



HAL
open science

Thermal induced changes of Lead Zirconium Titanate films and their consequences for liquid crystal devices applications

Marco Castriota, Stefano d'Elia, Salvatore Marino, Enzo Cazzanelli, Nicola Scaramuzza, Carlo C. Versace, Roberto Bartolino

► **To cite this version:**

Marco Castriota, Stefano d'Elia, Salvatore Marino, Enzo Cazzanelli, Nicola Scaramuzza, et al.. Thermal induced changes of Lead Zirconium Titanate films and their consequences for liquid crystal devices applications. *Philosophical Magazine*, 2010, 90 (16), pp.2223-2233. 10.1080/14786431003630850 . hal-00592299

HAL Id: hal-00592299

<https://hal.science/hal-00592299>

Submitted on 12 May 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**Thermal induced changes of Lead Zirconium Titanate films
and their consequences for liquid crystal devices
applications**

Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-09-Sep-0382.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	05-Dec-2009
Complete List of Authors:	castriota, marco; University of Calabria, department of physics d'elia, stefano; University of Calabria, department of physics marino, salvatore; University of Calabria, department of physics cazzanelli, Enzo; University of Calabria, department of physics Scaramuzza, Nicola; University of Calabria, department of physics versace, carlo; University of Calabria, department of physics bartolino, roberto; University of Calabria, department of physics
Keywords:	devices, electro-optical crystals, ellipsometry, ferroelectrics, films
Keywords (user supplied):	



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Thermal induced changes of Lead Zirconium Titanate films and their consequences for liquid crystal devices applications.

Marco Castriota, Stefano D'Elia, Salvatore Marino, Enzo Cazzanelli, Nicola

Scaramuzza, Carlo Versace and Roberto Bartolino.*

INFN-CNR-LICRYL Laboratory and CEMIF.CAL, Department of Physics, University of Calabria, via

P.Bucci 33B, Rende (CS), I-87036 (ITALY).

CORRESPONDING AUTHOR: scaramuzza@fis.unical.it

Abstract: Thin films of lead zirconate titanate (PZT) have been obtained by a modified sol-gel route on float glass and indium tin oxide (ITO) covered float glass substrates. Different thermal treatments have been performed on the deposited films in the range between 100 to 700 °C. Spectroscopic ellipsometry was used to investigate the optical properties of the deposited films, and the changing optical absorption spectra have been associated to the growth of two different crystal phases, pyrochlore and ferroelectric perovskite, as a function of annealing temperature. Moreover, a specific resonance at 1.9 nm, was detected when thin PZT films are deposited on ITO substrates and has been attributed to a particular charge distribution at the interface. Finally, the performance in rectifying the electro-optical response of asymmetric nematic liquid crystal cells have been tested for some of the films undergoing different thermal treatments.

1. Introduction

1
2
3
4 Electro-optic ceramics are considered very interesting materials for technological applications such as:
5
6 infrared detectors, electro-optic modulators, light-beam switching shutters, waveguides, ferroelectric
7
8 random access memories (FRAM), microelectromechanical actuators [1-3]. Among these materials, lead
9
10 zirconate titanate (PZT) has received great attention because of its ferroelectric and piezoelectric
11
12 properties, coupled to high optical transmittance, low reflectance and strong electro-optic Kerr effect
13
14 [4].

15
16 Due to their good optical properties, PZT thin films have been used recently as electrodes in
17
18 asymmetric nematic liquid crystal (ANLC) cells, where they induce a polarity-sensitive electro-optical
19
20 response of the liquid crystal layers [5]. Such effect has been previously obtained by inserting thin films
21
22 of metal oxides like WO₃ and V₂O₅, well-known for their applications to electrochromism in ANLC
23
24 cells. In fact the combination of electronic and ionic conductivities, typical for the abovesaid oxides, is
25
26 responsible also for the occurrence of peculiar charge distributions at the interfaces of these films inside
27
28 the ANLC cells; such distributions generate internal electric fields able to modify the electro-optical
29
30 effects of applied external fields on the liquid crystal layer [6-9].

31
32 In the case of inserted PZT films a different mechanism has been invoked: the internal field producing
33
34 the electro-optical rectified response should be related to the polarization of ferroelectric PZT [5].
35
36 Besides the recognition of the effect produced by the insertion of PZT films on the electrooptical
37
38 response of ANLC cells, previously reported [5], a further research step is carried out here to have some
39
40 correlation between the amount of the effect and the differences among the PZT films, due to their
41
42 thermal history, with the aim to optimize the application of these films to liquid crystal devices.

43
44 Thin films of lead zirconate titanate can be obtained by different techniques. In this work, they have
45
46 been obtained by sol gel synthesis, since it is one of the more versatile techniques for obtaining large
47
48 area electrodes that are necessary for some technological development. The synthesis method reported
49
50 here represent a modification of the procedures used in previous works [10-12], obtained by changing

Comment [TSF1]: Associate the reference to the specific application that they cover.

the temperature and the processing time. Moreover, a great attention has been given to the study of thermally induced transformations of the as-deposited films. The PZT films deposited on float glass and indium tin oxide (ITO) were annealed at different temperatures, to evaluate the effect of such treatments on the PZT structural morphology. The same kind of thermal treatment have been also performed on the substrates without PZT films to discriminate between thermally induced transformations of PZT films and the ones of the substrates. To gain information about the electronic and optical properties of the different film-substrate systems obtained, ellipsometric spectroscopy has been used. The optical models necessary to fit the ellipsometric data of both the substrates and the PZT layers have been chosen taking into account the main physical and chemical properties of the investigated layers. The float glass substrates were described by an optical Cauchy model for the dispersion law of the refractive index and by the Urbach model for the extinction coefficient, while a Lorentz optical model was used for both the annealed ITO thin films and PZT samples [13]. The ITO characterization has been performed by using different models for both ITO bulk and ITO rough surface. The bulk layer has been simulated by using a linear sum of Drude oscillators (conductive properties) and Lorentz oscillators (dielectric properties) [13]. The optical properties due to roughness of the surface layer were simulated by using the Bruggeman Effective-Medium Approximation (EMA), which combines a ITO layer containing a Lorentz oscillator (ϵ_{ITO}) and a layer made by voids (ϵ_{void}) [14].

Comment [TSF2]: Processing or mixing?

Comment [TSF3]: Redundant: chose one of the other.

Comment [TSF4]: This belongs to section 2

2. Experimental details

2.1. PZT sol- gel synthesis and thin films deposition

Lead Zirconate Titanate $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ (PZT) thin films, were obtained by hybrid (carboxylate and alkoxides) sol gel route and spin coating deposition of the obtained mother solution on float glasses and ITO (indium tin oxide)-glasses (sheet resistivity $\square_s = 20 \Omega/\square$, Unaxis GmbH and $R_{\text{sh}}=25\Omega/\square$, Balzers FAB) substrates.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

The reagents (all supplied by Sigma-Aldrich) used are Lead(II) acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, 99.999 %), Zirconium(IV) propoxide solution ($\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$, 70 wt. % in 1-propanol), Titanium(IV) isopropoxide ($\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$, 99.999 %), Acetic acid glacial (CH_3COOH , 99.99+ %), n-Propanol anhydrous ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, 99.7%), Ethylene glycol anhydrous ($\text{HOCH}_2\text{CH}_2\text{OH}$, 99.8%). Bi-distilled water has been used when necessary.

The sol-gel synthesis of PZT mother solution is schematized in Scheme 1 where the amount of the reagents and the operational conditions are indicated.

Except for the solution S7 (Scheme 1), the synthesis has been carried out under Argon atmosphere, inside an “humidity free” Glove Box, with water and oxygen concentrations lower than 0.01 ppm. The glove box has been equipped by two magnetic stirrers (thermal controlled) and by a technical balance. The chosen amount of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ has been calculated in such a way to obtain a 10% excess in mole of lead, which compensate the lead loss (as PbO) which occurs during the process. The amount of acetic acid used, in this work, is such that the total mol number of the acetic acid present in solution is twenty-five times the titanium mol number [10-12]. As it can be seen in Scheme 1, in order to obtain stable mother solution, the $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ have been dissolved in CH_3COOH , (Scheme 1), making the solution indicated as S1) by stirring and heating the solution up to 80°C for fifteen minutes. After two minutes at 80 °C, the heater was set at 70°C and when the solution was cooled down to the latter temperature the $\text{Zr}(\text{C}_3\text{H}_7\text{O})_4$ solution, has been added (Scheme 1, solution S2). Later on, after fifteen minutes, when the temperature is again 70°C and all the particles eventually formed are dissolved, the $\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$ was added (Scheme 1, solution S3_a). The resulting solution has been stirred for one hour at 70°C, for another hour on a cold stirrer (room temperature) (Scheme 1, solution S3_b) and left for another hour on a room temperature stage without stirrer (Scheme 1, solution S3_c).

When the solution is cooled down to room temperature, the rest part of CH_3COOH has been added (Scheme 1, solution S4) and the solution has been left to stir for 15 minutes. At this point the $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (Scheme 1, solution S5) has been added and again stirred for others 15 minutes.

At this time, the HOCH₂CH₂OH (Scheme 1, solution S6) has been added in order to obtain homogenous film (1 ml of HOCH₂CH₂OH for each 10 g Pb(CH₃COO)₂·3H₂O) [10-12] and then the solution has been sealed with parafilm and left to stir for one night.

Finally, the solution has been removed from the glovebox and 9 ml of bidistilled water have been added (Scheme 1, solution S7) before the spin coating.

The float glass and the ITO glasses substrates have been previously ultrasonically cleaned [5,6] and an SC10 CaLCTec s.r.l. spin coater has been used for the deposition. PZT thin films have been obtained at 1200 rpm for 25 s. Such films have been placed on a hot plate for 5 minutes at 300°C.

Later on, the films were subjected, for an hour, to different single thermal treatment in an oven in temperature range between 100 °C and 700 °C, each one separated by 100°C step.

2.2. Spectroscopic ellipsometry

The optical characterization of substrates and thin film samples was performed by using the Spectroscopic Ellipsometry technique. The VASE (Variable Angle of incidence Spectroscopic Ellipsometer) M2000F (J.A. Woollam) rotating compensator ellipsometer was used in the 250-1000 nm wavelength range. The ellipsometric spectra have been collected at different incident angles to improve the accuracy of layer modelling.

The structural and morphological properties have been estimated by using multilayer optical models compatible with the ellipsometric experimental results. Each layer has been depicted by an optical model whose fitting parameters were both thickness and its complex dispersion law [13].

The optical models together with the best fitting values have been calculated by WVASE32 application using the nonlinear Levenberg-Marquardt algorithm, which determines the minimum value of the Mean Square Error which is a measure of the likelihood of the fit [13].

2.3. Electro-optical responses collected by ANLC cells

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

The ANLC cells have been obtained by following the same procedure described before [5-9]. The ITO-coated glasses were used in ANLC cells as counter electrodes with respect to the PZT samples which were the working electrodes.

The electro-optical responses have been obtained by using a polarizing microscope Axioskop Pol (Zeiss). The transmitted light intensities have been collected by using a large area silicon photodiode (Hamamatsu) mounted on the polarizing microscope. The electrical signals proportional to the light intensities were collected by a digital oscilloscope (Tektronics, Mod. TDS 784). White light (the bulb of the microscope) have been used as light source. Without any applied voltage the maximum of the transmitted light it is obtained, since the liquid crystal is in planar alignment. When the external voltage is applied the liquid crystal switches toward the homeotropic alignment and simultaneously the light collected by the photodiode decreases.

3. Results and Discussion

The changes of optical constants due to different thermal treatments can be revealed, in the case of multi-layered systems like the ones under investigation here, by the spectroscopic ellipsometry, by using the proper modeling typical of such technique. Following this approach, the optical response of PZT layer has been simulated by three Lorentz oscillators to generate its pseudo-dielectric functions. When the PZT was placed on ITO covered float glass (Table 1), the introduction of a further Lorentz oscillator was necessary to generate a pseudo-dielectric function well fitting the ellipsometric experimental data. The surfaces roughness of PZT films has been simulated by using the Bruggeman EMA models with mixture of PZT layer and void, in similar way to the procedure applied to ITO substrates, obtaining as final result an effective dielectric function of the PZT roughness.

The dispersion laws of the optical constants, estimated for the float glasses annealed at different temperatures, are shown in Figure 1. It can be seen that the dispersion law for the float glasses substrates is not affected by the thermal annealing, while on the contrary the optical investigation performed on the

ITO covered float glasses shows that the optical properties of such substrate depend on the annealing temperature (Figure 1). The evaluated ITO thickness has small changes with temperature.

The typical model used to describe the conductivity of the ITO takes into account the carrier density determined both by the oxygen vacancies and by the doping tin atoms, acting as electron donors when the tin oxidation state is (IV), as in SnO_2 [15-17]. Of course, the annealing treatment, performed in oxidizing atmosphere, promotes the oxidation of the layer (reducing the oxygen vacancies and consequently reducing the amount of the charge carries) increasing the resistivity of the ITO layers.

The presence of the PZT layer (when the thickness is lower than 200 nm) does not change appreciably the oxidation phenomena for the ITO layer. In fact, different experimental observations on the ferroelectric PZT thin films, obtained by sol-gel synthesis and deposited on various substrates, show that these thin films do not affect, significantly, the diffusion of the atmospheric oxygen which can perform the oxidation of the ITO layer [18,19]. Thus, it is possible to assume that, during the thermal processes, the changes in structural and morphological properties of the substrates are only slightly affected by the presence of PZT thin layers.

The fitting procedure were performed by using the optical models obtained for the substrates at each temperature, maintaining the same fit parameters relative to the substrates, estimating only the fitting parameters of the PZT layers.

The estimated dispersion laws of PZT layers annealed at different temperature and on the different substrates are shown in Figure 2, where it is possible distinguish two absorption resonances in the Near-UV region. These bands are assigned to the presence of the two structural phases of PZT layers: the pyrochlore and ferroelectric perovskite phase [20, 21].

Moreover, a new small peak in the NIR region occurs for the PZT layer deposited on ITO coated glass, subjected to the higher temperature annealing treatments (see Figure 2). Such band, not detected for the others samples, seems to move towards lower energies as well as the annealing temperature increases. It has been tentatively assigned to the peculiar charge distribution at the interface, which

constitutes some kind of “intermediate layer” between ITO and PZT interface. Further investigations are on the way in order to better characterize such NIR-resonance.

The extinction coefficients of PZT thin films annealed at different temperatures have been used to estimate the optical band gaps energies of the pyrochlore and perovskite phases. Moreover, the electron transitions gaps energies have been estimated by the typical model used to describe an allowed direct transition [22].

Neglecting the exciton formation, the form of the absorption coefficient α as function of photon energy $h\nu$ depends on the joint density of the states, $N(E)$, involving the band across the Fermi level. For simple parabolic bands and direct transitions (allowed), the typical expression of the absorption coefficient $\alpha(h\nu)$, is:

$$(\alpha h\nu)^2 = A(h\nu - E_g^{opt}) \quad \text{with } \nu > E_g^{opt} \quad (1)$$

where E_g^{opt} is the energy gap and A is a constant, proportional to the probability of electron transition between occupied and empty states [22]. The extinction coefficients $k(\lambda)$, estimated by ellipsometry, are used to calculate the absorption coefficient $\alpha(h\nu)$ versus photon energy $h\nu$ by using the well-known formula:

$$\alpha(h\nu) = 4\pi \frac{k(h\nu)}{\lambda} \quad (2)$$

where, h is the Plank constant and λ is the light wavelength.

In Figure 2 (on the right) are shown the $(\alpha h\nu)^2$ functions versus photon energy $h\nu$, estimated as described above. The band gaps can be extracted by linear fit of the function $(\alpha h\nu)^2$ immediately above the edge of each absorption peak. The band gaps, obtained calculating the intercept of these lines with the photon energy axis, are indicated in Figure 2. First of all, it can be noticed that for the Glass/PZT

sample annealed at 700°C only one band appears and the associated band gap falls at 4.11 eV, while when the sample are treated at 500°C two bands occur at 3.69 eV and 4.20 eV. In summary, the optical band gaps obtained for the Glass/ITO/PZT samples are 3.70 eV and 4.11 eV, for the sample annealed at 600°C and 4.06 eV and 4.47 eV, for the samples annealed at 300°C. The NIR shift of the bands (and of the relative optical band gaps energies values) as well as the annealing temperature increases, observed in the Figure 2, is due to the PZT structural evolution from amorphous to polycrystalline phase [23-25].

Such values are consistent with the literature data that assign the lowest value, obtained from each sample, to the presence of the pyrochlore phase and the highest to the presence of ferroelectric perovskite phase, of the PZT with the same stoichiometric ratio ($Zr=0.53$, $Ti=0.47$) [20,21,26-29]. It means, that when the annealing temperature is lower than 600°C, the pyrochlore ($E_g^{opt} \approx 3.7eV$) and the perovskite ($E_g^{opt} \approx 4.2eV$) phases are coexisting. On the contrary, when the annealing temperature is higher than 600°C, the pyrochlore phase is completely converted in ferroelectric perovskite phase; for instance, in the GLASS/PZT sample annealed at 700°C (see Figure 2), the only band detected is assigned to the ferroelectric perovskite phase (the sample GLASS/ITO/PZT annealed at 700°C, has been not characterized by ellipsometry because of its deformation after such annealing treatment). However, the thermal induced structural evolution, similar to that observed on GLASS/PZT sample annealed at 700°C, has been detected by AFM and EFM (Electrostatic Force Microscopy) investigations, where the presence of ferroelectric dendritic structures has been shown [5]. These evidences indicate the same evolution of the PZT layer on GLASS/ITO substrates when such samples are subjected to the highest thermal annealing process [30].

Such structural evolutions are at the basis of the effect observed when GLASS/ITO/PZT samples are used as electrode in ANLC cells. In Figure 3 are shown the electro-optical responses measured in ANLC cells, containing as electrodes GLASS/ITO/PZT samples annealed at 500°C (on the bottom) and 600°C (on the top). The same optical responses are obtained from the two cells (Figure 3), polarity sensitive in both the cases: the liquid crystals molecules are affected by the electric field only for positive voltages

1 while for negatives ones they do not switch. (It should be remembered that at the beginning the
2 maximum of the light is collected by the photodiode; when the liquid crystals molecules change the
3 initial alignment the light intensity decreases)[5]. Such kind of response generates a plot (see Figure 3)
4 where transmitted light intensity and applied voltage appear “in opposition of phase”. The same
5 behavior has been obtained also in ANLC cells where the electrode was made by WO₃ film annealed at
6 600°C, while in the case of WO₃ films annealed at 100°C the electro-optical response appears “in
7 phase” to the applied voltage [6-9]. On the contrary, by using PZT films the observed electro-optical
8 responses appear always “in opposition of phase”, independently from the annealing temperature [5].

9 However, the electro-optical efficiency of the devices results remarkably dependent on the annealing
10 temperature of the electrode films. In fact, in order to obtain the same polarity sensitive electro-optical
11 responses, a voltage twice higher should be used for the ANLC cell containing PZT films annealed at
12 500°C with respect to that used for the ANLC cell containing PZT films annealed at 600°C. As reported
13 above, the increasing of the annealing temperatures favors the formation of the ferroelectric perovskite
14 structures, which remains the only existing structure for the highest annealing temperatures. It is
15 possible to assign to the increasing presence of such structure the better efficiency obtained from the
16 ANLC cell made with the PZT sample annealed at 600°C.

32 4. Conclusion

33 In conclusion, an easy way to grow Lead Zirconium Titanate, PbZr_{0.53}Ti_{0.47}O₃, (PZT) films, with
34 stoichiometric amount indicated in the formula, has been obtained by hybrid (carboxylate and alkoxides)
35 sol gel route and spin coating deposition of the mother solution on different substrates (float glasses,
36 ITO covered float glasses).The thermal induced structural evolutions of such films have been studied by
37 spectroscopic ellipsometry, to investigate specifically the changes of optical properties of the films,
38 relevant for the planned application in the field of liquid crystal cells. It has been seen that for lower
39 temperatures annealing the PZT layer is quite amorphous and it become polycrystalline when the
40
41
42
43
44
45
46
47
48
49

annealing temperature increases. Two phases have been identified, by comparison of the optical band gaps obtained during this work to the literature data: the pyrochlore phase and the ferroelectric perovskite phase.

It has been shown that the ferroelectric perovskite phase is the only phase which remains when the annealing temperature is 700°C. Unfortunately, analysis of the electro-optical response has been possible only for asymmetric nematic liquid crystals (ANLC) cell having PZT electrodes annealed at the maximum temperature of 600 °C; the great amount of ferroelectric perovskite present also in this case has been associated to the best efficiency for the wanted rectified switching of the liquid crystal layer.

To overcome such limit alternative annealing methods could be proposed, for instance CO₂ laser annealing, which can provide high heating rates on the PZT layer without deformation of the glass substrate. However, the effects of the phase transformation kinetics on the resulting properties of the films need also to be considered and studied by proper experiments, and such a task can be matter for further research, exceeding the aims of the present work.

Finally, the thermally induced formation of a peculiar interlayer between the ITO and PZT interface has been hypothesized. It should be responsible of the new band detected on the NIR region. Structural and chemical characterizations of such new layer are on the way. The preliminary Raman spectroscopic investigations seem to be very promising in order to individuate the nature of such layer.

ACKNOWLEDGMENT. The authors wish to thank Dr. Giuseppe De Santo and Dr. Tiziana Barone for their essential contribution during the PZT thin layers preparation.

REFERENCES

- 1
2 [1] D. Damjanovic, Reports on Progress in Physics 61 (1998) 1267.
3
4
5 [2] K. Uchino, Ferroelectric Devices, Marcel Dekker, Inc., New York NY, 2000.
6
7
8 [3] Y. Xu, Ferroelectric and their Applications, North-Holland, Amsterdam, 1991.
9
10 [4] J. Lappalainen, J. Hiltunen, V. Lantto, Journal of the European Ceramic Society 25 (2005) 2273.
11
12 [5] S. Marino, M. Castriota, G. Strangi, E. Cazzanelli, N. Scaramuzza, Journal of Applied Physics
13 102 (2007) 013112-1.
14
15
16
17 [6] M. Castriota, S. Marino, C. Versace, G. Strangi, N. Scaramuzza, E. Cazzanelli, Molecular
18 Crystals and Liquid Crystals 429 (2005) 237.
19
20
21 [7] G. Strangi, E. Cazzanelli, N. Scaramuzza, C. Versace, R. Bartolino, Phys. Rev E 62 (2000) 2263.
22
23
24 [8] E. Cazzanelli, S. Marino, V. Bruno, M. Castriota, N. Scaramuzza, G. Strangi, C. Versace, R.
25 Ceccato, G. Carturan, Solid State Ionics 165 (2003) 201.
26
27
28
29 [9] V. Bruno, M. Castriota, S. Marino, C. Versace, G. Strangi, E. Cazzanelli, N. Scaramuzza,
30 Molecular Crystal and Liquid Crystal 441 (2005) 27.
31
32
33 [10] G. Yi, Z. Wu, M. Sayer, J. Appl. Phys. 64 (1988) 2717.
34
35
36 [11] C. R. Martin, I. A. Akasay, J. Phys. Chem. B 107 (2003) 4261.
37
38
39 [12] Y. J. Song, Ph.D Thesis; Virginia Polytechnic Institute and State University, Blacksburg,
40 Virginia, USA, 1998.
41
42
43 [13] G. H. Tompkins, E. A. Irene, Handbook of Ellipsometry, William Andrew Inc, Norwich, New
44 York, 2005.
45
46
47 [14] D. E. Aspnes, Thin Solid Films 89 (1982) 249.
48

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- [15] F. O. Adurodija, L. Semple, R. Bruning, J. Mater. Sci. 41 (2006) 7096.
- [16] M. Berder, W. Seelig, C. Daube, H. Frankenberger, B. Ocker, J. Stollenwerk, Thin Solid Films 326 (1998) 72.
- [17] I. Hamberg, C. G. Granqvist, J. Appl. Phys. 60 (1986) R123.
- [18] Y. Matsui, M. Suga, M. Hiratani, H. Miki, Y. Fujisaki, J. Appl. Phys. 36 (1997) 1239.
- [19] S. G. Lee, K. T. Kim, Y. H. Lee, Thin Solid Films 372 (2000) 45.
- [20] A. Okada, J. Appl. Phys. 48 (1977) 2905.
- [21] H. Lee, Y. S. Kang, S. J. Cho, B. Xiao, H. Morkoc, T. D. Kang, G. S. Lee, J. Li, S. H. Wei, P. G. Snyder, J. T. Evans, J. Appl. Phys. 98 (2005) 094108.
- [22] N. H. Mott, E. A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, UK, 1979.
- [23] A. Wu, I. M. Miranda Salvado, P. M. Vilarinho, J. L. Baptista, Journal of the American Ceramic Society 83 (2000) 1379.
- [24] S. Trolier-McKinstry, J. Chen, K. Vedam, R. E. Newnham, Journal of the American Ceramic Society 78 (1995) 1907.
- [25] C. H. Peng, S. B. Desu, Journal of the American Ceramic Society 77 (1994) 1486.
- [26] Z. Hu, Z. Huang, Z. Lai, G. Wang, J. Chu, Thin Solid Films 437 (2003) 223.
- [27] M. P. Moret, M. A. C. Devillers, K. Worhoff, P. K. Larsen, J. Appl. Phys. 92 (2002) 468.
- [28] S. Yang, D. Mo, X. Tang, Ferroelectrics 287 (2003) 35.
- [29] S. Yang, D. Mo, X. Tang, J. Mater. Sci. 37 (2002) 3841.

[30] E. Bruno, M. P. De Santo, M. Castriota, S. Marino, G. Strangi, E. Cazzanelli, N. Scaramuzza, J.

Appl. Phys. 103 (2008) 064103.

For Peer Review Only

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

FIGURE CAPTIONS

Table 1. Description of the optical models used to characterize the samples and substrates annealed at the different temperatures.

Scheme 1. $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ (PZT) mother solution sol gel synthesis with the number of mole of each reagent and the procedure at each stage indicated. (RT indicates room temperature).

Figure 1. Dispersion laws estimated by using the multilayer optical models described in Table 1 for the float glasses and the ITO covered float glasses substrates annealed at different temperatures. The enlargement of the NIR spectra (on the top) shows the reduction of carrier concentration as well as the annealing temperature increases (Drude theory for free carries).

Figure 2. On the left and on the middle: dispersion laws estimated for PZT layers deposited on float glasses and ITO float glasses substrates; on the right: optical energies band-gaps extracted by linear fit of the function $(\alpha h\nu)^2$ immediately above the edge (see text).

Figure 3. Electro-optical responses (blue circle) of ANLC cells containing PZT layers annealed at 500°C (on the bottom) and 600°C (on the top) when the external applied voltage is applied (red solid line).

Table 1.

	Optical Models			
	(a)	(b)	(c)	(d)
Layer 1	Float Glass 1.1 mm	Float Glass 1.1 mm	Float Glass 1.1 mm	Float Glass 1.1 mm
Layer 2	/	ITO 85 ÷ 90 nm	PZT	ITO 85 ÷ 90 nm
Layer 3	/	Surface Roughness (EMA Model) 10 ÷ 20 nm	Surface Roughness (EMA Model) (<u>PZT+Surface Roughness</u> 110 ÷ 180 nm)	Surface Roughness (EMA Model) 10 ÷ 20 nm
Layer 4	/	/	/	PZT
Layer 5	/	/	/	Surface Roughness (EMA Model) (<u>PZT+Surface Roughness</u> 130 ÷ 200 nm)

Scheme 1. $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ (PZT) mother solution sol gel synthesis with the number of mole of each reagent and the procedure at each stage indicated. T_1 , T_2 and T_3 indicate the consecutive temperatures specified for each single step in the right side box. (RT indicates room temperature). All the solution, but the last one (S7), are prepared under Ar atmosphere.

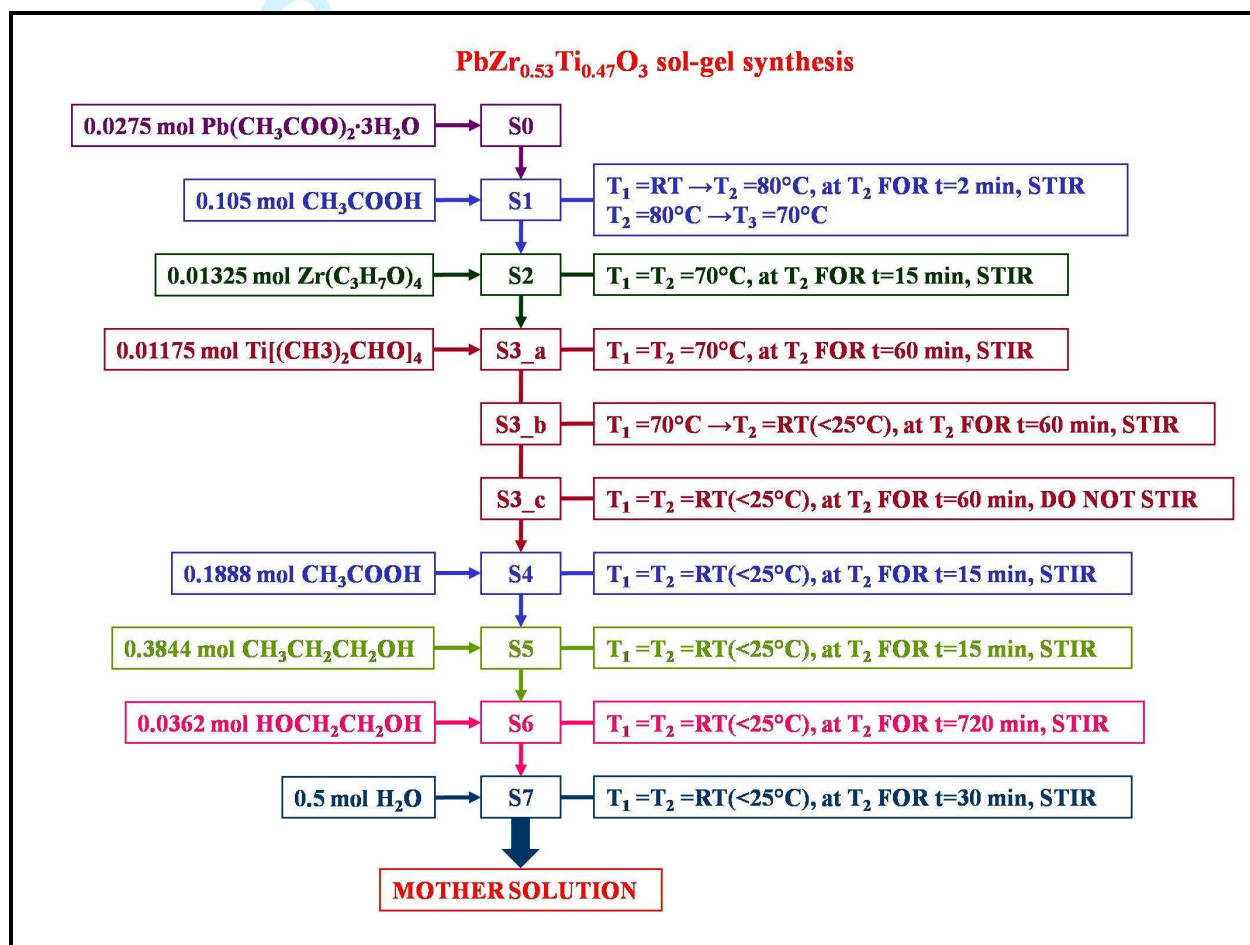
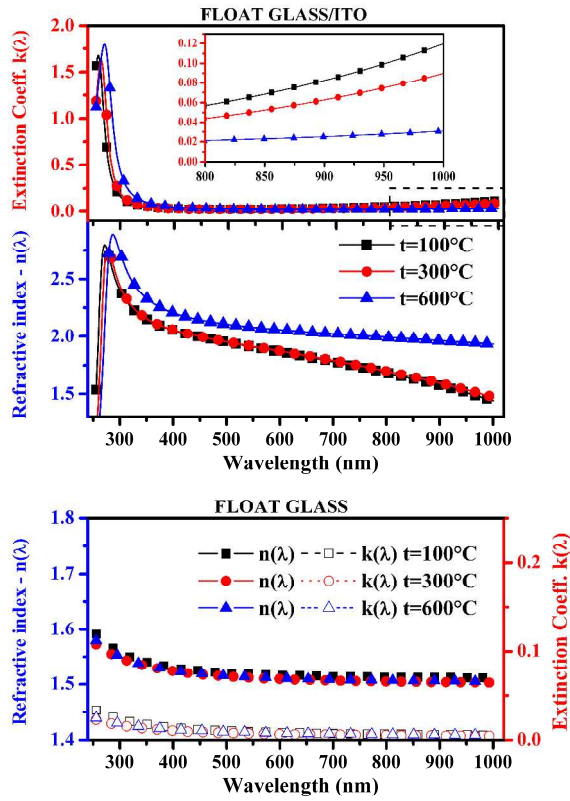
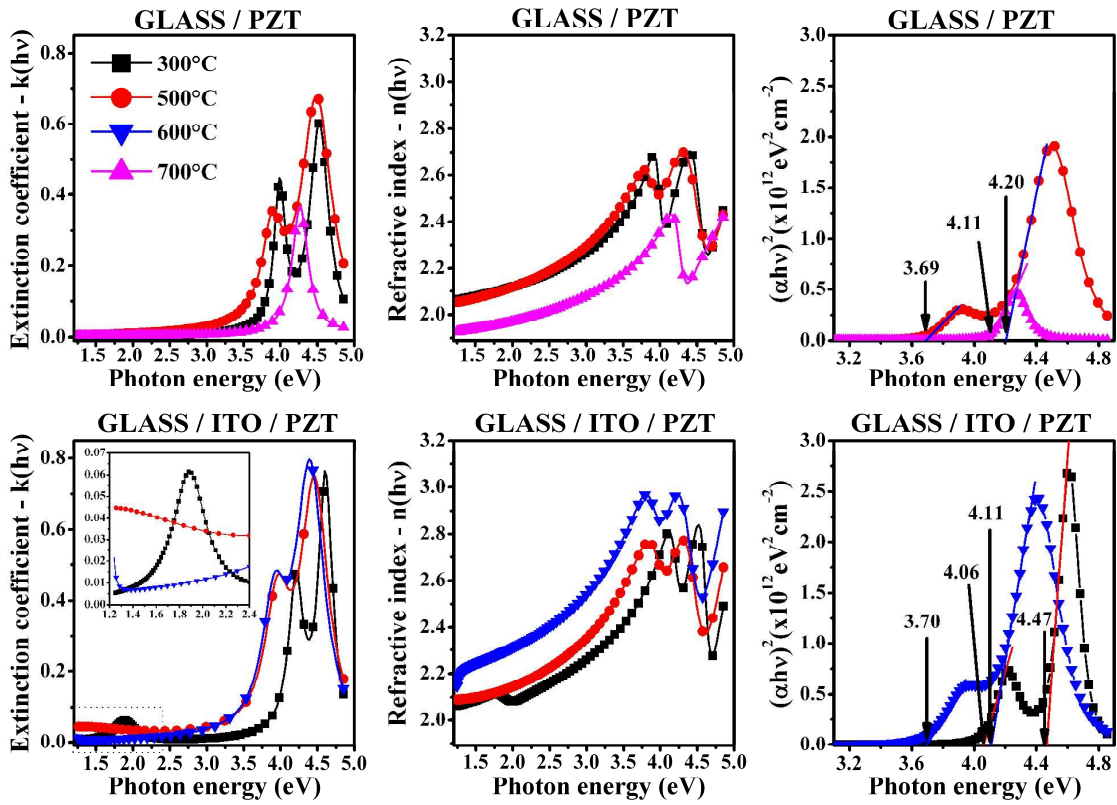


Figure 1.





Review Only

Figure 3.

