Local electrochemical deposition of thorium-229 targets and excitation of isomeric state by electron beam

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Abstract. The results of the study of local formation of thin-film coatings based on thorium oxide on SiO$_2$/Si(111) surfaces by electrochemical deposition. It is shown that as a result of electrochemical deposition of thorium atoms from an aceton solution of Th(NO$_3$)$_4$ with the presence of water on the silicon surface, local formation of thorium compounds occurs. Chemical analysis of the composition of the samples obtained by XPS showed the presence of compounds based on thorium, silicon, oxygen and carbon. It is shown that annealing for 6 hours at 600°C in the atmosphere leads to the departure of carbon, and the formed film consists only of thorium and oxygen. It is shown that such a system can be promising for further studies of the nuclear low-lying isomer transition in the 229Th isotope under electron beam irradiation. The method of excitation of isomeric thorium-229 nuclei by irradiation of a solid-state target based on thorium silicate with an electron beam is considered. The process of generating secondary electrons with a significant increase in the multiplication coefficient for electrons with energies in the range from 1 keV to 25 keV is considered. The values of the output function of isomeric nuclei and the excitation cross section of an isomeric transition in elastic scattering are obtained on the basis of numerical modeling and theoretical estimation.

1. Introduction
The creation of a new generation of time and frequency standards is currently of great interest. Creating such a standard with relative accuracy at the level of $10^{-19} – 10^{-20}$ will allow you to achieve new achievements in the field of fundamental research, such as checking the effects of General relativity, clarifying fundamental physical constants, and so on. The current time and frequency standards refer to "optical" standards, that is, they are based on the use of strongly forbidden transitions to long-lived electronic States of atoms placed in an optical lattice, or ions trapped in a quadrupole trap. However, there are a number of fundamental physical factors that limit the stability and reproducibility of the transition frequency at the $10^{-18}$ level. At the same time, the use of nuclear transitions, shielded from the surrounding world by an electronic shell, and, as a result, much less sensitive to external disturbances, would increase the accuracy of the time and frequency standard by several orders of magnitude. These transitions are in the absolute majority in the energy range from Kev to MeV, with the exception of the thorium-229 isotope, in which the energy of the first excited isomeric state is $8.27 \pm 0.17$ eV [1], which makes it available for existing vacuum ultraviolet laser sources. Unfortunately, precision measurement...
of the frequency of this isomeric transition is currently a challenge for the scientific community, which prevents the creation of a new standard of time and frequency based on it [2]. In this paper, we consider the creation of local coatings based on thorium-229 deposited on the surface of silicon oxide. The results of the study of the composition and structure of the obtained targets formed by electrochemical deposition from an acetone solution of thorium nitrate on the surface of SiO$_2$Si(111) are presented. It is shown that such a system can be promising for further studies of the nuclear isomeric transition in the thorium-229 isotope under electron beam irradiation. In particular, the value of the isomeric transition yield function has been obtained qualitatively by numerical modeling and theoretical estimation of the excitation cross section of the isomeric transition in inelastic scattering.

2. Experimental methods

One of the effective methods for radioactive target preparation from low concentration solutions is the method of electrochemical deposition. The key feature of the method is the possibility of the local deposition into an area of several hundreds of square microns. In present study the deposition process was carried out using original electrochemical cell from [3] and a modified technique. The Th layer was deposited onto Si(111) surface covered with thermal oxide SiO$_2$ of 0.1–0.6 µm width. A 50–3000 µm in diameter window can be made in SiO$_2$ by lithographic methods in order to obtain local spot of Th-229 in deposition process. During deposition process the electrochemical cell was filled with low concentration solution of thorium nitrate (preliminary purified acetone thinner was used). Series of experiments with a variety of SiO$_2$ layer widths, solution parameters, deposition spot diameters, deposition times, potentials between anode and cathode were carried out followed with analysis of surface morphology and chemical composition by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and alpha-spectrometry. The first obtained targets showed rather poor quality of chemical composition. The alpha spectrometry analysis revealed that lines of the entire decay chain are recorded, with the exclusion of gamma lines, with the following partial activities: $^{212}$Bi–1.756%, $^{212}$Po–3.29%5, $^{213}$Po–13.515%, $^{216}$Po–6.045%, $^{217}$At–14.886%, $^{220}$Rn–6.391%, $^{221}$Fr–13.906%, $^{224}$Ra–5.829%, $^{225}$Ac–13.971%, $^{228}$Th–5.638%, $^{229}$Th–13.521%. The alpha spectrum of the target formed from this material is shown in Fig. 1 (left). After a cascade of washings of thorium-229 solution in nitric acid in sorption columns with ion exchange resins a clean solution with Th-228 and Th-229 isotopes was obtained (see alpha spectrum in Fig. 1 (right).

![Figure 1. The alpha spectrum of the target formed from thorium-229 solution before (left) and after (right) a cascade of washings in sorption columns with ion exchange resins.](image-url)
The best result was obtained with 600 V potential difference between anode and cathode, 100 µg Th nitrate dissolved in 12 ml acetone, 200 µm window diameter and 30 min deposition time. XPS analysis showed the presence of carbon in the targets obtained so it was decided to carry out a high-temperature annealing at 600 °C for 6 hours at atmosphere in order to break carbon compounds. The followed XPS analysis showed the absence of carbon peaks. Also the Th4f/2 and O1s peak positions show that all thorium became oxidized. The additional annealing at 1350 °C for 30 h at atmosphere led to the solid-phase chemical reaction SiO2+ThO2=ThSiO4 that was proved by XPS measurements showed that the line shifts corresponding ThO2 is absent. Also the silicon lines on the spectra increase significantly. The Th/Si ratio calculated from the intensity of the Si(2p) and Th(4f/2) lines becomes close to one. It can be assumed that the entire ThO2 transformed to ThSiO4. Theoretically, the calculation in [4] predict a value of up to 7.8 eV for the thorium silicate phase but the studies of electronic structure made by EELS method estimates the bandgap value about 6.5 eV. From the mutual arrangement of zones for ThSiO4 target observed XPS measurements, it can be concluded that in order to transfer electrons from the top of the valence band to the bottom of the substrate (SiO2) conduction band, it is necessary to overcome a barrier of 8.6 eV. However, if the electron energy is insufficient to overcome such a barrier, but its value is in the range from 6.5 eV to 8.6 eV, such electrons will not be able to get into the conduction band of the substrate and will be effectively localized in the conduction band of ThSiO4. In relation to the problem of measuring the energy of a nuclear isomeric transition in 229Th nuclei during relaxation of excited thorium nuclei in the case of electron conversion, this circumstance can lead to the fact that the electrons will have a kinetic energy in the range from 7.3 eV to 8.3 eV. This range is covered by a potential barrier of 8.6 eV. Thus, in the case of an isomeric state decay through an electron conversion channel, an electron entering the conduction band of ThSiO4 formed on the SiO2 surface remains localized within it and forms an electron-hole pair. This circumstance will lead to an increase in fluorescence at the wavelength corresponding to the width of the ThSiO4 band gap, due to the annihilation of electron-hole pairs. Therefore, it can be assumed that the use of the ThSiO4/SiO2 system as a thorium-containing medium when registering a unique low-lying nuclear isomer transition in the 229Th isotope will increase the lifetime of the excited state and increase the probability of its relaxation through fluorescence.

The typical SEM-image and X-ray emission spectrum for the obtained thorium-229 targets by local electrochemical deposition are presented in Fig. 2. Also Fig. 3 shows profile Auger-spectrum taken from the line at the same sample feature.

3. Computer modeling and discussion

In current study the estimation of the number of excited isomeric Th-229 nuclei produced during electron beam irradiation of the obtained target was calculated. During the target irradiation with external high energy electron beam \(E_0 \sim 10 \div 20\) keV, a huge number of secondary electrons are excited in the target as a result of multiple inelastic scattering of the primary electron beam. These secondary electrons could cause Th-229 nucleus excitation as well. The total number of excited nuclei per time unit \(N_{is}\) can be estimated using the following expression:

\[ N_{is} = \sigma_{is} \lambda n N_{se} I_0 e \]

where \(\lambda \approx 10\text{–}6\) cm is mean free path (MFP), \(\sigma\) is thorium nuclei excitation cross-section, \(I_0 = 2 \mu A\) is a electron beam current, \(e\) is an absolute electron charge value, \(n \sim 10^{22} \div 10^{23}\) at./cm\(^3\) is atomic density, \(N_{se}\) is the number of secondary electrons born during the process. In order to calculate \(N_{se}\) a computer modeling was carried out using Java Monte Carlo Simulation of Secondary Electrons (JMONSEL) program [5] that provides calculation of secondary electron ensemble characteristics for known energy loss function. The last was obtained using electron
energy loss spectroscopy method for the target material. The calculations were made for different electron initial energy in the (1.0-25.0) keV. The results obtained shows the grows of the secondary electron number with the primary initial energy. The overall number of secondary electrons with energy suitable for possible thorium nuclei excitation (> 9 eV) is $N_{se} \sim 10^3$.

Let’s obtain the thorium nuclei excitation cross-section in electron collision process. As soon as the energy difference between ground and excited state of thorium-229 nuclei is 8.27 ± 0.17 eV [1] then the incident electron energy should be more than that value. The nuclear transition is magnetodipolar and is induced by the interaction of the magnetic moment of the core with the magnetic by the field of a scattering electron. Neglecting for simplicity the contribution from electron own the magnetic moment and using the standard expression of the first-order perturbation theory for the probability of transition per unit of time between the initial and final state of the system for fast electrons (expressed as plane waves in Born approximation) a matrix element of the electron-nuclei interaction operator for initial and final electron states can be found. Taking into account high electron energies ($E_0 \gg 8.27$ eV), an estimation of full cross-section for inelastic scattering can be found:

$$\sigma \simeq 1.3 \cdot 10^{-32} \text{ cm}^2.$$  

This value corresponds to the estimation obtained in [6]. Thus, for excited thorium-229 nuclei number per time unit one can obtain $N_{is} \sim 10^9 - 10^4$ s$^{-1}$. That means up to $10^4$ isomeric nuclei decays per second for initial electron energy in electron beam 10 keV and electron beam current 1 µA. Increasing the electron beam characteristics one can obtain higher value of $N_{is}$, thus excitation of Th-229 isomeric nuclei by an electron beam can be very promising from the point of view of experimental implementation.

In the current study the results of the study of local formation and chemical analysis of thin-film coatings based on thorium oxide on SiO$_2$/Si(111) surfaces by electrochemical deposition is presented. It is discussed that such a system can be promising for further studies of the nuclear low-lying isomer transition in the 229Th isotope under electron beam irradiation. The process of generating secondary electrons with a significant increase in the multiplication coefficient for electrons with energies in the range from 1 keV to 25 keV is considered. The values of the output...
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References
[1] Seiferle B, von der Wense L, Bilous P V, Amersdorffer I, Lemell C, Libisch F, Stellmer S, Schumann T, Düllmann C E, Pálffy A and Thirolf P G 2019 Nature 573 243–246
[2] Borisyuk P V, Kolachevsky N N, Taichenachev A V, Tkalya EV, Tolstikhina I Y and Yudin V I, 2019 Phys. Rev. C. 100 044306
[3] Parker W, Bildstein H and Getoff N 1964 Nuclear Instruments and Methods 26 55–60
[4] Shein I R, Shein K I and Ivanovskii A L 2006 Physics and Chemistry of Minerals 33 545–552
[5] Vladár A, Villarrubia J, Chawla J, Ming B, Kline R, List S and Sunday D 2015 Ultramicroscopy 154 15–28
[6] Tkalya E V, Akhrameev E V, Arutyunayn R V, Bol’shov L A and Kondratenko P S 2012 Phys. Rev. C. 85 044612