PZT thin films preparation by pyrosol process

A. El Bouchikhi[a*], E. Philippot[b], M. Et-tabirou[a]

[a]*Laboratoire de Physico-Chimie du Solide (LPCS), Université Ibn Tofail, Faculté des Sciences BP 133, 14000 Kénitra, Maroc*

[b]*Laboratoire de Physicochimie de la Matière Condensée, UMR 5617 CNRS, CC03, Université de Montpellier II, Sciences et Techniques du Languedoc, F34095 Montpellier cedex 5, France*

Lead Zirconate titanate [$Pb(Zr,Ti)O_3$] thin films were deposited on Si (111) substrates by pyrosol process based on the pyrolysis on a heated substrate of an aerosol produced by the ultrasonic spraying of a solution. The films were characterized by X-ray diffraction to control the morphology and the preferential orientation of the thin film.

1. Introduction

Lead zirconate titanate (PZT) ceramics are of interest because of their ferroelectric, piezoelectric and their electrical properties [1]. However, growth of a large and high quality single crystal of PZT is very difficult to achieve. Recent progress in thin film technology indicates the possibility of the preparation of single-crystal PZT thin films [2,3]. Such a single-crystal thin film is considered to be important for the investigation of the physical properties of PZT.

PZT thin films have great possibilities for integrated device applications, such as pyroelectric detectors [4], surface-acoustic wave (SAW) delay lines [5] piezoelectric vibrators [6] and optical switches [7].

In recent years, the applications of PZT thin films for nonvolatile random access memory (RAM) capacitors due to their large remanent polarizations and for dynamic RAM (DRAM) capacitors due to their high dielectric constants [8] have attracted much attention. The potentiel of combining the ferroelectric nonvolatility with the fast read-and-write characteristics of a DRAM has also been realized in the fabrication of non-volatile $DRAM_S$ (NV-$DRAM_S$) [9].

Lead zirconate titanate [$Pb(Zr,Ti)O_3$or PZT]is a perovskite-type ferroelectric material, and the crystal structure and ferroelectric properties depend strongly on the composition. Recent investigation [10,11] has shown that there are two kinds of crystal structure in the ferroelectric solid solutions of $Pb(Zr\text{-}Ti)O_3$ system. The compositions near the pure $PbTiO_3$ correspond to a tetragonal modification of perovskite structure with c/a□1.

To date,PZT thin films have been prepared by a variety of physical and chemical deposition methods. Methods utilized have included:magnetron sputtering [12,13] chemical deposition methods: MOD (Metallo-Organic Deposition) [14], and sol-gel [15]. The common feature of the physical deposition techniques is the necessity of deposition the films in high vacuum and sputtering or evaporating materials from a multicomponent material source. This implies that a complex set of conditions has to be brought together in order to obtain good quality films. These deposition techniques are generally costly and difficult to compensate for lead loss, although they are advantageous in preparing oriented or epitaxial PZT thin films as the produced species have relatively high mobility to from epitaxial nuclei on substrates. In contrast chemical solution based deposition methods like sol-gel processing of metal alkoxides are preferred because of their improved compositional control which allow high-quality growth and an ability to prepare uniformly doped thin films with small additive levels, compared to sputter deposition. Moreover this method is useful in processing cost reduction and large area fabrication.

In this paper, we report the preparation of $Pb(Zr_{0.52}\text{-}Ti_{0.48})O_3$ thin films by the "pyrosol" process (pyrolysis of an aerosol).

2. Experimental procedure

The deposition process used to perform experiments is based on the pyrolysis on a heated substrate of an aerosol produced by ultra-high frequency spraying of a solution. An ultrasonic bean is focused close to the materials to be deposited. Ultrafine droplets are produced above the surface of the liquid and convoyed by a carrier gas (air) close to the heated substrate which is placed in a furnace. The spray set-up is shown schematically in Fig.1. Owing to the very narrow droplet spectrum of the aerosol, a heterogeneous reaction occurs at the gas/substrate interface over a wide temperature range, leading to the CVD process. The precursors (metal, organic or mineral compounds) have to be selected according to the need of a high vapor pressure at a relatively low temperature, a long time maintenance of a stable vapor pressure, a deposition rate limited by transport of source gases, and no homogeneous nucleation in the vapor phase.

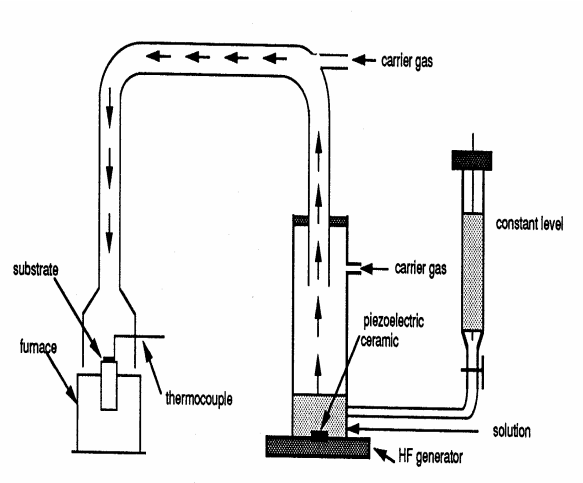


Figure 1: Schematic diagram of pyrosol process

In our experiments, the precursor compounds used for PZT were Lead acetate [$Pb(OOCCH_3)$], Zirconium acetylacetonate ($C_{20}H_{28}O_8Zr$) and titanium tri-n-butoxide
(Ti $[O(CH_2)_3CH_3]_4$). Methanol was used as solvent as it has a high dissociating power. The lead acetate concentration in the methanol was higher to 0.01mol/l. the solution were sprayed on to heated Si(111) substrate at a rate of 50ml/hour. The average working parameter in order to produce a stable spray and steady state flow are: generator frequency 800 KHz, power 90W, flow rate at lower part 100l/hour, at upper part 500l/hour.

Crystalline phases and preferred orientations in the films were analyzed by X-ray diffraction (XRD). The morphology and microstructure were observed by scanning electron microscopy (SEM) and composition of thin films were checked by EDS.

3. Results and discussion

Films of $Pb(Zr_{0.52}Ti_{0.48})O_3$ were deposited on silicon (111) substrate by spray pyrolysis process at different temperatures: 500-600°C. The crystalline structure of the films was determined by X-ray diffraction (XRD) patterns.

A series of experiments with various precursor concentrations were performed in order to examine the precursor concentration effects on the preferential crystal growth of PZT films formed on Si (111). For a lead acetate concentration in methanal lower than 0.01 mol/l, no thin film deposition was observed in the temperature range 400-600°C. Maybe the concentration is too small and the dissociated chemical species in the gas phase are volatilized before reacting so this concentration of active chemical species is not suitable to initiate at these processing temperatures the crystal growth which form the deposit onto the substrate. For a concentration of 0.015 mol/l crystallisation occurs when the substrate temperature reaches 500°C but the X-ray diffraction spectrum does not exhibit just the peaks of perovskite structure. A precursor concentration of 0.02 mol/l gives rise to crystallized thin films with perovskite structure but no specific orientations were found even by rising the substrate temperature up to 600°C as it can be seen from Fig.2a which show the X-ray diffraction patterns of a such deposited thin film at 600°C. In the temperature range 500-600°C we always obtained the perovskite structure with just some noticeable small variations of X-ray peaks intensity. By using the same experimental process of deposition, epitaxial growth of thin films were observed for a concentration of 0.025 mol/l and a substrate temperature of 560°C or higher. Fig.2b shows the X-ray diffraction pattern we obtained with these experimental conditions.

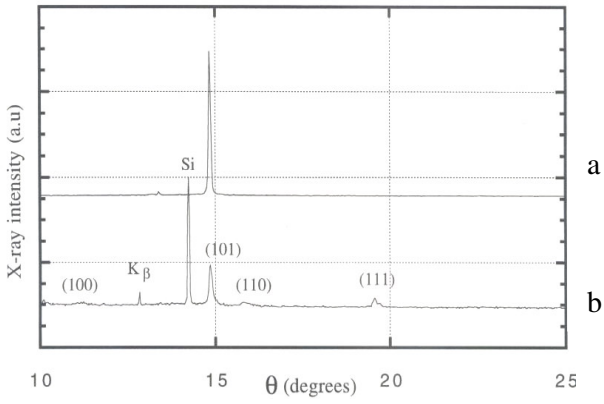
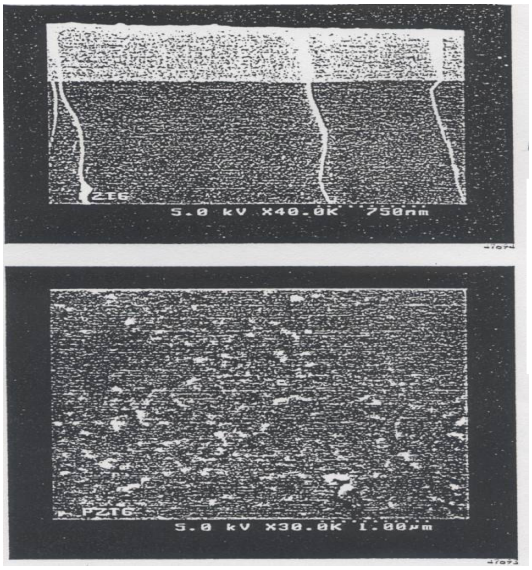


Figure 2: X-ray diffraction patterns (K_α Cu) of ($Zr_{0.52}Ti_{0.48}$)O_3Thin films on Si (111) at
a) 600°C, [Pb] = 0.02 mol/l
b) 560°C, [Pb] = 0.025 mol/l

An increasing of the precursor concentration to 0.03 mol/l did not change the results concerning the epitaxial growth of thin films which occurs at the same substrate temperature of 560°C. The orientation was still along (101) direction. A perovskite structure without specific orientation appeared at temperature as low as 440°C with this precursor concentration. Due to a lower deposition rate for the lowest concentration, the thickness of deposited thin film with a concentration of 0.02 mol/l was smaller than the one with 0.03 mol/l (for the same deposition time) and it is the reason why we observed the X-ray peak of Si (111) in Fig.2a.

These experimental results show with this deposition technique the crystal structure of the deposited thin films was not sensitive to the substrate temperature in the temperature range 500-600°C as soon as the precursor concentration was higher than 0.015 mol/l. Indeed all the crystallized thin films exhibited the perovskite structure.



a

b

Figure 3: Scanning electron micrographs of
a) the surface
b) The cross section of PZT thin film on Si (111) at T = 560°C

Fig.3a shows a SEM image of the surface of deposited films on Si (111) at 560°C. The films are continuous and we can not the presence of a grain structure on the surface. This structure is not due to the (101) orientation of the thin because we observed the same morphology for deposited thin films with perovskite structure. The observation of the fractured cross section of an oriented thin film (Fig.3b) showed no obvious grain structures, or columnar structures. Moreover as it can be seen on this picture no pores or cracks appeared which also confirmed the quite dense and pore free structure of PZT we obtained by this deposition technique. Film thickness was determined from cross sectional SEM observation of the film. The surface roughness of PZT was mostly caused by this micrograins structure and can be evaluated to be less than 60 nm.

With regard to the homogeneity of the layers obtained, and according to tests carried out on substrates of quarts and silicon, the films present varied orientations and characterised by a very heterogeneous aspect of surface. It thus appears that the quality of layers deposited is in close relationship to the nature and orientation of the substrate, but also with the quality of the thin interface layer / substrate.

4. Conclusion

Recent results of our study on PZT (52/48) based ferroelectric thin films were prepared by pyrosol process have been described. It was found that this technique can be successfully applied to the fabrication of highly homogeneous and crack-free perovskite PZT films on Si (111) substrate. For these materials, precursor concentrations and substrate temperature seem to be main parameters influencing the synthesis of oriented PZT thin films. As far as the pyrosol process is concerned, it presents some advantages compared with other traditional deposition methods. Indeed, not only it is a relatively low temperature process which allows fast deposition rate, but also its low cost and its ease of operation make it a suitable method to obtain good quality thin films of various materials.

Références :

[1] B. Jaffe, W.R-Cook and H.Jaffe, piezoelectric ceramics, Academic Press, New York, 1971.
[2] M.Ishida, S. Tsuji, K.Kimura, H.Matsunami and T. Tanaka : J-Cryt Grouth 45 (1978) 343.
[3]T.Okamura, M. Adachi, T. Shiosaki and A. Kawabata: Jpn.J.Appl.Phys.30(1991)1034.
[4] K.Iijima, Y.Tomita, R-takayama and I. Ueda : J.Appl.Phys.60(1986)361.
[5] H.Adachi,T.Mitsuyu and k.wasa:Proc.the 5th symp.Ultrasonic Electronics,Tokyo 1984,Jpn.J.Appl.Phys.24(1985) suppl.24-1,p.121
[6] k.Kushida and H. Takeuchi : Appl.Phys.lett.50(1987)1800
[7] K.Wasa, O.Yamazaki, H.Adachi, T. Kawaguchi and K.Setune : IEEE J. Ligth wave Tech . Lt.2 (1984) 710.
[8] G.H. HEARTLINE, in "Ceramic materials for electronics", edited by R.C Buchanan, Ch.3 (Marcel Debber, New York, 1986) p.184
[9] R.CUPPENS, P.K LARSEN and G.A.C.M.SPIERINGS, Microelectronic Eng. 19 (1992) 245.
[10] G.SHIRANE and K.SUZUKI, J.Phys .Soc.Japan 7 (1952) 333.
[11] G.SHIRANE, K.SUZUKI and A. TAKEDA, J.Phys.Soc.japan.vol.7,No.1,Jan-Feb.1952.
[12] Kenji IIJIMA, Ichiro UEDA and Koichi KUGIMITA,Japanese Journal of Applied Physics, Vol. 30, No. 9B, September, 1991, pp. 2149-2151.
[13] Kazuhide ABE, Hiroshi TONITA, Hiroshi TOYODA, Motomaso IMAI and Yukari YOKOTE, Japanese Journal of Applied Physics. Vol. 30, No.9B, September, 1991, pp. 2152-2154.
[14] Hiroshi MIKI and Yuzuru OHJI, Japanese Journal of Applied Physics. Vol. 33 (1994) pp. 5143-5146.
[15] P. GAUCHER, S.P.FAURE , P.BARBOUX, Integrated Ferroelectrics, 1992 . Vol.1, pp. 353-362.