Journal of the European Ceramic Society 21 (2001) 1151–1157

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Preparation of 9/65/35 PLZT thin films deposited by a dip-coating process

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Received 8 June 2000; received in revised form 20 November 2000; accepted 23 November 2000

Abstract

Crack-free polycrystalline PLZT (Pb,La)(Zr,Ti)O_3 thin films with the perovskite structure were prepared by dip-coating using the Pechinis process. Lead acetate, hydrated lanthanum carbonate, zirconium *n*-propoxide and titanium isopropoxide were used as raw materials. The viscosity of the solution was adjusted in the range of 20 to 56 cP and the films were deposited by a dip-coating process on silicon (100) as substrate. Solutions with ionic concentration of 0.1 and 0.2 M were used. Thin film deposition was accomplished by dipping the substrates in the solution with control of withdrawal speed from 5 to 20 mm/min. The thin films were thermally treated in two steps: at 300°C and 650°C. The influence of withdrawal speed, viscosity, heating rate and ionic concentration on the morphology of PLZT thin film was discussed.

Keywords: Dip-coating; Films; PLZT; Precursors-organic; Substrates; Surfaces

1. Introduction

Lead lanthanum zirconate titanate with the chemical formula $Pb_{1-x}La_x(Zr_yTi_z)_{1-x/4}O_3$ shows ferroeletric behavior and can be used in devices such as image displays, optorecording and optomodulating elements with large optoeletronic effects.[1] The physical methods used for preparing thin films, such as rf-sputtering,[2] laser ablation[3–6] metallo-organic decomposition[7] direct current sputtering,[8] ion beam sputtering[9] and molecular beam epitaxy[10] are not suitable for preparing large specimens or controlling the composition. On the other hand, the use of chemical methods leads to obtaining thin films with a good control over the stoichiometry and a lower synthesis temperature to obtain the crystalline phase. The chemical methods mostly utilized were sol-gel, polymeric precursors and organometallic decomposition (MOD). Among the process that use chemical precursors to deposit thin films, the more utilized are dip-coating and spin coating. Dip-coating is a very simple process used to deposit a thin film from a polymeric solution. In this process, a specified substrate is dipped in a uniform solution, after that it is withdrawn from the solution, dried, and heat-treated. Even for a multicomponent system such as PLZT, a uniform composition can be obtained since the cations are mixed in the solution. A coating can also be applied to prepare large and irregular shaped objects. Although films with good electrical, magnetic or optical properties have been obtained by this method, the films with ferroelectric and piezoelectric properties are usually obtained by physical methods.[11]

The polymeric precursor method can be divided into two groups.[12] The first is in situ polymerization of organometallic monomers and the second involves the preparation of a viscous solution system containing metal ions, polymers and a solvent.

This viscous solution can be easily converted into a thermoplastic gel at high polymer concentrations. The in situ polymeric precursors method has been used extensively to obtain ceramic powders with small particle size and in a single phase.[13–14] This method was originally developed by Pechini[15] and is based on the

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0955-2219/01/$ - see front matter
PII: S0955-2219(00)00341-1

chelation of a metallic cation by a carboxylic acid, such as citric acid, and further polymerization promoted by the addition of ethylene glycol and consequent polyesterification. However, this method has been little used to obtain thin films. Liu and Wang reported the deposition of $La_{1-z}Sr_zCo_{1-y}Fe_yO_{3-y}$ on dense or porous substrates using the polymeric precursors method.[16] They obtained nonporous and uniform crack-free film 400 nm thick with a single dip. According to Liu and Wang the most important parameter is the citric/metal ratio in controlling the deposition process.

Unfortunately, the disadvantage of polymeric precursor method for preparation of thin films is the appearence of cracking caused by development of stress during the thermal treatment used for the decomposition of the polymeric solution and formation of the ceramic film. In general, the appearence of cracks is lower in thinner films. The main reason is that in the thinner coatings the adhesion on the interface film-substrate is higher and a lateral shrinkage of film is suppressed. When the critical value for thickness of films is reached, the cracks cannot be avoided. To obtain the crack-free films it is necessary to control the parameters including characteristics of the solution such as viscosity and ionic concentration, substrate-film adhesion, conditions of heating and withdrawal speed. The differences between the thermal expansion coefficients of the film and the substrate has also influenced this behavior.[17] Moreover, the use of a clean room is advisable in order to avoid cracks and other contamination from the environment.

In the present work PLZT ferroelectric thin films were prepared by dip-coating using a polymeric solution. The conditions necessary for producing high-quality films were investigated.

2. Experimental procedure

The composition of PLZT used in this study was 9/65/35 with formula $Pb_{0.91}La_{0.09}(Zr_{0.65}Ti_{0.35})O_3$. Zirconium *n*-propoxide (Aldrich), titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and lead acetate (Merck) were used as raw materials. The precursor solutions of zirconium, titanium, lanthanum and lead were prepared by adding the raw materials to ethylene glycol and citric acid with heating and stirring. Appropriate quantities of solutions of Zr, Ti, Pb and La were mixed and homogeneized by stirring at 90°C. The PLZT polymeric solution was characterized by thermogravimetry (TG) and differential thermal analysis (DTA) aiming to determine the temperatures of decomposition and crystallization of the PLZT (SDT2960). The analyses were carried out in atmosphere of synthetic air (White Martins) at a heating rate of 3°C/min. α-Al_2O_3 was used as a standard. The solution viscosity was adjusted by addition of water in the range of 20 to 56 cP and measured by Brookfield viscosimeter (TC, 500). The films were deposited by a dip-coating process (MQCTL2000MP). The withdrawal speed of substrate from the solution was adjusted at 5, 10 and 20 mm/min, and the heating rate was adjusted at 5, 10 and 20°C/min. These conditions were used to obtain homogeneous and crack-free films. PLZT films obtained from polymeric solution were deposited on silicon (100) substrates (Nova Electronic Materials INC) with thickness of 330–430 μm and pre-annealed at 90°C in a hot plate for polyesterification, elimination of water and excess ethylene glycol. After the pre-annealing, the films were treated in two steps, first the heating rate was 1°C/min up to 300°C and second it was 5 to 20°C/min up to 650°C for 3 h. Films with 1, 2 and 3 layers were prepared. After each dip the films were treated at 650°C for 3 h. For the XRD the films deposited on Si substrate were placed on a glass support with a diameter of 4 cm and thickness of 3 mm. Phase analysis of the films were performed at room temperature using X-ray diffractometer (Siemens D-5000) under the following experimental conditions: 40 kV, 30 mA, $20 \leqslant 2\theta \leqslant 50$, $\Delta 2\theta = 0.02°$, $\lambda \mathrm{Cu}K_\alpha$ monocromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, step time = 10 s. The morphology and thickness of the annealed films were studied using scanning electron microscopy (Topcon SM-300). The PLZT film surfaces were analyzed without any cover or special preparation by incidence of secondary electrons while the thickness was measured from the transversal section.

3. Results and discussion

3.1. Preparation of the PLZT Film

3.1.1. Characterization of the polymeric solution

In order to determine the best condition of annealing and to obtain crack free PLZT thin films, a thermal analysis was perfomed. Fig. 1 shows the TG curves of the PLZT polymeric solution obtained from room temperature up to 800°C using a heating rate of 3°C/min. In this figure the existence of three stages of weight loss can be observed. The first stage (170 to 275°C) is related to elimination of water produced during the process of esterification and the excess of ethylene glycol. The second (275 to 400°C) corresponds to a break away of the polymeric chains formed by a polyesterification reaction. The third, between 400–460°C, is due to the decomposition of organic compounds, as it is in agreement with some literature data.[18] After that, no weight loss can be detected because the decomposition of the organic material has finished. The endothermic signals, in the range of 110–150°C and 190–230°C, were attributed to the evaporation of water and solvents,

respectively (DTA curve, Fig. 2). A very intense exotherm signal observed in the range of 400–450°C was assigned to the pyrolysis of organic ligands and crystallization of PLZT phase (DTA curve, Fig. 2). It should be noticed that above 460°C the PLZT stable phase was formed.

In previous studies it was observed that the films annealed at 650°C for 3 h were crystalline and showed good morphologic characteristics.[18] Therefore, in this work, the same conditions of annealing are used.

3.2. Characterization of the phase

Fig. 3 shows the XRD patterns of the films deposited on silicon (100) substrate using withdrawal speed of 5 mm/min, heating rate of 5°C/min, $\eta = 28$ cP and annealed at 650°C for 3 h. It was observed that the films are polycrystalline without preferential orientation and the peaks are located at $2\theta = 22°$; 31.3°; 38° and 44.78°. The main peak of PLZT crystalline phase at $2\theta = 31.3°$ were observed in Fig. 3b and c. The peak of second order for silicon (100) substrate at $2\theta = 33°$ can also be noticed (Figs 3a and b).

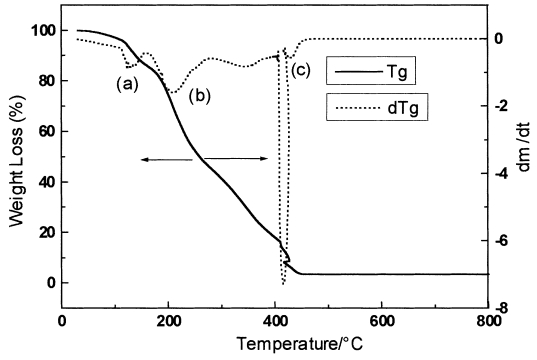

Fig. 1. TG curve of PLZT resin obtained in flow air and heating rate of 3°C/min.

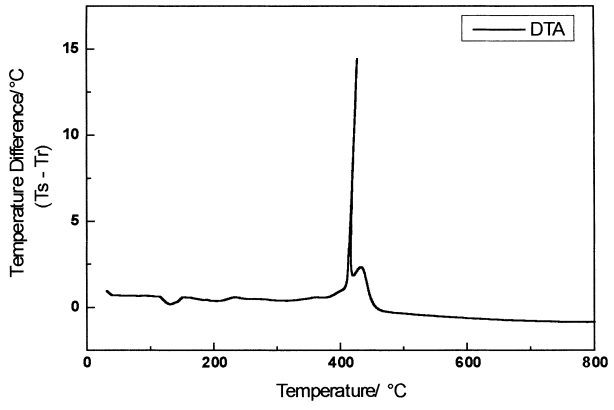

Fig. 2. DTA curve of PLZT resin obtained in flow air and heating rate of 3°C/min.

The peak of second order for silicon (100) substrate decreases when the number of layers increase. This indicates that a large amount of material on substrate surface influences the appearance of higher intensities diffraction peaks (Fig. 3c).

It can be supposed that the appearance of a broad peak in the range of $2\theta = 33°$ to 36° only for one layer was caused by the small amount of material on silicon substrate. The amorphous phase of the glass support was detected by X-ray diffraction.

Previously, it was noticed that for viscosity lower than 20 cP and for one layer the silicon substrate reacted with PbO at the temperatures higher than 600°C, resulting in formation of the $PbSiO_4$ phase.[18] This effect was not observed for the viscosity of 28 cP, as it was not investigated in their case.

3.3. Morphology of the PLZT film

3.3.1. Effect of the withdrawal speed

The solution with the highest viscosity (56 cP) was chosen to determine the convenient withdrawal speed. In fact, it is necessary to control the withdrawal speed to prevent that the thickness of the films promoting the formation of cracks and bubbles after annealing. To justify the best withdrawal speed, speeds of 5, 10 and 20 mm/min were used to prepare the films with 1, 2 and 3 layers.

The films were deposited on silicon (100) substrate and annealed at 650°C for 3 h and their surfaces were analysed by scanning electron microscope. The micrographs of films obtained from the solution with viscosity of 56 cP and prepared with 3 layers are shown in Fig. 4. The films prepared with a withdrawal speed of 5 mm/min show smaller size of cracks than films prepared with a withdrawal speed of 10 and 20 mm/min (Fig. 4a). It can be observed in Fig. 4b and c, that the films obtained with a withdrawal speed of 10 and 20 mm/min, show a higher number of cracks due to the presence of excess of

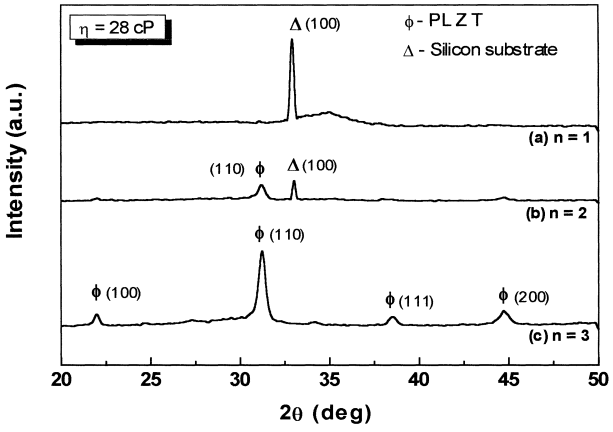

Fig. 3. XRD patterns of PLZT films ($\eta = 28$ cP, 0.1 M) annealed at 650°C for 3 h: (a) 1 layer; (b) 2 layers; (c) 3 layers.

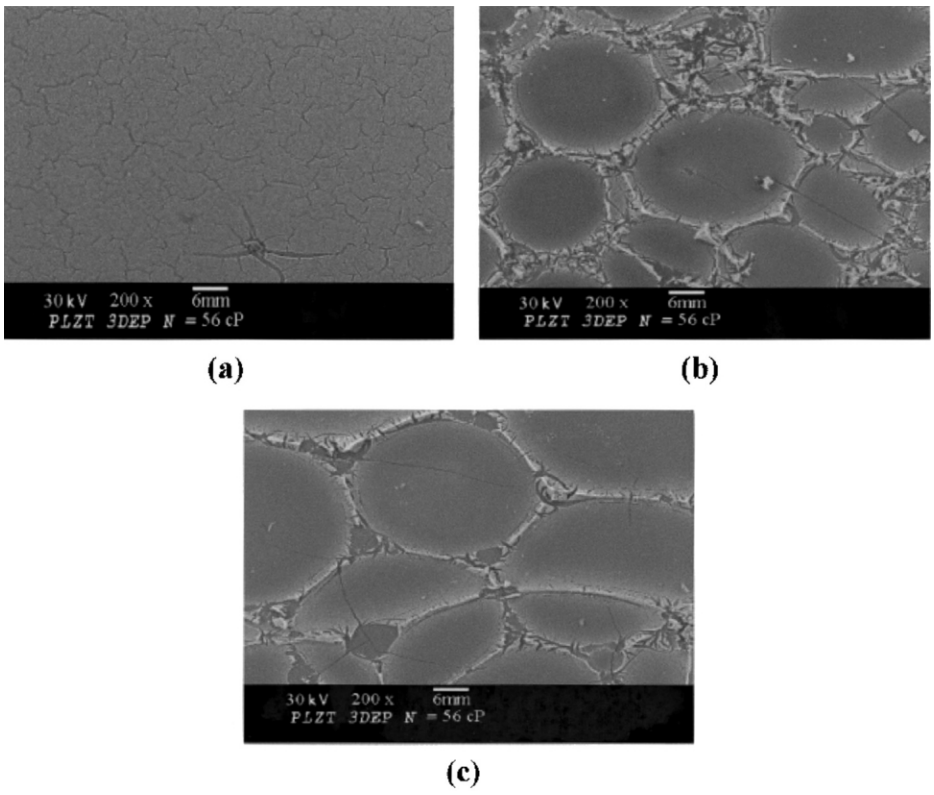

Fig. 4. SEM micrographs of PLZT film surfaces ($\eta = 56$cP) obtained on silicon (100) with different withdrawal speeds and annealed with heating rate of 5°C/min at 650°C for 3 h: (a) 5 mm/min, (b) 10 mm/min, (c) 20 mm/min.

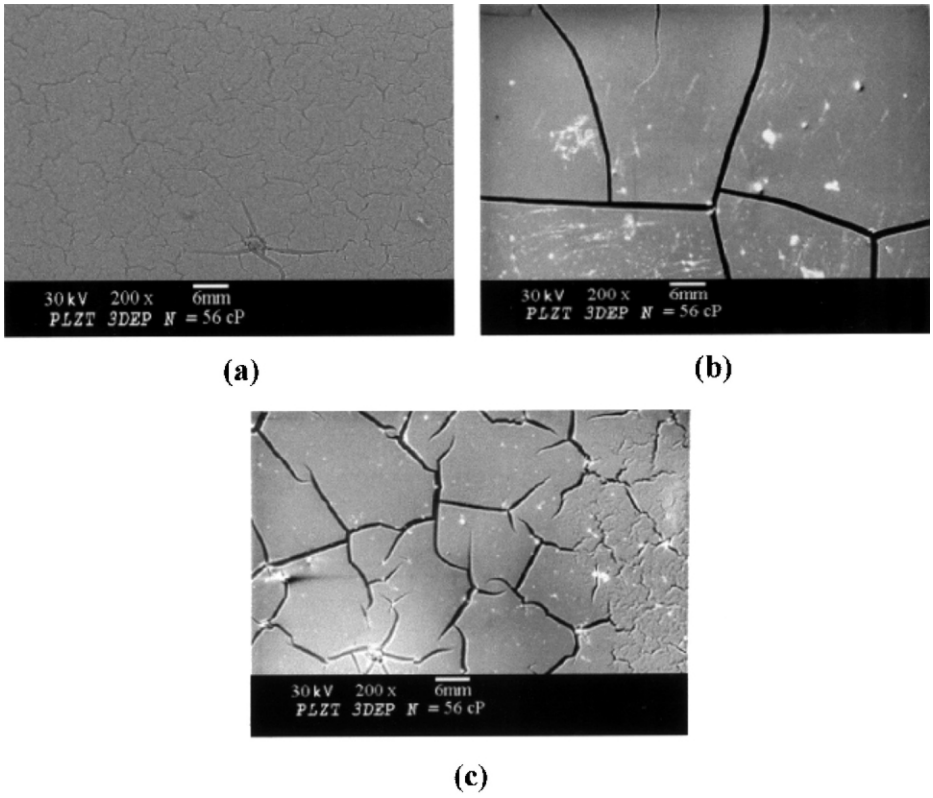

Fig. 5. SEM micrographs of PLZT film surfaces ($\eta = 56$ cP) obtained on silicon (100) with speed of 5 mm/min and annealed at 650°C for 3 h at different heating rates: (a) 5°C/min; (b) 10°C/min; (c) 20°C/min.

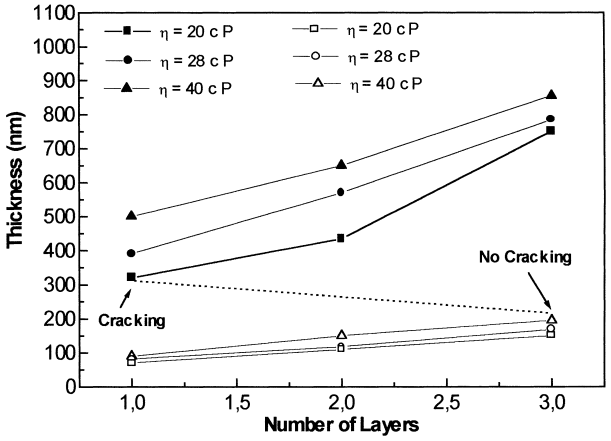

Fig. 6. Thickness versus number of layers after annealing at 650°C for 3 h. Closed symbols (0.2 M) and open symbols (0.1 M).

material on substrate surface. The cracks of the films were influenced during annealing due to the differences in the thermal expansion coefficient of the ceramic material and silicon substrate (heat capacity $= 3\times10^{-6}$ C^{-1} for Si and heat capacity $= 5.6\times10^{-6}$ $°C^{-1}$ for PLZT).

Therefore, the best withdrawal speed of substrate from the solution was 5 mm/min, pointed to the fact that the higher rate leads to the appearence of cracks and bubbles in the films.

3.3.2. Effect of the heating rate

The decomposition speed of the organic material from the deposited layer is also a very important parameter which can induce cracks in the microstructure. Taking this into account the heating rate was changed from 5 up to 20C/min aiming to establish the best condition of heating rate to obtain films with good characteristics. It is observed in the micrographs (Fig. 5) that the increase of the heating rate, for the same viscosity and withdrawal speed, leads to a higher number of cracks. Higher heating rates lead to faster organic decomposition and increases the shrinkage rate.

3.4. Effect of the ionic concentration

It is well known that the thickness of the layer is a function of viscosity, ionic concentration of the solution and withdrawal speed. As shown in Fig. 6, the film thickness, after annealing at 650°C for 3 h using a heating rate of 5°C/min, increases with the increase of the number of layers, viscosity and ionic concentration. The films obtained from solution with 0.2 molar concentration of ions show a larger thickness than the films obtained from solution with 0.1 molar concentration of ions. The critical thickness for appearence of cracks is in the range of 195 to 320 nm and can be identified by the dashed line in Fig. 6. This indicates that the cracks are

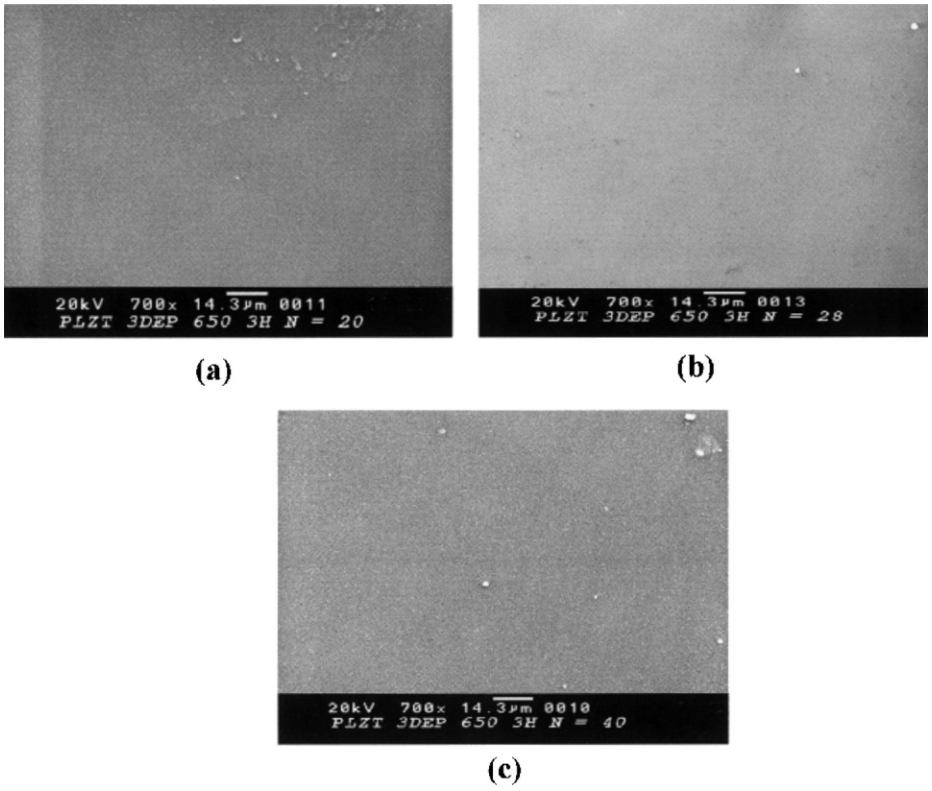

Fig. 7. SEM micrographs of PLZT film surfaces (0.1 M) obtained on silicon (100) with speed of 5 mm/min, heating rate of 5°C/min and annealed at 650°C for 3 h at different viscosities: (a) $\eta = 20$ cP; (b) $\eta = 28$ cP; (c) $\eta = 40$ cP.

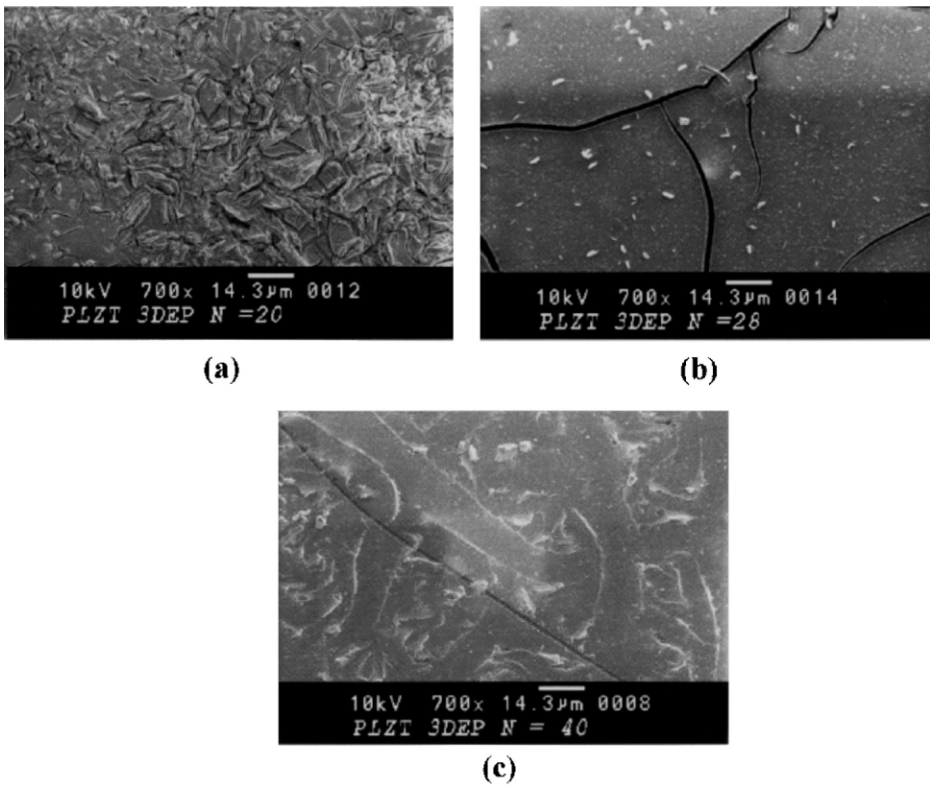

Fig. 8. SEM micrographs of PLZT film surfaces (0.2 M) obtained on silicon (100) with speed of 5 mm/min, heating rate of 5°C/min and annealed at 650°C for 3 h at different viscosities: (a) $\eta = 20$ cP; (b) $\eta = 28$ cP; (c) $\eta = 40$ cP.

controlled by ionic concentration of solution. Obviously, films obtained from solution with the same viscosity but smaller ionic concentration (0.1 M) show a smooth morphology and crack-free surface (Fig. 7). The same conclusions can be drawn from films obtained from solutions of differents viscosities but the same ionic concentration (0.1 M).

3.5. Morphology of the crack

It was emphasized that the control of the viscosity and ionic concentration of solution, heating condition, withdrawal speed as well as the differences in the thermal expansion coefficients of film and substrate show very important factors and have to be considered in the preparation of thin films. For example, for the same conditions of withdrawal speed, heating rate and ionic concentration but by different viscosities (Fig. 8), the various morphologies of cracks can be noticed. One kind of crack shown in Fig. 8a has the appearance of a rosette, which is short and branching from the center. This kind of rosette can be observed over the whole surface of the film and occurs at lower viscosities. The other kinds of crack have the appearance of a long straight line and can be observed in Fig. 8b and c. These cracks are observed in films obtained from solution with higher viscosity.

4. Conclusion

Homogeneous and crack free PLZT thin films were obtained by organic citrate solutions deposited by dip-coating on Si (100) substrate. To obtain the homogeneous PLZT films it is necessary to adjust the heating rate during annealing, withdrawal speed of the substrate from the solution, viscosity and ionic concentration of the solution. The best conditions to obtain the films are: heating rate of 5°C/min, withdrawal speed of 5 mm/min, viscosity in the range of 20 to 40 cP and ionic concentration of 0.1 molar. In these conditions crack-free PLZT films can be obtained up to a thickness of 195 nm.

Acknowledgements

The authors acknowledge the Brazilian agencies CNPq, CAPES and Fapesp for financial support of this work.

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