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Effect of Pressure and Temperature on Preparing PZT Films

تأثير الضغط ودرجة الحرارة على تحضير أفلام رقيقة من الرصاص والزركونيوم والتيتانيوم

Sharif Musameh

Physics Department, Faculty of Science, An-Najah National University, Nablus, Palestine.

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Abstract

Ferroelectrics lead zirconate titanate (PZT) thin films were fabricated by pulsed laser deposition on Pt coated Si substrate. The effect of oxygen partial pressure, substrate temperature and time of ablation on the film orientation and composition will be presented. It was found that highly (111) textured PZT films could be grown with careful selection of ablation conditions which are: the oxygen pressure is 300 mT, substrate temperature is 605 C and the ablation time is 16 minutes.

ملخص

الأفلام الرقيقة والمكونة من عناصر التيتانيوم، الزركونيوم والرصاص (PZT) والتي تمّ تحضيرها بواسطة الترسيب الموجي باستخدام الليزر على شرائح بليتنيوم (Pt) والمطلي بالسيليكون (Si)

تركز الدراسة على تأثير الضغط الجزئي للأكسجين ودرجة حرارة الشريحة وزمن التعريض لليزر على اتجاه الإحداثيات للأفلام الرقيقة وعلى طبيعة تركيبة الشريحه.

لقد خلصت الدراسة إلى ان اتجاه احداثيات [111] لأفلام (PZT) يُمكن أن يتم تحضيرها تحت الشروط التالية وهي أن يكون الضغط الجزئي للأكسجين 300 ميلي تود وأن حرارة الوسط للفيلم هي 605 درجة مئوية ومدة الترسيب 16 دقيقة.

Introduction

Lead zirconate titanate $PbZr_{1-x}Ti_xO_3$ (PZT) ceramics and its doped variants show very interesting and useful ferroelectric, pyroelectric, elecctro-optic and piezoelectric properties[1]. Ferroelectric is a class of nonlinear dielectric that exhibit an electric field dependent dielectric constant [2]. There is a considerable interest in these thin films because of their potential for low operation and low cost processing [1-3]. Remnant polarization in thin films of PZT is of considerable interest in nonvolatile memory applications, optical image storage devices, optical modulators, optical switches and other applications[3,5,6,8] .

PZT ferroectric memory capacitors have been synthesized by different film deposition techniques including sol – gel deposition [4, 6], sputtering [7-9], and metallo – organic chemical vapor deposition [10-11], and pulsed laser deposition [12-13]. In the work reported here, pulse laser deposition (PLD) is the method of choice because it has a primary advantage over other physical vapor deposition methods (evaporation, sputtering, etc.) in its ability to deposit high quality films of complex metal oxide materials which relative ease. PLD has been widely used since the late 1980’s as the preferred method to obtain high Tc super conducting thin films. PLD is selected since it leads to highly oriented and finer microstructure PZT films [9,13,20].

If the structure of ferroelctric distorted along the principal axis or the body diagonal, then the center cation is not stable at the center of the unit cell. Rather it has energy minimal in two distinct position ± from the center along the direction of the distortion. The center cation may be moved to either minimum (switched) by applying moderate electric field in that direction. The feroelctric properties of these crystals arises from the swithable dipoles formed by the displacement of the center cation with respect to the negative charged oxygen octahedron. The polarization of the crystal can be written as $P = \pm Nqx$, where N is the number of unit cell in the crystal, q is the charge on the center ion, and x is the displacement of the center cation with respect to the oxygen octahedron. In rhomboheral PZT, the center cation has energy minimal along the body diagonal, which defines the switching axis [4,9,15,18-19]. In this paper, the attention is focused on the effect of oxygen pressure of PLD deposition and substrate temperature on film growth rate and on its composition.

The reason for this study is to obtaine the (111) plane because it is the most important ferroelectric crystallize in the perovskite structure, which is the simple cubic unitcell with a large cation on the corners, small cation in the body center and oxygenat the face center. The center cation may be moved to either minimmum (switched) by applying an electric field in that directin and this could has many application in the technology and the industry.

Experiment

Pulsed laser deposition (PLD) has been used to deposit good quality thin films including such as ferroelectrics, superconductors, and piezoelectric films. 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 produces 7 ns pulses of 35 nm (UV) light at a frequency of 10Hz. The energy output is ~ 200mJ/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 a quartz window into the chamber and onto the target. The mirror is mounted on a programmable position controller who rotates it 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 rotable post, which allows several targets to be mounted simultaneously. The substrate is mounted on a rotable heater block placed in front of the target. The substrate temperature may be set fromroom temperature up to 900 C. The oxygen partial pressure (pO_2) or atmospheres in the chamber during deposition may be controlled using gas flow regulators.

PZT films with Zr/Ti ratios of 55/45, and 85/15 (refereed to as PZT – 55/45 and PZT -85/15, respectively) were deposited using pulsed laser ablation on substrate held at different temperatures and oxygen pressures.

A small section of the substrate was masked off during deposition to allow an access to the bottom Pt – electrode. An array of 50x50-μm tops, Pt- was formed using photolithography and sputtering [9,16-17].

The effect of oxygen partial pressure and temperature on growing PZT films on Pt- coated Si substrates was investigated by X – ray diffraxtion (XRD). A Seimen's DIFF 300 X – ray diffractometer was used.

Results and discussion

In this paper, the effect of oxygen partial pressure and temperature in growing PZT films of substrate Pt-coated Si was investigated by x-ray diffraction. PZT films were synthesized by PLD using different ablation conditions. These include ablation time, substrate temperature during ablation and oxygen partial pressure inside the chamber. Another parameter that could influence the growth process is the nature of the substrate. In this study we used Pt/Ti/SiO_2/Si substrate to grow all films reported in the paper. Figure 1. Shows X-ray diffraction pattern of the substrate prior to film deposition which is showing lines intensities versus the 2- Thetaθθ (θ) diffraction angle for one of the substrate which was used to grow the PZT films. The diffracted lines shown are Pt (111) and (200) at 40.05° and 43.79° respectively, in addition to Si (001) at 37.67°

The fact that a strong Pt (111) reflection [3,6,9] is shown indicates a very high (111) orientations of Pt film. The choice of Pt substrate on Si has to do with the switching phenomenon in PZT ferroelectrics films. PZT in the rhombehedral phase has a switching direction along the (111) direction of the unit cell [3,9,17]. It is also as important to obtain a single perovskite phase when PZT films are grown. Any amount of the undesired pyrochlore phase [1,8] will reduce the film unswitchable.

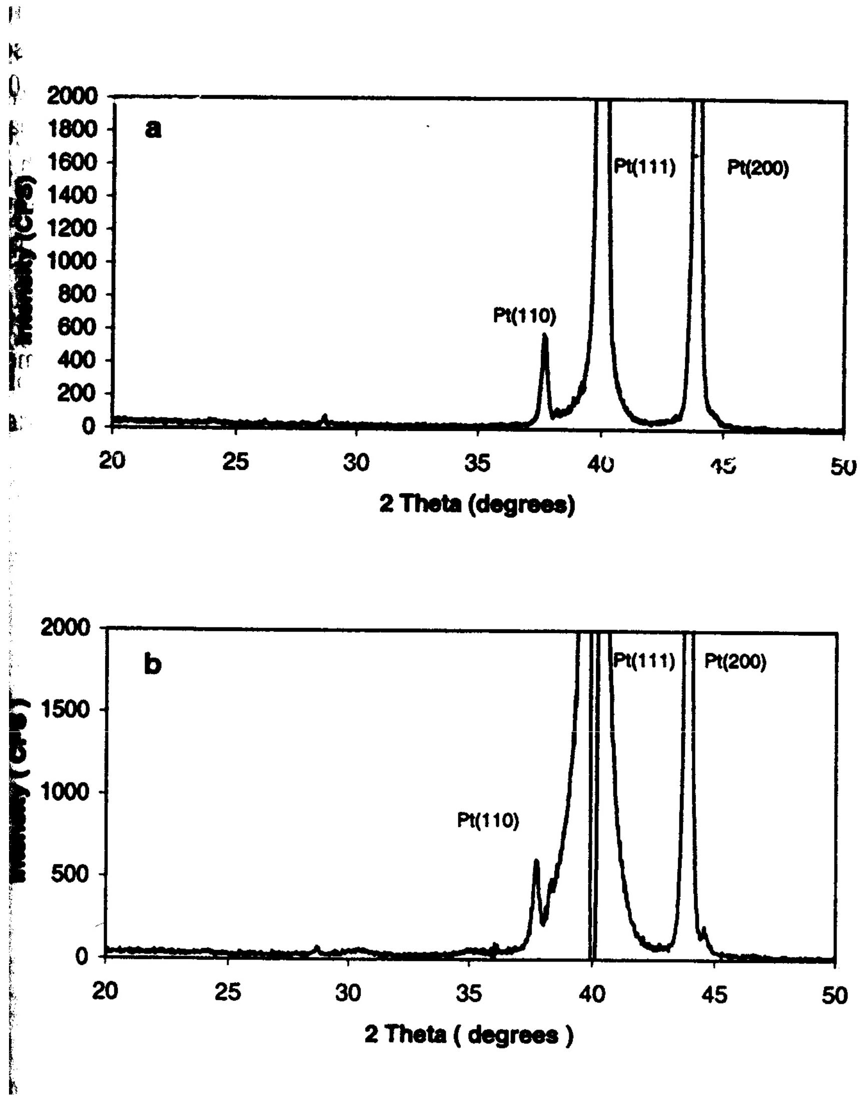

Figure 1: X – ray diffraction for the Pt /Si substrate only used for the PZT – 85/15 and PZT – 55/45 composites as shown in **a** and **b** respectively.

Figure 2. Shows the X – ray diffraction of the PZT 85/15 films grown at 605°C and 620°C temperature, with 300-mTorr oxygen partial pressure, while ablation time was kept to 6 minutes. The major phase detected was the pyrochlore phase with a small amount of PZT. Such film will be of no use since pyrochlore is present in a large proportion of the film composition. It is also worth noting that PZT (111), (110) and (100) peaks are present. The relative peak intensities PZT phase (i.e. I_{111} / I_{110} / I_{100}) are 100/30/19 for figure 2.a, and for 2.b, 100/88/38. These ratios are small as compared them with the other figures and also there is a pyrochlore phase, which is a clear indication that PZT was grown with limited preferential (111) growth direction. This become clear when PZT films intensities were compared with similar orientation of polycrystalline PZT where relative intensities are (15/100/12) from JCPDS films- International Center for Diffraction Data[9,13]. We can say here that the thermal energy needs more time to overcome the binding energy for the atoms in the substrate.

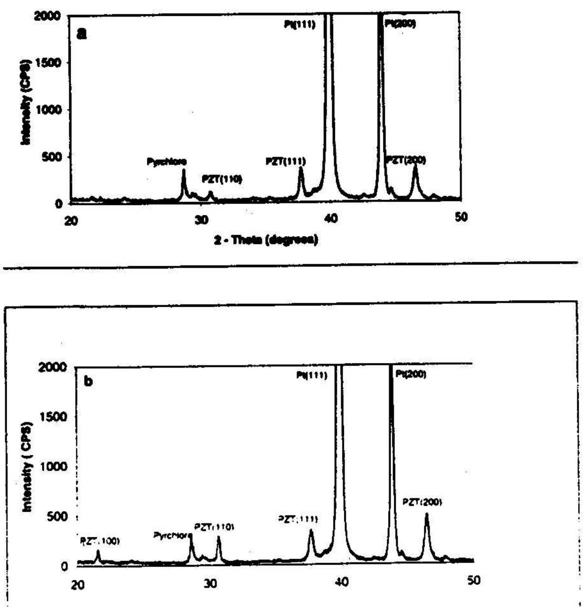

Figure 2: X – ray diffraction for 85/15 composite at temperature 605, 620° C, ablation time 10 minutes and Oxygen Pressure (pO_2) of 300 mTorr as shown in **a** and **b** respectively.

Figure 3, on the other hand shows X–ray diffraction patterns of PZT films grown at 610°C temperature with oxygen partial pressure of 250 and 300 mTorr. The abalation time however, was increased to 10 minutes instead of 6 minutes used earlier. It is clear that the pyrochlore phase disappeared and a higher degree of (111) orientation was achieved. The relative peak intensities were (100/17/30) and (100/15/25) in fig.3 (a) and 3(b) respectively. The above results clearly showed that ablation time longer than six minutes is needed in order for the pyrochlore phase to disappear. This could be attributed to the crystallization time needed for PZT film to grow under these current deposition conditions. A pure pervoskite phase was obtained when ablation time was increased to 10 minutes as shown in figure 3(b). The other observation, which must be noted here, is the effect of time and temperature on film orientation. More (111) orientation was obtained at longer time and at higher oxygen partial pressure in the range of deposition conditions used in this study.

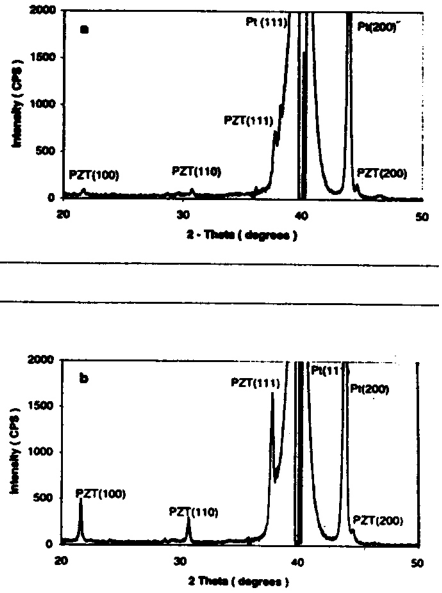

Figure 3: X – ray diffraction for 85/15 composite at temperature 610 C, ablation time 10 minutes, Oxygen Pressure (pO_2) of 250 and 300 mTorr as shown in **a** and **b** respectively.

Similar experiments were also conducted on different PZT compositions. Fig. 4 shows X–ray diffraction pattern of PZT (55/45) grown for 10 minutes, using oxygen partial pressure of 300 mTorr, while the deposition temperature was changed from 605 to 635 C. The relative intensities are ($I_{111}/I_{110}/I_{100}$) = (100/72/120), (100/50/60) for 4a and 4b respectively. This indicates higher (111) orientation with the increase of deposition temperature, which makes the crystallization to take place and to be easier along the other index.

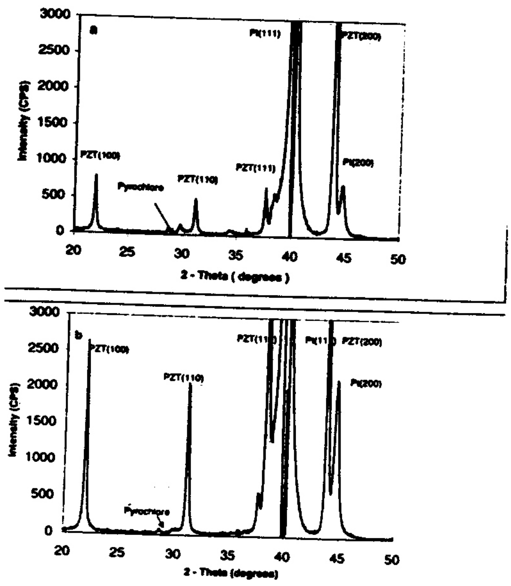

Figure 4: X – ray diffraction for 55/45 composite at temperature 635, 625°C, ablation time 16 minutes and Oxygen Pressure (pO_2) 300 mTorr on Dimos substrate as shown in **a** and **b** respectively.

In figure 5, PZT 55/45 was grown at oxygen pressure of 300 mTorr, ablation time 16 minutes and two temperatures of 615 and 605°C. The relative intensity ratios were (100/24/36) for figure 5a and (100/9/4) for figure 5b. This indicates that the film grown under the previous conditions exhibits the best desirable film orintation for usage in memory applications. This is due to enhanced switching properties along the (111) direction, and these conditions are the best to grow this kind of films, which makes the crysallizations to take place along the desirable orintation.

As we see from the graphs, 5b and 3b are the highest ratios obtained for the 55/45 and 85/15 ratio. The main difference between the two ratios is the ablation time needed, the 55/45 ratio needs more ablation time than the 85/15 ratio because the crysallization process takes more time to take place to overcome the binding energy with this close ratio. It has been observed that the temperature 605C° is the needed temperature to deposite the emitted atoms to the (111) plane because each plane needs specific energy (3/2 KT) to arrange atoms into different planes [16,18].

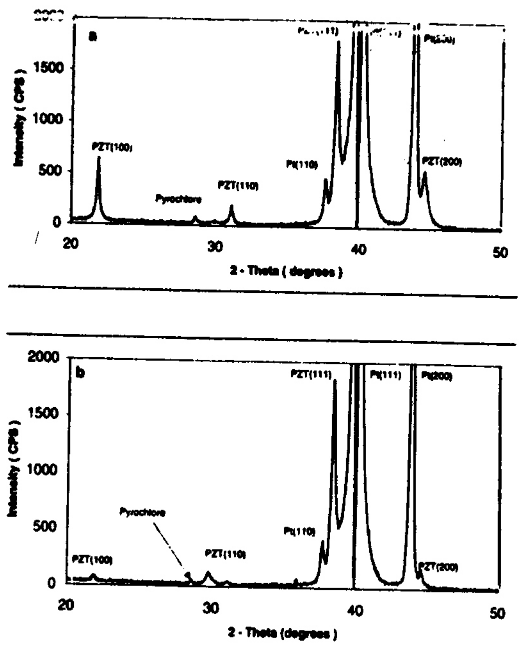

Figure 5: X – ray diffraction for 55/45 composite at temperature 615, 605°C, ablation time 16 minutes and Oxygen Pressure (pO_2) 300 mTorr on Dimos substrate as shown in **a** and **b** respectively.

For the time of ablation, the heat rate of flow (Q) needs time to reach a value which is enough to increase the kintic energy of the atoms to be emitted for the PLD. The rate of the heat flow is not linear with time [16,19-20].

Conclusion

Pure phase PZT films were successfully grown using pulse laser deposition method. Furthermore, highly oriented (111) PZT films could be grown by careful selection of the substrate, the ablation time, substrate temperature and the appropriate oxygen partial pressure. This clearly indicates that PLD could be used to grow PZT films for memory applications. The suitable conditions are 10 and16 minutes for ablation time, 605° C substrate temperature and 300 mT for the oxygen partial pressure.

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