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Dielectric properties of $Ca(Zr_{0.05}Ti_{0.95})O_3$ thin films prepared by chemical solution deposition

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Abstract

$Ca(Zr_{0.05}Ti_{0.95})O_3$ (CZT) thin films were grown on Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) substrates by the soft chemical method. The films were deposited from spin-coating technique and annealed at 928 K for 4 h under oxygen atmosphere. CZT films present orthorhombic structure with a crack free and granular microstructure. Atomic force microscopy and field-emission scanning electron microscopy showed that CZT present grains with about 47 nm and thickness about 450 nm. Dielectric constant and dielectric loss of the films was approximately 210 at 100 kHz and 0.032 at 1 MHz. The Au/CZT/Pt capacitor shows a hysteresis loop with remnant polarization of $2.5\,\mu C/cm^2$, and coercive field of 18 kV/cm, at an applied voltage of 6 V. The leakage current density was about $4.6 \times 10^{-8}\,A/cm^2$ at 3 V. Dielectric constant–voltage curve is located at zero bias field suggesting the absence of internal electric fields.
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Keywords: Dielectric properties; Thin films; Chemical solution deposition; CZT

1. Introduction

Recently, several papers have investigated the dielectric and ferroelectric properties of thin films for use as a capacitor for future generations of dynamic random-access memory (DRAM) [1–4]. However, these perovskite present lead in their composition, which contain certain degree of toxicity. Therefore, the development of new environmentally friendly materials is important [5]. The effect of substitution of Ti by Zr in ABO_3 perovskites such as: $PbTiO_3$ [6], $BaTiO_3$ [7] and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ [8] promote improvements in the dielectric properties of these materials. The effects of heterovalent substitutions of titanium ions give rise to various behaviors including relaxor [9] and phase transitions [10], particularly the ferroelectric $\longrightarrow$ paraelectric transition have been investigated in $BaTiO_3$. The homovalent substitutions of barium for calcium [11] or strontium [12] have shown improvement in dielectric constant.

$CaTiO_3$ is orthorhombic with space group *Pbnm* below 1380 K, and belongs to another ‘‘orthorhombic’’ structure space group *Cmcm* between 1380 and 1500 K. At 1500 K, it transform into ‘‘tetragonal’’ structure with space group *I4/mcm*. Above 1580 K, it becomes ‘‘cubic’’ structure with space group $Pm\bar{3}m$ [13]. However, $CaZrO_3$ is an orthorhombic perovskite with space group *Pbnm*, and does not exhibit any phase transitions in pressure of 8.7 GPa at room temperature using single crystal X-ray diffraction measurements [14]. Recently, perovskite calcium zirconate titanate $Ca(Zr_xTi_{1-x})O_3$ was prepared via an acetic acid-modified sol–gel process and solid-state reaction. However, the stoichiometric phase was obtained only upon heating at 1473 K [15,16].

In this work, we focus on the preparation of the $Ca(Zr_{0.05}Ti_{0.95})O_3$ (CZT) thin films obtained through the soft chemical method, as described elsewhere [17,18], with good structural, microstructural, and dielectric

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characteristics on $Pt/Ti/SiO_2/Si$ substrates annealed at 928 K for 4 h under oxygen flow.

2. Experimental procedure

$Ca(Zr_xTi_{1-x})O_3$, with $x = 0.05$, thin films were synthesized through the polymeric precursor method (PPM). Calcium carbonate (99.9% purity Aldrich), titanium(IV) isopropoxide (97% purity Aldrich), zirconium *n*-propoxide (99.9% purity NOAH-Technologies), ethylene glycol (99% purity J.T. Baker) and citric acid anhydrous (99.5% purity J.T. Baker) were used as starting materials. Titanium citrate and zirconium citrate were formed by the dissolution of titanium(IV) isopropoxide and zirconium(IV) *n*-propoxide in aqueous solutions of citric acid, respectively, under constant stirring. These solutions were homogenized and were mixed in a molar proportion of 5:95 of zirconium and titanium, respectively. The citrate solution was stirred at 353 K to obtain a clear and homogenous solution. Calcium carbonate was dissolved in water, and then it was added in a stoichiometric quantity to the titanium–zirconium citrate solution. After the homogenization of the solution containing Ca^{2+} cations, ethylene glycol was added to promote the citrate polymerization by the polyesterification reaction [19]. The citric acid/ethylene glycol ratio was fixed at 60:40. The solution was annealed up to 353–373 K under stirring to eliminate water until a viscosity of 13 mPa. s by controlling at this stage, a clear resin was obtained, and it was used to deposited CZT thin films onto.

The CZT thin films were spin coated on $Pt/Ti/SiO_2/Si$ substrates by a commercial spinner operating at 6500 rpm for 15 s (spin-coater KW-4B, Chemat Technology). After deposition, the CZT films were kept at 423 K on a hot plate for 10 min to remove residual solvents. The heat treatment was carried out in two stages: initial heating at 623 K for 4 h at a heating rate of 274 K/min to promote the pyrolysis of the organic materials, and finally the films were annealed at 928 K for 4 h at a heating rate of 274 K/min. The three CZT layers were obtained crystallizing each layer in a furnace tube for 4 h under oxygen atmosphere until the desired thickness was reached.

The structure of the CZT thin films was analyzed by X-ray diffraction in the $\theta - 2\theta$ mode scan, recorded on a Rigaku diffractometer (Rigaku-DMax 2500PC) using Cu-Kα radiation. The microstructure of the thin films was examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) and thickness was evaluated by observing the cross-section of the films using a high-resolution field-emission gun scanning electron microscopy FEG-SEM (Supra 35-VP, Carl Zeiss). The electric properties were measured by an Au/CZT/Pt capacitor structure. The Au top electrode area $3.1 \times 10^{-4}\,cm^2$ was deposited by sputtering through a designed mask onto the film surfaces. Dielectric characteristics of the capacitor were measured a Hewlett-Packard (HP4192A) impedance/gain phase analyzer and a Radiant Technology RT6000HVS in a virtual ground mode, respectively. The leakage current–voltage (*I–V*) characteristic was determined with a voltage source measuring unit (Keithley 237). All the measurements were taken at room temperature.

3. Results and discussion

Fig. 1 presents the XRD of CZT thin films deposited on $Pt(1\,1\,1)/Ti/SiO_2/Si(1\,0\,0)$ substrates by a chemical-soft method. Only peaks of the main phase were detected suggesting that substitution of Ti by 5 mol% Zr does not induce any secondary phase formation. The split of the (2 0 0) and (1 2 1) peaks into two duplets, (3 2 1), (2 4 0) and (0 4 2) peaks into three triplets indicates the orthorhombic perovskite-type structure with space group *Pnma* and lattice parameters $a = 5.446\,\text{Å}$, $b = 7.651\,\text{Å}$, and $c = 5.346\,\text{Å}$ were obtained by the analysis of XRD pattern using the FULLPROF program.

The average grain size and the surface roughness of the CZT thin films were estimated using an AFM. The surface morphology was obtained using an area of 500×500 nm as shown in Fig. 2. Analysis of AFM data indicated that the CZT thin films present a homogeneous, smooth and crack-free surface. This indicates that the chemical-soft method allows the preparation of films with controlled morphology. The surface morphology of the CZT films, the average grain size and surface roughness are shown in Fig. 2 and Table 1.

The thickness of the CZT thin films was obtained for field-emission scanning electron microscopy (FEG-SEM) in Fig. 3. From the micrograph it is possible to observe clearly the interface between the layers. The thickness of the CZT thin films through this process are shown in Table 1.

Fig. 4 shows the frequency dependence of the dielectric constant and dielectric loss of the CZT thin film on Pt/Ti/

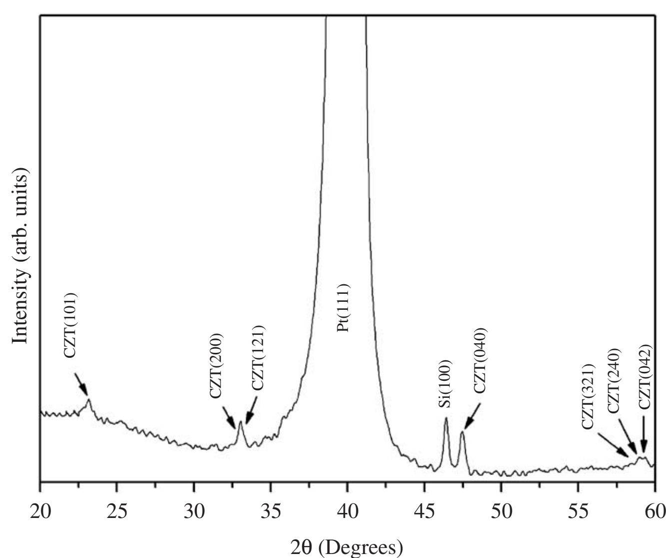

Fig. 1. XRD patterns of CZT film annealed at 928 K for 4 h in oxygen atmosphere.

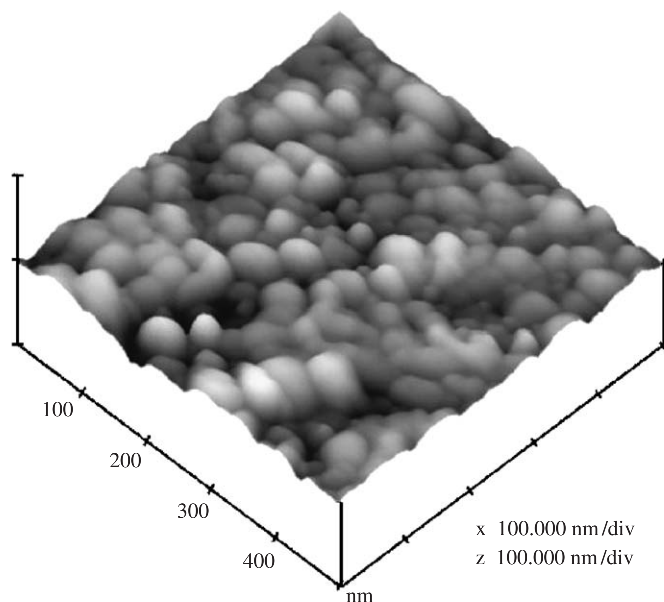

Fig. 2. AFM micrograph for CZT thin film annealed at 928 K for 4 h in oxygen atmosphere.

Table 1
Data obtained for CZT thin films measured at room temperature

Time of thermal treatment (h)	4
Average grain size (nm)	47.5
Average roughness (nm)	4.3
Average thickness (nm)	450
Remnant polarization ($\mu C/cm^2$)	2.5
Coercive field (kV/cm)	18

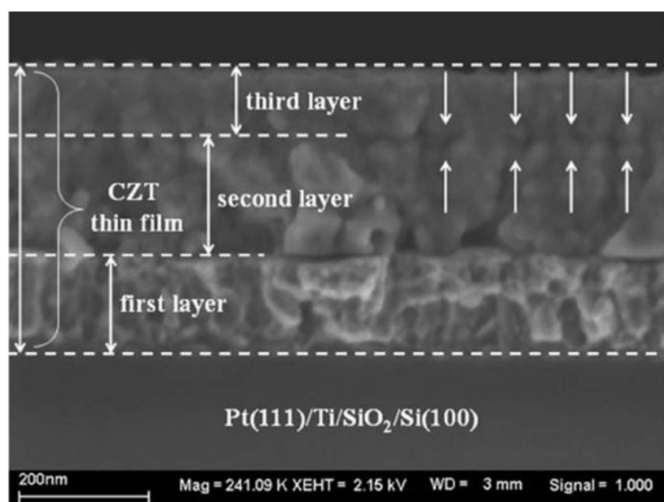

Fig. 3. FEG-SEM micrograph (241.000X) of CZT thin film grown on Pt/Ti/SiO_2/Si substrates.

SiO_2/Si substrates. The dielectric constant shows a slight decrease and the dielectric loss slowly increases with increasing frequency. The dielectric constant value at a frequency of 100 kHz is 212 and dielectric loss of 0.032 at

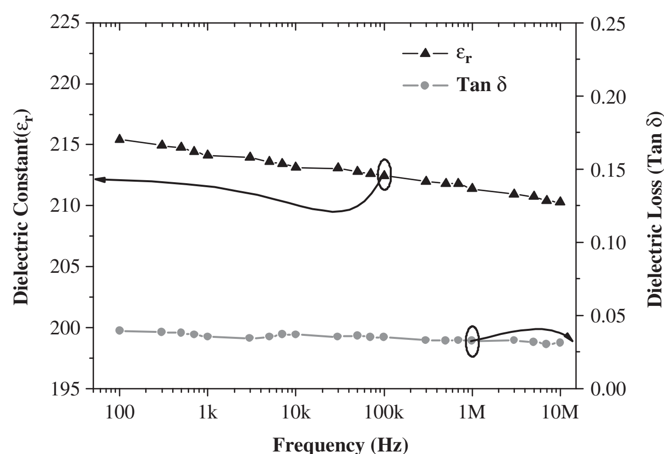

Fig. 4. Frequency dependence of the dielectric constant and dielectric loss of the CZT thin film with a Au/CZT/Pt configuration.

1 MHz at room temperature. This value of the dielectric constant is larger than the one reported by Fujii et al. [20] in $CaTiO_3$ deposited by excimer laser deposition. The dielectric constant is 120 at room temperature, and the dielectric loss is not reported. Also, $CaTiO_3$ thin films grown by pulsed laser deposition reported by Hao et al. [21] present a dielectric constant of 150 at room temperature and dielectric loss about 0.0045. The dielectric loss of the CZT film is larger presenting small variation with the increase in frequency. In contrast, $CaZrO_3$ thin films deposited by the sol–gel method present a low dielectric constant near 20 [22]. Chen et al. [23] showed that with the increase in the strontium concentration, the dielectric constants increase due to the electronic and ionic polarizations of strontium compared with calcium.

CZT thin films deposited on Pt/Ti/SiO_2/Si substrates exhibit ferroelectric characteristics, as seen in Fig. 5. Hysteresis loops measured at room temperature for CZT thin films annealed at 928 K, with applied voltage of 6 V is shown. CZT thin films showed dielectric characteristics with remnant polarization (P_r) and coercive field (E_c) showed in Table 1. The lower P_r value observed in CZT thin films are similar with the values reported by James and Prakash [24] in BZT films due the clamping effect and domain strain [25]. The switching in films with fine grains is relatively difficult. The domain walls with larger grains are easy to switch under external field compared with perovskits with small grains. Similar phenomena found in $PbTiO_3$ and $SrBi_2Ta_2O_9$ thin films were reported for the fine and larger grains [25,26].

Fig. 6 displays the typical dielectric constant–voltage (DC–V) curves for CZT thin films with the applied volt age region from 12 to -12 V.

The dielectric constant exhibited a hysteresis loop that depended on the sweep direction of the bias voltage, confirming the dielectric properties for CZT thin films. A general bell-shape of CD–V measurement was obtained with a cycling of the bias voltage up and down at room temperature. The dielectric constant–voltage dependence is

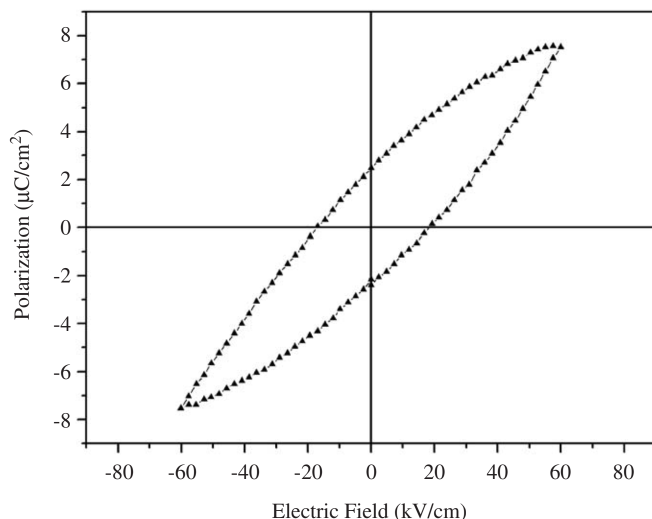

Fig. 5. *P–E* hysteresis loops for CZT thin films annealed at 928 K for 4 h in oxygen atmosphere.

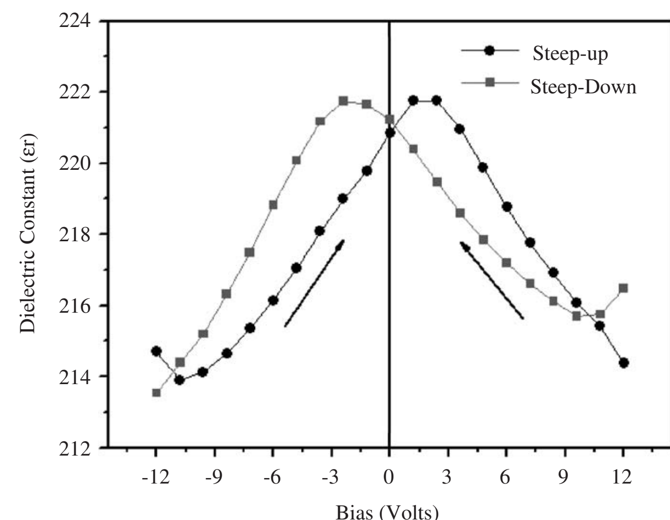

Fig. 6. Dielectric constant in dependence of voltage for CZT film annealed at 928 K for 4 h in oxygen atmosphere.

strongly nonlinear, confirming the dielectric properties of the film resulting from domain switching. The C*D–V* curve is symmetric around the zero bias axis, indicating that the films contain only few movable ions or charge accumulation at the film electrode interface.

A typical leakage current characteristic of CZT thin films, measured with a voltage step of 0.1 V and elapsed time of 1.0 s for each voltage, is shown in Fig. 7. The top electrode was biased positively. Fig. 7 shows the measured current density(J) vs the electric field(E) in a log(J) vs log(E) plot for CZT thin films. Two clearly different regions were observed. The current density increases linearly with external electric field in the low electric field region suggesting an ohmic conduction, characteristic of the Schottky emission mechanism. With increasing external field, the current density increases exponentially, characteristics of the Poole–Frenkel emission mechanism.

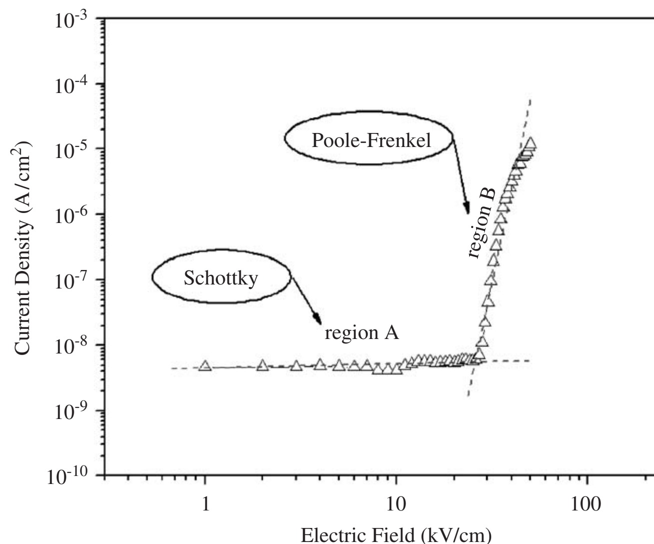

Fig. 7. Current density–electric field characteristics for CZT thin film annealed at 928 K for 4 h in oxygen atmosphere.

The leakage current density levels at 3 V were $4.6 \times 10^{-8}\,\mathrm{A/cm^2}$.

Both the Schottky and Poole–Frenkel emissions stem from lowering a Coulombic potential barrier. Schottky emission is also considered an electrode-limited conduction mechanism and occurs at low voltages, where the electrons at the surface of a metal or semiconductor transit above the potential barrier. The Poole–Frenkel emission mechanism involves a superimposed constant electric field and a localized potential, where the applied field enhanced electron emission from Coulombic donor-like centers or holes from acceptor centers [27].

4. Conclusions

Polycrystalline, homogenous and crack-free CZT thin films were prepared by the soft chemical method. The CZT thin films consisted of fine grains of approximately 47 nm, a low surface roughness (rms 4.3 nm) with a film thickness of 450 nm. The dielectric constant and dielectric loss (tan δ) at 100 kHz and 1MHz were 212 and 0.032, respectively, and the leakage current density at 3 V was about $4.6 \times 10^{-8}\,\mathrm{A/cm^2}$. *D–V* characteristic was observed for the CZT thin films deposited at 928 K with symmetry curve in the maximum dielectric constant that was observed in the vicinity of the spontaneous polarization switch. The film shows ferroelectricity behavior at room temperature. The results of these studies reveal the promising potential of CZT thin films as a new lead-free ferroelectric material with possible applications in random access memory.

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References

[1] A.I. Kingon, S. Srinivasan, Nat. Mater. 4 (2005) 233–237.
[2] T.X. -Gui, D.A. -Li, C.H.L. -Wah, Chin. Phys. Lett. 20 (2003) 2039–2041.
[3] J. Zhai, X. Yao, Z. Xu, H. Chen, J. Am. Ceram. Soc. 89 (2006) 354–357.
[4] D. Bao, N. Mizutani, X. Yao, L. Zhang, Appl. Phys. Lett. 77 (2000) 1203–1205.
[5] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Nat. Mater. 432 (2004) 84–87.
[6] N. Tohge, S. Takahashi, T. Minami, J. Am. Ceram. Soc. 74 (1991) 67–71.
[7] J. Zhai, X. Yao, J. Shen, L. Zhang, H. Chen, J. Phys. D: Appl. Phys. 37 (2004) 748–752.
[8] L.P. Lv, S.T. Zhang, J. Wang, Y.F. Chen, Z.G. Liu, X.N. Zhao, G.X. Cheng, J. Phys. D: Appl. Phys. 38 (2005) 1355–1360.
[9] A. Dixit, S.B. Majumder, R.S. Katiyar, A.S. Bhalla, Appl. Phys. Lett. 82 (2003) 2679–2681.
[10] A. Dixit, S.B. Majumder, P.S. Dobal, R.S. Katiyar, A.S. Bhalla, Thin Solid Films 447 (2004) 284–288.
[11] M. Toyoda, M.U.Y.S. Lubis, J. Sol–Gel Sci. Technol. 16 (1999) 7–12.
[12] S. Zafar, R.E. Jones, P. Chu, B. White, B. Jiang, D. Taylor, P. Zurcher, S. Gillepsie, Appl. Phys. Lett. 72 (1998) 2820–2822.
[13] B.J. Kenndey, C.J. Howard, B.C. Chakoumakos, J. Phys.: Condes. Matter 11 (1999) 1479–1488.
[14] N.L. Ross, T.D. Chaplin, J. Sol. Stat. Chem. 172 (2003) 123–126.
[15] J. Xu, A.P. Wilkinson, S. Pattanaik, Chem. Mater. 12 (2000) 3321–3330.
[16] I. Levin, E. Cockayne, M.W. Lufaso, J.C. Woicik, J.E. Maslar, Chem. Mater. 18 (2006) 854–860.
[17] A.Z. Simões, M.A. Ramírez, A.H.M. Gonzalez, C.S. Riccardi, A. Ries, E. Longo, J.A. Varela, J. Solid State Chem. 179 (2006) 2206–2211.
[18] I.A. Souza, A.Z. Simões, S. Cava, L.S. Cavalcante, M. Cilense, E. Longo, J.A. Varela. J. Solid State Chem. 179 (2006) 2972–2976.
[19] T. Salmi, E. Paatero, P. Nyholm, Chem. Eng. Proc. 43 (2004) 1487–1493.
[20] T. Fujii, A. Fujishima, T. Hirano, T. Kobayashi, Appl. Phys. Lett. 62 (1993) 3204–3206.
[21] J. Hao, W. Si, X.X. Xi, R. Guo, A.S. Bhalla, L.E. Cross, Appl. Phys. Lett. 76 (2000) 3100–3102.
[22] T. Yu, C.H. Chen, X.F. Chen, W. Zhu, R.G. Krishnan, Cer. Int. 30 (2004) 1279–1282.
[23] C. Chen, D. Huang, W. Zhu, X. Yao, Appl. Surf. Sci. 252 (2006) 7585–7889.
[24] A.R. James, C. Prakash, Appl. Phys. Lett. 84 (2004) 1165–1167.
[25] S.B. Ren, C.J. Lu, J.S. Liu, H.M. Shen, Y.N. Wang, Phys. Rev. B. 54 (1996) 14337–14340.
[26] M. Nagata, D.P. Vijay, X.B. Zhang, S.B. Desu, Phys. Stat. Sol. A. 157 (1996) 75–82.
[27] C. Chaneliere, J.L. Autran, R.A.B. Devine, B. Balland, Mater. Sci. Eng. R. 22 (1996) 269–322.