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X- RAY DIFFRACTION OF FERROELECTRIC PZT THIN FILMS

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انحراف الأشعة السينية من أفلام دقيقة ذو إستقطاب كهربي عفوي والأفلام مكونة من (PZT)

ملخص: يتعلق هذا البحث باستخدام انحراف الأشعة السينية (X-ray) في أفلام الكهروحديدية الدقيقة والمكونة من عناصر تيتانيت ، زيكرونيوم والرصاص بنسب مختلفة والمعروفة باسم (PZT).
من هذه الطريقة تم تحديد موقع الشوائب الغير معروفة وأيضاً اتجاه الذارات (111) تم إيجاده لكل فيلم .

Abstract: In this paper, the x- ray diffraction were taken for different ratios of Ferroelectric Lead Zirconate Titanate (PZT) thin films. From this method, the (PZT) locations were defined and the (111) orientations were found for each film.

Introduction

Lead -Zirconate -Titanate (PZT) ceramics and its doped variants show very interesting and useful ferroelectric, electro -optic and piezoelectric properties [1,2]. PZT films have many applications due to their high electromechanical coupling cbefficients,K., and high relative dielectric constants (ε_r). Recently, thin films offerroelectric materials have become of great interest in device applications such as piezoelectric vibrators [3], surface acoustic wave (SAW) devices [4], pyro lctric detectors [5], and nonvolatile random access memories [6]. Ferroelectric materials exhibit spontaneous electric polarization, the direction may be switched by applying a sufficiently large electric field. Just as ferromagnetic as well exhibit hysterics in the relation between magnetism and applied magnetic field, ferroelectric materials exhibit hysteresis in the relationship between polarization (P), and the applied electric field (E), [10,15]. A second property of ferroelectric materials is that as the temperature increases, the magnitude of the spontaneous polarization decreases, and finally disappears at a critical temperature, called the Curie temperature (T_c). The change in electrical properties, from ferroelectric to paraelectric, is typically the result ofa structural phase change that occurs at T_c [12,14]. Ferroelctric ceramics are of particular interest because they are chemically and mechanically stable at

room temperature, and relatively easy to prepare in the form of polycrystalline samples [10,13]. The most important ceramic ferroelectrics crystallizes ... in the perovskite structure, which can be described as a simple cubic unit cell with a Pb^{2+} cation at the corners, a Ti^{4+} or Zr^{4+} cation in the body center and O^{2-} anions at the face - center [11,13]. The structure offerroellectric ceramics below the Curie temperature becomes slightly distorted -typically along a principal axis or the body diagonal, due to that, the center cation is not stable at the center of the unit cell. It has energy minima in two distinct positions, ± x, from the center along the direction of distortion [8]. The center cation may be moved to either minimum (switched) by applying an electric field in that direction. The ferroelectric properties of these crystals arise from the switchable dipoles formed by the displacement of the center cation with respect to the negatively charged oxygen octahedron [8,13].

The films were prepared by the pulse laser deposition (PLD) technique, the most promising characteristics of the laser ablation method are the following:(I) there is insignificance difference in the composition between the target material and the deposited film. (2) Small targets can be used which may be made relatively easily. (3) Deposition in a high oxygen pressure is possible because of the absence of energy sources such as filaments for the electron emission, heaters for the evaporation, or discharge electrodes in the system. (4) The vacuum system and controlled atmosphere are independent of the

laser apparatus. (5) Even materials with a high melting point can be easily deposited if the material strongly absorbs the laser light, [7,9].

Experimental.

The films were prepared by the pulse laser deposition (PLD) technique. During the PLD process a short pulse light enters the deposition chamber through a window and impinges on a target of the material to be deposited. A few hundred angstroms of the target surface is vaporized into a cloud of material (plume), which expands in the chamber and is deposited onto a substrate placed in front of the target. A frequency tripled, Q switched Nd-YAG laser produces7 ns pulses of 35nm (UV) light at *a frequency of 10 Hz. The energy output is 200 mJ/pulse yielding an energy of ~ 0.8 J/cm*^{2} per pulse when the beam reaches the target. The beam passes through a quartz lens (f =100cm) and is reflected by a dielectric mirror positioned at 45

degrees to the beam. Finally the beam passes through a quartz window into the chamber and onto the target. The mirror is mounted on a programmable position controller that rotates about two ... perpendicular axes. This allows the beam to be aimed at various positions on the target: typically it raster across the target. The target is mounted on rot table post, which allows several targets to be mounted simultaneously. The substrate is mounted on a rot table *J heater block placed in front of the target. The substrate temperature may be set from room temperature up to 900 °C. The oxygen partial pressure (pO) or atmospheres in the chamber during deposition may be controlled using gas flow regulators.*

A small section of the substrate was masked off during deposition to allow an , access to the bottom Pt-electrode. An array of 50x50 -um top Pt-electrodes was formed using photolithography and DC-sputtering described in elsewhere [7,8,9].

PLD method used to grow different films of approximately 0.3 J.um thick of $PbZr_{o.55}$ *Tio.45O3* (PZT -55/45), $PbZr_{O}$.6S *Ti0.35* (PZT- 65/35), PbZrO.7S *Tio.2sO3* (pZT - 75/25), and $PbZr_{O.8S}$ *Tio.1SO3* (pZT- 85/15). These films were deposited using targets with 30% excess PbO, on Pt -Ti -SiO_2 -Si substrates held at 605 C^{O} in 300 mTorr of 0_2 with target -substrate distance of ~ 3 cm between the two surfaces. The Zr/Ti ratio was achieved by means of a novel technique for depositing compositionally varied multi - layer structures [13,15].

The film' s dimension are approximately 2 by 2 cm. The films were placed on the top of clay fixed on a plastic holder, then they were mounted horizontally in the radiation protection housing into the D501 Diffractmeter, equipped with a mechanically coupled 2θ and θ drive. This Diffractometer can be used for almost all applications ofx -ray diffraction techniques, such as structure research, phase analysis, and stress. The Diffractometer was used to determine preferred orientations (textures).

The radiation emanating from the line focus of the x- ray tube is diffracted at the specimen (PZT film), and recorded by a solid detector of which has a window of 0. 125mm, resolution less than 260 eV at 0.5V, area of 2x12 mm square, and it is bias at - 500 Volts. The film is rotated at a constant angular speed, whereas the detector moves "-"' I about the film at double the angular speed. The diffraction angle (2θ) is thus always equals to double the

glancing angle (θ). Whenever the Bragg condition is.fulfilled, the primary beam is reflected at the film to the detector. The intensity of the reflected radiation is measured by means of the detector and the connected electronic measuring system, while the angular position of the reflections is indicated at the goniometer. The K13 reflections can be suppressed by means of a filter or the diffracted beam monochromator. In order to define the irradiated film area, two apertures are arranged between the tube and the film. The second aperture shields the strong scattered radiation of the first aperture. A third aperture used to suppress undesired scattered radiation from the PZT film.

Results

The deposition ofhigh quality PZT films required the optimization of various parameters through the systematic adjustment of deposition parameters [8]. An ideal PZT film is phase -pure, (111) -oriented, which is the switching direction for rhombohedral ***J I*** phase, exhibits P -E hysteresis loops of high electrical resistance ($>10^8$ Ω). The primary adjustable parameters include PbO content of the target, substrate temperature, oxygen partial pressure pO2, distance from the target to the substrate, and type of substrate [8,10]. In general each of these parameters affected the chemical composition and phase, crystallographic orientation, thickness, P -E hysteresis loop, and the resistivity of the films to varying degrees [8,13,15].

Figure 1, shows the result of the x- ray diffraction pattern of PZT -85/15 film, which is deviated from an ideal PZT film of phase -.pure, (111) -orientation. The locations and *J the lines are assigned by comparing the results to standard and to the tables. In this film,* the formations of a Pb cause a pyrochlore phase due to the type of substr te. The most influential parameter identified on the formation of this phase was the type of substrate used [10,13]. The substrates consisted of(lll) Pt- coated Si wafers -some containing a Ti layer to facilitate adhesion of the Pt as the samples used in figures 2, 3 and 5. It was found that use of substrates not containing the Ti adhesion layer always resulted in films of the pyrochlore phase. Substrates containing the Ti adhesion layer were less likely to form the pyrochlore phase [8,15].

The excess PbO content of the target also influenced whether or not the pyrochlore was formed [8]. Targets fabricated via traditional powder

processing routes initially containing as much as 30% molar excess PbO were required to avoid pyrochlore, although some of the excess PbO was undoubtedly lost through volatilization during target processing. This film was grown at 250 mTorr and at temperature of 650 C^{O}, which iare out the range of substrate temperatures and oxygen partial pressures needed to grow an -ideal film [8].

Figure 2, shows the x- ray diffraction pattern of PZT -55/45 thin film, as the intensity ,....*J J* counts per second (CPS) versus the 2- θ (degrees), one can see from the figure that the PZT orientation (111) is so large compared to the other PZT orientations and also the pyrchlore is so small. The other peaks also determined the Pt locations. Figure 3 shows the x -ray diffraction pattern of PZT -65/35 film, which is grown on another substrate which contains Ti adhesion layer, again the peaks and the locations are well defined for the PZT and Pt because the ablation parameters are suitable for this ratio.

From figure 4, which is the x- ray pattern of PZT -75/25 film, grown in the same substrate as the PZT -55/45. In fig. 4, there is small pyrochlore compare to the PZT, (111) orientation, this is may be due to chemical composition and crystallographic orientation which results from the pulse laser deposition.

Figure 5 is the x -ray diffraction pattern of the PZT -85/15 film, with no pyrochlore at all in this film, this is due to the proper ablation conditions that are used to grow the film. As mentioned before, the films are grown at 605 C^{O} and oxygen pressure of 300 mTorr.

The x -ray beam penetrated the whole film and into the substrate. It can be seen that the relative intensity of the perovskite (111) peak is so large with respect to that of the pyrochlore peak in all figures except for fig.l. This is an indication that the transformation of the perovskite phase starts at the substrate -film interface and propagates through the film to the surface.

The XRD profile of the films revealed the preferred orientation of single -phase PZT film to (111) as shown in Figures 2 to 5. However, only pyrochlore of low crystallinity was formed as shown in Figures 1,2 and 4.

Conclusion

X -ray diffraction technique is a proper way to find the impurities and locate the exact position of the orientations in the grown PZT thin films with different ratios of Zr/Ti. The (111) -oriented PZT thin films, were found that

the best ablation conditions are of substrate temperatures of605 C^{o} and oxygen pressure of 300 mTorr.

References

1. A.Okade, J.Appl.Phys. 48 (1977) 2905.
2. ChiK. Kwok, Seshu B. Desu and Lee Kammerdiner, Mat.Res.Soc.Symp.Proc. Vol.200 (1990) 83.
3. V. Kushida and H. Takeuchi, Appl.Phys.Lett. 50, (1988) 1800.
4. K.Sreenivas and M.Sayer, J.Appl.Phys. 64, (1988) 1484.
5. K. Iijima, Y. Yomita, R. Takayama, and I. Veda, J. Appl. Phys. 60, (1986) 361.
6. J. F. Scott, J. Appl. Phys. 64, (1988) 1666.
7. H. Kidoh, T. Ogawa, A. Morimoto and T. Shimizu, Appl. Phys. Lett. 58 (1991) 2910.
8. S. M. Musameh accepted at Najah Research Journal.
9. B.E. Watts, F. Leccabue, G. Bocel1i, G. Calestani, F. Calderon, 0. de Melo, P.P. Gonzalez, L. Vidal and D. Carrillo, Materials Lett. Vol. 11, No.5, 6,7 (1991) 183.
10. J.F. Scott, Ferroelectrics review 1, (1998).
11. D.M. Smyth, Ferroelectrics 151, (1994) 115.
12. I.K.Yoo, S.B. Desu, and J. Xing, Mat. Res. Soc. symp.proc.310, (1993) 1231.
13. M. Brazier, M. McElfresh, and S. Mansour, Appl. Phys. Lett. (a) *72, (1998) 1121.*
14. R. Dat, J. K. Lee, 0. Auciello, and A. I. Kingon, Appl. Phys. Lett. 67, (1995) 572.
15. M. Brazier, M. McElfresh, and S. Mansour, Appl. Phys. Lett.74, (a), .(1999) 299.

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