MEASURING BIMODAL CRYSTALLOGRAPHIC TEXTURE IN FERROELECTRIC $PbZr_xTi_{1-x}O_3$ THIN FILMS

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ABSTRACT

A powder x-ray diffraction method has been developed to quantify textured volume fractions in thin films. It has been applied to {111}, {100} and randomly oriented $PbZr_xTi_{1-x}O_3$ in 200 nm thick films used for ferroelectric random access memory applications. The integrated and peak intensities of 100, 110, 200 and 222 Bragg peaks from an untextured PZT film were determined by applying a thickness correction to a θ-2θ scan obtained from random powder of the same composition as the film. X-ray scans were made on the same peaks from the PZT film specimens. The distributions of grain orientation for the {111} and {100} populations in the films were determined from ω scans which were obtained from the films using 100, 200 and 222 scattering angles and corrected for defocussing and absorption. To determine the total volume fraction of each population of grains, the ratios of the integrated film peak intensities to the corrected powder integrated peak intensities were multiplied by the integrals of the corrected ω scans.

INTRODUCTION

Many thin film materials exhibit properties that depend on the crystallographic texture of the film. It has been shown by several authors that a correlation between processing properties and texture exists for ferroelectric thin films [1-3]. In order to develop physical models that relate texture to ferroelectric properties it is necessary to have a method that can quantify the volume fraction of textured material within a film. Without this quantification it is difficult to separate the effects of texture from other changes in film structure, e.g., grain size and density, that can also strongly influence ferroelectric performance. Previous work has shown that $PbZr_xTi_{1-x}O_3$ (PZT) thin films often consist of {100}, {111} and random textures. A method for determining the volume fraction of each type of texture using x-ray diffraction (XRD) θ-2θ scans was developed by Fox [4]. This method required several assumptions in order to calculate the volume fractions from the XRD integrated peak intensities. This paper presents an improved measurement and analysis method for determining textured volume fractions. For this method ideal texture is not assumed (as in Fox) but instead the texture profiles, the angular distributions of the textured crystallites, are measured and explicitly incorporated into the analysis.

EXPERIMENTAL

A θ-2θ scan was obtained from randomly oriented $PbZr_{0.4}Ti_{0.6}O_3$ powder doped with La, Ca and Sr. The peak centroid ($2\theta_H^R$), peak intensity (P_H^R) and integrated intensity (I_H^R) of each hkl Bragg peak (hkl≡H) were determined. The powder spectrum had many overlapping peaks, and the integrated intensities for these peaks were found by fitting a Pearson VII function to each Bragg peak. Film specimens with a thickness of 200 nm and having the same composition as the powder were prepared by RF magnetron sputtering onto 150 mm diameter Si/SiO_2 (600nm)/Ti (20 nm)/Pt (175 nm) substrates. The films were crystallized by rapid thermal annealing at 725 °C

for 20s in flowing O_2. Two specimens, taken from the center and edge regions, respectively, of the PZT-coated wafer were analyzed. A θ-2θ scan from each specimen showed both {100} and {111} texture. For the random powder, 101 was the strongest peak, but for the films the 101/110 doublet was either extremely weak and not resolvable, or non-existent, consistent with the film containing little or no random material. Higher resolution scans of the 100, 101/110, 200 and 222 film lines were obtained; the 101/110 doublet was measured to characterize the random material. The 111 peak was not measured because it overlapped with the 111 peak from the Pt substrate; the 222 peak was more separated. The film peak centroids ($2\theta_H^F$), peak intensities (P_H^F) and integrated intensities (I_H^F) were determined. Using the $2\theta_H^F$ scattering angles for 100, 200 and 222, ω-scans were obtained from the films. For each ω scan, the background was measured with an ω scan using a scattering angle about 2° from the Bragg peak position; the background was subtracted from the Bragg peak ω scan to give the intensity profiles, $P_H^F(\omega)$. All the x-ray data were collected using a powder diffractometer with monochromatic $CuK\alpha_1$ radiation .

THEORY

The central assumption of any XRD texture analysis is that the integrated intensity of a Bragg peak is proportional to the volume fraction of material diffracting into that peak. Let the volume fraction of H-oriented grains in random powder be F_H^R. Following Warren [5], we can write the integrated H intensity:

$$I_H^R = C_H F_H^R p_H \tag{1}$$

where p_H is the multiplicity of reflection H, and C_H is a constant depending on H and the diffractometer settings. To compare with intensities from a film t thick, the peak and integrated intensities from a random powder are corrected for film thickness and density:

$$\begin{aligned} I_H^R{}' &= I_H^R A_H \\ P_H^R{}' &= P_H^R A_H \end{aligned} \tag{2}$$

where $A_H = 1 - \exp(-2\mu t / \sin\theta_H^R)$ and μ is the x-ray linear absorption coefficient.

We assume that a non-zero I_{101}^F is entirely due to the presence of a randomly oriented volume fraction in the film. The random fraction contributes integrated intensity, I_H^{FR}, to each textured peak from the film so that each total integrated intensity from the film, I_H^F, is a sum:

$$I_H^F = I_H^{FR} + I_H^{FT} \tag{3}$$

where I_H^{FT} is the integrated intensity due to the textured grains. The random integrated intensities from the powder and film are in direct proportion so that:

$$I_H^{FR} / I_{101}^{FR} = I_H^R{}' / I_{101}^R{}' \qquad \text{for any peak H} \tag{4}$$

Compared to the thickness-corrected integrated intensity from the random powder, $I_H^R{}'$, the integrated intensity for the textured portion of the film, I_H^{FT}, is divided by the multiplicity factor because only one of the p_H sets of planes in the H-oriented grain population contributes to I_H^{FT}. The volume fraction of H-oriented material in the film is $M_H(0)$ times the H-oriented volume fraction in the powder; thus, $M_H(0)$ is the preferred orientation of the PZT grains in units of multiples of a random distribution (MRD). Therefore:

$$I_H^{FT} \big/ (A_H I_H^R) = M_H(0) / p_H \tag{5}$$

Combining (3), (4) and (5) and solving for $M_H(0)$ gives:

$$M_H(0) = p_H\left\{\frac{I_H^F}{I_H^R A_H} - \frac{I_{101}^F}{I_{101}^R A_{101}}\right\} \quad (6)$$

For the random fraction of the film, the MRD value, M_{rand}, is the ratio of the integrated intensity for the film to the thickness-corrected integrated intensity for the powder and is given by:

$$M_{rand} = I_{101}^F / (I_{101}^R A_H)\,. \quad (7)$$

$M_H(0)$ gives the volume fraction of the PZT film that is exactly H-oriented. This is the volume fraction calculated using only information from the θ-2θ scans from the powder and the film, as done by several authors[1-3]. The ω-scans, $P_H^F(\omega)$, show how the texture of the film varies as a function of angular deviation from exact H alignment, and they provide more complete texture information. The film texture is assumed to be axisymmetric; thus $P_H^F(\omega)$ is independent of specimen orientation about the film normal. The raw ω scans are corrected for absorption and defocus by calculating the random ω scan from the θ-2θ scan of the H peak and dividing $P_H^F(\omega)$ by the calculated random scan [6]. The corrected ω scans are denoted $P_H^F{}'(\omega)$; they contain a random contribution which is constant over ω, P_H^{FR}, so that:

$$P_H^F{}'(\omega) = P_H^{FT}{}'(\omega) + P_H^{FR} \quad (8)$$

To find the random contribution to the film peak intensity, P_H^{FR}, we assume that the ratio of the integrated intensity to the peak intensity (the peak integral breadth) is the same for both textured and random contributions to H, i.e. $I_H^{FR} / P_H^{FR} = I_H^F / P_H^F$. Substituting for I_H^{FR} from eqn. (4):

$$P_H^{FR} = P_H^F \frac{I_{101}^F}{I_H^F}\frac{I_H^R{}'}{I_{101}^R{}'} \quad (9)$$

The MRD profile of H-oriented grains as a function of ω, $M_H(\omega)$, equals $P_H^{FT}{}'(\omega)$, normalized to equal one at ω = 0 and multiplied by $M_H(0)$:

$$M_H(\omega) = M_H(0)\frac{P_H^F{}'(\omega) - P_H^{FR}}{P_H^F{}'(0) - P_H^{FR}} \quad (10)$$

For a random material, the volume fraction oriented between ω and ω+dω, $V_R(\omega)$, is given by:

$$V_R(\omega)\,d\omega = 2\pi \sin\omega\, d\omega / 4\pi \quad (11)$$

The volume fraction of the H component of the film oriented at ω, $V_H(\omega)$, is given by:

$$V_H(\omega) = M_H(\omega) V_R(\omega) \quad (12)$$

The total volume fraction of H-oriented material, V_H, is found by integrating $V_H(\omega)$ from ω = 0 to π. With a 2-circle diffractometer the ω scan is limited to +/- θ_H, but if $P_H^F{}'(\omega)$ falls to P_H^{FR} within this range, $V_H(\omega)$ is zero above that angle. We plot $P_H^F{}'(\omega)\sin\omega$; this rises from 0 at ω = 0, peaks, and then falls to a minimum at ω_o. It rises again if there is random material in the film such that $P_H^{FR} \neq 0$. We set the upper limit of integration in eqn.(11) to ω_o. Thus:

$$\begin{aligned} V_H &= \frac{M_H(0)}{2\left(P_H^F(0) - P_H^{FR}\right)}\left\{\int_0^{\omega_o} P_H^F{}'(\omega)\sin\omega\, d\omega - P_H^{FR}(1 - \cos\omega_o)\right\} \\ &= M_H(0)\, X_H \end{aligned} \quad (13)$$

V_H measures the H-oriented volume fraction in the range 0 < ω < ω_o. The term X_H is the integral of the intensity from the H-textured material over all orientations (based on the assumption of axisymmetric texture) divided by the peak intensity from the H-textured material,

and it is a measure of the breadth of the texture distribution, analogous to the integral breadth of a Bragg peak. For a given $P_H^F{}'(\omega)$ profile shape, X_H scales with the square of the full width at half maximum height (FWHM) of the profile, and therefore knowledge of the profile shapes for each textured volume fraction is essential to the correct quantification of the volume fractions. V_{rand} is calculated from the assumption that $V_{rand} = V_{101}$; using eqn. (12) with $P_{101}^F{}'(\omega) = P_{101}^F(0)$, $P_{101}^{FR} = 0$ and $\omega_o = \pi$, we find that $V_{rand} = M_{rand}$. The volume fraction sum, $V_{TOT}\,(= V_{100} + V_{111} + V_{rand})$ should equal 1, but in experiments to date has been somewhat larger (1.5 to 3.0); this is currently under investigation. The volume fractions are normalized to give V_H^{norm} :

$$V_{100}^{norm} = V_{100} / V_{TOT}; \qquad V_{111}^{norm} = V_{111} / V_{TOT}; \qquad V_{rand}^{norm} = V_{rand} / V_{TOT}. \qquad (13)$$

RESULTS AND DISCUSSION

Figure 1 shows the raw ($P_H^F{}'\omega)$) and corrected ($P_H^F{}'\omega)$) 100 ω scans from the center specimen and demonstrates that the corrections for the raw data are significant: the raw profile is narrower, and it is skewed to negative ω whereas the corrected profile is almost perfectly centered, at ω=0.01°; and the correction factor is 2.5 at ω = ±5°, rising to over 10 at higher ω values. Thus, except when the film is highly textured, simple ω scans are not adequate to characterize the texture, particularly as the corrections depend on the scattering angle of the Bragg peak, being greatest for low Bragg angles. Figure 2 shows the corrected ω scans ($P_H^F{}'(\omega)$) for 100, 200 and 222 peaks from the center specimen, scaled to have the same $P_H^F{}'(0)$ intensity. The corrected 100 and 200 profiles are very similar, confirming the validity of the correction algorithms [5], but the 200 data extend to higher ω in Fig. 1, due to the higher 200 Bragg angle, and therefore the 200 data were used for the calculations of textured volume fractions. The profiles for 200 and 222 are different in shape in that the 222 profile has a lower full width at half maximum intensity but extends out to higher ω values. As will be seen, although the 200 and 222 profiles are different in shape, the texture breadth parameters, X_{200} and X_{222}, are similar.

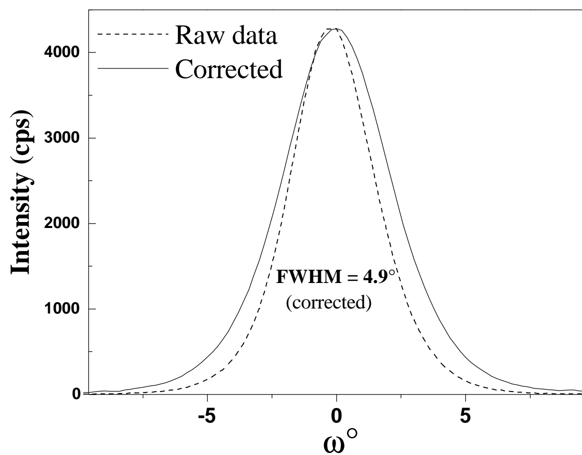

Figure 1: Raw and corrected 100 ω scans from wafer center

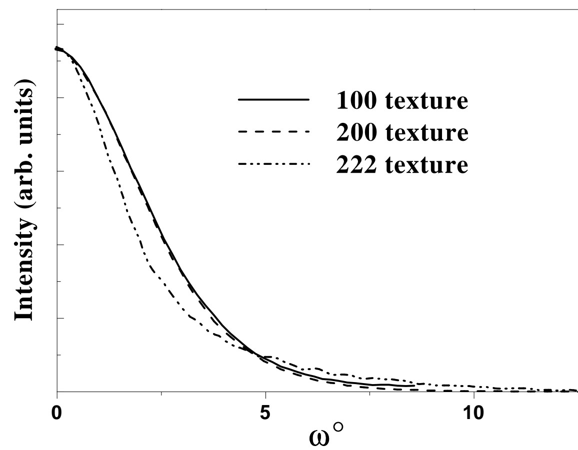

Figure 2: Scaled 100, 200 and 222 texture profiles from wafer center

Table I: Integrated intensities from random PZT powder

hkl	Integrated peak (cps°)	Corrected for t = 200nm	Multiplicity p_H	hkl	Integrated peak (cps°)	Corrected for t = 200nm	Multiplicity p_H
001	50.9	11.6	2	111	98.2	13.4	8
100	64.0	14.3	4	002	63.6	7.7	2
101	408.2	67.6	8	200	107.7	12.8	4
110	159.0	26.0	4	222	21.5	1.5	8

A θ-2θ scan was obtained from the random PZT powder. The integrated intensities of the 001, 100, 101, 110, 111, 002, 200 and 222 peaks, I_H^R, were found by direct integration of the data, or by curve fitting for overlapping peaks such as 100 and 001. They are listed in Table I, together with the intensities corrected for the thin film factor as in eqn.(2), $I_H^R{}'$, and the multiplicities of these peaks, p_H.

Table II lists the integrated and peak intensities from the film specimens, I_H^F and P_H^F, for the 200 and 222 Bragg peaks. Equation (6) is used to calculate the $M_H(0)$ values which are normalized in the next column. The texture breadth values, X_H, calculated using eqn.(12), and the normalized volume fractions, V_H^{norm}, are given in the next two columns. The last three columns contain I_{101}^F from which M_{rand} (eqn. (7)) and V_{rand}^{norm} (eqn.(14)) are calculated. The measurements were carried out twice on both specimens and for each specimen the volume fraction results from the two sets agree well. Thus, in this case, the technique yields results that are repeatable to 8% or better for the smaller volume fraction and 3% for the larger. The results show that both specimens are primarily {111} textured, with a smaller volume fraction of {100} material and between 2% and 3% of random material in the center specimen but no random material in the edge specimen. The {100} fraction is about twice as large in the center of the wafer as at the edge. The random fraction of 0.35% shown for one of the edge specimen results is not reliable as the 110/101 film peak barely exceeded the noise level.

Table II: Integrated and peak intensities and calculated texture values for PZT film specimens

hkl	I_H^F cps°	P_H^F cps	$M_H(0)$	$M_H(0)$ norm %	X_H	V_H^{norm} %	I_{101}^F	M_{rand}	V_{rand}^{norm} %
			Center specimen - data set 1				3.3	0.034	2.0
200	1126.7	2272.1	351.2	17.5	0.00072	15.1			
222	305.0	351.1	1651.8	82.5	0.00084	82.8			
			Center specimen - data set 2				3.7	0.038	2.6
200	1173.1	2110.1	365.9	18.9	0.00074	18.2			
222	290.0	346.7	1570.4	81.1	0.00075	79.2			
			Edge specimen - data set 1				0.0	0.0	0.0
200	485.00	824.8	151.1	6.9	0.00078	8.2			
222	375.80	454.0	2035.0	93.1	0.00065	91.8			
			Edge specimen - data set 2				1.0	0.0103	0.35
200	516.7	777.0	161.0	7.4	0.00084	9.2			
222	373.0	425.7	2019.4	92.6	0.00066	90.4			

Most of the PZT peaks are multiplets, and therefore the intensity of any individual peak is difficult to determine with high accuracy, even with curve fitting techniques, which rely on specific functions fitting the peak profiles accurately. The spectra from the films also contain 111 and 222 Pt peaks which are more intense than the PZT peaks by at least one order of magnitude. Curve fitting showed that the Pt/PZT peak overlaps did not affect the ω scans significantly but did reduce the accuracy of the I_H^F values for 200 and 222. The accuracy of the volume fractions determined by this technique, particularly in the case where there is a large random fraction, has not yet been rigorously analyzed but peak overlap is clearly one of the major sources of errors (as it is with any diffraction texture analysis). The lack of standard thin film specimens with known texture properties is also an impediment to a full error assessment.

The agreement between the {100} and {111} volume fractions determined by peak integral ratios ($M_H(0)$ norm%) and the full analysis (V_H^{norm} %) is relatively good in this case, primarily because X_{200} and X_{222} differ by at most 25% and the films have a large majority of one orientation, {111}. In situations where the differently textured volume fractions are similar in size, small differences in the FWHM of the corrected ω scans produces significant differences in the X_H term as discussed above. For an example of this, see Fig.3 in reference 6; further analysis of the data from the BST thin films presented in this paper shows that the {110} volume fraction based on peak integrals is underestimated by 50% compared with the full volume fraction analysis presented here. In a specimen with a significant random fraction, the random fraction cannot be determined with any accuracy solely from peak integral ratios because X_{rand} is by definition one and is therefore more than three orders of magnitude larger than X_{200} and X_{222}. This work has shown that in the general case, quantification of volume fractions of textured material requires analysis of the orientation distribution in each textured volume fraction, especially when the degree of preferred orientation is different in the textured volume fractions, or the differently oriented volume fractions are similar in size.

CONCLUSIONS

A technique for quantifying the relative abundances of specific preferred grain orientations in a thin film using a powder x-ray diffractometer has been described. The x-ray peak intensities from the film and from a random powder with the same composition as the film were measured. The texture profiles of the grain populations with different preferred orientation directions were measured taking absorption and defocus into account. The volume fractions were determined from the ratios of the integrated intensities from the random powder and the film in conjunction with the texture profiles. The technique has been applied to PZT films.

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