Study Of DC Conduction Mechanism in Ferroelectric Pb(Zr,Ti)O$_3$ and (Pb,La)TiO$_3$ Thin Films

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It is of great significance to investigate into the details of the dc conduction in ferroelectric thin films. The magnitude of leakage current is usually one of the most concerned issues for the applications of these films. Resistivity degradation of the films under constant dc field stress, which leads to time-dependent dielectric breakdown (TDBB), is another important issue intrinsically related to dc conduction. The present paper summarizes the studies on DC conduction observed in ferroelectric thin films while considering Pb-based perovskites as specific examples by the quite flexible multi-ion-beam reactive sputtering (MIBERS) system.

Great efforts have been involved emphasizing the process control related to composition, structure and properties of the resultant films. A multi-Ion beam reactive sputter deposition of complex oxide films has been chosen in the present work, as it promises utmost flexible control over cationic/anionic ratios, while also allows to introduce a secondary reactive ion assistance during growth of films. Due to the versatility of the present deposition approach, two major approaches were taken as shown in Fig.1, which illustrates a) effects of minor changes in composition on structure, microstructure and properties, while the other part b) signifies the importance of controlled low-energy ion bombardment to modify the growth process, microstructure and electrical properties of ferroelectric thin films. Furthermore, this technique can be easily combined with controllable low energy ion bombardment which was proven to offer great opportunities to modify growth process, microstructure and physical properties of the films. Recently, efforts have been directed towards using multiple targets, sputtered by either a single ion beam or multiple ion beams. The configuration of multiple targets with multiple ion beams seems noticeably attractive as it allows high flexibility and good control over stoichiometry, uniformity and reproducibility.

A. Relationship between Composition-Structure-DC conductivity of (Pb,La)TiO$_3$ Thin Films:

An understanding of the relationships between composition and microstructure is highly advantageous when trying to engineer the properties of a thin film. By knowing the
types of phases and connectivity of those phases, mixing rules can be used to predict the property dependence on composition. For the PLT films studied, the dependence of the electrical properties on composition can be understood by applying mixing rules to the simplified microstructure models for textured and non-textured films.

The dc resistivity measured through the thickness of the film is given as an example of an electrical property which illustrates the relationship between composition, microstructure, and properties. As shown in Figure 2, textured films exhibit a high dc resistivity (on the order of $10^{13} \ \Omega \cdot $cm) which decreases slowly with increasing PbO excess. At the transition between $<100>$ texture and non-textured, the resistivity drops discontinuously to a low resistivity (on the order of $10^{9} \ \Omega \cdot $cm). Because a mercury probe was used for the top electrode and the Pt substrate layer was used for the bottom electrode there are two curves, labeled Pt cathode and Hg cathode, which refer to measurements for opposite electric field polarities. The resistivity difference for the two polarities increases with increasing PbO content due to an increasing thin film surface roughness (resulting from PbO evaporation) which alters the contact between the Hg electrode and the PLT film. A model of the resistivity dependence on excess PbO is presented in Figure 2. This model applies the mixing rules developed by Hanai to the simplified microstructure model. In Figure 2, curve A is calculated assuming a continuous perovskite phase with a resistivity of $10^{14} \ \Omega \cdot $cm, and curve B is calculated assuming a continuous second phase of PbO with a resistivity of $10^{8} \ \Omega \cdot $cm. Curve A applies to textured films while curve B applies to non-textured films. The dashed vertical line marks the empirically determined transition between textured and non-textured microstructures. The heavy solid line indicates the portion of the calculated curve that corresponds to the experimental curves in Figure 2. Such a close correlation between the experimental and calculated behavior of the resistivity not only supports the validity of the simplified microstructure model.

B. Low energy Oxygen Ion Bombardment Approach:

The difference in dc behaviors between the bombarded films and the non-bombarded films is revealed more clearly by I-V and TDDB measurements. Figure 3 shows the TDDB characteristics of both bombarded films and non-bombarded films annealed at 680°C for 2 h. The bombardment-induced effect on TDDB is significantly large. For a dc field of 450 kV/cm, the non-bombarded films break down in 50 min, while the bombarded films do not break down for up to 925 min. The difference in TDDB stems from the difference in I-V behavior.
Figure 3. Current with time for bombarded and non-bombarded PZT films.

Figure 4. I-V behavior of bombarded and non-bombarded PZT thin films.

Figure 4 shows the results of I-V measurements for both bombarded films and non-bombarded films, annealed at 600°C for 2 h. The ohmic resistivity of the bombarded films (~3×10¹¹ Ω·cm) is about one order of magnitude higher than that of the non-bombarded films (~3×10¹⁰ Ω·cm). The onset voltage of the space-charge-limited conduction (indicated by the slope change of the logI-logV curve, from approximately unit to 2 or larger) is much higher for the bombarded films (~12 V) than for the non-bombarded films (~3 V). Also, the bombarded films have much higher dielectric breakdown strengths than the non-bombarded films (~770 kV/cm and ~350 kV/cm respectively). For films annealed at temperatures higher than 600°C, the difference in I-V behavior between the bombarded films and the non-bombarded films is reduced as both groups become more resistive. The effect of low-energy oxygen ion bombardment is more visible for films processed at lower temperatures. Since TDDB is a long-term degradation behavior, even a small difference in the dc resistivity can still lead to a significant difference in TDDB.

C. I-V characteristics of ultrafine grain PZT thin films:

Type I: varistor type characteristics

Figure 5 shows one typical J-E curve which is usually observed in well-annealed films. As mentioned above, the curve was obtained by conjoining the segment of long-term response for low field region (AB) and the segment of short-term response for high field region (B'C'). It can be noted that in this case these two segments can meet one another and virtually there is no gap of uncertainty between B and B'. More strikingly, this type of curve features a strong nonlinear J-E dependence.

Five regions can be distinguished by using the nonlinearity coefficient, α, which is defined as the slope of lnJ-lnE plot (J=CEα and α=dlnJ/dlnE, where C is a constant). Linear J-E dependence (ohmic conduction) is observed only at very low fields (region I, 0-4 kV/cm). In the wide intermediate field region, α continuously decreases from nearly 1 to
Type II: space charge limited conduction (SCLC)

Figure 6 shows another typical J-E curve which is observed in some moderately annealed films. Unlike the previous type, the long-term segment (AB) and the short-term segment (B'C') in this case do not meet one another, indicating the coexistence of polarization and time-dependent dc degradation effects between B and B'. An approximate transitive arc (BB') is therefore needed to connect the two segments. This type of J-E curve clearly exhibits four different $\alpha$ regions; however changes in $\alpha$ are less dramatic than those in the previous case. In the low field region, the $\alpha$ is close to unity (region I, 0-30 kV/cm). Followed is the transition region where the $\alpha$ varies from approximately 2 to 3.5 (region II, 30-100 kV/cm). The next is a region characterized by an $\alpha$ of about 9 (region III, 100-130 kV/cm). At higher fields, the $\alpha$ becomes 2 to 3.5 again (region IV, above 130 kV/cm). This type of J-E curve can be easily modeled in terms of the SCLC theory: region I follows Ohm's law; region II corresponds to the shallow trap square law; region III seems to be the region of trap filled limit (TFL); and region IV corresponds to the trap free square law.

Figure 5. I-V behavior of ultrafine grained PZT films indicating varistor type response.

Figure 6. J-V response of ultrafine grain PZT films indicating SCLC behavior.