ELSEVIER

Applied Surface Science 127–129 (1998) 466–470

applied surface science

Pulsed laser deposition of superionic ceramic thin films: deposition and applications in electrochemistry

Michel Meunier [a,*], Ricardo Izquierdo [a], Lahcen Hasnaoui [a], Eric Quenneville [a], Dentcho Ivanov [d], François Girard [c], François Morin [b], Arthur Yelon [a], Michael Paleologou [c]

[a] *Department of Engineering Physics and Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), École Polytechnique de Montréal, P.O. Box 6079, Station 'centre-ville', Montréal, Québec, Canada H3C 3A7*

[b] *Institut de Recherche d'Hydro-Québec (IREQ), P.O. Box 1000, Varennes, Québec, Canada J0L 2P0*

[c] *Pulp and Paper Research Institute of Canada (PAPRICAN), 570 St-John Blvd., Pointe-Claire, Québec, Canada H9R 3J9*

[d] *Microelectronics Center, New Jersey Institute of Technology, 121 Summit St., Newark, NJ 07102, USA*

Abstract

Pulsed laser deposition (PLD) has been used to prepare two types of superionic ceramic thin films: (i) NASICON (Na superionic conductor) for a Na ion selective membrane and (ii) the mixed electronic and oxygen conductors $La_{1-x}Sr_xMnO_{3\pm\delta}$ (LSM) for the cathode in solid oxide fuel cells. NASICON thin films have good ionic conductivity with resistivities between 3×10^3 and 5×10^4 Ω cm at room temperature and they have low surface particle densities depending upon the deposition conditions. When NASICON is deposited on polymeric (Raipore) membranes frequently employed for Na selectivity, the composite membranes show a significant increase of current efficiency of 23% for the production of sodium hydroxide from sodium sulfate using electrolysis. For LSM, very smooth and dense thin films are produced by PLD with the perovskite structure after an anneal at 950°C. © 1998 Elsevier Science B.V.

Keywords: Pulsed laser deposition; Ceramic thin films; Na superionic conductor

1. Introduction

Electrochemical devices are used in a variety of applications in the biological, medical, chemical, pulp and paper and other industries. Superionic ceramic conductors are used for their high ionic conductivity in many of these devices such as membranes, solid oxide fuel cells or gas sensors. Examples of these materials are NASICON (Na superionic conductor), ceramics of average composition $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, where x varies between 0 and 3 [1,2], and the mixed electronic and oxygen conductors of the family $La_{1-x}A_xBO_{3\pm\delta}$ with A = Ba, Ca, Sr, B = Cr, Fe, Mn, Co, where $0<x<1$ [3–7]. Until recently, all electrochemical devices using these solid ionic conductors were made either from bulk material or thick films (> 0.1 mm). In order to obtain high current densities, it is necessary to produce thin components, reducing the resistance. Furthermore, in some applications like oxygen sensors, integration of these devices requires that the sensing materials be in the form of thin films. How-

* Corresponding author. E-mail: meunier@phys.polymtl.ca.

0169-4332/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0169-4332(97)00674-0

ever, such thin films are difficult to produce by conventional techniques, because of the inherent problem of maintaining exact stoichiometry. Even sputtering deposition leads to a significant loss of some volatile elements such as Na and P from NASICON thin films (L. Pouliot, A. Lecours, R. Izquierdo, D. Ivanov, A. Yelon, J.F. Currie, unpublished). As their conductivity and stability is strongly dependent upon the composition, good control of film stoichiometry is very important. Due to the intrinsic advantage of being able to transfer the stoichiometry from the target, pulsed laser deposition (PLD) [8] has been successfully used to deposit these thin films by our group [9,10] and by others [11,12]. In this paper, we present recent results on the production of these thin films and their applications in electrochemistry.

2. Experimental

The PLD system has been described previously [9]. Very briefly, an excimer laser (248 nm, 30 Hz) beam is focused to a 1×2 mm^2 ellipse, giving an energy density of 0.28 to 2 J/cm^2 at the target. The target-to-substrate distance can be varied from 4 to 10.5 cm and the operating pressure, from vacuum (10^{-6} Torr) to a partial O_2 pressure of 0.3 Torr. The area of deposition was varied from 3×3 to 7×7 cm^2.

Film compositions were measured by X-ray photoelectron spectroscopy (XPS). The film thicknesses were measured using a Dektak profilometer in order to obtain the average growth rates. The crystallography of the deposited films was evaluated using X-ray diffraction (XRD). The morphology was studied by scanning electron microscopy (SEM) and by atomic force microscopy (AFM).

3. PLD of sodium superionic conductor (NASICON)

3.1. NASICON thin film properties

Bulk NASICON is a solid solution of $NaZr_2(PO_4)_3$ and $Na_4Zr_2(SiO_4)_3$ yielding average composition $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, where x varies between 0 and 3. It has a high ionic conductivity which depends upon the value of x, and is maximal for $x \approx 2$ [2]. The targets were prepared from a mixture of $ZrSiO_4$ and $Na_3PO_4 \cdot 12H_2O$ powders, pressed at 500 bars and sintered at 1200°C for at least 6 h. Films were deposited on Si, SiO_2/Si and Si_3N_4/Si substrates as well as on a polymeric substrates such as Raipore R-4010 to form an ion selective composite membrane. Deposition rates ranging from 0.002 to 0.03 nm/pulse were obtained with a target-to-substrate distance of 5.5 cm and energy densities ranging from 0.7 to 2 J/cm^2. Depending on laser fluences and target used, NASICON thin films deposited on all types of substrates, have low particle density of dimensions < 0.1 μm, and low roughness as measured by AFM.

The compositions of the target and films deposited on Si and Si_3N_4/Si are the same within a few percent for a substrate temperature varying from 25 and 500°C [9]. However, composition of films deposited at room temperature onto Raipore substrates show very small or even zero Na content at the surface of the films. In Table 1, we show the composition of the target as well as of NASICON films deposited on Si_3N_4/Si and Raipore substrates, placed side-by-side in the processing chamber. Since Na is present in the film deposited on the Si_3N_4/Si substrate, we exclude the formation of volatile compounds as the cause of the Na depletion. After the deposition of the first few monolayers, further deposition takes place onto a ceramic in both cases. Thus, we do not expect that a sticking coefficient difference could explain the Na depletion for thick films. When the Raipore membrane was modified by dipping it into a Na_2SO_4 solution for a few hours

Table 1
Composition, in at%, of as-deposited PLD NASICON thin films as analyzed by XPS. The NASICON thin films were deposited on Raipore and Si_3N_4/Si during the same deposition

	Target (at%)	NASICON film on Raipore (at%)	NASICON film on Si_3N_4/Si (at%)
Zr	5	13	7
O	60	70	60
P	6	3	5
Na	23	1	21
Si	6	12	8

before the deposition, Na depletion was substantially reduced or not observed at all. We, therefore, suppose that Na diffusion into the polymer is the cause of depletion from the ceramic. Similar behavior is observed when NASICON films are deposited on SiO_2/Si substrates. In this case, elastic recoil detection (ERD) measurements show that Na concentration increases in the interior of the ceramic film. Despite the Na depletion, these composite membranes show excellent electrochemical behavior as we shall show below.

Resistivity measurements were performed using impedance spectroscopy [9]. Resistivity at room temperature is between 3×10^3 and 5×10^4 Ω cm, depending upon the deposition conditions. From resistance measurements between 30 and 400°C, the activation energy was found to be between 0.33 and 0.5 eV, increasing with increasing resistivity. These values are in good agreement with those obtained on a pellet having the same composition as the target. However, the measured resistivities are slightly greater than the best reported values for bulk crystalline NASICON, 1×10^3 Ω cm [2] and for bulk amorphous NASICON 2×10^3 Ω cm [13].

Based on our XRD measurements, deposition at room temperature leads to a predominantly amorphous phase at lower fluences (below about 1.0 J/cm^2) and to microcrystalline materials at higher fluences (> 1.5 J/cm^2). Crystalline thin films are produced using a rapid thermal anneal at temperature not exceeding 900°C, to prevent stoichiometry variations.

3.2. Application of NASICON thin film as an ion selective membrane

One of the major applications of ion selective membranes is their use in electrolysis and bipolar membranes electrodialysis cells for the splitting of salts into their component acid and base [14]. Polymeric membranes are usually used because large areas are relatively easy to manufacture, and it is relatively simple to build leak-free systems. However, they present problems of selectivity and fouling, which reduce efficiency and life. Ceramic membranes do not present these problems but, because of the thickness necessary for mechanical stability, they usually have high resistance. Taking the advantages of both types, we have combined the two types of material in a composite membrane, formed by a superionic ceramic thin film deposited onto an appropriate polymeric membrane [10,15]. For application to Na salts splitting, we used NASICON thin films deposited onto Raipore®.

Efficiency and DC polarization measurements were performed using a cell consisting of two Pt covered electrodes, two electrolyte compartments and a 1 cm^2 cation selective membrane separating these compartments [10,16]. The current efficiency of the composite membrane was measured from the production of NaOH from the electrolysis of sodium sulfate. When a voltage is applied between the two electrodes, the sodium ions migrate through the membrane towards the negative electrode. The initial concentrations of Na_2SO_4 in the anolyte compartment and NaOH in the catholyte compartment were both 1 M. The performance of the membranes was evaluated by measuring the current efficiency for the production of sodium hydroxide from sodium sulfate using electrolysis. This is defined as the ratio of the actual quantity of base equivalent produced to the expected quantity calculated using Faraday's law, from the current density applied: $I \times t = n \times F$ where I is the current density, t is the duration of the application of the current density, n is the number of equivalents expected and F the Faraday constant (96 486 C mol^{-1}). Results in Table 2 show that the cumulative efficiency at high concentrations increases from 56% for the Raipore membrane to 69% for the composite membrane, representing a 23% improvement from the initial characteristics. The

Table 2
Efficiency and lifetime results of ion selective NASICON composite membranes for salt splitting

	Polymeric membrane alone	Polymeric membrane covered by NASICON deposited by PLD
Efficiency (no iron)	56%	69%
Lifetime (accelerated test with 275 ppm of ferrous sulfate)	4 days	> 26 days

No iron was present in the base cumulative current efficiency experiment.

increase of efficiency is due to the fact that the composite membrane is more selective against H^+ ions than the Raipore membrane [10,16]. The level of membrane performance was maintained for over 100 days of continuous operation, confirming its durability.

The life of a membrane can also be influenced by its resistance to fouling agents such as iron, calcium and magnesium. The fouling process occurs through the precipitation of the hydroxide salts of these agents inside the membrane when they cross and encounter a relatively high concentration of hydroxide on the catholitic side of the membrane. To compare the resistance of each membrane to fouling, we performed an accelerated test in the same electrolysis cell, but with the anolyte charged with 275 ppm of ferrous sulfate, leading to a much larger iron concentration than typically encountered. After only 4 days of operation, the Raipore membrane failed. In contrast, the composite membrane functioned for 26 days in the same conditions, and was still operating when the experiment was terminated. Thus, development of these composite membrane represents a very promising technological advance [15].

4. PLD of mixed electronic and oxygen superionic conductor (LSM)

Mixed electronic and ionic conductors with the perovskite structure such as ABO_3 (A = Ba, Ca, Sr, La, etc., and B = Cr, Fe, Ti, Mn, Co, etc.) have a relatively high electronic conductivity and a high oxygen diffusion coefficient, because they can tolerate a high oxygen deficiency [3–7]. For the application in solid oxide fuel cells (SOFC), one composition of this family is $La_{1-x}Sr_xMnO_{3\pm\delta}$ with $x = 0.5$ (LSM) which has the advantage of having a thermal expansion coefficient similar to the one of the solid electrolyte ZrO_2–Y_2O_3, thus preventing mechanical failure at operating temperatures > 800°C. LSM is one of the best materials for the cathode electrode in SOFCs.

The LSM targets were prepared by a modified glycine-nitrate process [17,18] whereby solutions of the nitrate salts are mixed into the required ratios and a gel is made by combining with glycine and by concentrating the final solution. This gel is then combusted to give a powder of the final desired oxide composition. The targets, with $x = 0.5$, were isostatically pressed into pellets and brought close to full theoretical density by sintering in pure oxygen at ~ 1500°C. LSM particulate-free, dense, films can be deposited at 2 J/cm^2 in our PLD system on various substrates such as Al_2O_3 and Si_3N_4/Si at growth rate of 0.01 nm/pulse. This gives an average growth rate of 1 μm/h at 30 Hz. From our XPS analysis shown in Table 3, compositions of the as-deposited films are almost identical to the target composition and for anneals below 950°C. However, film degradation occurs in anneals at 1200°C for 2 h because of a solid state reaction with the alumina substrate. From our XRD measurements, films are amorphous after deposition at room temperature and become crystalline with the perovskite structure after annealing at 950°C for 2 h. Conductivity measurements in air further indicate that the films are very stable and results are very reproducible up to 850°C and become unstable at 950°C. At 850°C, the absolute conductivity is 100 $(\Omega\ \mathrm{cm})^{-1}$ slightly lower than the bulk value of 300 $(\Omega\ \mathrm{cm})^{-1}$ at this temperature [19], probably due to the surface roughness of our alumina substrates. Characterization of these films are in progress and their applications in solid oxide fuel cells or as O_2 membranes are under study.

Table 3
Composition, in at%, of as-deposited and annealed PLD LSM thin films as analyzed by XPS

	Target	Film as deposited	Annealed at 700°C	Annealed at 950°C	Annealed at 1200°C
O	54	55	58	60	70
Sr	11	13	15	17	5
Mn	22	20	17	15	10
La	13	12	10	8	15

5. Conclusion

High quality NASICON and LSM thin films can be deposited by PLD. Efficient composite ion selective membrane can be fabricated by depositing a thin film of NASICON by PLD on a Raipore membrane.

Acknowledgements

The authors acknowledge, for financial support, the Natural Science and Engineering Council of Canada (NSERC), Pulp and Paper Research Institute of Canada (PAPRICAN), and the Fonds pour la formation de Chercheurs et l'Aide à la Recherche (FCAR) of Quebec. They also acknowledge the technical help of Jean-Paul Lévesque.

References

[1] H.Y.-P. Hong, Mater. Res. Bull. 11 (1976) 173.
[2] J.B. Goodenough, H.Y.-P. Hong, J.A. Kafalas, Mater. Res. Bull. 11 (1976) 203.
[3] O. Toft Sorensen (Ed.), Non Stoichiometric Oxides, Academic Press, New York, 1981.
[4] B.C.H. Steele, in: T. Takahashi (Ed.), High Conductivity Solid Ionic Conductors, World Scientific, Singapore, 1989, p. 142.
[5] T. Takahashi, H. Iwahara, Denki Kagaku 35 (1967) 433.
[6] J.A. Kilner, R.J. Brook, Solid State Ionics 6 (1982) 237.
[7] R.L. Cook, A.F. Sammells, Solid State Ionics 45 (1991) 311.
[8] D.B. Chisey, G.K. Hubler, Pulsed Laser Deposition, Wiley, New York, NY, 1994.
[9] R. Izquierdo, F. Hanus, Th. Lang, D. Ivanov, M. Meunier, L. Laude, J.F. Currie, A. Yelon, Appl. Surf. Sci. 96–98 (1996) 855.
[10] R. Izquierdo, E. Quenneville, D. Trigylidas, F. Girard, M. Meunier, D. Ivanov, M. Paleologou, A. Yelon, J. Electrochem. Soc. 144 (1997) L323.
[11] M. Mocrette, P. Barboux, A. Laurent, J. Perrière, Solid State Ionics 93 (1997) 283.
[12] L.G. Coccia, G.C. Tyrrell, J.A. Kilner, D. Waller, R.J. Chater, I.W. Boyd, Appl. Surf. Sci. 96–98 (1996) 795.
[13] J.P. Boilot, Ph. Colomban, Solid State Ionics 18/19 (1986) 974.
[14] M. Palleologou, J.-N. Cloutier, P. Rananyergtm, R.M. Berry, M.K. Azaeniouch, J. Dorica, Pulp Paper 95 (1994) T386.
[15] A. Yelon, M. Paleologou, D. Ivanov, R. Izquierdo, M. Meunier, US Patent, submitted April 97.
[16] F. Girard, R. Izquierdo, E. Quenneville, M. Meunier, D. Ivanov, M. Paleologou, A. Yelon, to be published.
[17] F. Morin, G. Trudel, Y. Denos, Solid State Ionics 96 (1997) 129.
[18] L.A. Chick, L.R. Pederson, G.D. Maupin, J.L. Bates, L.E. Thomas, G.J. Exharos, Mater. Lett. 10 (1992) 6.
[19] J.A.M. van Roosmalen, J.P.P. Huijsmans, E.H.P. Cordfunke, in: F. Grosz, P. Zegers, O. Yamamoto, S.C. Singhal, H. Iwahara (Eds.), Proc. of the 2nd Int. Symp. on Solid Oxide Fuel Cells, Rept. no. EUR 13546en, 1991, pp. 507–517.