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Porous Germanium Anode Material for Lithium-Ion Batteries

S.M. Khantimerov, R.R. Fatykhov, V.V. Bazarov, N.M. Lyadov, N.M. Suleimanov

Abstract: ***This work is devoted to the development of porous germanium anode material for lithium-ion batteries. Samples of porous germanium were fabricated by ion implantation of Co^+ ions in single-crystal germanium plates. The surface morphology of porous germanium samples with an increase in the implantation dose of Co^+ ions was studied. Scanning electron microscopy study revealed that the implantation leaded to the formation of porosity of the surface and the surface morphology differed for different doses of implantation. It is assumed that the obtained Ge material with a porous surface can be used as effective anode material in lithium-ion batteries and will show an increased capacity and charge / discharge rate relative to traditionally used graphite.***

Keywords: anode material, electrode, ion implantation, Li-ion accumulator, porous germanium

I. INTRODUCTION

Nowadays intensive research in the world is given to electrochemical storage and energy conversion, in particular to Li-ion accumulators (LIA). This is due to the fact that LIA (in comparison with lead-acid storage batteries, etc.) have a higher specific energy density, operating voltage and relatively low weight, which allowed them to be widely used as an energy source in modern electronic devices [1]. In addition, LIA are considered as promising autonomous sources of energy for electric vehicles, power satellites [2].

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***** Correspondence Author
Khantimerov Sergey Mansurovich*, Zavoisky Physical-Technical Institute (ZPhTI) - Subdivision of the «Federal Research Center «Kazan Scientific Center of the Russian Academy of Sciences», Kazan, 420029, Russian Federation. Email: khantim@mail.ru
Fatykhov Ranis Radikovich, Zavoisky Physical-Technical Institute (ZPhTI) - Subdivision of the «Federal Research Center «Kazan Scientific Center of the Russian Academy of Sciences», Kazan, 420029, Russian Federation. Email: nice.fatyhov@mail.ru
Bazarov Valery Vyacheslavovich, Zavoisky Physical-Technical Institute (ZPhTI) - Subdivision of the «Federal Research Center «Kazan Scientific Center of the Russian Academy of Sciences», Kazan, 420029, Russian Federation. Email: bazarov@kfti.knc.ru
Lyadov Nikolay Mikhailovich, Zavoisky Physical-Technical Institute (ZPhTI) - Subdivision of the «Federal Research Center «Kazan Scientific Center of the Russian Academy of Sciences», Kazan, 420029, Russian Federation. Email: nik061287@mail.ru
Suleimanov Nail Muratovich, Zavoisky Physical-Technical Institute (ZPhTI) - Subdivision of the «Federal Research Center «Kazan Scientific Center of the Russian Academy of Sciences», Kazan, 420029, Russian Federation. Email: nail.suleimanov@mail.ru

Despite the high characteristics of LIBs, the rapid development of technologies imposes higher requirements on the development of an efficient design of electrode systems and methods for the rapid recharging of such energy sources in order to increase their specific energy characteristics, lifetime, charge/discharge cyclicity and reduce the destruction of electrode materials.

As is known, LIA consist of a cathode and anode, which Traditionally, LIA consist of a cathode and anode, which are separated by an electrolyte, but their boundaries are transparent to lithium ions. The principle of LIA operation is based on periodic intercalation and deintercalation of lithium ions into the materials of the anode and cathode (see Fig. 1).

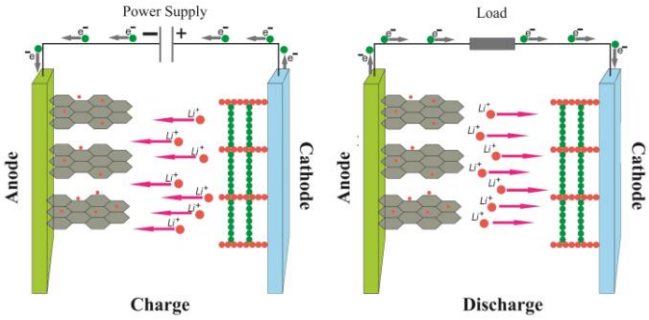

Fig. 1. The principle of LIA operation: charge and discharge

As the cathode, lithium oxides of transition elements, in particular $LiCoO_2$, are used. A lot of investigations are dedicated to studying the properties of this cathode material in order to improve its specific characteristics [3, 4]. However, much efforts has also been devoted to anode research. LIA use graphite as a commercial anode material, which has a theoretical capacity (372 mA·h/g) and a specific surface area (90 m^2/g), which is insufficient to obtain batteries with high capacitive characteristics [5]. Recently, elements of group IV, such as Si, Ge, are being studied as potential substitutes for graphite because of their higher capacitive characteristics. It is known that Si has a high theoretical capacity corresponding to the composition of $Li_{15}Si_4$ and equals to 3579 mA·h/g, which is about 10 times higher than that of graphite [6]. However, a significant drawback of these materials is that silicon lattices expand by 300% from the initial size during the introduction of lithium ions. This leads to the destruction of the electrode, to the weakening of contact with the current collector. For example, in the work [7] E.V. Astrova et al. studied the morphology of silicon anodes of lithium-ion batteries subjected to cyclic tests at different durations.

It was found that the observed degradation of the discharge capacity of electrodes based on macroporous silicon was due to the mechanical destruction of silicon walls and the formation of the amorphous Si-Li phase, which occured already at the initial stage of testing.

As a result of electrode degradation, the capacity and battery life were significantly reduced.

Compared to graphite, Ge has a high gravimetric capacity (1384 mA·h/g for $Li_{15}Si_4$) [8, 9]. Despite the high theoretical capacity of silicon, germanium has several advantages:

1) A high electronic conductivity, since the band gap for Ge (E_g = 0.66 eV) is less than that of the Si (E_g = 1.12 eV);

2) A high diffusion coefficient of lithium ions: for Ge this value is approximately two orders of magnitude higher than that of Si at room temperature [10, 11].

Thus, the use of germanium as an anode material can significantly increase the recharging speed of the battery. It should be noted that during the intercalation of lithium ions into crystalline germanium, electrode destruction can also occur. This problem can be solved, for example, by forming germanium with a porous structure.

This work is devoted to the development and study of a new anode material based on porous germanium.

II. MATERIALS AND METHODS

Samples based on porous germanium were obtained using the technique described in our previous works [12, 13]. The implantation was carried out on an IBI-3 ion accelerator designed to produce monoisotopic beams of singly charged ions of various elements with energies up to 100 keV under high vacuum conditions with an ion current of several μA / cm^2.

During ion implantation, single-crystal plates (c-Ge) with a size of 1.5 x 1.5 cm and a thickness of 500 μm were implanted with Co^+ ions with energy of 40 keV and, as a result, the surface layer of the plate acquires a porous structure.

In our case, we obtained Ge samples implanted with Co^+ ions with the dose D = $2.4 \cdot 10^{16}$ ion/cm^2 and D = $6 \cdot 10^{16}$ ion/cm^2 with an energy of 40 keV and a current density in the ion beam of 1-2 μA/cm^2.

To study the surface morphology of the samples, high-resolution scanning electron microscopy (SEM) Carl Zeiss EVO 50XVP was used. The study of the samples was carried out at room temperature.

III. RESULTS AND DISCUSSION

SEM images of the Ge plate of the initial and implanted with Co^+ ions with a dose of $2.4 \cdot 10^{16}$ ion/cm^2 and $6 \cdot 10^{16}$ ion/cm^2 are shown on Figures 2a, 2b, and 2c, respectively. Based on the data obtained, it can be assumed that implantation of Co^+ ions leaded to formation of pores in the surface layers of Ge plate.

Moreover, depending on the dose of implantation, the size and shape of the pores could vary. It is assumed that the porous structure of the obtained samples will allow lithium ions intercalate unimpeded into the sample and increase the charge/discharge rate.

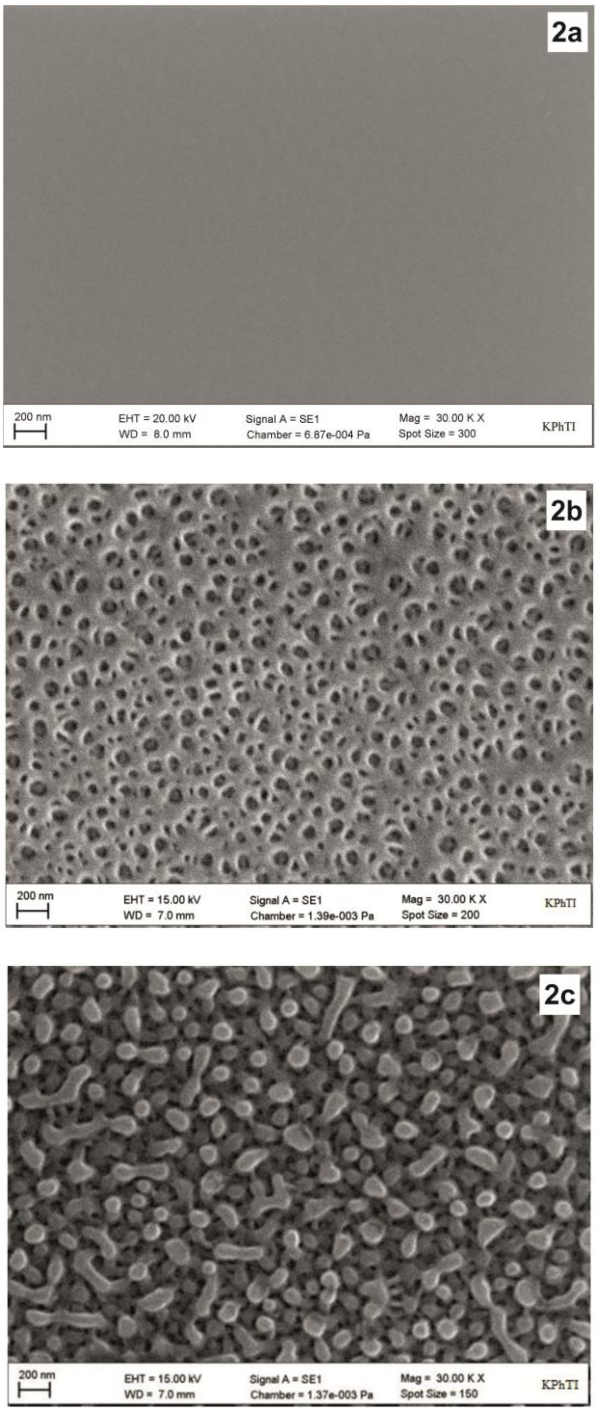

Fig. 2 Electron microscopic images of a fragment of the Ge surface: initial (2a), implanted with cobalt ions at a dose of $2.4 \cdot 10^{16}$ ion/cm^2 (2b), implanted with cobalt ions at a dose of $6 \cdot 10^{16}$ ion/cm^2 (2c).

IV. CONCLUSION AND FUTURE SCOPE

In this work, the porous germanium was prepared by ion implantation of Co^+ ions into single-crystal germanium plates. The surface layer of the initial and implanted at different dose of Co^+ ions samples was studied by scanning electron microscopy. It was found that as a result of irradiation with Co^+ ions, a significant change in the surface and the formation of pores occurs.

It is assumed that the porosity of the germanium surface will allow to avoid electrode destruction the intercalation of lithium ions into germanium. Besides, such structure may result in lithium ions to be adsorbed both on the surface and in the pores, therefore, increasing the capacity and charge / discharge rate relative to traditionally used graphite. In subsequent experiments, investigations of the charge-discharge characteristics of such material will be performed.

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AUTHORS PROFILE

Khantimerov Sergey Mansurovich, corresponding author, is presently working as Senior Fellow in Laboratory of the Physics of Carbon Nanostructures and Composite Systems of the Department of Chemical Physics in Zavoisky Physical-Technical Institute FRC Kazan Scientific Center of RAS located in Kazan, Russia. He obtained his Candidate of Physico-Mathematical Sciences degree in Zavoisky Physical-Technical Institute FRC Kazan Scientific Center of RAS in 2015 year. The results of his work were published in 42 peer-reviewed journals and proceedings. He is a leader of 2 projects connected with the development of nanostructured composite materials. His areas of research include nanomaterials, Li-ion batteries, fuel cells, carbon nanotubes, composite material, electrophysics, chemical physics.

Fatykhov Ranis Radikovich is presently working as Junior Research Fellow in Laboratory of the Physics of Carbon Nanostructures and Composite Systems of the Department of Chemical Physics in Zavoisky Physical-Technical Institute FRC Kazan Scientific Center of RAS located in Kazan, Russia. He obtained his Bachelor's Degree in Kazan State Power Engineering University in 2014 year. He obtained his Master's Degree in Kazan State Power Engineering University in 2016 year. His areas of research include Li-ion batteries, cathode and anode materials for Li-ion batteries, carbon nanotubes, nanomaterials. He is a member and a leader of research projects in the field of Li-ion batteries and carbon nanotubes.

Bazarov Valery Vyacheslavovich is presently working as Senior Fellow in Laboratory of Radiation Physics of the Department of radiation exposure to materials in Zavoisky Physical-Technical Institute FRC Kazan Scientific Center of RAS located in Kazan, Russia. He obtained his Candidate of Physico-Mathematical Sciences degree in Kazan State Power Engineering University in 2003 year. His areas of research include ion implantation, high temperature superconductivity. He published 72 works in peer-reviewed journals and proceedings. He is a member and a leader of research projects in the field of Li-ion batteries, high temperature superconductivity and ion implantation.

Lyadov Nikolay Mikhailovich is presently working as Research Fellow in Laboratory of Radiation Physics of the Department of radiation exposure to materials in Zavoisky Physical-Technical Institute FRC Kazan Scientific Center of RAS located in Kazan, Russia. His areas of research include ion implantation, optics, nonlinear optics, magnetism, ion-stimulated deposition. He published 80 works in peer-reviewed journals and proceedings. He is a member of research projects in the field of Li-ion batteries, carbon nanotubes and ion implantation.

Suleimanov Nail Muratovich Muratovich is presently working as Leading Researcher and is a Head of the Laboratory of the Physics of Carbon Nanostructures and Composite Systems of the Department of Chemical Physics in Zavoisky Physical-Technical Institute FRC Kazan Scientific Center of RAS located in Kazan, Russia. He obtained his Doctor of Physico-Mathematical Sciences degree in Zavoisky Physical-Technical Institute FRC Kazan Scientific Center of RAS in 1997 year. He published 57 works in peer-reviewed journals. His areas of research include Li-ion batteries, fuel cells, hydrogen storage, supercapacitors, carbon nanotubes, nanomaterials, magnetic phenomena, metals, nanoparticles, electrophysics, superconductivity, electrochemical energy sources. He is a leader and a member of research projects in the field of Li-ion batteries and magnetic materials.