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Electrical/Microstructural Characterization of Dielectric Thin Films Prepared on Transparent Substrates

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ABSTRACT

$Pb(ZrTi)O_3$ thin films were prepared on transparent conducting oxides, through sol-gel processing. The processing variables such as spin velocity, spin time and annealing temperature were investigated using a statistical design of experiments. Dielectric properties were determined through capacitance-voltage measurements and electrical characterizations evaluated using current-voltage characteristics. The leakage current is determined mainly by annealing. The capacitance and breakdown voltage is found to be independent of the processing variables. The sophisticatedly controlled PZT thin films have been confirmed through microscopic images.

Key Words : $Pb(ZrTi)O_3$, Dielectric Properties, Electrical Properties, Annealing Temperature.

1. INTRODUCTION

Ferroelectric materials have been one of the emerging materials in semiconductor memories, micro-electromechanical systems (MEMS), smart microsensors etc.[1-5] Among those ferroelectrics, lead-zirconate-titanate, ($Pb(ZrTi)O_3$, PZT) thin films have been recognized as one of the excellent candidates for the above high-performance applications, since the PZT thin films possess significant polarization-electric field hysteresis, high dielectric constants, stability in high electrical fields, and optical transparency in visible light regime, in addition to piezoelectric characteristics. In particular, the superior dielectric constant and electrical insulating feature can be adapted into the inorganic dielectric layers constructed in inorganic electroluminescent displays in the form of thin and thick films.

In order to apply PZT thin films to electroluminescent devices, sol-gel processing can be employed onto the transparent conducting oxides, i.e., indium-tin oxides deposited on glass substrates High dielectric constant materials enhance the luminescent devices, especially in inorganic electroluminescent materials in the form of multilayered device structures[6]. The conventional inorganic electroluminescent devices have been fabricated through screen printing methods. The applicability of inorganic electroluminescent devices has been evolved into high-brightness flat panel displays, involving thin film depositions in dielectric and phosphorus layers.. The inorganic electroluminescent thin films are composed of the insertion of the luminescent materials between dielectric layers deposited on the high conducting electrodes, i.e., metals or transparent conducting oxides[6,7].

A majority of relevant studies have been focused on fabrication of display devices rather than elementary understanding on the component materials[7]. This work is aimed to improve the application of high-permittivity dielectric constants through the optimization in the electrical/dielectric properties in PZT thin films. The electrical/dielectric features were investigated using current-voltage characteristics and frequency-dependent capacitance, respectively, along with the microstructural imaging analysis.

2. EXPERIMENTAL

ITO (Indium Tin Oxide)-deposited glass of the dimension 2cm×2cm, was used as underlying substrates for PZT thin films. The thickness of the ITO

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thin films was estimated to be approximately 1600 by FESEM (JSM 6700F, JEOL, Tokyo, Japan). The ITO-coated glasses were cleaned according to the procedure described elsewhere[8].

PZT thin films were deposited onto the ITO-coated substrates through sol-gel processing which employed a commercial solution mixture (INOSTEK, KOREA): the relative proportion of Zr to Ti is 48:52 and the lead (Pb) content is of 10% excess, in order to compensate for the volatile characteristics of the corresponding constituent in PZT thin films, Pb. The sol-gel solution was dispersed for forming the PZT thin layers, using a spin coater. Usually, four spin coatings were performed in a single PZT thin film deposition: the spin coating was repeated with the annealing of 500°C with 5 min. Based on the above preliminary treatment, the design of experiments (DOE) was performed as a function of processing variables, i.e, spin velocity, spin time, and annealing temperature. The detailed experimental conditions are shown in Table 1.

For the electrical characterization, the top electrodes were prepared onto PZT thin films using the shadow metal masks. Aluminum was deposited to 100nm with the diameter of approximately, 220 mm. The corresponding electrical properties were characterized using a high-resistivity electrometer, (KE 6517, Cleveland, Ohio, USA). The dielectric features were investigated using a low-frequency impedance analyzer (HP 4192A, Palo-Alto, California, USA). The cross-sectional view was observed using Field-Emission Scanning Electron Microscopy.

3. RESULTS AND DISCUSSION

Design of experiments were performed according to the combination shown in Table 1, in order to estimate the effect of processing variables on the electrical/dielectric properties in the PZT thin films.

Since the final temperature is fixed by the inherent limitations in PZT thin film processing, the sol-gel processing was intensively investigated in terms of spin velocity, spin time, and the immediate treatment temperature applied prior to the final annealing at 500°C. The resultant output parameters were monitored to the aim to optimizing the electrical insulation along the high dielectric constant, i.e., breakdown field, capacitances, and leakage current are shown in Table 2.

In the breakdown voltage analysis, the main effects and interactions are not statistically significant at the significance level of 0.05 as shown in Fig. 1. The capacitances seem to be independent of the processing variables in sol-gel processing in Fig. 2. Unlike those of the breakdown voltage and capacitance, the leakage current is found to be primarily affected by annealing temperature, as shown in the original leakage current (of Fig. 3) and the corresponding Pareto chart of Fig. 4.

Table 1. Experimental conditions employed in the design of experiments. (A: spin velocity [rpm], B: spin time [sec], and C: annealing temperature [°C])

Run Number	A	B	C
1	4000	30	300
2	4000	10	300
3	4000	30	400
4	4000	10	400
5	3500	20	350
6	3000	10	300
7	3000	30	400
8	3000	10	400
9	3000	30	3000

Table 2. Experimental results performed in the order given in Table 2. Log (L.C.) is the logarithmic of leakage current. V_{BR} is the breakdown voltage, and capacitance.

Run No.	V_{BR} [V]	Capacitance [F]	Log (L.C.) [A]
1	27.3	5.39E-11	-10.4425
2	30.6	6.01E-11	-10.2967
3	21	3.01E-11	-11.5406
4	22	2.74E-11	-11.9281
5	7.4	2.91E-11	-11.3036
6	5.8	6.68E-11	-9.9281
7	5.8	3.06E-11	-11.1337
8	10.7	6.14E-11	-11.5467
9	15.7	5.68E-11	-10.2832

The detailed effects in main effect plots and interaction plots are shown in Figs. 5 and 6, The main effects plot indicates that the leakage current is not determined by the change in spin velocity and spin time but the annealing temperature controls mainly the leakage current. The leakage current decreases with increasing the annealing temperature. It should be noted that the leakage current obtained from the center point is not significantly deviated along the linear prediction estimated from the corresponding corner points. The interaction plot of Fig. 6 exhibits no significant two-factor interactions in spin velocity, spin time, and annealing temper-

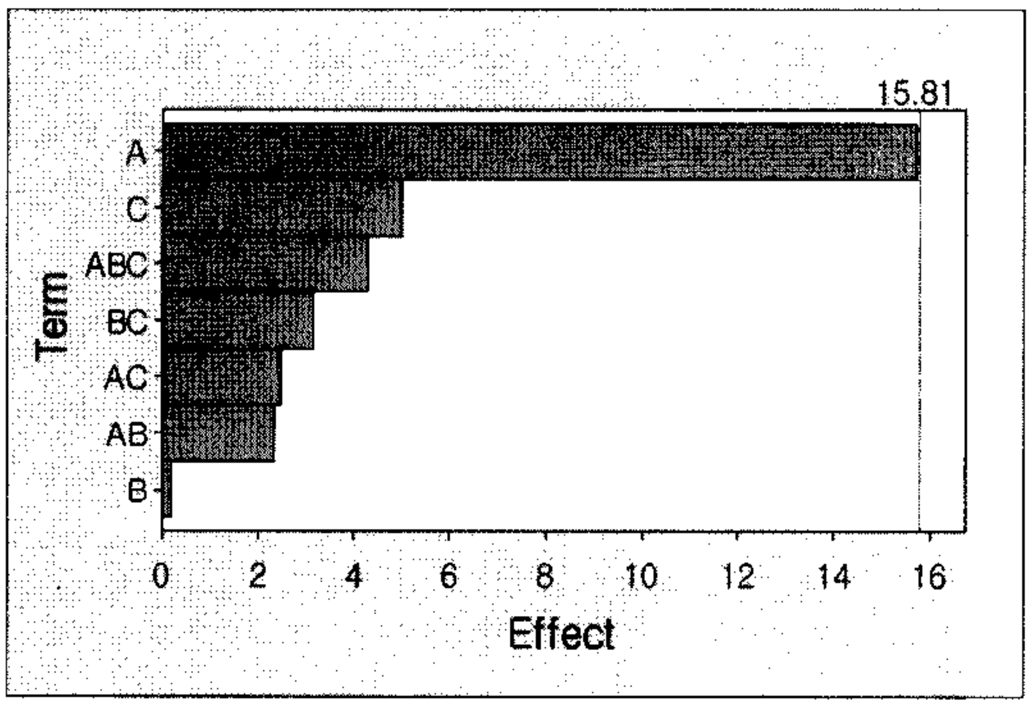

Fig. 1. Pareto chart of V_{BR} at the level of α=0.05.

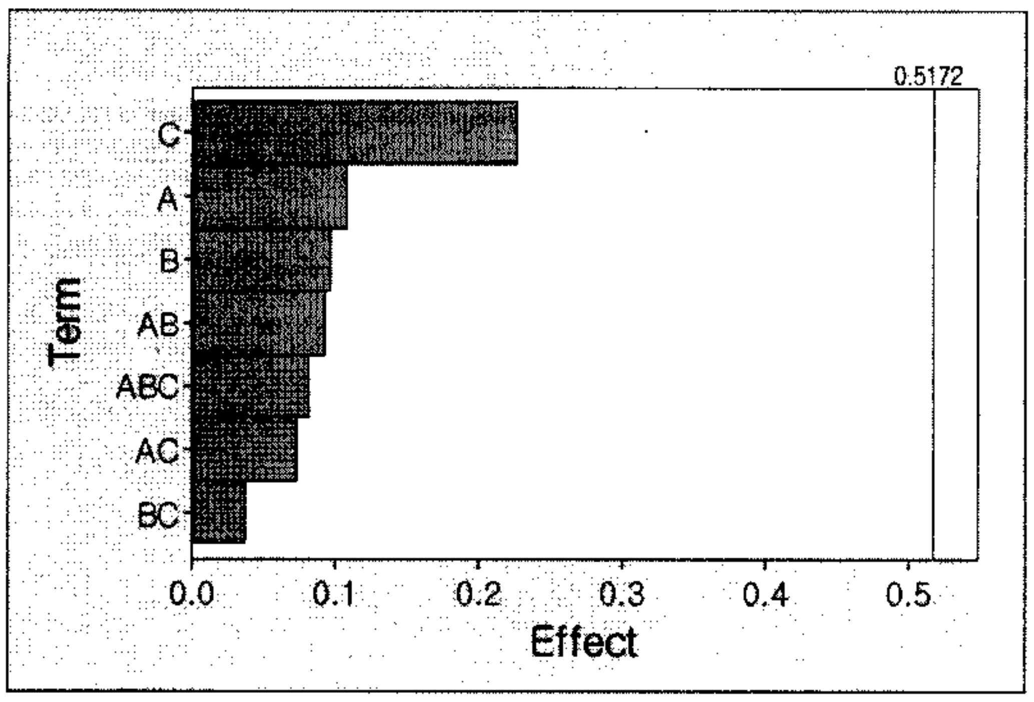

Fig. 2. Pareto chart of Log(C) at the level of α=0.05.

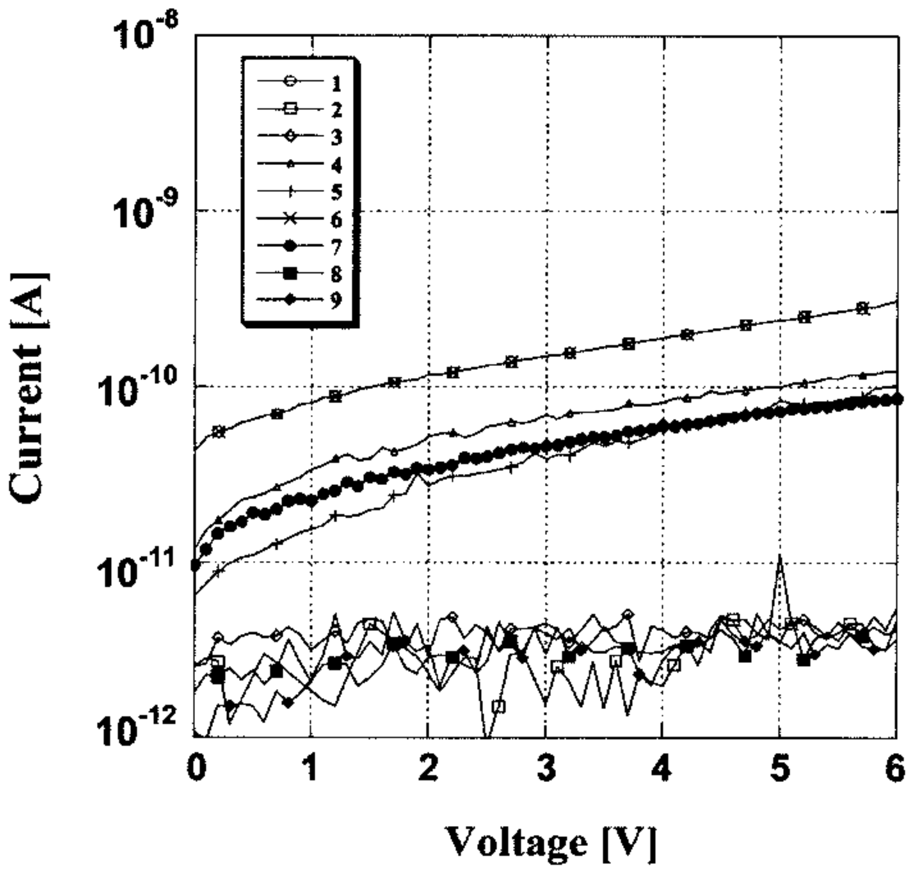

Fig. 3. Current-voltage characteristics in the PZT thin films.

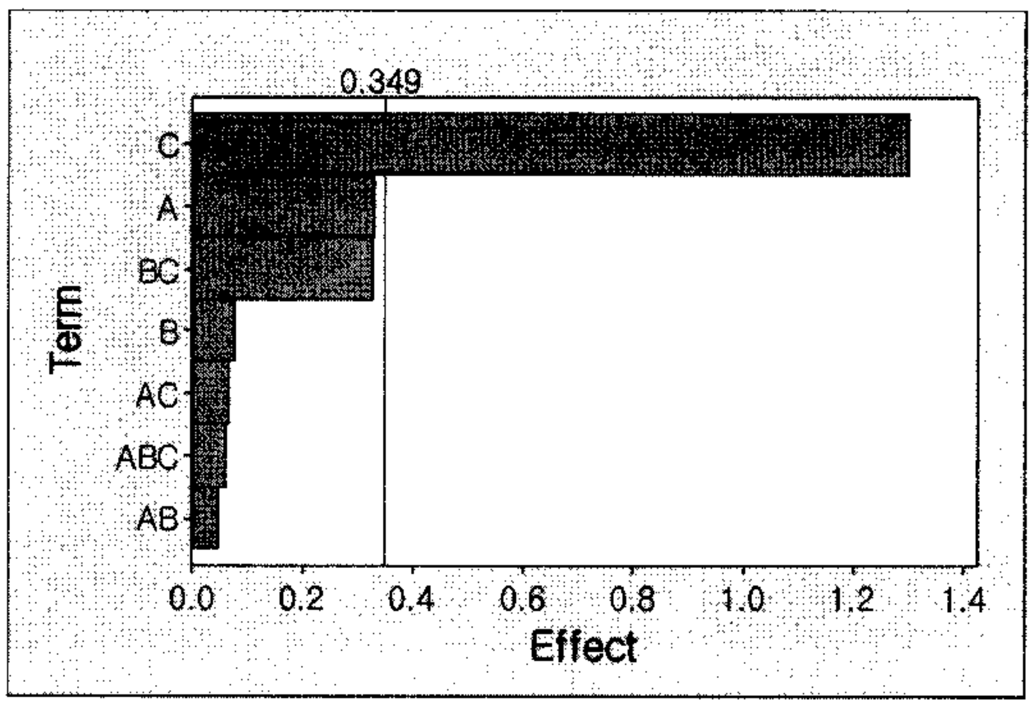

Fig. 4. Pareto chart of Log(L.C.) from experiment in the PZT thin films

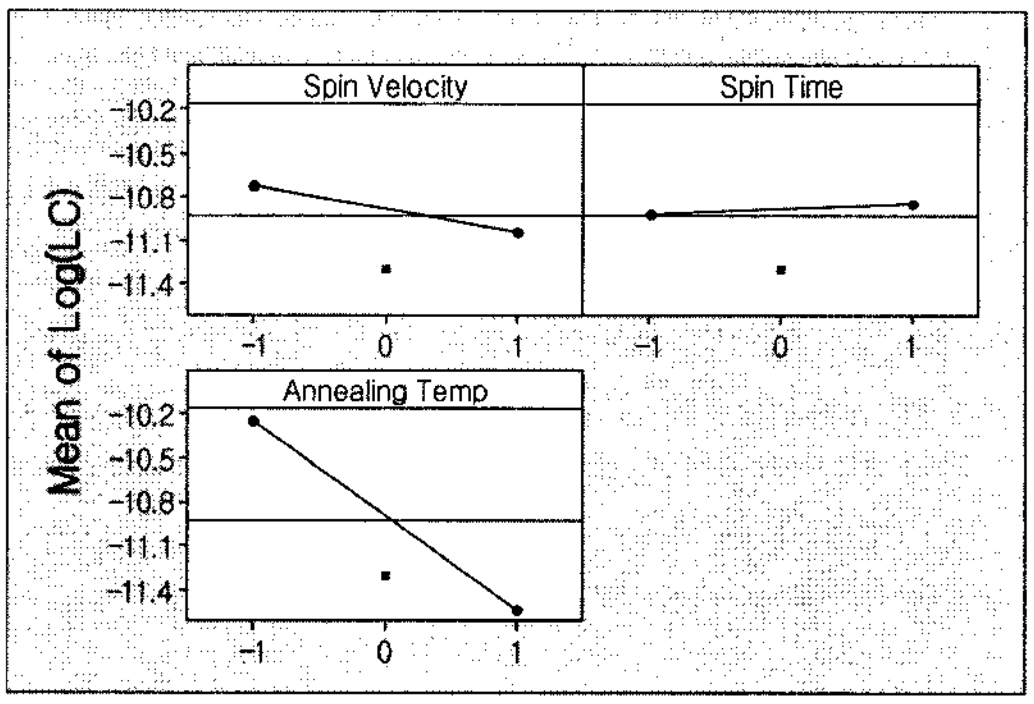

Fig. 5. Main effects plot for leakage currents in the PZT thin films.

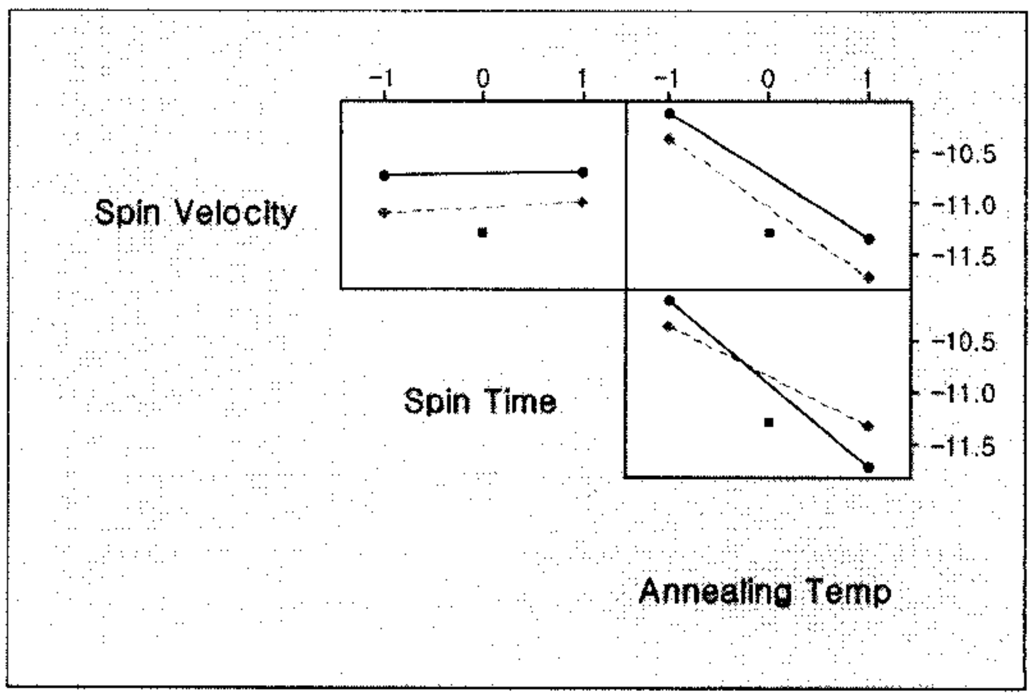

Fig. 6. Interaction plot for leakage current in the PZT thin films.

ature.

Since the current work adopts the full 2^3 factorial design with one center point, we can estimate the relative importance of all relevant effects and interactions and model a process of PZT thin film deposition statistically. The system can be modeled with regard to the output parameter, Y, in terms of the processing variables, as the following

$$Y = B_0 + B_1x_1 + B_2x_2 + B_3x_3 + B_1B_2x_1x_2 + B_1B_3\,x_1x_3 + B_2B_3\,x_2x_3 + \varepsilon \qquad \text{[Eq. 1]}$$

where i) x_1, x_2, and x_3 represent primary factors A, B, and C, respectively, ii) x_1x_2, x_1x_3, and x_2x_3, represent two-factor interactions between A and B, A and C, and B and C respectively, and iii) $x_1x_2x_3$ represent a three-factor interaction. B_0 is a grand-average calculated using all experimental outputs. ε is a random error in order to compensate for the difference between experimental values and predictions from a proposed equation [9]. The estimated effects and coefficients are summarized in Table 3. In this work, A is spin velocity, B spin time and C annealing temperature. As shown in Pareto chart and main effects plot, the output value is determined by only the single main effect of C, i.e., by annealing temperature. Eq. (1) is then approximated at the significance level of 0.05, to the following equation,

$$Y = B_0 + B_3x_3 + \varepsilon \qquad \text{[Eq. 2]}$$

Eq. (2) is rearranged like the following

$$\text{Log (LC)} = -10.89+(-0.65)x_3 \qquad \text{[Eq. 3]}$$

Table 3. Estimated effects and coefficients for log (LC) in coded units.(A; spin velocity, B: spin time and C: annealing temperature.

	Effects	Coefficient
Constant	-	-10.89
A	-0.33	-0.16
B	0.07	0.04
C	-1.30	-0.65
AB	-0.05	0.02
AC	0.07	-0.03
BC	0.33	0.16
ABC	-0.06	-0.03
Center Points		-0.042

In other words, the PZT thin film can be designed with special emphasis on the leakage current. The concurrent capacitance and breakdown voltage can be estimated to be independent of the processing conditions. Therefore, the optimization on the output parameters can be achieved only by focusing on the leakage current. In order to elucidate the microstructural feature in PZT thin films, one of the specimens, i.e., Run 9 was characterized using Secondary Electron Microscopy. The SEM image of Fig. 7 shows no defects: the dense PZT thin films were deposited using sol-gel processing. The optimized PZT thin films can be applied to the thin film inorganic electroluminescent devices which require superior insulation and high dielectric constants.

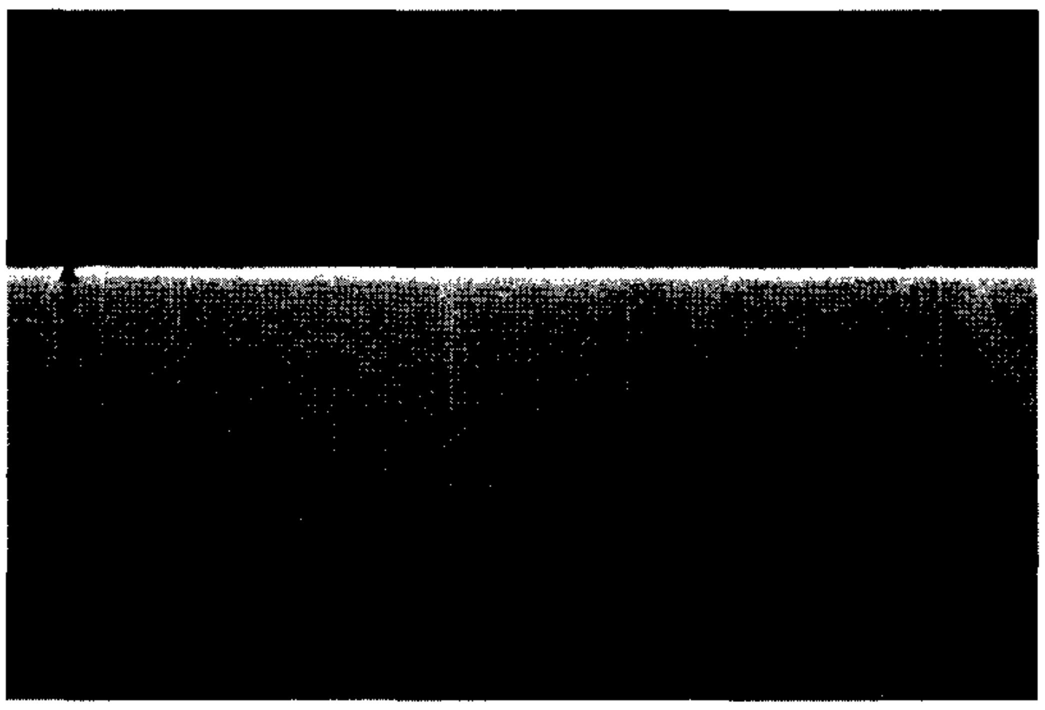

Fig. 7. Cross-sectional image of a PZT thin film (of Run number 9).

4. CONCLUSION

High-quality PZT thin films were deposited on ITO-coated glass substrates. The electrical/dielectric features were estimated using current-voltage measurements and capacitance measurements. The leakage current was found to be controlled by annealing temperature. However, the breakdown voltage and capacitance were not affected by the processing variables. The superior feature of high-dielectric constant in thin films can be combined with the high-brightness in inorganic electroluminescent display devices. Furthermore, the cross-sectional image revealed defect-free thin films without high fraction of pores.

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