ATOMIC LAYER DEPOSITION OF LITHIUM OXIDE, TIN OXIDE, AND LITHIATED TIN OXIDE NANOFILMS FOR HIGH PERFORMANCE THIN FILM BATTERIES ANODES

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Abstract

In recent years atomic layer deposition has proved to be a successful method of fabrication and modification of electrodes for lithium-ion batteries and thin film power sources. Tin oxide demonstrated considerable excellence over currently used materials for thin film batteries anodes, however, lithiated tin oxides are expected to show even better performance. In this research nanofilms of LiOx, SnO_2 and lithiated tin oxide were deposited by atomic layer deposition (ALD) using lithium hexamethyldisilylazide ($LiN[Si(CH_3)_2]_2$, LiHMDS), tetraethyl tin ($Sn(C_2H_5)_4$, TET) as the metal-containing reagents and water or ozone or oxygen plasma as co-reagents. The monocrystalline silicon (100) and stainless steel (316SS) were used as supports. The thickness of the films was measured with spectral ellipsometry. The composition was studied by X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. Regardless of the type of co-reagent, the resulting films are unstable under long-term storage in air, but their stability is significantly improved by ALD of aluminum oxide with a thickness of several nanometers. The optimal temperature range was about 250-300 °C for deposition of lithium oxide, tin oxide, and lithium-tin oxide nanofilms. It was observed the remarkable influence of the type of co-reactant on the properties of the prepared nanofilms.

Keywords: Li-ion batteries, lithium oxide, anodes, lithiated tin oxide, thin film electrodes, atomic layer deposition

1. INTRODUCTION

Development of new materials for high-performance power sources is one of the most actual tasks for modern material science. Li-ion batteries (LIBs) are the most successful and perspective type of power sources which are actively used in hybrid electric vehicles and portable electronics [1,2]. Nowadays one of the most promising and interesting trends in the development of materials for lithium-ion batteries is thin film technologies [3,4]. Thin film power sources are the most progressive and sometimes the only possible ones for nanodevices such as smart cards, microchips with integrated power supplies, for various portable devices, medical implants and etc. [5,6]. To create such nanodevices, it is necessary to develop a reliable and successful technology for their production. In this case, the most significant is the method of producing thin-film electrodes.

Among the variety of methods it should be noted the atomic layer deposition (ALD) which is actively used in microelectronics [7,8] and also has broad prospects for producing of catalysts [9], biomaterials [10], photovoltaic devices [11] etc. 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, high aspect ratio and complex 3-dimensional substrates [12,13]. The ALD is based on a sequence of chemical reactions of gaseous reagents with the substrate surface separated in time by inert gas purges, which makes the self-limited growth of the films is possible [12,13]. Due to this features the ALD is ideal for preparation of thin film electrodes [14]. Today tin

oxide thin film anodes are regarded as the most perspective for LIBs due to safety, cycleability and specific charge capacity (theoretically - 1491 mAh/g) [15-17]. But lithiated tin oxide probably is more perspective due to its better stability during many charge/discharge cycles [18,19].

In this work, we are studying the processes of ALD lithium oxide, tin oxide and lithium-tin oxide prepared using lithium hexamethyldisilylazide (LiHMDS), tetraethyl tin (TET) as the metal-containing reagents and water or ozone or oxygen plasma as co-reagents and also, we are trying to find the optimal parameters for ALD of lithium oxide and lithium-tin oxide thin films.

2.   MATERIALS AND METHODS

Monocrystalline silicon (100) substrates (20x20 mm) and 316SS stainless steel plates, 16 mm in diameter were used as support for tin oxide, lithium oxide and lithium-tin oxide deposition. Before deposition silicon and stainless-steel supports were cleaned in an ultrasonic bath in acetone and deionized water for 10 min. After that, the substrates were dried in the inert gas atmosphere.

Atomic layer deposition was carried out with commercial "Picosun R-150" setup. Tetraethyltin ($Sn(C_2H_5)_4$ - TET) and remote oxygen plasma were used for tin oxide deposition. The more detailed the procedure is described in [20]. For lithium oxide ALD lithium hexadimethyldisilazide ($LiN[(CH_3)_3Si]_2$ - LiHMDS) and different co-reagent (ozone, water and remote oxygen plasma) were used. The power of plasma was 2500-3000 W. To find optimal regimes for deposition we varied the reactor temperature in the range of 250-300 °C. Stabilization of lithium oxide was carried out by additional of Al_2O_3 ALD coating (50 cycles) using trimethylaluminium (TMA) and water. All depositions were performed as follows. After pulsing of reagent (TET - 0.1s, LiHMDS - 0.1s, TMA - 0.1s) precursor had been injected for a certain pulse time, the excess of the precursor was purged (4-6s) with nitrogen (99.999 %) before the counter-reactant was introduced. Pulse times for co-reagents were H_2O - 0.1s, ozone - 4s, oxygen plasma - 10s. The temperatures of reagent containers were TET - 65 °C, LiHMDS - 150 °C, TMA-25 °C.

The thickness of the films was determined by spectral ellipsometry (SE) and Scanning Electron Microscopy (SEM). The ellipsometry setup "Ellips-1891 SAG" (Novosibirsk, the Russian Federation) ensured the accuracy in measuring the thickness equal to 0.3 nm. The measurements were carried out at 5-9 points of the support surface. Scanning electron microphotographs (SEM) showing plan-views and cross-sectional views were obtained using the SEM Zeiss Merlin. The microscope spatial resolution was around 1 nm. X-ray photoelectron spectra (XPS) were registered with a "Thermo Fisher Scientific Escalab 250Xi" spectrometer. The samples were excited by Al Kα (1486.7 eV) X-rays in the vacuum of 7×10^{-8} Pa. The binding energy scale was referenced using the C1s 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 regimes were used.

3.   RESULTS AND DISCUSSION

The initial results showed that films of lithium oxide obtained using water were hydrolyzed very quickly when stored in air condition (discoloration and the presence of a significant gradient of thickness after 1 day of storage). The samples deposited using of plasma and ozone was less prone to hydrolysis. However, they also hydrolyzed during prolonged storage in air. In this regard, the samples of lithium oxide were future deposited using ozone, water and oxygen plasma as co-reactants and stabilized with alumina. To this end, immediately after the synthesis, films were coated by ALD with aluminum oxide using trimethylaluminum and water (**Table 1**).

Table 1 Characteristics of the samples

Short name	Reagents	Temperature (°C)	Number of cycles	Passivation (number of cycles)	Thickness, nm	Growth per cycle (nm)
Li-O$_3$-300	LiHMDS+ozone	300	500	Al$_2$O$_3$ (50)	26.5±0.8	0.048±0.001
Li-H$_2$O-250	LiHMDS+water	250	400	Al$_2$O$_3$ (50)	290±25	0.64±0.06
Li-H$_2$O-300	LiHMDS+water	300	400	Al$_2$O$_3$ (50)	500±100	1,11±0.22
Li-O$_2$-250	LiHMDS+O$_2$ plasma	250	400	Al$_2$O$_3$ (50)	165±25	0.37±0.06
Li-O$_2$-300	LiHMDS+O$_2$ plasma	300	400	Al$_2$O$_3$ (50)	70±22	0.16±0.05
Li-O$_3$-Sn-1-1	LiHMDS+O$_3$+TET+O$_3$	300	(1+1)*500	no	28±0.8	0.028±0.001
Li-H$_2$O-Sn-1-3	LiHMDS+H$_2$O+TET+O$_2$ plasma	250	(1+3)*200	no	67±5	0.084±0.006
Li-O$_2$-Sn-1-3	LiHMDS+O$_2$ plasma +TET+O$_2$ plasma	300	(1+3)*380	no	170±25	0.11±0.02

The samples obtained using H$_2$O showed a growth rate of more than 1 nm (**Table 1**), which is much larger than the thickness of the monolayer. In addition, they are quickly hydrolyzed in the air, forming crystals (presumably lithium hydroxide) despite the stabilization of the surface with Al$_2$O$_3$ (**Figure 1a, c**). The use of O$_2$ plasma and O$_3$ at 300 °C gives a growth per cycle of 0.16 and 0.048 nm, respectively. These samples are less prone to hydrolysis (**Figure 1b, d**). Uncontrolled growth of films deposited with LiHMDS and H$_2$O was observed earlier [21]. It appears that the use of water leads to uncontrolled growth due to the reservoir effect, where the bulk of the film absorbs water providing a large supply of hydroxide groups in addition to the self-limiting surface reaction. Any LiOH thereby formed in the bulk of the film may react with the subsequent pulses of LiHMDS leading to a growth rather limited by the thickness of the deposited film [21].
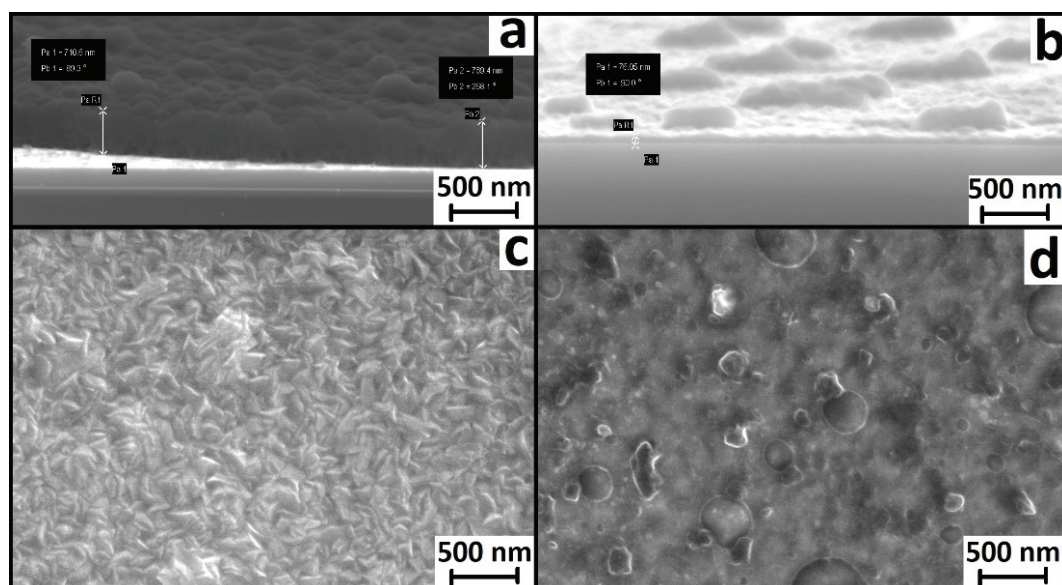

Figure 1 SEM profile and in-plane images of the films prepared by ALD at 300 °C using LiHMDS and water - a), c), or O$_2$ plasma as co-reagents - b), d).

The films of tin oxide were deposited using TET and oxygen plasma. A detailed description of the process was described earlier [20, 22]. Despite the fact that it is possible to obtain films at low temperatures (up to 200 °C) [23], the temperature range 250-300 °C is the optimal [20]. The use of this temperature range is applicable to the deposition of tin oxide using ozone and oxygen plasma [20]. A similar temperature range is also applicable to lithium oxide. Thus, the range of 250-300 °C is optimal for the deposition of lithium-tin oxides.

Then we obtained thin films of complex oxides using the sequential pulses of LiHMDS+O_3+TET+O_3. This sequence represents one supercycle ALD. The number of supercycles was 500. The XPS data showed that only Li, O and C are present on the surface of the samples. Moreover, Sn is either absent or its concentration is much less than 1 %.

In connection with this fact, for further work, we increased the number of TET pulses, and also oxygen plasma was used as a co-reagent, which is more active then ozone. The samples were obtained using supercycles: LiHMDS+H_2O+(TET+O_2 plasma)*3 - sample Li-H_2O-Sn-1-3 and LiHMDS+O_2 plasma+(TET+O_2 plasma)*3 - sample Li-O_2-Sn-1-3. According to XPS, these samples contained Sn on the surface, but its atomic concentration does not exceed 1 % (**Figure 2a**). In the bulk of the film, the Sn concentration exceeds 4 at. % (**Figure 2b**), however, the concentration of Si (> at. 12 %) is significantly increased. The presence of silicon in the films was observed earlier and is associated with the low reactivity of silicon containing a precursor (LiHMDS) under the ongoing ALD reactions [24,25].
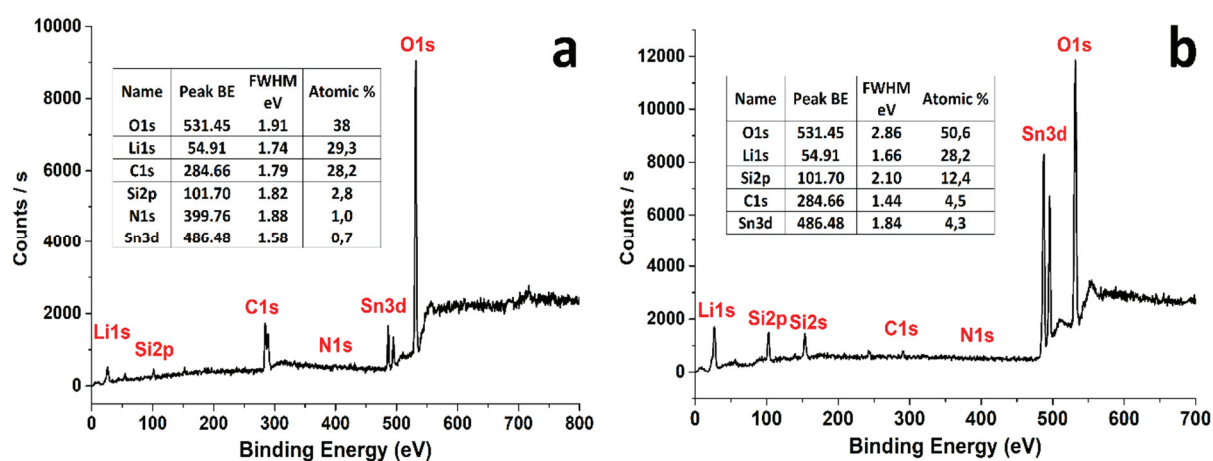
Figure 2 XPS survey spectra of the sample Li-H_2O-Sn-1-3 before - a) and after ion-etching - b)

TOF-SIMS study of lithium oxides coated with aluminum oxide revealed that aluminium is presented presumably on the surface. Secondary ions were detected both in the form of AlO^+, and $LiAl^+$, $LiAlO_2^+$ (**Figure 3a**). Thus, aluminum on the surface is present both in the form of an oxide (Al_2O_3) and as a complex oxide ($LiAlO_2$). However, the concentration of aluminum on the surface is a very small. The concentration of silicon in the surface layer is much lower than in the bulk of the film. Probably, the source of silicon in the bulk is the incompletely reacted precursor (LiHMDS) [24,25].
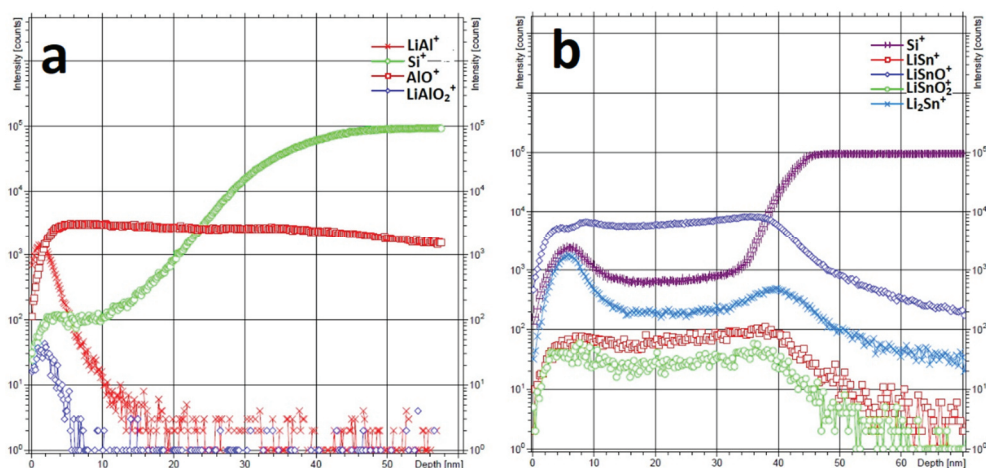
Figure 3 TOF-SIMS profiles of the samples Li-O_2-300 - a) and Li-H_2O-Sn-1-3 - b)

TOF-SIMS study of lithium-tin oxides revealed that tin concentration is very low, especially on the surface (**Figure 3b**). This result is in good agreement with the XPS data. In the sub-surface layer, the concentration of Li_2Sn^+ and $LiSnO^+$, as well as of Si^+, increases, while $LiSnO_2^+$, $LiSn^+$ practically does not change. The XPS and TOF-SIMS data show that the coating contains a lot of silicon but little nitrogen and carbon, which could also remain in the coating from the precursor. In addition, it can be assumed that lithium, silicon and tin form a mixture of complex oxides and the sub-surface layer rather thick (about 10 nm) and significantly different in composition from bulk.

4.   CONCLUSION

Nanofilms of lithium oxide, tin oxide and lithiated tin oxide were successfully deposited by ALD using lithium LiHMDS or/and TET as the precursors. It was revealed that lithium oxide is nonstable at storage in air conditions but can be stabilized by ALD alumina coatings. The lithiated tin oxide can be prepared by ALD using LiHMDS, TET and O_2 plasma as co-reactant, but the resulting films have a relatively low concentration of tin (~4.3 at. %) and a remarkable concentration of silicon (>12 % at. %). Nevertheless, the results showed that the increase in the number of TET pulses in each supercycle of ALD can significantly increase the concentration of tin and probably lead to the producing of lithiated tin oxide which is promising material for high-performance Li-ion anodes.

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