AIP Review of Scientific Instruments

Novel method for determining the Curie temperature of ferroelectric films

Chi Kong Kwok and Seshu B. Desu

Citation: Review of Scientific Instruments **64**, 2604 (1993); doi: 10.1063/1.1143876
View online: http://dx.doi.org/10.1063/1.1143876
View Table of Contents: http://scitation.aip.org/content/aip/journal/rsi/64/9?ver=pdfcov
Published by the AIP Publishing

Novel method for determining the Curie temperature of ferroelectric films

Chi Kong Kwok and Seshu B. Desu[a)]
Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

(Received 12 January 1993; accepted for publication 20 May 1993)

A novel technique to measure the Curie temperature of ferroelectric thin films has been developed. The method is based on identifying changes in slope of film stress versus temperature plot. At the Curie temperature, ferroelectric films undergo a phase transition from ferroelectric phase to paraelectric phase. Due to this phase transformation, physical properties of films such as elastic constants and coefficients of thermal expansion also change at the Curie temperature. Consequently, at this temperature the temperature coefficient of film stress changes since it is related to elastic constants and thermal expansion coefficient. Thus, by measuring the film stress as a function of temperature, the Curie temperature can be determined. The Curie temperatures measured by this method are in good agreement with the literature values. Small discrepancies that were observed can be attributed to the intrinsic stresses present in the films.

The high values of switchable spontaneous polarization, dielectric constant, pyroelectric coefficient, piezoelectric coefficient, and electro-optic coefficient of ferroelectric films have been exploited for several applications including nonvolatile electronic memories, dynamic random access memories, infrared detectors, acoustic transducers, waveguide devices, and optical memories.[1] The upper operating temperature of these devices is limited by the Curie temperature (T_C) of the ferroelectric film because above the Curie temperature the material becomes paraelectric and loses all of its interesting ferroelectric properties. Therefore, for a given application the Curie temperature limits the choice of material. For example, because of its low T_C $BaTiO_3$ is not a preferred material for nonvolatile memory applications when compared to $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), although the ferroelectric properties are comparable. In addition to limiting the material choice, T_C also limits the amount of dopants used to improve certain characteristics of a material since the dopants can reduce the Curie temperature. For example, La doping of $Pb(Zr_{1-x}Ti_x)O_3$, despite its advantages, is limited to around 2 at. % because La additions reduce T_C in a linear manner at the rate of ~37 °C per at. % La.[2]

The nature of ferroelectric to paraelectric transition (i.e., sharp versus broad transition) and T_C are, in general, sensitive functions of microstructure, dopant concentration, and more importantly, state and amount of mechanical stress.[3] For thin films, mechanical stresses are very important since stresses are always present in the film, unless they are free standing. For example, it is shown that compressive stresses of the order of 400 MPa increased T_C of $BaTiO_3$ thin films by about 29 °C.[4]

It is apparent from the above discussion that an accurate determination of T_C of ferroelectric films is crucial. Although several standard techniques are available, most of these require the deposition of electrodes because they depend on changes in the temperature dependence of electrical properties (e.g., polarization, dielectric constant). In this letter, a simple method is reported for determining the Curie temperature of ferroelectric films, which does not require any electrodes. In this technique, T_C of a ferroelectric film is obtained from the slope changes in film stress versus temperature plots. Concomitantly, the effect of film stress on the Curie temperature can also be evaluated. In addition, using this method the elastic stiffness and thermal expansion coefficient of the film can also be obtained.[4]

The contribution of the thermoelastic component (thermal stress component) σ_{th}, arising because of the difference in the linear thermal expansion coefficients of the substrate and the film materials, to the total film stress σ_{tot}, is defined by the expression

$$\sigma_{th}=[E_f/(1-\nu_f)]\int_{T_1}^{T_2}(\alpha_s-\alpha_f)dT, \tag{1}$$

where E_f and ν_f are, respectively, the Young's modulus and Poisson's ratio for the film material; α_s and α_f are the linear thermal expansion coefficients of the substrate and film, respectively, and T_1 and T_2 is the temperature interval. From Eq. (1) the slope of a stress versus temperature plot can be related to the thermal expansion coefficient by

$$(d\sigma/dT)=[E_f/(1-\nu_f)](\alpha_s-\alpha_f). \tag{2}$$

For obtaining Eq. (2), the values of E, α, and ν are assumed to be independent of temperature, which is valid within the uncertainty of the experimental techniques employed.

For a given substrate, the slope of the stress-temperature curve is determined by the film properties E_f, ν_f, and α_f [Eq. (2)]. A change in the slope of the stress-temperature curve is expected at the Curie point because ferroelectric and paraelectric phases have different properties. Thus, by measuring the film stress as a function of temperature, T_C can be obtained, in principle, for a ferroelectric film. Similarly, other characteristic phase transition temperatures of the films can also be obtained. It should be pointed out that other components of total film

[a)]To whom all correspondence should be addressed.

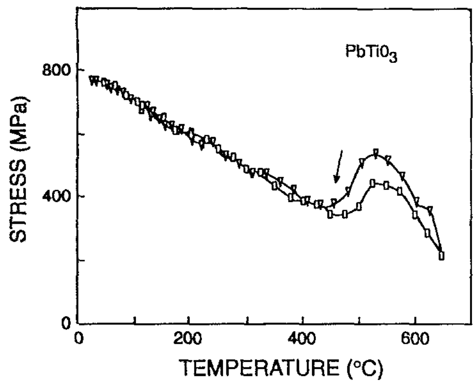

FIG. 1. Film stress of the 75/25 PZT film as a function of annealing temperature. The square symbols indicate measurements during heating, inverted triangles symbols indicate measurements during cooling.

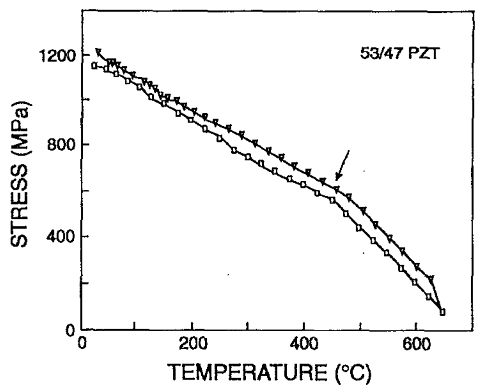

FIG. 2. Film stress of the 53/47 PZT film as a function of annealing temperature.

stress such as extrinsic and intrinsic stresses may have an influence on the nature of changes in the slope of the stress-temperature curve.

The stress of the films was measured using an optically leveraged laser-beam apparatus (Flexus F2400). This tester is capable of running *in situ* stress measurements at temperatures up to 900 °C. It uses a laser as the probing source and a position-sensitive detector to measure the displacement of the laser reflection from the wafer surface. These displacements are converted to radii of curvature. The sensitivity of this tester is limited to a radius of curvature of 4000 m, which corresponds to about 1.3 MPa for a 0.3 μm film on a 525-μm-thick Si substrate. For the case of a homogeneous, isotropic thin film deposited on a thick substrate where the film-substrate bond is strong enough to suppress slippage, the total film stress is related to the radius of curvature (R) of the substrate by Stoney's equation[5]

$$\sigma_{\rm tot}=[E_s/(1-\nu_s)](t_s^2/6t_f)(1/R), \qquad (3)$$

where t_s and t_f are thicknesses of substrate and film, respectively and $E_s/(1-\nu_s)$ is the biaxial modulus of the substrate.

PZT films with three compositions, Zr/Ti ratios of 0/100, 53/47, and 75/25 were deposited on 100-mm-diam Pt-coated Si wafers by a sol-gel process.[6] Film preparation by sol-gel process involves precursor (sol) preparation, hydrolysis, polycondensation, film formation, and sintering. In this study, PZT films were fabricated from sol-gel precursors (0.4 M) of lead acetate, titanium isopropoxide, and zirconium *n*-propoxide dissolved in glacial acetic acid and *n*-propanol. The proper amounts of Zr and Ti alkoxides were premixed in the presence of propanol and acetic acid before the addition of lead acetate. These solutions were hydrolyzed with appropriate amounts of water and were further diluted with propanol and acetic acid to form the final precursors. Thin films were deposited by spin coating on Pt-coated Si substrates using a spin speed of 3000 rpm. After spin coating, each film was dried at 150 °C for 5 min on a hot plate. Film thicknesses were around 0.3 μm after two coatings. The configuration of the PZT film on Pt wafers is as follows: PZT (0.3 μm)/Pt (400 nm)/Ti (30 nm)/SiO_2 (200 nm)/{100} Si substrate. Detailed description of the PZT film deposition can be found in Ref. 7.

For each sample, two identical heating-cooling cycles were run sequentially. The samples were heated in two identical annealing cycles from room temperature to 650 °C and cooled down to room temperature twice in ambient condition. The heating rate was 5 °C/min and the cooling rate was 2.5 °C/min. The main reason for annealing the samples in two cycles is that all irreversible transitions are presumably completed in the first cycle and the second heating-cooling cycle only involves the reversible Curie transition.

The stress-temperature plots of PZT films with Zr/Ti ratios of 75/25, 53/47, and 0/100 during the second heating-cooling cycles are shown in Figs. 1, 2, and 3, respectively. The square symbols indicate measurements during heating while inverted triangles symbols indicate measurements during cooling. All three plots exhibit similar stress response as a function of annealing temperature. However, the pure $PbTiO_3$ film has a more abrupt change in stress at temperatures around 450 °C. The film stresses of these PZT films decrease from initial stresses ranging from 800 to 1300 MPa in tension after the first annealing cycle. The decrease in stress is relatively linear with the annealing temperature until a break of linearity is observed at a higher temperature. Evidently, the variation of film stress as a function of annealing temperature is a reversible

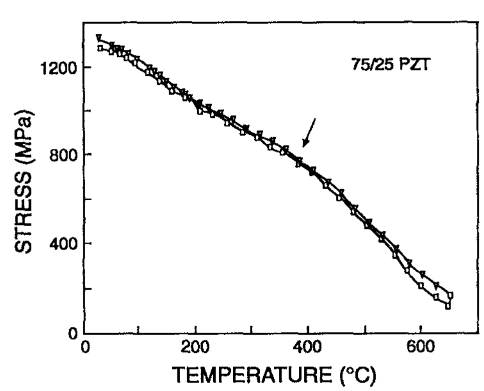

FIG. 3. Film stress of the $PbTiO_3$ film as a function of annealing temperature.

TABLE I. Curie temperature as a function of composition.

Composition	T_c^{expt} (°C)[a]	T_c^{ref} (°C)[b]
$PbTiO_3$	507± 8	490
53/47	439±10	411
75/25	356±13	335

[a] T_c^{exp}=Curie temperature measured in this experiment. Average of at least four measurements.
[b] T_c^{ref}=Curie temperature given in the literature (Ref. 6).

process. The stress-temperature profiles during heating matched very well to those during cooling. This indicates that the irreversible transitions and reactions are presumably completed after the first annealing cycle. As expected, changes in slope for the stress-temperature curves were observed at the Curie transition due to the changes in physical properties. When the samples underwent paraelectric (cubic) to ferroelectric (noncubic) transformations, the elastic constant and the coefficient of thermal expansion (α_f) of these samples also underwent a change. Consequently, these changes of elastic constant and α_f resulted in the discontinuity found in the stress-temperature profiles at the Curie temperature. Hence, Curie temperatures can be determined from these stress-temperature plots and their values are tabulated in Table I. It should be noted that the experimental Curie temperature values presented in Table I are the averages of at least four measurements.

The Curie temperatures of PZT films measured by the film stress method are in qualitative agreement with those obtained from the *bulk* PZT ceramics,[8] but Table I shows that they are 17–28 °C higher than in these corresponding bulk ceramics. This can be attributed to the large intrinsic stresses present in the films. The ferroelectric to paraelectric transition (at the Curie point) results in a volume decrease; the intrinsic tensile stresses would counteract this volume decrease and therefore increase the Curie temperature. For $PbTiO_3$, the volume change at T_C is very high when compared with PZT films. Therefore, the effect of extrinsic stress on temperature dependence of stress is significant for $PbTiO_3$. This may explain the nonlinear change in stress at T_C for $PbTiO_3$ (Fig. 3).

In summary, a novel method for determination of Curie temperature of ferroelectric films by film stress measurement is described. The Curie temperatures measured by the film stress method are in good agreement with the literature values for bulk materials. The discrepancy of Curie temperature can be explained by the large intrinsic tensile stresses present in the film.

[1] L. M. Sheppard, Ceram. Bull. **71**, 85 (1992).
[2] G. H. Haertling, Ferroelectrics **75**, 25 (1987).
[3] G. Arlt, D. Hennings and A. de With, J. Appl. Phys. **58**, 1619 (1985).
[4] S. B. Desu, J. Electrochem. Soc. (in press).
[5] G. Stoney, Proc. R. Soc. London A **82**, 172 (1909).
[6] J. Blum and S. Gurkovich, J. Mater. Sci. **20**, 4479 (1985).
[7] Chi Kong Kwok, Ph.D. dissertation, Virginia Polytechnic Institute & State University, July 1992.
[8] *Landolt-Bornstein Series, Vol. 3, Ferro- and Antiferroelectric Substances*, edited by K. Hellwege (Springer, Berlin, 1969), p. 269.