



Effect of Thermal Treatment Temperature on the Crystallinity and Morphology of LiTaO_3 Thin Films Prepared from Polymeric Precursor Method

A.H.M. GONZÁLEZ,^{1,*} A.Z. SIMÕES,¹ M.A. ZAGHETE,¹ E. LONGO² & J.A. VARELA¹

¹*Centro Multidisciplinar para o Desenvolvimento de Materiais Cerâmicos, Instituto de Química - UNESP/Araraquara, Rua Prof. Francisco Degni s/n, Quitandinha, Araraquara, São Paulo, Brazil, CEP 14801-970, P.O. Box 355*

²*Centro Multidisciplinar para o Desenvolvimento de Materiais Cerâmicos, Departamento de Química - UFSCar, Rod. Washington Luís km 235, São Carlos, São Paulo, Brazil, CEP 13565-905, P.O. Box 676*

Submitted February 5, 2003; Revised February 2, 2004; Accepted February 13, 2004

Abstract. Lithium tantalate thin films (LiTaO_3) with (50:50) stoichiometry were prepared by spin coating method using a polymeric organic solution. The films were deposited on silicon (100) substrates with 4 layers. The substrates were previously cleaned and then the solution of lithium tantalate was deposited by adjusting the speed at 5000 rpm. The thin films deposited were thermally treated from 350 to 600°C for 3 hours in order to study the influence of the thermal treatment temperature on the crystallinity, microstructure, grain size and roughness of the final film. X-ray diffraction (XRD) results showed that the films are polycrystalline and secondary phases free. The thickness of films was observed by scanning electron microscopy (SEM). The atomic force microscopy (AFM) studies showed that the grain size and roughness are strongly influenced by thermal treatment.

Keywords: lithium tantalate, thin films, polymeric precursor, crystallinity, morphology

1. Introduction

Lithium tantalate, LiTaO_3 , is a leading electro-optical material for active waveguides [1], surface acoustic wave devices [2], holographic storage [3] and electro-optic deflectors [4] because it has large non-linear optical coefficients, a high Curie point, a high electro-optic coefficient and excellent acousto-optic coefficient [5]. The performance of devices crafted from the bulk crystal is limited by the geometrical factors, size and thickness, rather than by the material properties. Therefore, the availability of this material in a high quality thin film form would increase its potential and open new areas for its application [6].

Recent progresses in ferroelectric thin-film technologies have produced a number of processes to prepare epitaxial or highly oriented ferroelectric thin films

for fabricating non-volatile memories, optoelectronic devices, miniature capacitors or surface acoustic wave devices [7]. The deposition of high-quality thin films is important to the fabrication of integrated electro-optic devices. Amorphous lithium tantalate films on a glass substrate [8], epitaxial films on sapphire substrates [9] and polycrystalline films on silicon or platinum substrates [6] have been grown by a large variety of physical and chemical deposition techniques such as chemical vapor deposition (CVD) [10], liquid phase epitaxy (LPE) [11], chemical beam epitaxy (MBE) [12], r. f. sputtering [13] and pulsed laser deposition (PLD) [14]. Most of these techniques, however, are not only expensive but also involve difficult stoichiometric quantification and complex equipment. Sol-gel processing [5], a solution-based method, is interesting due to the easier production of low cost, large area thin film. However, the commonly used alkoxide precursors to produce LiTaO_3 films by sol-gel methods are highly reactive and require careful control of the hydrolysis-condensation reaction.

*To whom all correspondence should be addressed. E-mail: alejgonz@posgrad.iq.unesp.br

The polymeric precursor process is an attractive method to prepare thin films, offering some advantages over other methods, such as accurate stoichiometric control, good compositional homogeneity, use of aqueous solution, high purity, low-temperature processing and low cost. For these reasons, the aim of the present study was to prepare high-quality LiTaO_3 thin films from polymeric precursor method. Subsequently, several studies were performed to verify the effect of thermal treatment on the crystallization process and morphology of the deposited films.

2. Experimental Procedure

Lithium and tantalum precursor solutions were prepared separately by polymeric precursor method. This method is based on metallic citrate polymerization with use of ethylene glycol. A hydrocarboxylic acid, such as citric acid, is used to chelate cations in aqueous solution. The addition of a glycol, such as ethylene glycol, leads to organic ester formation. Polymerization, promoted by heating the mixture, results in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix. Lithium carbonate, Li_2CO_3 , (Montedison) and tantalum ethoxide, $\text{Ta}(\text{OC}_2\text{H}_5)_5$, (Alfa Aesar) were used as raw materials. Figure 1(a) and (b) show the preparation schemes for lithium and tantalum solutions.

The lithium tantalate solution was obtained by mixture of individual solutions. Thermogravimetry (TG) and differential thermal analyses (DTA) of this solution were carried out to follow the decomposition and crystallization processes. Both analyses were performed on a Netzsch Simultaneous Thermal Analyzer, from room temperature to 1100°C using a heating rate of $5^\circ\text{C}/\text{min}$ in static air.

To deposit the films the viscosity of the lithium tantalate solution was adjusted at 20 cP by adding a controlled amount of deionized water. Silicon (100) substrates were cleaned with Extran solution (Merck) prior to use. Lithium tantalate films with 4 layers were deposited on substrates by spin coating method at a rotation speed of 5000 rpm for 30 s. Then, the thin films were thermally treated using a two-step heat treatment. A preheating at 300°C for 1 h with heating rate of $2^\circ\text{C}/\text{min}$ was used to eliminate water and excess ethylene glycol, and promote the polyesterification process. After that, the films were heated from 350°C to 600°C for 3 h with heating rate of $5^\circ\text{C}/\text{min}$ to reach the crystallization stage.

The crystallization process of the prepared films was analyzed by X-ray diffraction (XRD) using X-ray diffractometer (Rigaku Gergenfex, RINT2000 vertical goniometer). The film surface morphology was observed with an atomic force microscope (Digital Instruments Nanoscope IIIA). A scanning electron

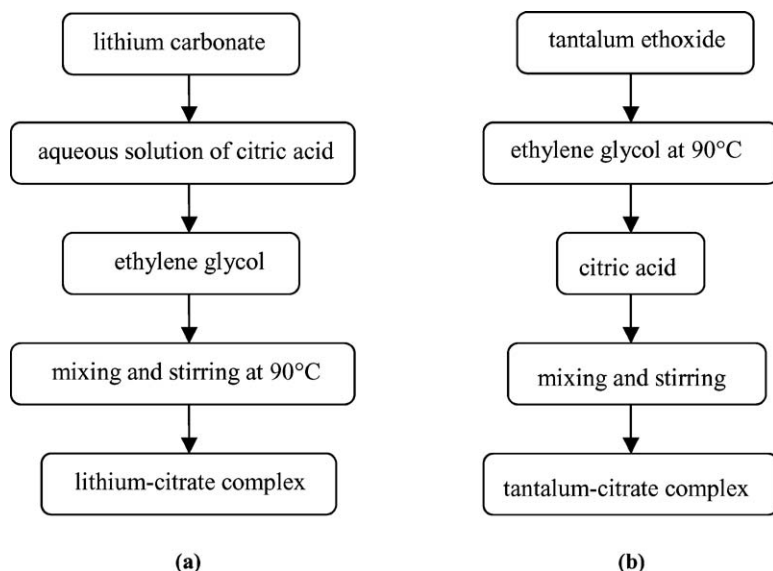


Fig. 1. Flow chart for the preparation of (a) lithium and (b) tantalum precursor solutions.

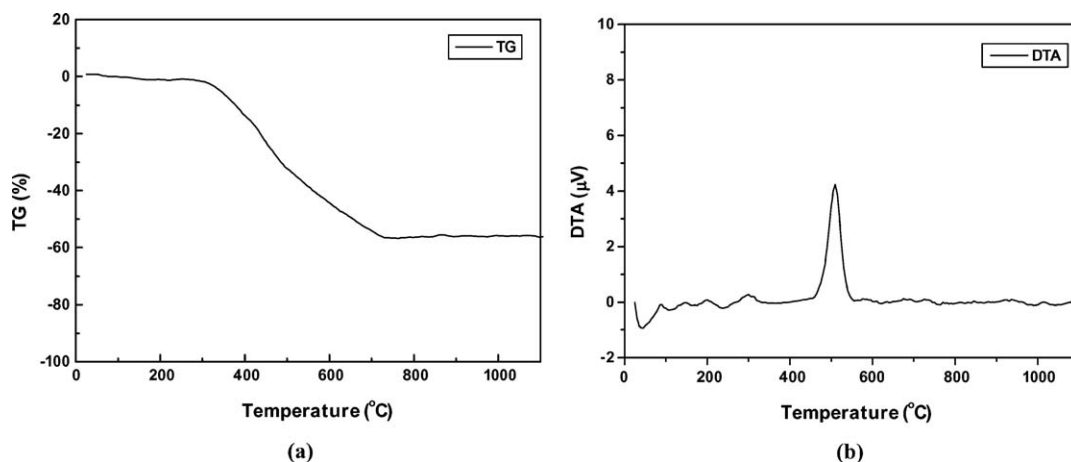


Fig. 2. TG (a) and DTA (b) curves of lithium tantalate solution.

microscope (Zeiss 940 A) was used to determine the thickness of films.

3. Results and Discussion

To define with accuracy the temperature that begins the crystallization process, a thermogravimetry-differential thermal analysis was performed. The thermal decomposition of the lithium tantalate solution is illustrated in Fig. 2. The TG curve, Fig. 2(a),

indicates an overall weight loss of 56% between 25 and 740°C. This weight loss is due to the dehydration and decomposition of organic matter. The DTA curve, Figure 2(b), shows an exothermic process at 510°C. The pronounced and sharp peak is related to the crystallization of the LiTaO₃ phase. This will be confirmed by XRD analysis of the deposited thin films.

Figure 3 shows the θ - 2θ scans, ranging from 20° to 65°, of the LiTaO₃ thin films annealed from 350°C to 600°C for 3 hrs. The results revealed that the films heat treated between 350 and 450°C were still amorphous.

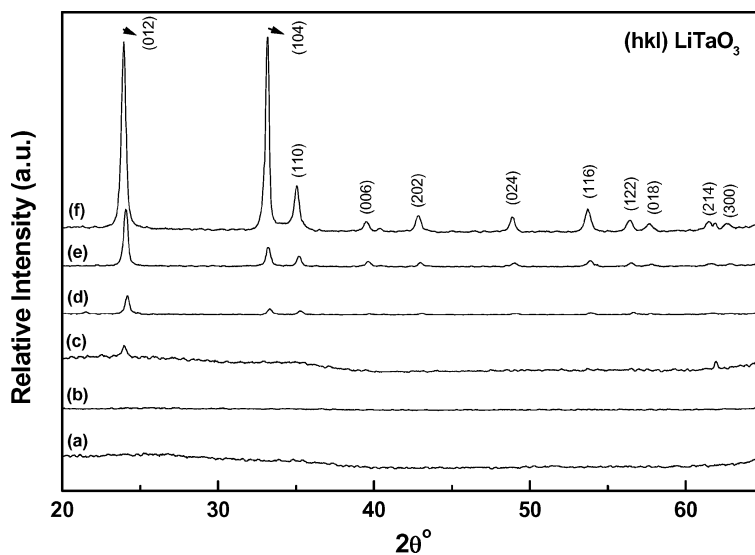


Fig. 3. XRD patterns of 4-layered LiTaO₃ thin films deposited on silicon (100) and thermally treated at: (a) 350°C/3h; (b) 400°C/3h; (c) 450°C/3h; (d) 500°C/3h; (e) 550°C/3h; (f) 600°C/3h.

For the thin film heat treated at 500°C, the corresponding XRD data exhibit diffraction peaks belonging to the formation of LiTaO_3 , which suggests the beginning of crystallization.

At this temperature the organic compounds were already gradually decomposing. A correlation between the process of phase crystallization and organic fraction elimination is therefore evident. Heating the thin film at 600°C leads to a highly crystalline phase.

The fact that no preferential orientation is observed indicates that the films are polycrystalline. There are significant difficulties for the growth of oriented

LiTaO_3 films on silicon substrates due to the following reasons.

- (1) LiTaO_3 has the hexagonal (rhombohedral) symmetry while Si crystallizes with the cubic structure [7]. These geometric mismatches are evidently not suitable for heteroepitaxy.
- (2) Stresses at the silicium-lithium tantalate interface due to differences in the structures as well as in thermal expansion coefficients can serve as an additional factor for the formation of imperfections and non-oriented growth.
- (3) Possible reactions between LiTaO_3 and Si can lead, not only to the production of undesirable phases

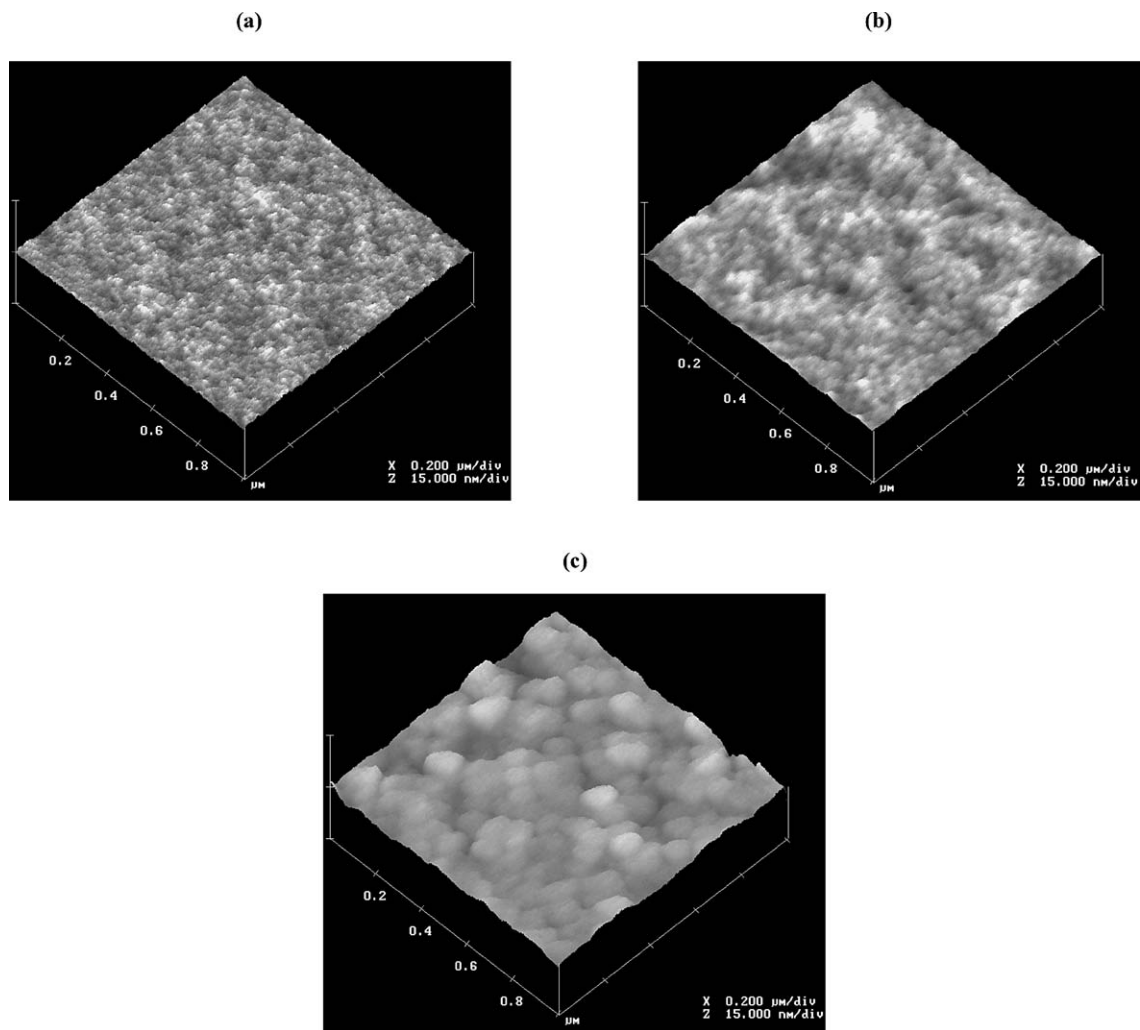


Fig. 4. AFM images of 4-layered LiTaO_3 thin films deposited on silicon (100) and thermally treated at: (a) 400°C/3 h; (b) 500°C/3 h; (c) 600°C/3 h.

at the thin film/substrate interface, but also to the diffusion of Si in the film.

Generally, epitaxial growth of thin films is facilitated by a lattice-matched starting substrate, as there is a tendency for the substrate to serve as a template for further crystalline growth of the film.

All peaks and associated planes represented in Fig. 3 are in agreement with the crystallographic data of the LiTaO₃ rhombohedral phase, obtained by JCPDS-International Center for Diffraction Data.

Average grain size and surface roughness of the LiTaO₃ thin films were estimated using a contact mode atomic force microscopy (AFM). The surface

morphology of the LiTaO₃ thin films thermally treated at 400, 500 and 600°C is illustrated in Fig. 4.

The microstructure study revealed that all surfaces are not only crack-free but also appear relatively smooth. It was observed that the thin films thermally treated at 400°C presented homogeneous surface, however it is still amorphous. At 500°C the beginning of the crystallization process is observed, which is followed by the growth of spherical grains with homogeneous grain size at 39, 59 and 102 nm, for temperature of 500, 550 and 600°C respectively. These results are in agreement with XRD analyses.

Table 1 summarizes the thickness, roughness and grain size data of the LiTaO₃ thin films prepared by polymeric precursor method.

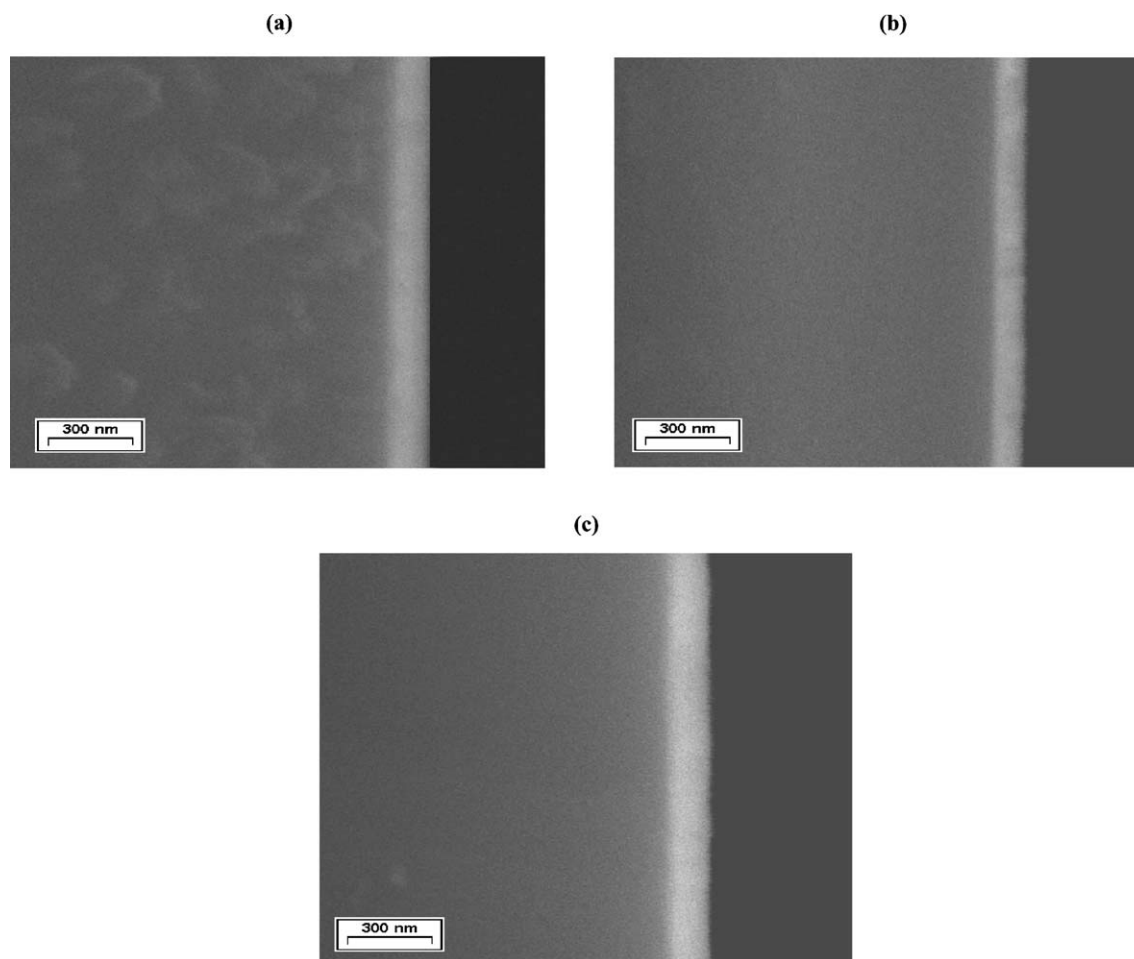


Fig. 5. Thickness micrographs obtained by SEM of 4-layered LiTaO₃ thin films deposited on silicon (100), and thermally treated at: (a) 400°C/3 h; (b) 500°C/3 h; (c) 600°C/3 h.

Table 1. Thickness, roughness and grain size of LiTaO₃ thin films deposited on silicon (100) by spin coating method and thermally treated at different temperatures.

Thermal treatment (°C/3h)	Thickness (nm)	Roughness (nm)	Grain size (nm)
350	134	0.2	–
400	130	0.2	–
450	109	0.3	–
500	116	0.3	39
550	127	0.5	59
600	152	0.8	102

To determine the thickness of LiTaO₃ thin films, high-magnification SEM observation (50,000×) was performed. The roughness data, R_{MS}, were obtained for an area of 1 μm × 1 μm. Surface roughness was calculated using the equipment's software routine.

It can be seen that the thickness of the films decreased with increasing the annealing temperature, between 350 and 450°C, due to the densification of films. However, as the temperature increased from 450 to 600°C, both thickness and roughness data of films increased. According to the authors, the change of the film surface texture with increased heat-temperature would be due to surface tension effects, which become predominant at high temperature.

Note that the grain size is mainly influenced by the temperature of annealing, which explains its variation according to the thermal treatment performed. The grain size typically increases with temperature due to enhanced surface mobility. Species diffusing on the surface can, therefore, reach growing crystallites reducing the density of nucleating sites. As the density of the nucleating sites decreases, the grain size should increase.

In this study, the film heat treated at 600°C presented a thicker surface. Also, the surface roughness of this film was highest. These behaviors are probably due to a natural thermodynamic process driven by interface energy-i.e., surface energy of the film and film-substrate interfacial energy.

Surface morphology and roughness are important for many LiTaO₃ thin film applications, especially for waveguides. Several factors may play a role in the improved surface smoothness of LiTaO₃ films, including improved surface kinetics and energetics and a better lattice match between the film and substrate.

Figure 5 shows the thickness images obtained from transversal section of thin films thermally treated at different temperatures. SEM analyses showed that the film/substrate interface presented a very good adhesion.

4. Conclusions

Polycrystalline LiTaO₃ thin films deposited on silicon (100) substrates were prepared from polymeric precursor method. In addition to their crystalline structure, the films exhibited smooth and relatively homogeneous surface.

The control of temperature during the thermal treatment is an important parameter in the formation of good-quality thin films since the grain growth and roughness surface are mainly influenced by the thermal process. When higher temperatures are used, the decomposition of organic material is faster and an improvement of the crystallization phase is noticed. On the other hand, the surface roughness of the film heat treated at 600°C was highest. Stress at the silicium-lithium tantalate interface due to differences in the structures as well as in thermal expansion coefficients probably is the reason for the formation of deteriorated surface.

Acknowledgments

The authors gratefully acknowledge the financial support of the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Proj. No. 01/06515-5 and 00/01991-0.

References

1. J.M. Mir and J.A. Agostinelli, *Journal of Vacuum Science Technology A*, **12**, 1439 (1994).
2. J. Koskela, J.V. Knuutila, P.T. Tikka, C.S. Hartmann, and V.P. Plessky, *Applied Physics Letters*, **75**, 2683 (1999).
3. J. Imbrock, S. Wevering, K. Buse, and E. Kratzig, *Journal of Optical Society of America B*, **16**, 1392 (1999).
4. G.J. Friel, R.S. Conroy, A.J. Kemp, B.D. Sinclair, and J.M. Ley, *Applied Physics B*, **67**, 267 (1998).
5. S.D. Cheng, C.H. Kam, Y. Zhou, X.Q. Han, W.X. Que, Y.L. Lam, Y.C. Chan, J.T. Oh, and W.S. Gan, *Thin Solid Films*, **365**, 77 (2000).
6. F. Gitmans, Z. Sitar, and P. Gunter, *Vacuum*, **46**, 939 (1995).
7. V. Bornand, P. Papet, and E. Philippot, *Thin Solid Films*, **304**, 239 (1997).

8. D.P. Gia Russo and C.S. Kumar, *Applied Physics Letters*, **23**, 229 (1973).
9. T.N. Blanton and D.K. Chatterjee, *Thin Solid Films*, **256**, 59 (1995).
10. T. Majima, H. Yamamoto, S.A. Kulinich, and K. Terashima, *Journal of Crystal Growth*, **220**, 336 (2000).
11. K. Kaigawa, T. Kawaguchi, M. Imaeda, H. Sakai, and T. Fukuda, *Journal of Crystal Growth*, **191**, 119 (1998).
12. R. Bellman and R. Raj, *Vacuum*, **48**, 165 (1997).
13. V. Bornand, I. Huet, P. Papet, and E. Philippot, *Annales de Chimie Science des Materiaux*, **26**, 49 (2001).
14. X.L. Guo, Z.G. Liu, S.N. Zhu, T. Yu, S.B. Xiong, and W.S. Hu, *Journal of Crystal Growth*, **165**, 187 (1996).