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Determination of the stoichiometry of AlN coatings by radioactivation with bunches of collectively accelerated deuterons

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The use of deuteron bunches collectively accelerated in a Luce diode to an average energy of 1200 ± 200 keV and a number of 10^{13} per shot is shown for the radioactive determination of the stoichiometry of AlN coatings with a known thickness. In each shot, the deuteron energy was determined by measuring the drift velocity of the virtual cathode collectively accelerating deuteron bunches, and the coating stoichiometry was determined with an accuracy of no worse than $\pm 5\%$ from the ratio of the activities of the ^{28}Al/^{15}O radionuclides induced in the nuclear reactions $^{27}\mathrm{Al}(d, p)^{28}\mathrm{Al}$ and $^{14}\mathrm{N}(d, n)^{15}\mathrm{O}$, respectively.

Keywords: collective ion acceleration, virtual cathode, radioactivation analysis, stoichiometry, coating

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Determining the stoichiometry of coatings from binary compounds of light elements, such as, for example, AlN, BN, and B_4C, at a known mass thickness or, conversely, their mass thickness at a known stoichiometry, is an important problem in materials science [1–7]. To solve this problem, it is possible to use beams of deuterons or protons accelerated on a cyclotron [8], however, such accelerators are complex, energy consuming, and require large rooms, which makes them inaccessible for even small-scale analysis. Much more compact, energy saving, cheap and affordable high-power pulsed ion accelerators based on forming lines with a diode voltage of 200–400 kV, which accelerate intense short-pulse (30–100 ns) ion beams to an energy of 200–400 keV, are widely used to modify surface properties [9], deposition of coatings from ablation plasma [10], but cannot be used to analyze even the lightest elements, not only because of the low energy, but also because of the large uncertainty in the energy spectrum of accelerated protons or deuterons. On the other hand, switching the polarity of the diode electrodes makes it possible, at a diode voltage of 200–300 kV, to accelerate electron bunches, which, in the Plutto–Luce diode geometry [11,12], form virtual cathodes that effectively accelerate ion bunches to the same specific energy in individual shots, but distributed according to the normal law in the range from 450 to 700 keV/a.m.u. [13] in a series of shots.

The use of a coating of deuterated polyethylene for the anode of the Luce diode makes it possible to accelerate bunches of nanosecond deuterons up to $2 \cdot 10^{13}$ per shot to an energy in the range of 1000–1400 keV [14], which may be sufficient for radioactivation analysis of a number of light elements by nuclear reactions of the type (d, n) and (d, p). The yield of such reactions from thick targets at a deuteron energy of about 1200 keV reaches $4.4 \cdot 10^{-6}$ for the $^{12}\mathrm{C}(d, n)^{13}\mathrm{N}$ reaction, decreasing due to the Coulomb barrier for heavier elements. Thus, for the reactions $^{14}\mathrm{N}(d, n)^{15}\mathrm{O}$ and $^{27}\mathrm{Al}(d, p)^{28}\mathrm{Al}$, the yields are $1.3 \cdot 10^{-7}$ and $0.85 \cdot 10^{-8}$ [14,15] respectively. The last pair of reactions is promising for analysis due to approximately the same and rather short half-lives of the radionuclides ^{15}O ($T_{1/2} = 122.24$ s) and ^{28}Al (134 s), which significantly reduces the contribution of systematic errors in the analysis error in determining the time parameters and makes it possible to repeat irradiation of the same sample already after 20 min.

A bunch of 10^{13} deuterons with an energy of 1200 keV produces about $6.5 \cdot 10^5$ nuclei of ^{15}O and $4.25 \cdot 10^4$ nuclei of ^{28}Al in a thick AlN stoichiometric coating. During the measurement time of ~ 2 min, about half of these nuclei due to decay will emit γ-quanta with energies of 511 and 1779 keV, the registration of which by a Ge detector with an efficiency of about 8 and 3%, respectively, will make it possible to register the number of counts in the total absorption peaks $0.52 \cdot 10^5$ (since two γ-quanta with energy 511 keV) and 625. The statistical deviation for 625 counts is $\pm 4\%$, which sets the error in determining the ratio of the number of ^{28}Al and ^{15}O nuclei induced in a thick AlN coating and, as a consequence, the error in determining the mass thickness of coatings or their stoichiometry at a known mass thickness. During magnetron deposition of thin AlN coatings, the ratio of N/Al atoms can vary from 1.7 to 0.4, i.e., from +70 to −60%, depending on the plasma power (see Fig. 3 in [4]); therefore, the development of available methods for determining stoichiometry with an error of up to ± 5–10% is relevant.

In this work, using the example of the analysis of AlN coatings deposited on high-purity silicon substrates with mass thicknesses measured using proton beams of the U-120 cyclotron [8], we study the possibility of determining the stoichiometry of coatings with known mass thicknesses

in relation to the activities of radionuclides ^{28}Al/^{15}O, induced in AlN coatings by up to 10^{13} deuterons per shot, collectively accelerated to an energy of 1200 ± 200 keV in a Luce diode based on the TEMP-4M accelerator.

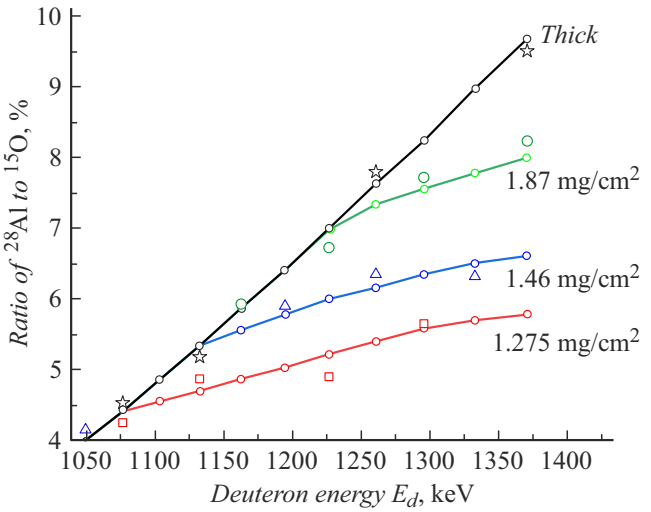
The experimental setup for collective ion acceleration in the Luce diode based on the TEMP-4M accelerator is described in detail in [13,14]. In contrast to [13], a drift tube made of stainless steel with a diameter of 4.4 cm and a length of 22 cm (from the anode) was used as a working chamber, which made it possible to transport bunches of collectively accelerated ions without losses to a target installed at a distance of 22 cm from the anode, and, in addition, significantly accelerated the pumping of the chamber to a pressure of 10^{-5} Torr. The deuteron energy E_d [keV] was determined from the drift time $\Delta\tau$ [ns] of the virtual cathode between the sensors, the distance between which is 8 cm, according to the following formula:

$$E_d = 1050/(8/\Delta\tau)^2 \approx 16.406\Delta\tau^2, \qquad (1)$$

where deuteron velocity is 1 cm/ns at an energy of 1050 keV.

The determination of the drift time over distances of 8 cm with an accuracy of 0.1 ns is expressed in the deuteron energy determination accuracy of ± 25 and ± 35 keV for $E_d = 1050$ and 1365 keV, respectively. Targets in the form of plates with the same dimensions $4 \times 1 \times 0.1$ cm made of aluminum nitride ceramics AlN and silicon with AlN layers deposited on them with known linear and mass thicknesses were installed at a distance of 22 cm from the anode in the center of the ion guide flange with a diameter of 4.4 cm. After each shot, the chamber was opened, and the sample, 1 min after irradiation, was transferred to a detector made of high-purity Ge Canberra) with a relative efficiency of 50%, surrounded by a lead shield 5 cm thick. The induced activity of ^{15}O and ^{28}Al radionuclides was measured for 2 min at total absorption peaks of 511 and 1779 keV, respectively. In this case, the statistics collected in the 511 and 1779 keV peaks was no less than $4 \cdot 10^4$ and 10^3 counts, respectively, which ensured the statistical error of the analysis no worse than $\pm 3\%$. The activity measurement at the 511 keV peak was repeated several times to control the possible activity of the ^{13}N radionuclide ($T_{1/2} = 9.965$ min), which could be formed from possible carbon contamination of the coatings by the $^{12}C(d, n)^{13}N$ nuclear reaction.

In addition to aluminum nitride ceramic plates, three AlN coatings on Si from among the witness samples were studied, for which the linear thicknesses were determined with an error of $\pm 0.1\,\mu$m using an MII-4 optical microinterferometer (AO LOMO, St. Petersburg): 4.6, 5.7, and 4.2 μm for the samples AlN-1, AlN-2 and AlN-3 respectively. Their mass thicknesses were determined as 1.46, 1.87, and 1.275 mg/cm^2 on the working samples of these coatings by the radioactive method using a proton beam accelerated at the U-120 TPU cyclotron [8], which were in agreement with the mass thicknesses of these coatings determined by weighing samples with an accuracy of ± 0.1 mg before and after deposition of coatings on silicon wafers (with



Theoretical (lines with small circles marking E_d gradation) and experimental (symbols) ^{28}Al/^{15}O ratios for an AlN plate (asterisks) and AlN coatings on Si with mass thicknesses of 1.275 (squares), 1.46 (triangles), and 1.87 mg/cm^2 (circles).

an area of 4 cm^2), which for AlN-1, AlN-2, and AlN-3 samples gave an gain of about 5.9, 7.5, and 5.1 mg and made it possible to estimate the mass thicknesses of the AlN coatings as 1.475, 1.875 and 1.275 mg/cm^2, respectively. The discrepancy between the mass thicknesses of the coatings obtained by these two methods, within the weighing error, indirectly indicates a negligible contribution of carbon and oxygen impurities adsorbed by the coatings. Samples of AlN coatings on Si and an AlN plate were irradiated with separate shots four times. The theoretical yield ratio ^{28}Al/^{15}O for stoichiometric AlN coatings of different thicknesses was calculated on the basis of data on this ratio for a thick AlN target given in [14] and data on the ranges of deuterons in nitrogen and aluminum according to [16].

The figure shows a comparison of the experimental results given in the table and the theoretical ^{28}Al/^{15}O yield ratios for stoichiometric AlN coatings with mass thicknesses of 1.87 (AlN-2), 1.46 (AlN-1) and 1.275 mg/cm^2 (AlN-3), and also for a thick AlN sample in the form of a plate. The table lists the deuteron energies Ed and the yield ratios of ^{28}Al/^{15}O nuclei in AlN samples, measured for each of the four shots for all the studied samples. The S value in the table shows the relative discrepancy between the experimental ^{28}Al/^{15}O ratios and the calculated values of these yields for samples of this thickness, expressed as a percentage of the calculated values. It can be seen from the figure that, due to the random dispersion of the deuteron energy in different shots, already three or four shots make it possible to judge the value of the stoichiometry or mass thickness of the studied thin coating from the branch from the „stem“ dependence for a thick target.

In this case, the discrepancies averaged over four shots for each sample, at known mass thicknesses, were treated as

Shot parameters

Shot number	Sample											
	Thick AlN			AlN-1			AlN-2			AlN-3		
	E_d, keV	Y_{Al}/Y_O, %	S, %	E_d, keV	Y_{Al}/Y_O, %	S, %	E_d, keV	Y_{Al}/Y_O, %	S, %	E_d, keV	Y_{Al}/Y_O, %	S, %
1	1133	5.18	−3	1050	4.15	3.75	1371	8.24	3	1296	5.65	1.25
2	1077	4.53	2.72	1333	6.32	−2.92	1227	6.73	−3.58	1133	4.87	3.62
3	1371	9.51	−1.76	1261	6.35	3.08	1296	7.72	2.12	1077	4.25	−3.63
4	1261	7.8	2.23	1195	5.9	2.08	1163	5.93	1.02	1227	4.9	−6.13
Average	1210	6.77	0.05	1210	5.68	1.5	1264	7.16	0.64	1183	4.92	−1.22
±S.D.	131	2.34	2.85	120	1.04	3.02	90	1.03	2.93	97	0.57	4.45

deviations from stoichiometry in the samples in cases where the standard deviations (S.D.)of these averaged discrepancies are much less than themselves. As can be seen from the table, the analysis error for all three coatings (±3−5%) and thick AlN was 2−3 times higher than possible deviations from stoichiometry (from +2 to −1%); therefore, it was concluded that the composition of the studied coatings is stoichiometric within the error.

Thus, we have shown the possibility of using deuteron bunches collectively accelerated by a virtual cathode in a Luce diode to an energy of 1200 ± 200 keV to determine the stoichiometry of AlN coatings at a known mass thickness. Alternatively, this method can be used to determine mass thickness of stoichiometric AlN coatings. Also, such a method can be applied to determine the stoichiometry of coatings of binary compounds of other light elements, such as BN and B_4C, by measuring the activity ratios of radionuclides ^{15}O and ^{11}C, ^{13}N and ^{11}C, respectively, formed in nuclear reactions $^{14}N(d, n)^{15}O$, $^{10}B(d, n)^{11}C$ and $^{12}C(d, n)^{13}N$.

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Conflict of interest

The authors declare that they have no conflicts of interest

References

[1] K. Ueno, E. Kishikawa, S. Inoue, J. Ohta, H. Fujioka, M. Oshima, H. Fukuyama, Phys. Status Solidi (RRL), **8** (3), 256 (2013). DOI: 10.1002/pssr.201308275
[2] J. Borges, N.P. Barradas, E. Alves, M.F. Beaufort, D. Eyidi, F. Vaz, L. Marques, J. Phys. D: Appl. Phys., **46** (1), 015305 (2012). DOI: 10.1088/0022-3727/46/1/015305
[3] L. Behera, N. Pandey, M. Gupta, AIP Conf. Proc., **2265**, 030310 (2020). DOI: 10.1063/5.0017482
[4] S. Cho, M. Lee, S. Lee, J. Chang, New Phys.: Sae Mulli, **67** (8), 929 (2017). DOI: 10.3938/NPSM.67.929
[5] H. Moreno Fernández, D. Rogler, G. Sauthier, M. Thomasset, R. Dietsch, V. Carlino, E. Pellegrin, Sci. Rep., **8**, 1293 (2018). DOI: 10.1038/s41598-018-19273-6
[6] M. Störmer, F. Siewert, H. Sinn, J. Synch. Rad., **23** (1), 50 (2016). DOI: 10.1107/S1600577515020901
[7] A.S. Kamenetskikh, N.V. Gavrilov, O.V. Koryakova, S.O. Cholakh, J. Phys.: Conf. Ser., **857**, 012017 (2017). DOI: 10.1088/1742-6596/857/1/012017
[8] V.A. Ryzhkov, V.A. Tarbokov, E.A. Smolyanskii, G.E. Remnev, Tech. Phys. Lett., **47**, 524 (2021). DOI: 10.1134/S106378502105028X
[9] T.J. Renk, P.P. Provencio, S.V. Prasad, A.S. Shlapakovski, A.V. Petrov, K. Yatsui, W. Jiang, H. Suematsu, Proc. IEEE, **92** (7), 1057 (2004). DOI: 10.1109/JPROC.2004.829024
[10] J. Zhang, H. Zhong, J. Shen, X. Yu, S. Yan, X. Le, Surf. Coat. Technol., **388**, 125599 (2020). DOI: 10.1016/j.surfcoat.2020.125599
[11] J.S. Luce, H. Sahlin, N.R. Crites, IEEE Trans. Nucl. Sci., **NS-20** (3), 336 (1973).
[12] A.A. Plyutto, K.V. Suladze, S.M. Temchin, E.D. Korop, Sov. Atom. Energy, **27** (5), 1197 (1969). DOI: 10.1007/BF01164972
[13] V.A. Ryzhkov, I.N. Pyatkov, G.E. Remnev, Nucl. Instrum. Meth. Phys. Res. A, **1042**, 167436 (2022). DOI: 10.1016/j.nima.2022.167436
[14] V.A. Ryzhkov, I.N. Pyatkov, E.V. Kibler, M.V. Zhuravlev, G.E. Remnev, Russ. Phys. J., **64** (1), 151 (2021). DOI: 10.1007/s11182-021-02311-8
[15] F.C. Young, in *Proc. of the Workshop on measurement of electrical quantities in pulse power systems* (National Bureau of Standards, Boulder, Colorado, 1981), NBS Special Publication 628, p. 107. https://nvlpubs.nist.gov/nistpubs/Legacy/SP/nbsspecialpublication628.pdf
[16] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, Nucl. Instrum. Meth. Phys. Res. B, **268** (11-12), 1818 (2010). DOI: 10.1016/j.nimb.2010.02.091

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