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Investigation of the effect of nitrogen ion irradiation on the lithium surface condition

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A comparison of the surface of solid lithium in the atomically pure state, after contact with oxygen, nitrogen and after irradiation with N^+ ions with an energy of 0.6 keV at a current density of $2\,\mu$A/mm^2 was carried out. The analysis of surface characteristics was carried out using electron Auger spectroscopy. To obtain an atomically pure surface, low-energy electron bombardment was used. It is shown that the contact of an atomically pure Li surface with oxygen leads to the formation of lithium oxide, and with nitrogen with a partial pressure of 10^{-6} Pa, lithium oxide and oxynitride in a mixture with free lithium atoms. Irradiation of lithium with nitrogen ions leads to the formation of the surface compound Li3N. It is noted that the resulting compound is unstable in ultrahigh vacuum and eventually decays to form lithium oxide due to interaction with the residual oxygen of the spectrometer chamber.

Keywords: lithium, vacuum, ions, electrons, surface.

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1. Introduction

The formation of thin films includes such processes as adsorption, the formation and growth of new phase nuclei, and their coalescence. To obtain a film with the desired properties, it is required to be able to control these processes. The traditional methods of control include the regulation of the substrate temperature and the deposition rate of the material. Another control opportunity — irradiation of the solid surface with ions that stimulate adsorption, nucleation and film growth [1].

A systematic study of ion-stimulated processes on the surface of solids, with the aim of elucidating the mechanism of condensation and growth of films, their regularities, has been carried out since 1973. A decisive role in the development of the study of ion-stimulated processes was played by the study of the effect of ion irradiation on the processes of formation, structure, and properties of carbon films [2].

The effect of ion irradiation on the growth and properties of the film is based on the following processes: ion-stimulated nucleation, ion-stimulated diffusion, ion-stimulated surface reconstruction, surface heating, generation and annealing of defects. Depending on the parameters of ion irradiation, any of these processes can become decisive for the resulting properties of the film.

The use of ions in the process of film formation allows to expand the opportunities of control by varying the energy of the ion beam, its density, and duration of exposure. The ion beam energy is the main parameter that determines the ions interaction with the surface. At sufficiently high energies, exposure to the beam can lead to the generation of extended defects in the bulk of the growing film, so the beam energy is chosen to be less than a certain critical energy [3]. The density of the ion flux allows to control the formation of nuclei, and the duration of exposure affects the kinetics of film growth, the rate of nucleation and diffusion [3].

Given these considerations , lithium subjected to irradiation with nitrogen ions can be proposed as an object of study of the formation of surface films. Such exposure can lead to the formation of lithium nitride on the surface of the film, which has many attractive properties. From a fundamental point of view, Li_3N is an excellent model system for studying ion dynamics [4]. In practice, lithium nitride has proven itself well in lithium battery production technology [4], and is also a well-known solvent catalyst for the synthesis of boron nitride [5]. The use of Li_3N as a hydrogen storage [6] is very promising.

2. Experimental part

Freshly prepared clean surfaces of lithium (LE-1, GOST 8774-58), which were bombarded with argon ions (HF, GOST 10157-79), oxygen (ultra high purity, grade 5.0) and nitrogen (HF, GOST 9293-74) were used as the objects of study.

The surface reactions of the ions of these gases with Li were studied using Auger electron spectroscopy. The spectra were obtained using an Auger spectrometer based

The energies of the Auger peaks of lithium, oxygen and nitrogen in various compounds

Li KLL, eV	Li_2O, eV	LiF, eV	LiH, eV	LiOH, eV	Li_3N, eV	O KLL, eV	N $KL_{2,3}L_{2,3}$, eV	Literature
58.0		43.0						[18]
48.8	37.0					506.0		[19]
51.0	42.0		36.0			512.0		[20,21]
53.0	42.0		44.8	44.8		509.5		[17]
52.3	40.7					509.5		[22,23]
52.0	38.0					510.0		[15,24]
51.5	40.5					505.0		[16]
			40 ± 1	40 ± 1				[25]
52.0	41.1				47.2	506.9	381.5	Our data

on the USU-4 [7] ultrahigh vacuum setup. The limiting residual pressure in the chamber of the Auger spectrometer was $5 \cdot 10^{-8}$ Pa. The energy of the probing electron beam with a diameter of 1 mm was 2 keV at a current of 1 μA. The spectra were recorded in the range from 0 to 1000 eV at a modulation voltage from peak to peak of 2 V. The selected recording mode is due to the fact that at higher current densities of primary electrons, lithium oxide dissociation was observed. To clean the surface of Li samples, we used an electron beam of the same energy at currents of $300-350\,\mu$A, and to obtain a surface compound of lithium nitride — N^+ ions ($E = 600$ eV, $J = 2\,\mu$A/sm^2).

3. Results and their discussion

It is known that the following main methods are used to remove surface-active impurities and obtain an atomically pure state of the surface of metals, semiconductors, and dielectrics: chemical and mechanical treatment, cleavage (in the case of single crystals), long-term high-temperature heating followed by short-term thermal flash treatment (for refractory materials), ion bombardment (usually by ions of inert gases) [8]. In case of reactive metals, the main impurity on the surface is oxygen, and therefore, cutting the sample under *n*-hexane [9] followed by scribing in inert media [10]. After such a mechanical treatment, the surface is far from an atomically pure state; therefore, already in the spectrometer chamber, bombardment with inert gas ions is practiced, since the insignificant thickness of the formed oxide layer makes it possible to remove impurities within reasonable time intervals. This method, along with simplicity, has disadvantages associated with mechanical action (deformation) on the surface under study.

Therefore, in this work we used a method consisting in cleaning the surface of alkali metals by bombardment with low-energy electrons [11]. The mechanism of surface cleaning by electron action in [11] is explained as follows. For low-energy electrons incident on the surface, electronic excitations due to inelastic interactions of primary electrons with adsorbed particles are of primary importance. In case of lithium, the impurity-free surface is characterized by the KLL transition, in which only lithium electrons at the internal K level and its valence electrons participate. For heavily oxidized Li, an Auger peak is observed due to the interatomic Auger transition $Li(K)O(L_{23})O(L_{23})$ [12]. In such Auger transitions, multiple ionization of the anion component occurs, followed by its ejection from the surface as a result of the Coulomb explosion [13]. The experiments showed that for lithium the best surface cleaning result was obtained for $E = 1000-2000$ eV ($300-350\,\mu$A/mm^2). The electron irradiation time depended on the state of the sample surface and was within 10–60 min.

In view of the fact that, under such influences, a transition to a liquid state is possible, leading to the sample flowing from its holder in the ultrahigh-vacuum chamber of the spectrometer, before bombardment, the sample was oxidized in an oxygen atmosphere with a partial pressure of 10 Pa. Due to this, the metal was kept in a thick-layer oxide „bag“ practically without changing the shape of the sample.

According to our data, the atomically clean lithium surface is characterized by a peak KLL — 52.0 eV (Fig. 1, *a*). When Li reacts with oxygen to form Li_2O, this peak shifts by 10.9 eV and is fixed already at 41.1 eV (Fig. 1, *b*). In this case, as well as in [14], our spectra were obtained after exposing 66 Lengmuir to oxygen. A similar result was obtained in [15]. In literature [17] similar changes in the spectrum are reported, when, after the reaction of Li with hydrogen, an Auger peak was recorded in the Auger spectra at an energy of 42.0 eV. Due to the same profile and energy position of lithium KLL, it was possible to distinguish Li_2O from LiH only by the presence of the 506.9 eV oxygen line. Literature [15–25] and our data on the energy position of the Auger peaks of lithium, nitrogen and oxygen in various compounds are given in the table.

In literature, we found only one work [14], in which the interaction of nitrogen with the surface of lithium was reviewed. The authors [14] made measurements on clean lithium surfaces after exposure to O_2, CO_2 and N_2. It was found that the reaction of Li with oxygen (O_2, CO_2) causes the appearance of lines Li_2O — 38.0 eV and oxygen 510.0 eV with their subsequent increase in amplitude. It is noted that the contact of Li with nitrogen is also characterized by the presence of a peak at 38.0 eV in the spectrum at rather intense peaks of oxygen (510.0 eV) and carbon (270 eV). The authors [14] explained the nature of

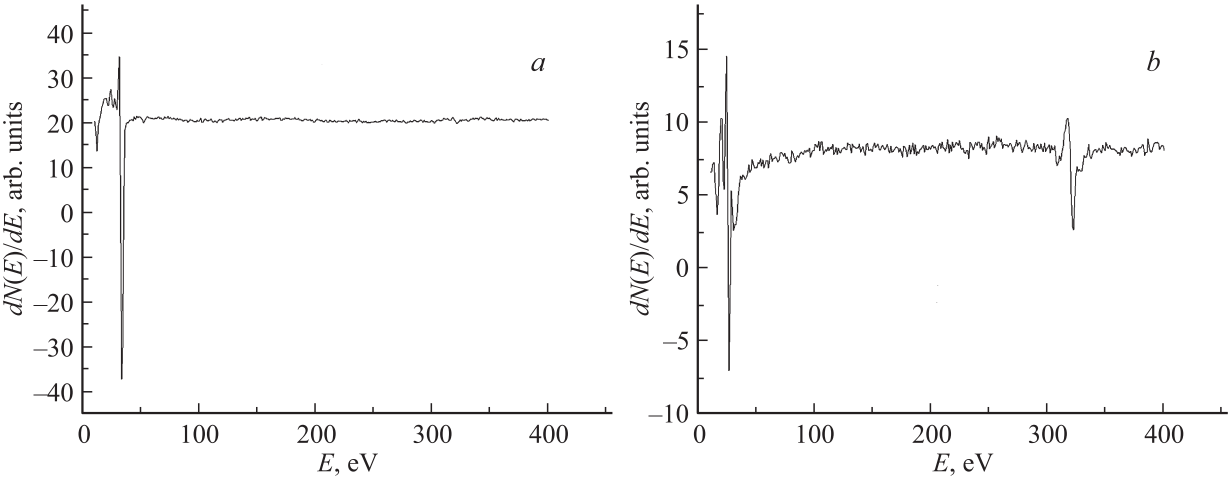

Figure 1. Auger spectra of an atomically clean lithium surface obtained by irradiating the surface with electrons with = 2000 eV at a current of 300 μA for 30 min (*a*) and after exposure to oxygen medium (66 Lengmuir) (*b*) at room temperature.

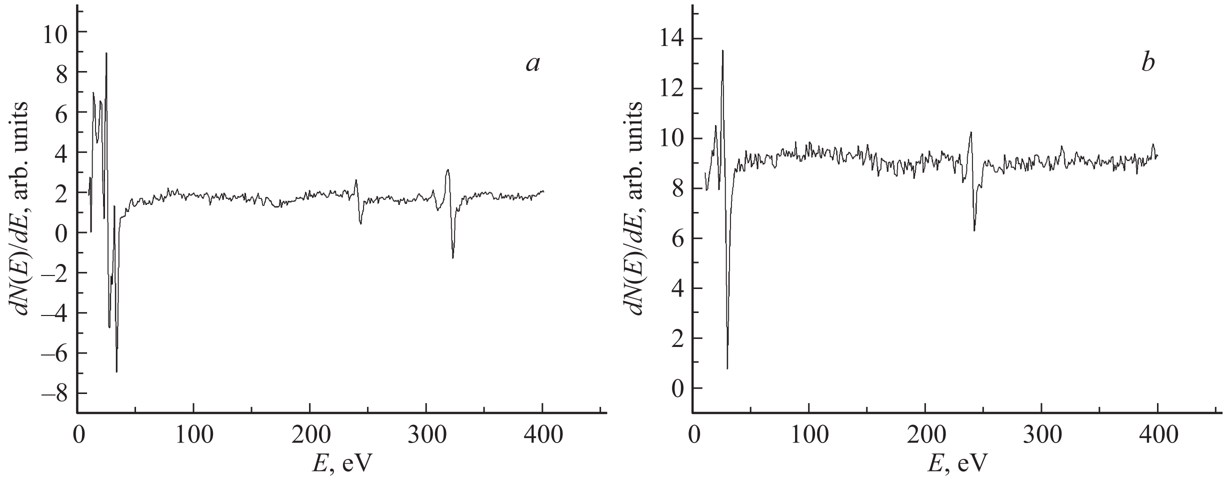

Figure 2. Auger spectra of the surface of lithium at room temperature: *a*) after exposing $1 \cdot 10^4$ Lengmuir to nitrogen; *b*) after 30 min. bombardment with nitrogen ions.

the peak at 38.0 eV by the formation of lithium oxynitride with a significant content of lithium oxide in the surface layer. In conclusion, the authors conclude that nitrogen practically does not interact with lithium at doses from $4 \cdot 10^4$ to $5 \cdot 10^8$ Lengmuir, while the oxidation of lithium with the formation of Li_2O is already observed at 66 Lengmuir O_2 [14]. What stands out in this work is that for all the studied interactions with gases, an Auger peak of Li with one energy — 38.0 eV was observed.

The results obtained in this work confirm the conclusions made in [14]. Exposure of a Li sample in a nitrogen atmosphere at the indicated doses gives spectra similar to those given in [11]. Figure 2, *a* shows the characteristic Auger spectrum after exposure to N_2 with a dose of $1 \cdot 10^4$ Lengmuir. Besides, as in [14], the presence of oxygen on the surface of lithium is noted, but unlike [14], our spectra do not contain carbon. There were significant differences from the literature data for the lithium peak. If one peak was recorded in [14] at 38.0 eV, then, as can be seen in Fig. 2, *a*, there is a split peak with energies of 41.1 and 52.0 eV. Let us note that these Auger peaks (table) refer to lithium oxide and unbound lithium atoms, respectively. In addition to the nitrogen peak, there is also an intense oxygen peak, the appearance of which is due to the influence of residual oxygen in the spectrometer chamber. Thus, our data also indicate that a significant difference in the rates of the reaction between oxygen and nitrogen and lithium leads to the formation of a film consisting mainly of lithium oxide in a mixture with lithium oxynitride and free Li.

Bombardment of the surface of lithium with nitrogen ions significantly changes the Auger spectra. It is seen (Fig. 2, *b*) that N^+ irradiation stimulates the interaction of nitrogen with lithium. First, a significant amplitude of the nitrogen Auger peak is noted in the almost complete absence of oxygen and carbon, as well as a new energy position of the lithium Auger peak — 47.2 eV (table). The nitrogen Auger

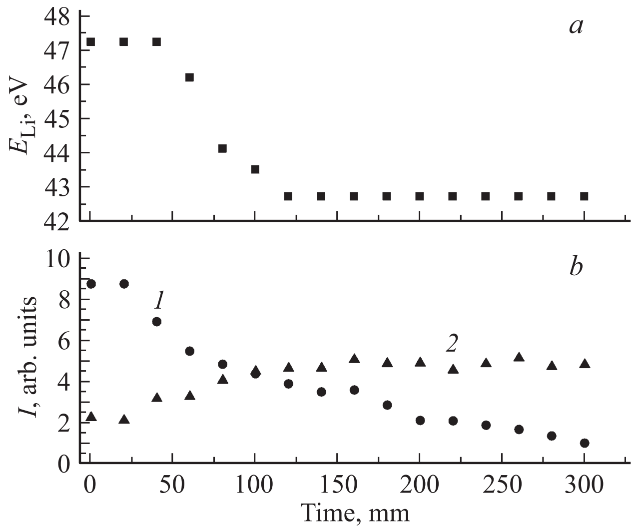

Figure 3. Changes in the intensities (a) of the Auger peaks of nitrogen (1) and oxygen (2) and the energy position of the Auger peak of lithium (b) with the holding time in vacuum $1 \cdot 10^{-6}$ Pa for the sample after 30 min bombardment with nitrogen ions ($E_p = 600$ eV, 2 μA/mm^2).

peak N $KL_{2,3}L_{2,3}$ is recorded at an energy of 381.5 eV, which agrees with [17]. Since only nitrogen and lithium are present in the spectrum, the Li 47.2 eV peak can be associated with the generation of Auger electrons as a result of an interatomic transition involving lithium and nitrogen electrons, for example, $K(Li)L_1(Li)L_{23}(N)$.

Based on the obtained intensity ratio I_{Li}/I_N (Fig. 2, b), the surface concentration was calculated using the equation that takes into account matrix effects [26]. For matrix correction, when calculating the surface concentration, we used such physical parameters as the electron free-path length, the backscattering factor, the ionization cross section of the inner shell, etc. [26]. The calculations showed that the surface concentrations of lithium and nitrogen correspond to the Li_3N stoichiometry. The formation of lithium nitride is also evidenced by the shift of the Li KLL Auger peak by 4.8 eV towards lower energies. This is due to the appearance of a strong chemical bond between the atoms, which leads to a shift in the internal hybridized electronic levels compared to their energy in isolated atoms (the so-called chemical shifts). The range of nitrogen ions with an energy of 600 eV in lithium is commensurate with the escape depth of Auger electrons Li KLL in the energy range 40–50 eV and is 1–2 monatomic layers, so it can be argued that surface compound of lithium nitride.

The resulting compound turned out to be unstable and decomposed in ultrahigh-vacuum at room temperature with the formation of lithium oxide at the expense of oxygen in the residual gaseous medium. This assertion can be supported by data on changes in the Li energy (KLL 52.0 eV) and amplitudes of nitrogen Auger peaks ($KL_{2,3}L_{2,3}$ 381.5 eV), oxygen (KLL 506.9 eV) with holding time in ultrahigh vacuum ($1 \cdot 10^{-6}$ Pa) (Fig. 3). It can be seen in Fig. 3, a that, with time, the intensity of the nitrogen Auger peak decreases (1) with an increase in the amplitude of the oxygen peak (2). Simultaneously with it the lithium Auger line shifts from the position characteristic of lithium nitride (47.2 eV) towards the energy position corresponding to Li_2O — 41.1 eV (Fig. 3, b).

4. Conclusion

Let us specify the main results of the performed study. An alternative method was used to clean the lithium surface, which consisted in electron bombardment with $E = 2000$ eV at $J = 300\,\mu$A/mm^2. It has been specified that the energy position of the Auger peak Li can be used as a good indicator of either the purity of the lithium surface or the presence of a surface compound — Li_2O, Li_3N. It is shown that exposure of an atomically clean lithium surface to oxygen ($1 \cdot 10^{-6}$ Pa) results in the formation of a film consisting of free Li, Li_2O, and LiON. The use of nitrogen ions with $E = 600$ eV, $J = 2\,\mu$A/mm^2 allowed to obtain a Li_3N surface compound.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M.B. Guseva. Soros. obrazovat. zhurn. **10**, 106 (1998). (in Russian).
[2] D.M. Pout, G. Foti, D.K. Jacobson. Modifitsirovaniye i legirovaniye poverkhnosti lazernymi, ionnymi i elektronnymi puchkami. Mashinostroenie, M. (1987). 423 p. (in Russian).
[3] V.G. Babaev, M.B. Guseva. Izv. AN SSSR. Ser. fiz. *37*, *1*, 2596 (1973).
[4] Y. Yan, T. Cui, Y. Li, Y.M. Ma, J. Gong, Z.G. Zong, G.T. Zou. Eur. Phys. J. B **61**, 397 (2008).
[5] V.B. Shipilo, O.V. Ignatenko, N.A. Shempel, I.I. Azarko, S.A. Lebedev. Neorgan. materialy **44**, *3*, 310 (2008). (in Russian).
[6] Y. Nakamori. Appl. Phys. A **80**, 1 (2005).
[7] O.G. Ashkhotov, I.B. Ashkhotova, M.A. Aleroev, T.T. Magkoev. Zhurn. fiz. khimii **91**, *7*, 1171 (2017). (in Russian).
[8] D. Vudraf, T. Delchar. Sovremennye metody issledovaniya poverkhnosti. Mir, M. (1989). 564 p. (in Russian).
[9] K. Wang, P.N. Ross Jr., F. Kong, F. McLarnon. J. Electrochem. Soc. **143**, 422 (1996).
[10] G.L. Powell, G.E. McGuire, D.S. Easton, R.E. Clausing. Surf. Sci. **46**, *2*, 345 (1974).
[11] O.G. Ashkhotov, I.B. Ashkhotova. Pribory i tekhnika eksperimenta **6**, 109 (2019). (in Russian).

[12] H.H. Madden, J.E. Houston. J. Vacuum Sci. Technology **14**, 412 (1977).

[13] V.V. Nikitin, Elektronno-stimulirovannyye protsessy v tverdykh telakh. OGTI, Orsk (2005). 120 p. (in Russian).

[14] D.J. David, M.H. Froning, T.N. Wittberg, W.E. Moddeman. Appl. Surf.Sci. **7**, *3*, 185 (1981).

[15] R. E. Clausing, D. S. Easton, G. L. Powell. Surf. Sci. **36**, 377 (1973).

[16] J.P. Tonks, M.O. King, E.C. Galloway, J.F. Watts. J. Nucl. Mater. **484**, 228 (2017).

[17] L.E. Davis, N.C. Macdonald, P.W.Palmberg G.E. Riach. Handbook of Auger Electron Spectroscopy. Physical Electronics Inc. Minnesota (1976). 253 c.

[18] N. Ishidaa, D. Fujita. J. Electron. Spectroscopy Rel. Phenomena **186**, 39 (2013).

[19] J. Engbæk, G. Nielsen, J.H. Nielsen, I. Chorkendorf. Surf. Sci. **600**, 1468 (2006).

[20] L. Buzi, Y. Yang, F.J. Domínguez-Gutierrez, A.O. Nelson, M. Hofman, P.S. Krstic, R. Kaita, B.E. Koel. J. Nucl. Mater. **502**. 161. (2018).

[22] Ch.F. Mallinson, J.E. Castle, J.F. Watts. Surf. Sci. Spectra **20**. 113 (2013).

[23] W. W. Coghlan,R. E. Clausing. A Catalog of Calculated Auger Transitions for the Elements. Oak Ridge National Laboratory Report ORNL-TM-3576. **11**, (1971).

[24] D.M. Zehner, R.E. Clausing, G.E. McGuire, L.H. Jenkins. Solid State Commun. **13**. 681 (1973).

[25] C.E. Holcombe, G.L. Powell, R.E. Clausing. Surf. Sci. **30**, 561 (1972).

[26] V.A. Gorelik. Elektron. Prom-st., *11–12*, 47 (1978). (in Russian).

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