as a function of temperature, applied voltage duration, and bias. Tests are typically accomplished using a voltage staircase program, as shown in Fig. 5. As illustrated, prior to breakdown, the typical response of the sample to a voltage step is a high leakage current transient, followed by decay toward steady state. After a prescribed time interval the voltage is then stepped to a higher value by a programmed increment, typically two volts. Eventually, as the voltage is increased to the critical value, breakdown occurs, as indicated in the present example by the excessively high current which results from the application of -70 V to the sample. One other feature of Fig. 5 is worth mentioning. Leakage current results are shown for step durations of 60 seconds. It is apparent that this time period is inadequate to allow for the attainment of steady state leakage currents, as discussed earlier.

Results for the effects of temperature on breakdown strength are illustrated in Fig. 6, for PZT 53/47 with a Pt top electrode, PZT 53/47 with a RuO₂ top electrode, and PLZT 5/50/50 with a Pt top electrode. A step duration of 5 minutes was used. Typical breakdown fields ranged from 600 kV/cm to 1000 kV/cm. Unlike the proposed model of Klein,¹⁸ surprisingly, we do not observe the expected decrease in breakdown strength with increasing temperature. For PZT 53/47, the highest breakdown strengths were observed at a temperature of 75°C. At this temperature, the films with RuO₂ top

Fig. 5. Typical I - t plot for voltage staircase program used to evaluate dielectric breakdown. Test conditions are indicated in the plot.

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Fig. 6. Effects of temperature, top electrode material, and composition on breakdown. Results are shown for positive bias. PZT films ($\sim 0.8 \mu\text{m}$) fired at 650°C for 30 minutes; PLZT 5/50/50 film ($\sim 0.8 \mu\text{m}$) fired at 675°C for 30 minutes.

electrodes displayed breakdown strengths higher than those with Pt top electrodes. Breakdown strengths for these films approached 1 MV/cm . At 125°C , the films with Pt top electrodes yielded higher breakdown strengths. Since the results presented represent the averages of numerous measurements, typically 6 - 8 trials per test condition, and there was good repeatability from capacitor to capacitor for a particular test condition, it is believed that, contrary to expectations, the PZT films did indeed exhibit higher breakdown strengths at 75°C than at room temperature. The lanthanum-doped PLZT 5/50/50 sample displayed a somewhat different trend; breakdown strength increased with increasing temperature. At room temperature, the lanthanum-doped sample displayed the lowest breakdown strength. With increasing temperature, however, the breakdown strength of the sample continued to increase, and at 125°C , the lanthanum-doped sample exhibited a higher breakdown strength than either of the PZT samples.

This apparent increase in breakdown strength with increasing temperature would seem to imply that at elevated temperatures, there exists a mechanism which contributes to improved breakdown performance. Potentially, this could be related to some type of self-healing phenomenon, which is also affected by doping. This final result would seem to indicate that in addition to electrode/film interface effects, defect chemistry can also play a role in breakdown behavior.

The effects of bias sign on the temperature dependence of breakdown have also been characterized. For samples tested under negative bias (i.e., top electrode biased negative with respect to the bottom electrode), similar results were obtained; i.e., for the PZT films, higher breakdown strengths were observed at 75°C. In general, breakdown strengths observed under negative bias were lower than under positive bias conditions, irrespective of temperature. The combined results of electrode effects on breakdown and the dependence on bias sign indicates that electrode/film interface effects are important in defining breakdown behavior. Finally, we have also evaluated temperature, bias and electrode effects with shorter step durations and obtained similar results. Maximum breakdown strengths are not obtained at the lowest test temperature.

Effects of voltage step duration on breakdown strength are shown in Fig. 7 for the Pt/PZT/Pt capacitor structure. As predicted by Klein,¹⁸ longer step durations resulted in lower breakdown strengths. As seen in the figure, this effect was more pronounced at higher test temperatures. At 125°C, as step duration was increased from 10 seconds to 5 minutes, breakdown strength decreased from ~ 1 MV/cm to ~ 660 kV/cm. The results are in qualitative agreement with those of Moazzami,¹⁹ who observed a decrease in apparent breakdown strength for longer stress times. A more direct comparison of the results is difficult due to a number of differences in test conditions.

Fig. 7. Effect of voltage step duration (stress time) on dielectric breakdown strength at 21°C, 75°C and 125°C for PZT 53/47 thin films with Pt electrodes.

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Fig. 8 Relationship between voltage step duration and reciprocal breakdown field; circles: $0.8 \mu\text{m}$ PZT 53/47; squares: $0.2 \mu\text{m}$ PZT 50/50 from Ref. 20.

These results may also be used to obtain an estimate of capacitor reliability by plotting step duration (stress time) versus reciprocal breakdown field, as has been presented by previous authors.²⁰ Results are shown in Fig. 8 for Pt/PZT/Pt capacitors tested at 125°C . The results of Sudhama²⁰ are also shown in the figure for comparison. Based on this plot, reasonable capacitor lifetimes, ($> 10^8$ seconds) are expected. The longer predicted lifetimes for the films of the present study may simply be due to the thicker nature of our films.

CONCLUSIONS

We have investigated the dielectric, leakage, and breakdown characteristics of PZT, PLZT and PNZT thin films for decoupling capacitors. The dielectric properties of the films, $k' \sim 800$, $\tan\delta \sim 0.02$, as well as the temperature and field dependence of the dielectric properties appear reasonable for this application. Under applied electric field, the temperature dependence of k' was reduced. Leakage characteristics of the films were significantly improved through the incorporation of either A- or B-site donor dopants. By incorporating 5 mol % La or Nb, film leakage was decreased by approximately a factor of 10^3 . Breakdown characteristics of the films were dependent on doping and

electrode materials. In general, acceptable breakdown fields were observed for the films, and reasonable capacitor lifetimes are expected.

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