

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/NO2008/000468

International filing date: 23 December 2008 (23.12.2008)

Document type: Certified copy of priority document

Document details: Country/Office: NO
Number: 2007 6696
Filing date: 28 December 2007 (28.12.2007)

Date of receipt at the International Bureau: 23 January 2009 (23.01.2009)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
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Bekreftelse på patentsøknad nr
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2007 6696

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Formation of a lithium comprising structure on a substrate by ALD

The present invention relates to a method for formation of a lithium comprising surface layer on a substrate.

5 There has in later years been a large emphasis on improving methods for the formation of thin material layers on substrates of various kinds in order to produce amongst others electrolytes. It has long been a goal to produce as thin as possible, as well as defect free layers of Lithium comprising materials on a substrate in a controlled fashion. This has been of particular interest for application in battery technology. However the earlier described methods are cumbersome and expensive, and there is a great need for cheaper and better production methods. ALD (atomic layer deposition, also known as atomic layer chemical vapour deposition, ALCVD, or atomic layer epitaxy ALE) presents all the necessary properties for the formation of thin film layers upon a substrate, however it has been thought that it would not prove possible to use ALD techniques for compounds only having a single ligand such as lithium. It has been thought that single 15 ligand compounds could not possibly be deposited using an ALD method, as the single ligand of lithium would react with the surface such that there would be no self-limiting growth mechanism to prevent further growth according to the ALD principle. This has empirically been proven to be false as is shown in the present application that describes a method for the formation of thin film lithium-comprising layers on a substrate.

20

Short description of the ALD method

ALD also known as atomic layer chemical vapour deposition, ALCVD, or atomic layer epitaxy, ALE, is a thin-film-deposition technique that relies on alternating self-terminating gas-to-surface reactions. The film is formed by sequential pulsing of two or 25 more reactants, using purging with inert gas between the precursor pulses to avoid gas-phase reactions. Operated under ideal conditions this process ensures saturation of all surfaces with precursor for each applied precursor pulse. The growth of the film will therefore depend on the saturation density of the involved precursor during a pulse.

30 Unlike most other deposition and crystal growth techniques the growth is in the ideal case not dependent on the distribution of the precursors or rate of formation of growth steps on the crystallites forming the film. The growth thus follows a somewhat different type of dynamics and ensures even growth on all exposed surfaces for each pulse.

Background art

There are a large number of patent applications describing various aspects of thin film Li-deposition; however the majority pertain to different deposition methods such as pulsed laser deposition, sputtering, and the like. These methods present different issues to which solutions must be found, for instance laser deposition and sputtering may be harmful to the substrate due to the high energy impact of the deposited method upon the substrate. Furthermore these methods are difficult to control in an adequate manner and in such applications wherein layer thickness control is of vital importance the methods may prove difficult to apply. There is additionally the difficulty of providing a defect free or pinhole free layer which is desired in many industrial applications so that there is no leakage between layers or in some applications no contact between layers. By sputtering or by laser deposition techniques it is very difficult to ensure that the entire surface is covered and a defective film may result. An area wherein it is especially important to provide defect free layers is in battery technology wherein lithium-comprising layers are to be separated by electrolytes allowing for the passage of lithium ions, but wherein no contact should be made between the layers to avoid an irreversible reduction in the battery efficiency. The layers should preferably be as thin as possible to provide the least resistance to the passage of the ions, and thus layer control is of the utmost importance.

20

P. Fragnaul et al. in J. Power Sources 54,362 1995 proposes a CVD method for the deposition of thin films of the active cathode materials LiCoO_2 and LiMn_2O_4 by chemical techniques. Low pressure chemical vapour deposition is described as being successful at readily preparing LiCoO_2 at temperatures ranging from 450 to 650 °C; however, in order to prepare the spinel phase LiMn_2O_4 , temperatures greater than 600 °C were required. No mention is made of the use of ALD or ALE technology.

WO00/25378 to Menachem et al. describes a method for forming a battery in which CVD techniques are used to form an electrolyte barrier in a Li-solid state battery. However, CVD differs widely from ALD in that CVD and MOCVD are not self-limiting reactions as is ALD, and they are thus more difficult to control. There are also issues in that the reaction temperature must be very closely monitored, and in that there might occur undesirable side reactions whilst performing the deposition. In contrast

30

ALD proposes a simple self-limiting reaction wherein a monolayer of the desired compound may be deposited on a substrate, and wherein each layer formation reaction is self controlled.

5 US20070026309 to Notten et al. describes a method for forming a solid battery wherein the anode and cathode are separated by an electrolyte. There is a description of the electrolyte layer being a lithium comprising electrolyte wherein said lithium comprising electrolyte is deposited by either Physical Vapor Deposition (PVD), Chemical Vapor
10 Deposition (CVD), and/or Atomic Vapor Deposition (AVD). However there is no mention of how this is to be performed, and the sequential listing of alternative methods for the production of said electrolyte is merely a listing of known gas phase deposition methods. No mention has been found of the authors citing an ALD methodology as described in the present invention elsewhere in the art. On the contrary the authors themselves have in WO2006092747 solely proposed the use of MOCVD in the
15 production of the Li layers, this being a clear indication that the inventors have in fact not used ALD methodology to produce the Li layers. If the authors had proposed the use of ALD in the production of Li comprising layers, they would as persons skilled in the art have recognised the beneficial aspects of the method as such, and would have proposed using ALD instead of MOCVD. EP06710932 / WO2006056963 to the same
20 authors are variations on the same theme of the above invention.

Short summary of the invention

The hereinafter described invention seeks to overcome at least some of the shortcomings of the background art and comprises a method for formation of a Li-
25 comprising layer on a substrate by atomic layer deposition comprising the following steps:

- a) providing a substrate in a reaction chamber wherein said reaction chamber is arranged for gas-to-surface reactions,
- b) pulsing a lithium precursor through said reaction chamber,
- 30 c) reacting said lithium precursor with at least one surface of said substrate,
- d) purging of said reaction chamber

- d1) by sending a purge gas through said reaction chamber for the purging of the reaction chamber or
d2) by evacuating said chamber, and
e) repeating steps b) to d) a desired number of times in order for the formation of a thin
5 film layer of a lithium comprising material upon said at least one surface of said
substrate.

Further advantageous embodiments of the invention are described in the hereinafter enclosed dependant claims.

10

In one aspect the present invention provides a method which may result in an electrolyte comprising no or a limited number of pin holes. When applied in batteries this method will provide a lower efficiency loss over time.

- 15 In another aspect the invention may provide improved sensor materials for sensors for measuring the concentration of alkali ions in liquids.

In another aspect the invention may provide improved LiNbO_3 thin films. Due to its unique electro-optical, photoelastic, piezoelectric and non-linear properties Lithium
20 Niobate is widely used in a variety of integrated and active acousto-optical devices.

The invention may also provide improved Lithium Tantalate which exhibits unique electro-optical, pyroelectric and piezoelectric properties combined with good
25 mechanical and chemical stability and, wide transparency range and high optical
damage threshold. This makes LiTaO_3 well-suited for numerous applications including electro-optical modulators, pyroelectric detectors, optical waveguide and SAW
substrates, piezoelectric transducers etc.

The figures are solely intended for illustration purposes and should not be construed in
30 any manner limiting the invention:

Figure 1 is a representation of the Li_2CO_3 deposition rate as a function of deposition temperature for an embodiment of the invention.

Figure 2 is a representation of growth rate as a function of pulsing ratio of precursor cycles, compared to the deposition rates of binary processes according to an embodiment of the invention. There is an alternating deposition of Li and La compounds.

5 Figure 3 is a representation of the compositional change of Li-La containing films as a function of pulsing ratio of each of the Li and La precursors according to an embodiment of the invention.

Embodiments of the invention

10 The present invention will hereinafter be described with reference to the enclosed figures, tables and examples. Although specific methods have been provided as examples of embodiments of the invention, it will be clear to a person skilled in the art that variants of the invention are within the scope of the invention.

15 The present invention discloses a method for the production of lithium-comprising thin film layers by Atomic layer deposition (hereafter ALD) wherein a substrate is to be provided by a thin preferably defect free layer of a lithium comprising compound. The method comprises pulsing of a lithium precursor into a reaction chamber wherein is arranged a substrate which is to be furnished with a lithium comprising layer. If
20 required, an inert purge gas is pulsed through the reaction chamber after each pulse of lithium comprising precursor, or after each sequence of lithium precursor pulses, or even concurrently with the precursor. Alternatively several purge pulses may be performed between each lithium precursor pulse. In some instances purging the chamber may be performed simply by evacuating the chamber. With each lithium
25 precursor pulse cycle, a layer of lithium-containing material will be deposited upon the substrate such that in a layer by layer fashion the lithium-containing material will be deposited upon the substrate surface according to the ALD principle.

The main and surprising effect of the invention is that it has proven possible to deposit a
30 lithium layer on a substrate using ALD in spite of the fact that lithium and other alkali metals are provided with a single ligand in gaseous phase for reaction. It has heretofore been thought that alkali metals would not be suitable for ALD methods as the ligand on

the Li-precursor would undergo reactions with the active sites on the surface and form part of a volatile specie and not take part in a self hindering mechanism. In this way the surface would be terminated by Li-atoms who are significantly smaller than their anionic counterparts and easily be adsorbed into the film and not be able to produce a suitable terminating layer to prevent further reactions on the anionic counterparts of the film surface. This has now empirically been proven to be wrong, which is surprising and contravenes a prejudice of the art.

Accordingly the present invention provides a new method for applying a thin film comprising an alkali metal on a surface by use of the ALD technique.

In order for activation of the surface between each deposition cycle it may in an embodiment of the invention be necessary to include introducing an oxygen precursor in the cycle to incorporate oxygen moieties on the surface after each deposition. Any suitable oxygen precursor such as for instance water, O₃ or any other oxygen comprising gaseous compound may serve the purpose as will be evident to a person skilled in the art. This oxygen containing precursor is often referred to as the oxidizer in the literature, even though there may be no clear redox reaction taking part in the main formation of the film. The oxygen precursor may be pulsed into the reaction chamber in a manner resembling that of the pulsing of the precursor material. An illustration of the rate of deposition of Li per deposition cycle according to an embodiment of the invention upon a substrate with interceding oxidisation by O₃ is given in fig. 1. The deposition is temperature dependent, with deposition at higher temperatures being less effective than at lower temperatures. Although it is preferable to first pulse the metal phase through the reaction chamber for deposition upon the substrate, it may in some instances be preferable to pulse said oxygen comprising precursor prior to pulsing the metal comprising precursor through the chamber. The precise manner of pulsing may vary, as ALD methods, and variants thereupon, as such are known. However the deposition of Li-comprising and alkali-metal compounds as such is novel.

30

The deposition temperature should be adjusted such that the deposition occurs at the best possible rate, however, as is evident, the temperature must not be too high such that

the substrate is damaged, or the precursor decomposes noticeable. Fig. 1 illustrates use of Li(thd) (lithium 2,2,6,6-tetramethylheptane-3,5-dionate) as a lithium precursor. Li(thd) is stable to about 400 °C which thus for this precursor defines the highest possible deposition temperature. Using other precursors, higher or lower deposition temperatures may be envisaged, depending on the physico-chemical properties of the precursor and the substrate. Amongst other possible precursors are found organo-metallic compounds such as lithium alkoxides or alkyls, bimetallic or multimetallic compounds such as M-Li compounds, where M may be another metal from the periodic table and where both M and Li may be incorporated into the film, this last group of precursors may include compounds such as Ti-Li-, La-Li- and Ti-La-Li-organic compounds. This evidently encompasses a large number of possible precursors that may be used, wherein each may be chosen for the specific use on a specific substrate or chosen due to economic, environmental or other considerations. The invention is not limited to a single precursor, and the use of a plurality of different precursors may be envisaged.

A separate consideration concerns the specific pulsing scheme to be used for pertaining to the duration of each pulse and to the pulse sequence. Each pulse sequence may be varied according to need, however the pulse duration of each precursor should be such that there is sufficient time for the entire substrate surface to have reacted with the precursor. Typical precursor pulse durations may range from about 0.1 to about 2 seconds, preferably from about 0.5 to about 1 second, often about 0.8 seconds. In a similar manner, the purge pulse durations should also be tailored to ensure that the purge has been effective. Typical purge pulse durations may range from about 0.8 to about 3 seconds or longer even up to 6-12 seconds, but often the purge pulse will have a duration of 1-2 seconds. Purge pulse durations may vary significantly depending upon which precursor has been used, and whether the purging pulse occurs after a possible oxidising pulse as described above. A purge of the reaction chamber may be carried out in several different ways. The main importance of the purge is to avoid that there are undesirable gas phase reactions between different types of precursors. A purge may consist of an additional pulse of an inert gas capable of removing excess and unreacted precursors from the previous pulse. A purge may alternatively be carried out by

evacuating the chamber by reducing the pressure and in this way remove excess and unreacted precursor from the previous pulse. Alternatively the purge may be effectuated by using the flushing effect of a carrier gas directing the precursor to the substrate and carrying away any by-products. The carrier gas may be used in a pulsewise or continuous manner. Some reactions may occur with a minimum of physisorption of excess precursor to the substrate so that a purging period may be virtually absent. The same considerations with respect to the purging pulse durations are relevant to the duration of the oxidising pulse (oxygen containing precursor), which may range from about 0.1 to about 2 seconds, preferably from about 0.5 to about 1 second, often about 1.2 seconds depending on the oxidiser. As is evident, shorter or longer pulses of each specific compound may prove necessary depending on the surface reaction kinetics as will be evident to a person skilled in the art.

An example of a possible pulsing sequence may thus be:

0.8s/1.2s/1.5s/2.0s Metal-precursor/purge/oxygen-precursor/purge.

Using these pulses in an embodiment of the invention one achieves a layer composition as described in table as measured by a TOF-ERDA (time of flight elastic recoil detection analysis) method.

Table 1: Layer composition for an example of an embodiment of the invention

Deposition temperature	Li	O	C	H	Na	F
185°C	33	49	17	0.22	0.33	0.25
225°C	33	48	18	0.2	0.21	0.29

Using Li(thd) as the metal precursor and O₃ as the oxidiser this results in the deposition rate as shown in fig. 1. The pulsing sequence is repeated as many times as is necessary in order to form the desired layer thickness. The layer thickness may be measured by any appropriate method or estimated based on empirical data.

A main purpose of the invention as such is to produce an electrolyte layer suitable for use in lithium battery applications. As such it has been considered advantageous to provide an electrolyte layer comprising further to said lithium layer a lanthanum comprising layer. Thus in an embodiment of the invention, further to the pulses of lithium comprising precursor a lanthanum comprising precursor is pulsed through the reaction chamber for reaction and subsequent deposition upon the substrate.

Lithium as such has long been of major interest in the development of thin film batteries, in particular with respect to its use as an anode, due to its very high energy density of about 3,800 mAh/g and to its very high conductivity. However the reactive nature of Li has necessitated the use of large amounts of excess lithium due to that Li typically reacts with the electrolyte resulting in reaction losses. Previous efforts have been concentrated upon the use of Lipon (lithium phosphorous oxynitride) electrolytes, however Li-La-Me systems, where Me is a metal, may present much higher lithium conductivities and would as such prove more effective than the previously studied Lipon electrolytes.

Accordingly an object of the invention is to provide an electrolyte comprising a desired proportion of Li and La compounds using ALD methodology. This will result in a method according to the invention whereby the Li precursor and La precursor will be furnished to the reaction chamber in a predetermined sequence such that the desired composition of the layer is achieved. The specific composition may depend on which use is intended for the electrolyte as will be evident to a person skilled in the art. As for the other compounds to be deposited upon the substrate, the pulse lengths may vary and depend upon the reaction kinetics on the surface. The La precursor pulse duration may typically vary between 0.5 to about two seconds, preferably about 0.8-1.5 seconds. An example of a deposition cycle may thus be:

0.8-1.5s/1.2s/1.5s/2.0s Li(thd)/purge/oxygen precursor/purge
 0.8-1.5s/1.2s/1.5s/2.0s La(thd)₃/purge/oxygen precursor/purge

Any suitable La precursor may serve as is evident to a person skilled in the art, in one embodiment of the invention the La precursor is a metal-organic La-compound. In this example use is made of a La(thd)₃ precursor.

- 5 Figure 2 shows an illustration of the variation of the growth rate of the resulting deposited layer with respect to the percentage of Li(thd)/O₃ cycles. Figure 3 correspondingly illustrates relative amount of Li deposited upon the substrate with respect to the percentage of Li(thd)/O₃ cycles.
- 10 Using a TOF-ERDA measurement, it has empirically been found that the composition of the layer of each compound varies according to table 2 in this embodiment of the invention.

Table 2: Layer composition for an example of an embodiment of the invention

% Li pulses	La	Li	Li/La ratio	O	C	H	Na	F
16.7	20	3	11.1	61	14	1.4	<0.1	0.4
50	15	9	36.7	58	17	1.5	0.1	0.25
75	7	22	75.9	54	16	0.6	0.8	0.4
90.9	2	30	94	50	17.5	0.3	0.5	0.33

15

In one embodiment of the present invention includes further incorporating Ti into the structure thereby obtaining a Li-La-Ti-O layered compound. Ti can be included by a process similar to the La process described above but applying for instance TiCl₄ as a precursor and H₂O as oxygen comprising precursor. Applicable Ti precursors include
 20 for instance halogenides of Ti, Ti-Li- and Ti- organometallic or metalorganic compounds.

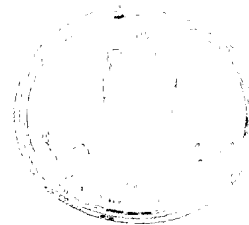
Equivalent to this process other metal organic, organo metallic, or halogenides may be included in the Li comprising film.

25

It is thus to a large degree possible to design the electrolyte according to the needs of the task. Amongst possible uses for this electrolyte are as a thin-film barrier between Li layers in a thin-film battery, and it as one of the objects of the present invention to provide such an electrolyte. Although battery technology is one of the possible uses of the present method, it should be clear that other possible uses of the ALD method for depositing Li-layers on a substrate are foreseen. Although exemplified above for use in a battery this will not be the only application for the present invention.

The present invention has thus proposed a method for the formation of thin Li-comprising layers on a substrate using an ALD-method.

While embodiments of the invention have been described, it is understood that various modifications to the disclosed process and its implementation may be made without departing from the scope of the invention as define by the subsequent claims.



C l a i m s

1.

A method for formation of a Li-comprising layer on a substrate by atomic layer

5 deposition comprising the following steps:

a) providing a substrate in a reaction chamber wherein said reaction chamber is arranged for gas-to-surface reactions,

b) pulsing a lithium precursor through said reaction chamber,

c) reacting said lithium precursor with at least one surface of said substrate,

10 d) purging of said reaction chamber

d1) by sending a purge gas through said reaction chamber for the purging of the reaction chamber or

d2) by evacuating said chamber, and

e) repeating steps b) to d) a desired number of times in order for the formation of a thin

15 film layer of a lithium comprising material upon said at least one surface of said substrate.

2.

A method according to claim 1 wherein each step of the process is independently

20 repeated a desired number of times.

3.

A method according to claim 1 wherein steps b) through d) are repeated with independently chosen lithium precursors in step b).

25

4.

A method according to any one of the claims 1-3 wherein an oxidising gas is pulsed through said reaction chamber such that the resulting deposition sequence comprises

a) providing a substrate in a reaction chamber wherein said reaction chamber is
30 arranged for gas-to-surface reactions,

b) pulsing a lithium precursor through said reaction chamber,

c) reacting said lithium precursor with at least one surface of the substrate,

d) purging of said reaction chamber

- d1) by sending a purge gas through said reaction chamber for the purging of the reaction chamber or
- d2) by evacuating said chamber, and
- e) pulsing an oxygen precursor through said reaction chamber,
- 5 f) reacting said oxygen precursor with said at least one surface of said substrate,
- g) sending a purge gas through said reaction chamber for the purging of the reaction chamber,
- h) repeating steps b) to g) a desired number of times in order for the formation of a thin film layer of a lithium comprising material upon said at least one surface of said
- 10 substrate.

5.

A method according to claim 4 wherein each step of the process is independently repeated a desired number of times.

15

6.

A method according claim 4 wherein further to the described steps, a lanthanum comprising precursor is pulsed through the reaction chamber such that the reaction resulting sequence comprises:

- 20 a) providing a substrate in a reaction chamber wherein said reaction chamber is arranged for gas-to-surface reactions,
- b) pulsing a lithium precursor through said reaction chamber,
- c) reacting said lithium precursor with a surface layer of the substrate,
- d) purging of said reaction chamber
- 25 d1) by sending a purge gas through said reaction chamber for the purging of the reaction chamber or
- d2) by evacuating said chamber,
- e) pulsing an oxygen precursor through said reaction chamber,
- f) reacting said oxygen precursor with said at least one surface of said substrate,
- 30 g) sending a purge gas through said reaction chamber for the purging of the reaction chamber,
- h) pulsing a lanthanum precursor through said reaction chamber,

- i) reacting said lanthanum precursor with said at least one surface of said substrate,
- j) sending a purge gas through said reaction chamber for the purging of the reaction chamber,
- k) pulsing an oxygen precursor through said reaction chamber,
- 5 l) reacting said oxygen precursor with said at least one surface of said substrate,
- m) sending a purge gas through said reaction chamber for the purging of the reaction chamber,
- n) repeating steps b) to m) a desired number of times in order for the formation of a thin film layer of a lithium and lanthanum comprising material upon said at least one surface
- 10 of said substrate.

7.

A method according to claim 6 wherein each step of the process is independently repeated a desired number of times.

15

8.

A method according claim 6 or 7 for the production of a Li-La-Ti-O layered compound.

9.

- 20 A method according to any one of the above claims wherein the lithium precursor is chosen from a metal-organic compound such as lithium 2,2,6,6-tetramethylheptane-3,5-dionate, a lithium alkoxide or a lithium alkyl.

10.

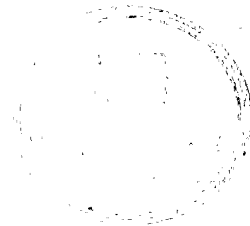
- 25 A method according to any one of the above claims wherein the lithium precursor is a bimetallic compound such as Ti-Li compounds.

12.

- 30 A method according to any of the above claims for the production of a lithium-comprising thin film battery.

13.

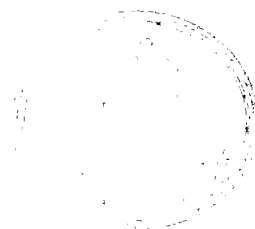
A method according to any of the above claims for the production of a lithium-comprising electrolyte thin film for use in a battery.



Abstract

P60704585NO00

The present invention discloses a method for the formation of lithium comprising layer on a substrate using an atomic layer deposition method. The method comprises the sequential pulsing of a lithium precursor through a reaction chamber for deposition upon a substrate. Using further oxidising pulses and or other metal containing precursor pulses, an electrolyte suitable for use in thin film batteries may be manufactured.



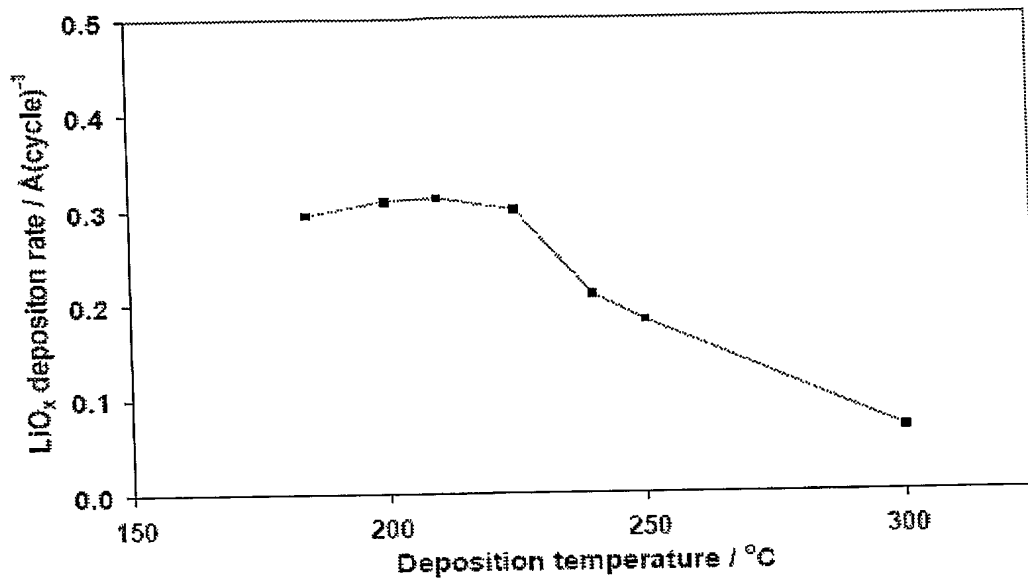


Figure 1

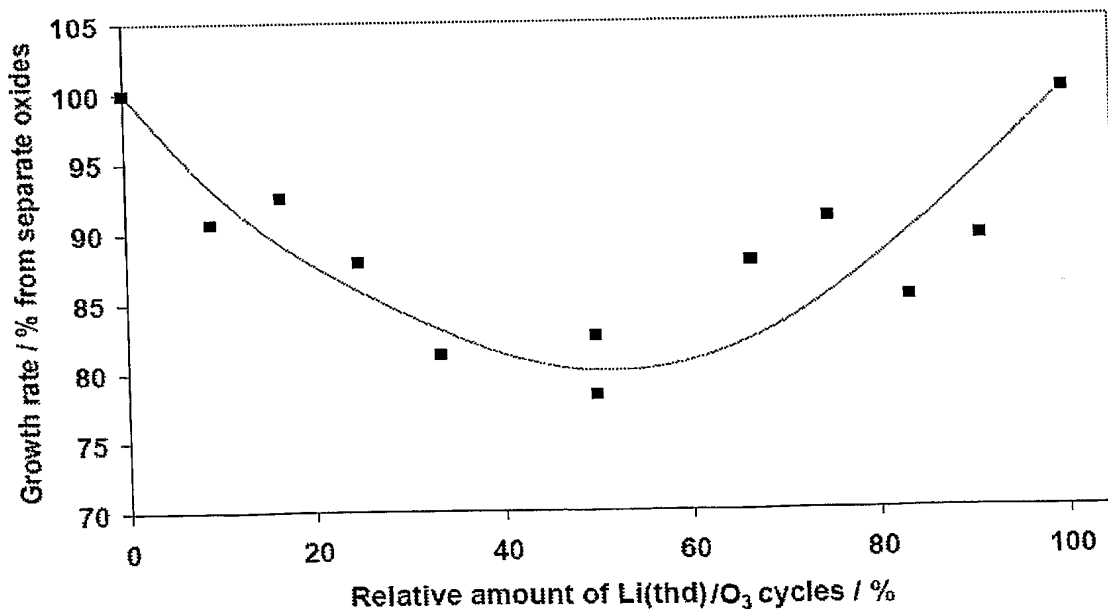
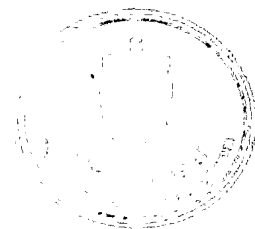


Figure 2



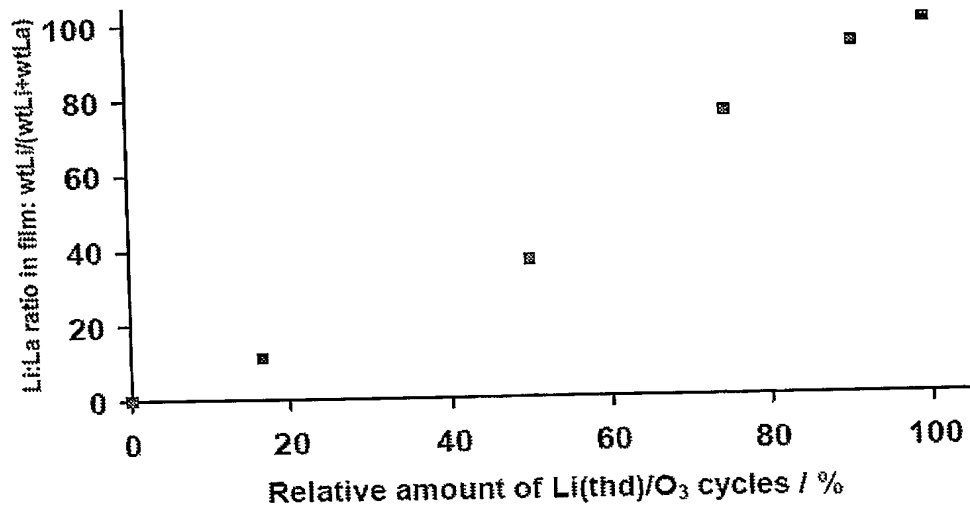


Figure 3

