Article

Atomic layer deposition of Li-Me-O thin films as electrode materials for nanodevices power sources

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Abstract: Nowadays the development of nanoscale power sources with a long battery life is required for novel nanoelectronic devices, such as wireless sensors, biomedical implants, smart cards and others. Lithiated metal oxides (Li-Me-O) are widely used in Lithium-ion batteries (LIBs). Depending on the type of metal Li-Me-O can be applied as cathode, anode or electrolyte materials. Atomic layer deposition (ALD) due to its precision control over thickness, purity, and uniformity over large areas of applied coatings can be applied as appropriate method for synthesis of a different type of thin film LIBs materials. In present work the deposition of Li-Sn-O (anode) and Li-Al-O (electrolyte) by ALD is considered. The prepared films were investigated with use of X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry.

Keywords: Atomic layer deposition, nanodevices, thin films power sources, lithiated metal oxides

1. Introduction

Development of new materials for high-performance power sources is one of the most actual tasks for modern material science. For some applications such as nanodevices, smart cards, microchips with integrated power supplies, some medical implants, etc thin films power sources are the only ones that can be applied. Li-ion batteries (LIBs) are widely used in high energy density applications such as portable electronics, electric vehicles, drones etc [1]. Thanks to their high energy density and cycle life LIBs electrochemical system is considered for fabrication of thin film power sources [2].

To implement thin film LIBs, it is necessary to develop and use a reliable and successful technology for their production. The most significant is the method of obtaining thin-film electrodes. Among the variety of methods, the atomic layer deposition (ALD) actively used in microelectronics [3] should be noted. ALD deserves specific attention due to its unique features, such as good conformity and absence of pinholes and defects, high precision of thickness and composition controllability and a capability to deposit high quality coating both on planar and on complex 3-dimentional substrates with high aspect ratio [4,5]. The ALD technology is based on a sequence of chemical reactions of gaseous reagents with the substrate separated in time by inert gas purges, which makes the self-limited growth of films possible [4,5].

Tin oxide thin films as anode is regarded as one of the perspective materials for LIBs due to safety, cycle life and high specific discharge capacity (theoretically – 1491 mAh/g) [6,7]. The properties of tin oxide can be improved by its lithiation.

Lithium aluminum oxide possess relatively high li-ion conductivity and can be regarded as possible candidate for electrolyte of solid state power source.

In present publication we communicate the results of synthesis by ALD of lithium oxide, tin oxide, lithium-tin oxides and lithium-aluminum oxide as composite films lithium-tin oxide with deposited film of aluminum oxide.

2. Materials and Methods

Monocrystalline silicon (100) substrates (20x20 mm) and 316SS stainless steel plates, 16 mm in diameter were used as a substrates. Before deposition silicon and stainless-steel substrates were washed in an ultrasonic bath in acetone then in deionized water for 10 min. After cleaning procedure the substrates were dried in inert gas atmosphere.

Atomic layer deposition was carried out with use of commercial "Picosun R-150" setup in the laboratory "Functional Materials", SPbPU. Lithium hexadimethyldisilazide ($LiN[(CH_3)_3Si]_2$ – LiHMDS), Tetraethyltin ($Sn(C_2H_5)_4$ – TET), trimethyl aluminium (TMA), water, ozone, remote oxygen plasma (2500-3000 W, the frequencies were 1.9-3.2 MHz) were used to deposit films. The maintained temperatures during ALD process for reagent vessels with TET – 65°C, LiHMDS – 130-170 °C, TMA-25 °C. The excess of precursor was purged (pulse time 4-6 seconds) with nitrogen (99.9999%) before the counter-reactant was introduced. The synthesis was conducted at low pressure – 8-12 hPa. Reactor temperature varied in the range of 200-300°C. The denotation of samples and synthesis conditions are presented in Table 1.

Table 1. Description of deposition process.

Name	Com-n	A	t_A, s	B	t_B, s	C	t_C, s	D	t_D,s	T, °C	nC
Al(nC)	**Al_2O_3**	**TMA**	**0.1**	**H_2O**	**0.1**	–	–	–	–	**200-300**	**50-150, 500**
Al(O_3)	**Al_2O_3**	**TMA**	**0.1**	**O_3**	**4**	–	–	–	–	**300**	**50**
H2O(nC)	**Li-O**	**LiHMDS**	**0.1**	**H_2O**	**0.1**	–	–	–	–	**200-300**	**400-500**
Li-Al-O	**Li-Al-O**	**LiHMDS**	**0.1**	**H_2O**	**0.1**	**TMA**	**0.1**	**H_2O**	**0.1**	**250**	**500**
Li-O	**Li-O**	**LiHMDS**	**0.5**	**O_3**	**4**	–	–	–	–	**300**	**500**
Li-Sn-O	**Li-Sn-O**	**LiHMDS**	**0.1**	**O_3**	**4**	**TET**	**0.1**	**O_2**	**10**	**300**	**300**
PO_2 (nC)	**Li-O**	**LiHMDS**	**0.1**	**O_2**	**10**	–	–	–	–	**200-300**	**400-500**

Note: Com-n – composition, A, B, C, D – reagents, t_A, t_B, t_C, t_D – pulse time (seconds), T – reactor chamber temperature, nC – number of cycles (A-D).

The notations of the samples used in the article can be decrypted by example – H2O(500)+Al(100): 500 cycles of wafer treatment by LiHMDS, nitrogen purge, water vapors, nitrogen purge followed 100 cycles of TMA, nitrogen purge, water vapor, nitrogen purge.

The growth rate was calculated on the base of number of cycles and thickness of the films which was determined by spectral ellipsometry (SE). The ellipsometry setup "Ellips-1891 SAG" (Novosibirsk, the Russian Federation) ensured the accuracy in determining the thickness of films equal to 0.3 nm in the film thickness range of 1–100 nm. The measurements were carried out at 5-9 points of the support surface. X-ray photoelectron spectra (XPS) were registered with use of "Thermo Fisher Scientific Escalab 250Xi" spectrometer. The samples were excited by Al Kα (1486.7 eV) X-rays in vacuum of 7×10^{-8} Pa. The sample charging was automatically compensated. The binding energy scale was referenced using the C 1s carbon line (284.8 eV). The depth profiles of elemental concentrations were examined by time-of-flight – secondary ion mass spectroscopy (TOF.SIMS 5 instrument, ION-TOF GmbH, Germany). Depth profiles of the elements were recorded in dynamic SIMS mode using the primary ion gun (Bi^+ at 30 keV energy and 3.1 pA measured sample current, area 70x70 μm) for analysis and Cs (0.5 keV, area 120x120 μm) for sputtering. Both positive and negative ion modes were used. The total analysis (sputtering) time for each mode was 4 minutes.

3. Results and Discussion

3.1 Growth per cycle

The Li-O films were deposited with two pairs of precursors LiHDMS / H_2O vapors and LiHDMS / O_2 plasma. Despite of method of synthesis the deposited films have been changing their color in time during their contact with air atmosphere. The change of color may be caused by augmentation of films thickness and their composition after reaction with water vapors presented in air. In order to hinder this adverse reaction the samples were placed in argon (H_2O content less than 10 ppm) filled Glove box (VGB-6, MTI). The samples were withdrawn immediately before carrying out of measurements. To prevent hydration reaction, it was proposed to deposit alumina thin layer by ALD process.

The effect of temperature on the growth rate of Li-O films and Li-O modified by alumina are shown on Figure 1. For the films Li-O deposited with use of oxygen plasma the growth rate diminishes with increase of temperature. The same influence of temperature we observed earlier for SnO_2 films [8]. The growth rates of H2O(500)+Al(100) and Po2(400)+Al(50) films are similar. For both samples the maximum growth rate is observed at 250°C and may be caused by secondary processes [9, 10] lead to nanocrystal formation and/or formation lithium aluminate. The minimal values of growth rates (0.16-0.22 nm per cycle) are observed for the synthesis at 300°C and they are consistent with growth rates observed for ALD process [4,5,8].

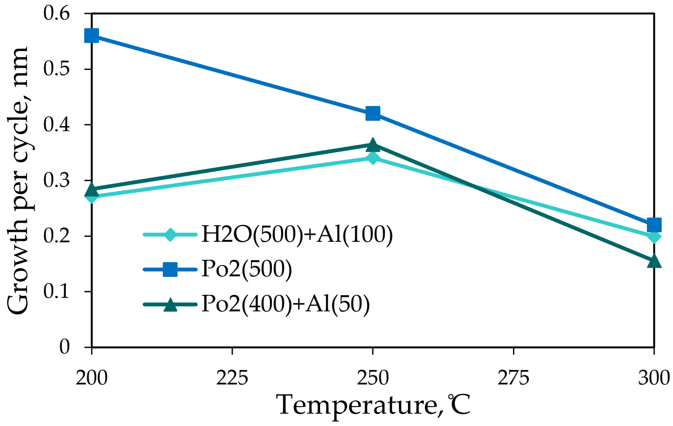


Figure 1. The influence of temperature on average growth rate of Li-O films and Li-O films modified by alumina

The growth rates for films of different composition deposited at 250 °C are presented on the Figure 2. The growth rates calculated for Li-Al-O and Al_2O_3 are consistent with values determined for films deposited by ALD process [4]. The estimated average growth rate for Li-O films modified by alumina is higher than theoretical values and it diminished with increase of number of TMA/H_2O treatment cycles. It is possible that in our case the deposited film of alumina doesn't fully protect the Li-O film. Assuming that the alumina growth rate is constant one can conclude that the use of LiHMDS/H_2O provide higher growth rate than LiHMDS/O_3 precursors. Probably 250°C in not enough temperature for full desorption of water molecules from Li-O film surface and part of the film deposits according to chemical vapor deposition process [11]. Thus, in order to avoid uncontrollable growth of films Li-O water free process should be used.

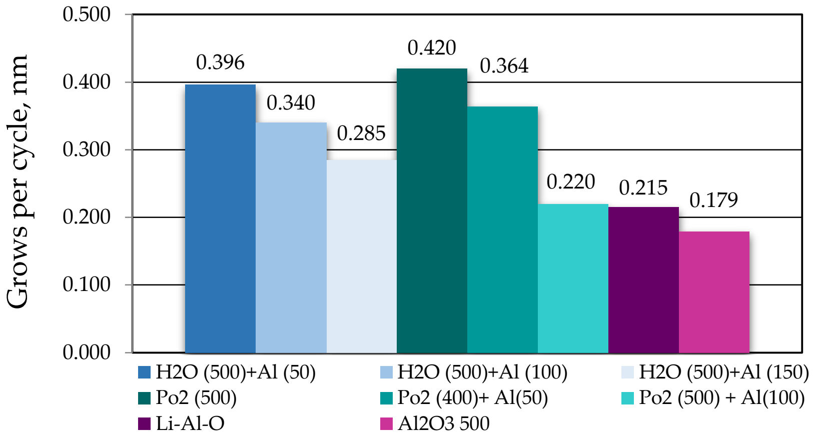
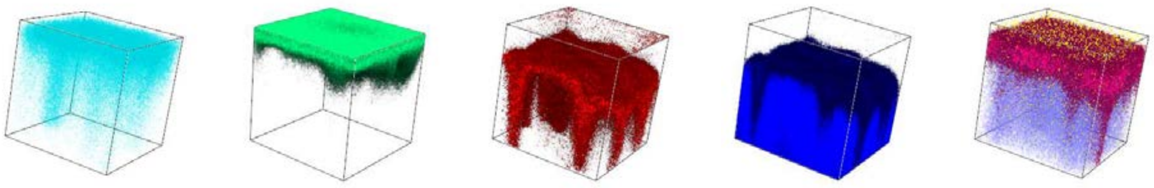


Figure 2. Growth per cycle of thin films with different chemical composition deposited at 250°C

The influence of synthesis conditions on the growth rate of SnO_2 was investigated in our previous paper [4]. The approximate value of growth rate of films obtained at 250-300 °C varied from 0.06 to 0.09 nm per cycle. The thickness of obtained Li-Sn-O films (300 °C, 300 cycles) varied in the range 27.4-30.4nm, thus the growth rate varied in the range 0.09-0.1 nm per cycle.

3.2 Depth distribution of elements

Depth distribution of elements was studied with use of TOF SIMS. The analysis of Li-O films modified by alumina (Po2(500)+Al(100)) was carried out in positive (Figure 3 (a) and 3 (b)) and negative (Figure 3 (c), 3 (d), 3 (e)) modes. In positive mode at the beginning of analysis (external surface) the lithium ions were fixed. With increase of sputtering time the concentration of lithium diminished and after 2 minutes it was close to the value of error. On contrary the concentration aluminum ions increased with the sputtering time. In the negative mode at initial time of sputtering the $LiOH^-$ were detected that were followed by AlO^-, OH^- and O^- were detected. Despite of attempt to cover and protect Li-O film it is still presented on the external surface of the sample. Alumina seemed to diffuse through Li-O film during synthesis or vice versa lithium diffuse to the external surface. Thus, the deposited alumina film does not protect Li-O film and estimated increased growth per cycle is due to its hydration.



(**a**) (**b**) (**c**) (**d**) (**e**)

Figure 3. Elemental composition of Li-O+Al(O_3): (**a**) Al^+ ions; (**b**) Li^+ ions; (**c**) OH^- ions; (**d**) O^- ions; (**e**) magenta – AlO^-, yellow – $LiOH^-$ ions, and purple – wafer (Fe, 316SS).

According to TOF SIMS analysis (negative mode) of Li-Sn-O film the anions containing Li, Sn and O are presented in the film. Lithium (Figure 4 (a), 4 (b)) is distributed uniformly across the depth the film. LiOH$^-$ are mainly present at the external surface of investigated film. Tin anions were found in inner layers of the film, but their quantity was much smaller than anions containing lithium. Probably Li precursor interacts more actively with the surface groups than Sn precursor and this result in smaller quantity of Sn in the film. Thus in order to increase quantity of Sn in the film more long pulses or greater number of pulses are required.

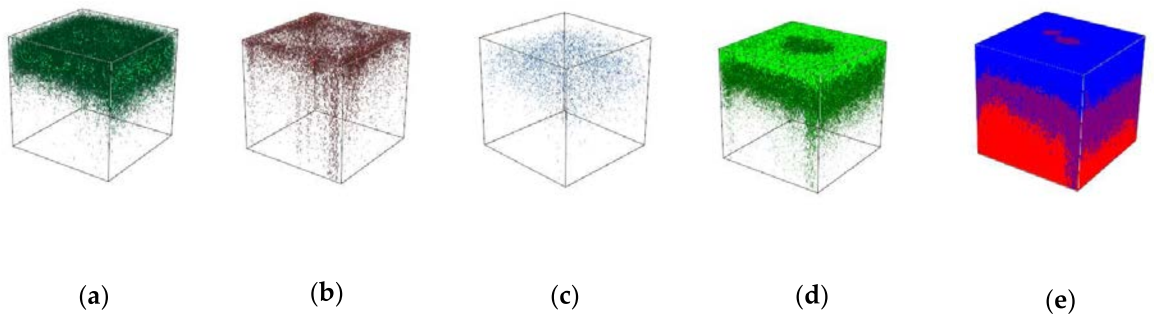


Figure 4. Elemental composition of Li-Sn-O thin film: (**a**) dark green Li$^-$; (**b**) LiOH$^-$; (**c**) Sn$^-$, (**d**) green – OH$^-$; (**e**) blue – O$^-$, red – wafer (Si, silicon (100)).

3.3 Chemical state of surface atoms

XPS analysis of deposited films showed the presence of peaks with binding energy corresponding to O 1s, C 1s Li 1s and Al 2p for Li-Al-O and O 1s, C 1s Li 1s and Sn 3d for Li-Sn-O films. The maximums with binding energy corresponding for Si 2p and N 1s were not found, therefore these elements belonging to the lithium precursor are not presented in the external layers of the deposited films. Apparently the unsymmetrical from of O 1s peak and additional maximum in the area of low binding energy (523 eV) may be caused by the presence of hydroxyl groups or by organic impurities containing oxygen. The registered additional maximum in the region of 280 eV (C 1s) may also signify about the presence of organic impurities.

4. Conclusions

The thin films of different compositions (Li-O+Al-O, Al-O, Li-Al-O, and Li-Sn-O) were deposited by ALD method. The minimal growth rate per cycle which is close to reported values intrinsic for ALD was observed at 300^{o}C. The modification of Li-O films by alumina (less than 100 cycles of treatment) may only hinder but cannot prevent the hydration of surface. When water is applied as a second precursor for Li-O films deposition with use of LiHMDS the growth rate is higher than in case of use of oxygen plasma. The elemental analysis of Li-O films modified by alumina showed that lithium is presented on the external surface whereas alumina is found in deep layers of the film. The observed phenomena maybe caused by diffusion of lithium or aluminum. The quantity of tin in Li-Sn-O films is smaller than the quantity of lithium. Probably more long pulses are required to obtain Li-Sn-O film with equimolar quantity of Li and Sn.

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Conflicts of Interest: The authors declare no conflict of interest.

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