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Investigation of the Structural and Optical Properties of La-doped PZT Films on Transparent Conductive Oxide Ga-doped Zinc Oxide (GZO) Substrates

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Abstract

Lanthanum-doped $(Pb_{(1-y)}La_y)(Zr_{0.65}Ti_{0.35})O_3$ (PLZT) thin films with y=8, 9, 10 mole-% were prepared by sol-gel spin coating on gallium-doped zinc oxide (GZO) coated glass substrates. The effect of the processing conditions such as pyrolysis steps and duration, annealing temperature were investigated as the parameters to achieve single phase microstructure. Final annealing temperature and time was decided as 725ºC for 1 hour for all the PLZT films. Two-phase structure was observed, and it was concluded that pyrolysis steps are very dominant process on the properties. Optical measurements were done in the wavelength range of 300-2500 nm. The average transmittance level of the films annealed at 725ºC were found in between ~70% -80% in the visible region and band gap levels were calculated as ~3.29 eV.

Ga-katkılanmış Çinko Oksit (GZO) Saydam İletken Oksit Üzerindeki Lantan-katkılanmış PZT Filmlerin Yapısal ve Optik Özelliklerinin İncelenmesi

Özet

Lantanum katkılanmış $(Pb_{(1-y)}La_y)(Zr_{0.65}Ti_{0.35})O_3$ (PLZT) ince filmler, y=%8, 9, 10-mol oranları ile sol-jel döndürme kaplama yöntemi kullanılarak galyum-katkılanmış çinko oksit (GZO) kaplı cam altlıklara kaplanmıştır. Piroliz aşamaları ve süreleri, tavlama sıcaklıkları gibi proses koşullarının tek fazlı mikroyapının eldesine etkileri incelenmiştir. Nihai tavlama sıcaklık ve süresi tüm PLZT filmler için 725ºC'de 1 saat olarak belirlenmiştir. Çift faz gözlenmiş ve bunun sonucunda piroliz aşamasının özellikler üzerinde önemli bir etken olduğu değerlendirilmiştir. 300-2500 nm dalga boyu aralığında optik ölçümler gerçekleştirilmiştir. Filmlerin geçirgenlik seviyeleri görünür ışık bölgesinde ~70% -80%, bant aralığı ise ~3.29 eV olarak hesaplanmıştır.

1. INTRODUCTION

Lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) and lead lanthanum zirconate titanate, $(Pb_{1-y}La_y(Zr_{1-x}Ti_x)_{1-y/4})O_3$ (PLZT) are two well-known materials because of their excellent electrical properties in bulk and thin film form, but also, their optical properties are another important factor about this wide-usage.[1] The compositional range named as morphotropic phase boundary is the most studied composition for these materials. This is preferred because of the coexistence of tetragonal and rhombohedral phases increases the electrical properties of the material.

Lanthanum, as a dopant, occupies the A-site of the PZT perovskite structure. It is known that this relocation results with formation of B-site vacancies to maintain charge balance.[2,3] PLZT, like PZT, is a material with high electrical properties but its optical properties were more interested by researchers. This material has high response speed, transmittance and electro-optic coefficient which are so important for possible applications. Studies have shown that when dopant amount is 8, 9, 10%-mol for PLZT, there is a significant increase in the optical properties. It is important to achieve high crystallinity for the desired optical properties. Conventional heat treatment processes are not efficient for this aim, therefore rapid thermal annealing (RTA) is more preferably used to achieve higher crystallinity.[4-6]

Thin film form of these materials is mostly considered for optical applications and for an optical usage most preferred substrate type that can be used is glass. Despite being inexpensive it is hard to have high crystallinity on this amorphous material. Also, for any electro-optic application, films must have a bottom electrode. At this point transparent conductive oxides (TCOs) take place. Indium doped tin oxide (ITO) is a well-known TCO material with its wide band-gap value between 3.5-4.3 eV and transmittance levels in UV-IR regions. By using ITO substrates, Khodorov et. al. showed that the 455 nm PLZT coatings can result with a transparency between 50-70% in the visible range of spectrum. This result was promising for PLZT as an electro-optic coating on ITO because of the possibility to improve the optical performance by using the parameters of the coating method like in this article.[6-8] Another widely used TCO is gallium-doped zinc oxide (GZO). Due to toxicity of indium, zinc oxide was researched as an alternative material. Its low charge carrier level was increased by aluminum or gallium doping and studies have shown Ga-O bonds resulted with better coherency, electrical stability and less distortion of the structure.[9-11]

In this study, PLZT thin films were coated on GZO coated glass substrates by sol-gel spin coating method and processing steps were followed from the literature.[6,12-19] It was aimed to show the possibility of coating PLZT thin films on GZO successfully (without any surface defects, peelings etc.) which is not widely studied in the literature and also to find the optimum coating parameters of PLZT films for comparable optical results with the films coated on ITO substrates. Therefore, it was aimed to contribute to electro-optic coating knowledge with a glass-GZO-PLZT sandwich structure.

2. METHODS

In this study, La-doped lead zirconate titanate $(Pb_{1-y}La_y(Zr_{1-x}Ti_x)_{1-y/4})O_3$ (PLZT) thin films with y=8, 9, 10 mole-% were prepared by sol-gel spin coating method on gallium-doped zinc oxide (GZO) coated glass substrates (provided by Şişecam Science and Technology Center, Turkey). All precursor solutions were prepared with 5 mole-% Pb excess in order to compensate Pb loss that occurs during annealing process. Lead acetate trihydrate, $C_4H_6O_4Pb.3H_2O$ (Merck), lanthanum acetate hydrate, $La(CH_3CO_2)_3.xH_2O$ (Sigma-Aldrich), zirconium n-propoxide, $Zr(O(CH_2)_2CH_3)_4$ (Alfa-Aesar), and titanium n-butoxide $Ti(O(CH_2)_3CH_3)_4$ (Alfa-Aesar) were used as source materials. 2-methoxyethanol, $CH_3O(CH_2)_2OH$ (Sigma-Aldrich) was used as the main solvent. The preparation route of all precursor solutions was done in light of our previous studies with a fixed concentration at 0.4M.[13,15,16] Phase analysis was done using an X-ray diffractometer (XRD) (Bruker D8 Advanced). The microstructure of the thin films was examined by a scanning electron microscope (SEM) (Philips XL30). The grain size, finer features and surface morphology of the thin films were determined using a Nanoscope IV (Digital Instruments) scanning probe microscope (SPM).

3. RESULTS AND DISCUSSION

3.1. Phase Analyses and Microstructural Examinations

XRD patterns of $(Pb_{0.91}La_{0.09})(Zr_{0.65}Ti_{0.35})O_3$ (PLZT (9/65/35)) films annealed at 650°C and 725°C for 1h were given in Fig. 1(a). Based on the DTA-TG analysis (not shown here), a two-step pyrolysis process was applied, initially at 200ºC for 2 min followed by 430ºC for 5 min. The high intensity peak that was observed in both cases at the 2θ=34º was the main diffraction peak of the GZO layer on the glass substrate. In the case of the films annealed at 650ºC for 1h, only a single and weak peak around the 2θ=29º was observed in the XRD pattern, which belongs to the pyrochlore phase (PDF #00-027-1201). This result indicated that annealing at 650ºC was not enough to induce crystallization of the perovskite phase. When the annealing temperature was increased to 725ºC, a full perovskite phase was obtained with several diffraction peaks clearly visible. The films had a $[110]_{pc}$ preferred orientation, as indicated by the higher than expected intensity of the (110) peaks compared to a random polycrystalline ceramic with perovskite structure. This dominant preferred orientation can be attributed to a lattice match with GZO substrate. A low intensity peak was still observable at around 2θ=29º, which was an indication of the persisting presence of the pyrochlore phase. Based on these initial results, PLZT films were prepared on GZO with La content of 8, 9 & 10 mole-%, named as PLZT (8/65/35), PLZT (9/65/35) and PLZT (10/65/35), respectively. The temperatures of the first and second pyrolysis steps were fixed at 200ºC and 430ºC, and the annealing temperature was fixed at 725°C for 1h for the rest of the study. XRD results of these films were also given in Fig. 1(b) (PLZT PDF#00-046-0336). However, the duration of the pyrolysis steps was investigated as a parameter to control the nucleation and growth of the perovskite phase.

Fig. 2 shows representative SEM micrographs of two PLZT films with different pyrolysis durations. From Fig. 2, a two-phase microstructure was obtained with round, grain-like features with light contrast (monikered as the 'rosette phase' and the second phase with a dark contrast (called the 'matrix phase').[16] From our previous studies[15,16] on antiferroelectric lead zirconate thin films, this two-phase microstructure is believed to arise as a result of heterogeneous nucleation and growth of the perovskite phase. According to EDS analyses, matrix phase was found to be lead-deficient compared to the rosette phase.[13,14] Similar results were also reported in previous papers from our group.[13-18] The cross-sectional SEM micrograph of the films (not shown here), indicated that the thickness of the GZO coated glass substrate and PLZT films were as ~300 nm and ~600 nm, respectively.

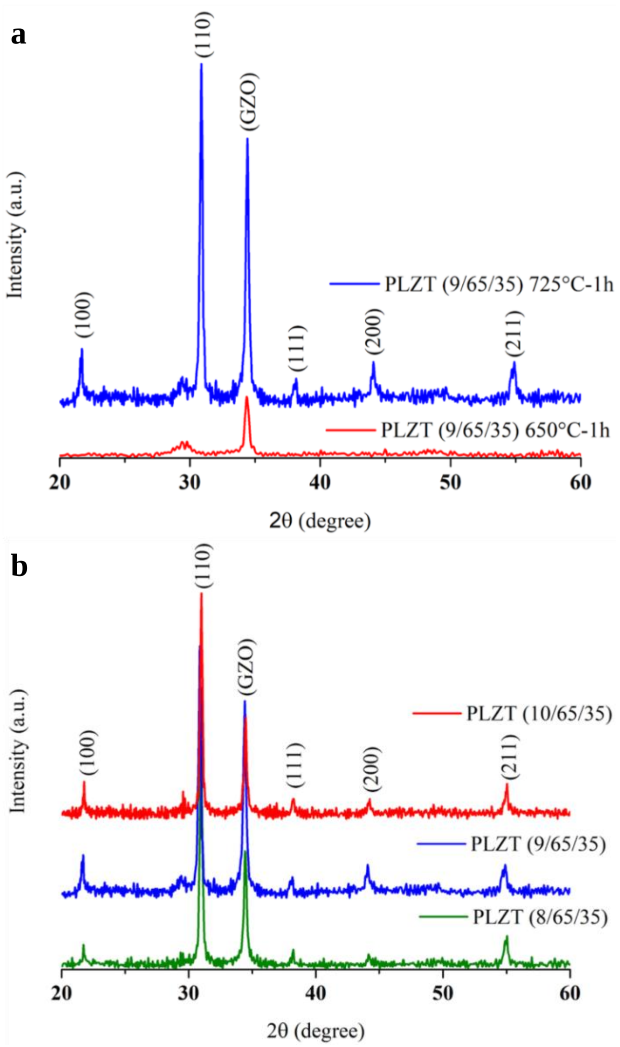

Figure 1. XRD patterns of the (a) PLZT (9/65/35) films annealed at various temperatures and (b) PLZT films with various La content.

Further investigation of the microstructure by using scanning probe microscope given in Fig. 3 indicated that the matrix is a polycrystalline phase with nanograins. The rosette phase was also found to be a polycrystalline region, but with larger, submicron grains. The rosettes were found to nucleate from a central grain and then grew radially with the growth of additional neighboring grains (Fig. 3(a)). The growth process was found to propagate until the neighboring regions impinged upon each other (Fig. 3(b)). When the XRD, SEM and SPM findings were evaluated together, the rosettes could be identified as a crystalline perovskite and matrix phase could be identified as a mixture of pyrochlore and perovskite phases with very fine grains.

The ratio of rosette phase was calculated from the scanning electron micrographs using image analysis. Table 1 summarizes the results, and from these findings it was clear that the ratio of the rosette and matrix phases depended on the pyrolysis duration and the final annealing temperature. Very low rosette phase ratio was observed for the samples annealed at 650ºC and this result was supported by XRD given in Fig. 1. When the annealing temperature was increased to 700ºC and 725ºC, the ratio of the rosette phase was increased for all three La-doped compositions. As an example, for PLZT (9/65/35) film, the ratio of rosette phase was calculated as ~69% and ~80% (Fig.2(a)) for the samples annealed at 700ºC and 725ºC.

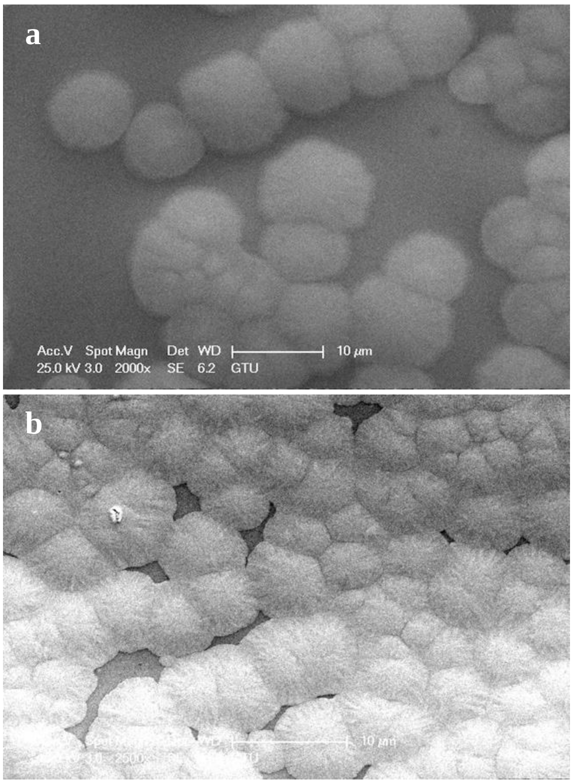

Figure 2. SEM micrographs of PLZT (9/65/35) films with different pyrolysis conditions annealed at 725ºC: (a) 200ºC for 2 min and 430ºC for 10 min and (b) 200ºC for 5 min and 430ºC for 15 min.

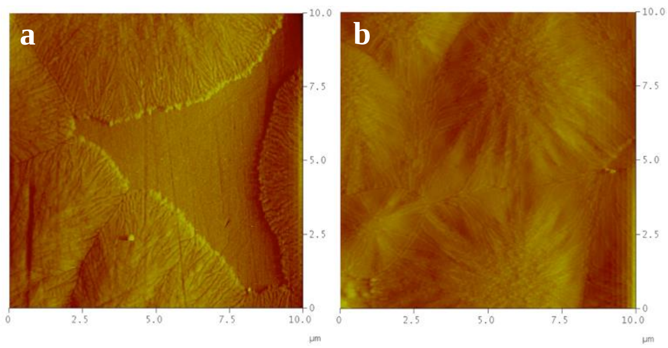

Figure 3. Scanning probe microscope images of PLZT (9/65/35) films annealed at 725ºC for 1 hour. Pyrolysis conditions were (a) 200ºC for 2 min and 430ºC for 5 min and (b) 200ºC for 5 min and 430ºC for 10 min.

The duration of the pyrolysis steps was investigated as the main parameter in the processing of films, because our previous studies[14], indicated that the pyrolysis step is very effective on the first nucleation in the microstructure. When Table 1 is evaluated as a whole, the pyrolysis duration was found to be more effective in controlling the rosette phase ratio in the PLZT (9/65/35) films, where increasing the first and the second pyrolysis durations both caused a general increase in the rosette ratio. The highest rosette ratio was obtained as ~94% for 9 mole-% La-doped film using the pyrolysis step as 200ºC for 5 min and 430ºC for 15 min. A correlation between La content and the pyrolysis duration has not been observed.

3.2. Optical Analyses

The optical properties of the films were characterized by UV- VIS measurements. Total film thickness was taken as ~600 nm for calculations. Measurements were done in the range of 300 nm-2500 nm wavelength range using UV-VIS spectrometer.

Table 1. The pyrolysis conditions and ratio of rosette phase in PLZT thin films.

La-content	Pyrolysis Conditions		Rosette Ratio
(mole-%)	at 200ºC (min)	at 430ºC (min)	(%)
PLZT (8/65/35)	2	5	91
	2	10	88
	5	5	92
	5	10	88
	5	15	88
	10	10	86
PLZT (9/65/35)	2	5	75
	2	10	60
	5	5	76
	5	10	88
	5	15	94
	10	10	82
PLZT (10/65/35)	2	5	83
	2	10	92
	5	5	83
	5	10	86
	5	15	86
	10	10	72

In Fig. 4(a), optical transmittance spectra of PLZT films with 8, 9 and 10 mole-% La doping, pyrolyzed at the same conditions and annealed at 725ºC were given. All films showed higher than 65% optical transmittance (T) in the visible range. The oscillations in T arose from the interference due to reflection from the top surface of the film and the interface between the film and substrate.[8] In the Fig.4(b), transmittance vs. wavelength spectra was given for the PLZT (9/65/35) films obtained with various pyrolysis conditions. There was no remarkable change in the films. Although the highest transmittance values in the visible range have been obtained in the PLZT (9/65/35) films with the highest rosette ratio, a direct and conclusive correlation has not been observed between the rosette ratio and the transmittance values of the films. At the same time, the average transmittance of PLZT on GZO coated glass substrate is 70%-80% in visible region.

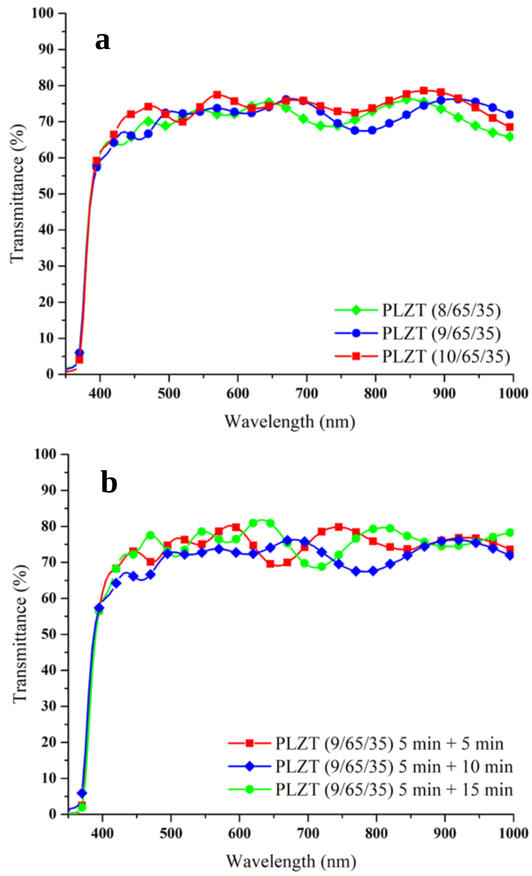

Figure 4. a) Optical transmittance of PLZT films with different La content and obtained at 200ºC for 2 min and 430ºC for 5 min pyrolysis condition, (b) PLZT (9/65/35) films with various pyrolysis conditions.

The optical band gap (E_g) values of the films were calculated from absorption edge of the UV-VIS results using the equation given below [18]:

$$ahv = (v - E_g)^{1/2} \quad (1)$$

The direct band gaps of the films were found to range from 3.29 eV to 3.31 eV. A significant variation or a strong shift of the band gap has not been observed with La content or the pyrolysis conditions, because the rosette ratio was above a certain threshold in all cases. In the UV region, electromagnetic radiation was entirely absorbed by the PLZT films.

4. CONCLUSIONS

PLZT films were prepared by sol-gel spin coating method on the GZO coated glass substrates without any seeding layer for the first time. Two phases microstructure, rosette and matrix, was observed for almost all films. The direct band gaps of the PLZT films with various La content was calculated from transmission measurements as ~3.29 eV. A significant variation has not been observed with La content or the pyrolysis conditions. The transmission value of PLZT(9/65/35) film with the highest rosette ratio, 94%, was found to be as 70-80% in visible region. Although the desired optical properties could be achieved by these substrates, the effect of the high temperature annealing on the conductivity of the GZO layer will be investigated for electrical characterization of the PLZT films. There were no remarkable changes between the values of the optical transmittance of the PLZT films with 8, 9 and 10 mole-%. But the highest transmittance value of PLZT (9/65/35) is attributed to the improve- ment of rosette phase, with 94% ratio, using 200ºC for 5 min and 430ºC for min pyrolysis condition.

This study has shown:

- It is possible to coat PLZT thin films on GZO layers without any peeling and physical interface problem.
- By using GZO as an alternative TCO material to ITO, similar transparency levels with ITO based structures can be achieved in the visible region.
- Pyrolysis conditions has effect on optical transmittance but its effect on the band-gap values is negligible.

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