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Development of the anode for a lithium-ion battery based on nanoporous germanium formed by the implantation with silver ions

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In this work, the possibility of using a nanoporous Ge layer (p-Ge), formed by implantation with Ag^+ ions on a single crystal c-Ge substrate, as an anode electrode for a lithium-ion battery was studied. For this, the ion implantation of c-Ge substrutes was carried out at an energy of $E = 30\,\text{keV}$, a current density of $J = 5\,\mu\text{A/cm}^2$, and a dose of $D = 1.3 \cdot 10^{16}\,\text{ion/cm}^2$. It was shown that the obtained spongy Ag:p-Ge layers, consisting of intertwining Ge nanowires, demonstrate a high Coulomb efficiency ($> 97\%$) after the first cycle and show up to 79.5% of reversible capacity after 1000 cycles.

Keywords: nanoporous germanium, ion implantation, anod, lithium-ion battery.

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In recent years, significant practical efforts were focused on the search of new materials for anodes of lithium-ion batteries (LIB). As shown in the overview [1], the role of working anode in LIB is played by graphite. However, the limited energy capacity of graphite in relation to accumulation of Li^+ ions in its volume dictates the need for the use of new more effective materials. Theoretical evaluations show that considerably higher capacities (as compared to graphite) may be inherent to other substances composed of group IV elements, such as Si, Ge, Sn etc. Among these materials the most attractive is Si that possesses the highest capacity ($> 4000\,\text{mA}\cdot\text{h/g}$) when the $Li_{15}Si_4$ silicide is formed in the process of intercalation of Li^+ ions into Si [2]. Ge is not less promising for the use as LIB anodes, demonstrating higher coefficient of diffusion of Li^+ ions when forming Li_xGe_{1-x} germanides, as compared with Si [3]. In addition, the intrinsic high electron conductivity of Ge allows significant increase in speed of battery charging/discharging with keeping sufficiently high capacity. However, when using substances composed of group IV elements as LIB anodes, there are arising problems which are related to mechanical destruction of the electrode under its cyclic lithiation/delithiation. One of methods to resolve this problem is the use of nanoporous materials, which make it possible to reduce the mechanical stresses. In this context certain achievements are obtained on layers of nanoporous Ge (p-Ge) [4].

To produce LIB anodes from p-Ge, various chemical technologies are used, such as electrochemical deposition from solutions [5], chemical deposition from vapor phase on glass opal structures [6], reduction of GeO_2 by gaseous H_2 [7], etc. A certain interest is presented by the physical method to create layers of p-Ge for the LIB anode by implantation of c-Ge substrates with Ge^+ ions, as a result of which the layers of p-Ge are formed in the form of honeycomb [8]. Earlier in [9] the possibility to form spongy implanted layers of p-Ge composed of Ge nanowires was demonstrated at high-dose low-energy implantation of c-Ge/Ag:p-Ge substrates with Ag^+ ions. In literature, it is shown the possibility to use Ag^+ ions to improve performance of LIB anode materials, in particular, the Si/Ag composite material [10] or $Li_4Ti_5O_{12}$ nanocrystal material coated with Ag nanoparticles Ag [11]. This work is focused on the investigation of the possibility to use spongy layers of Ag:p-Ge to produce LIB anodes. The choice of Ag^+ ions is due to the increase in conductivity of p-Ge layers with nanoparticles of Ag in their structure as compared with the conductivity of pure p-Ge, which is demonstrated in literature [12].

The smooth polished plates of c-Ge with a thickness of $150\,\mu\text{m}$ with crystal-lattice orientation (111) were used as substrates for the ion implantation. The implantation was carried out by ions of Ag^+ with $E = 30\,\text{keV}$, $D = 1.3 \cdot 10^{16}\,\text{ion/cm}^2$ at $J = 5\,\mu\text{A/cm}^2$ on an ILU-3 ion accelerator at a normal angle of incidence of the ion beam on the c-Ge surface. $AgNO_3$ salt was loaded into the chamber of the accelerator source as a working substance to produce Ag^+ ions. A Merlin (Carl Zeiss) scanning electron microscope (SEM) was used with an accelerating voltage of 5 keV and a current density of 300 pA to observe the morphology of sample surface. Fig. 1 shows SEM-image of Ag:p-Ge sample, from which it follows that the implanted surface is a spongy structured layer composed of intertwined Ge nanowires with an average diameter of $\sim 15\,\text{nm}$.

Profiles of impurity distribution in ion implantated samples were evaluated by means of simulation by SRIM-2011 software. The obtained results show that implanted Ag^+

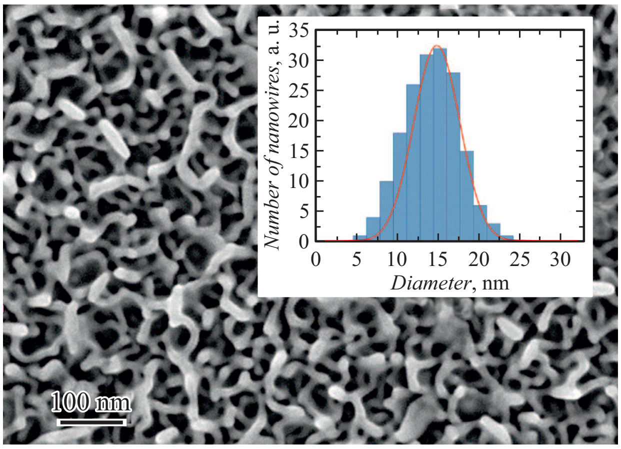

Figure 1. SEM-image of the c-Ge surface implanted with Ag^+ ions at $E = 30\,keV$, $J = 5\,\mu A/cm^2$ and $D = 1.3 \cdot 10^{16}\,ion/cm^2$. The histogram of Ge nanofilaments distribution by diameters is shown in the insert.

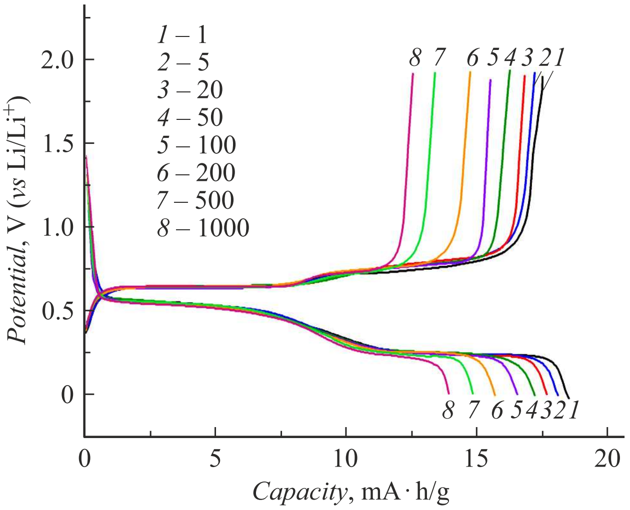

Figure 2. Charging-discharging curves of the LIB anode based on Ag:p-Ge for different numbers of cycles.

ions are distributed in Ge in accordance with Gaussian curve with maximum at a depth of $\sim 14.6\,nm$ and the straggle of $\sim 6.9\,nm$, therefore thickness of the doped layer is about 28.4 nm according to the evaluation.

The electrochemical study of Ag:p-Ge as LIB anode were carried out by the galvanostatic method using a three-electrode electrochemical cell at room temperature. A Ag:p-Ge sample was used as a working electrode, while plates of metal Li were used as a counter electrode and a reference electrode. Size of the working electrode was $0.2 \times 1\,cm$, its thickness was $500\,\mu m$. The solution of $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DEC) ($1.0\,M$ $LiPF_6$ in EC/DEC = 50/50 (vol/vol)) was used the as an electrolyte. Voltage profiles and cycle characteristics were investigated in a voltage range of $0.01-2\,V$ in relation to Li/Li^+ at a charging/discharging rate of 0.2 C. Fig. 2 shows galvanostatic curves of charging/discharging process for the Ag:p-Ge sample that reflect the process of incorporation and extraction of lithium in p-Ge at direct current. In the case of the cathode polarization the potential shifts in the negative direction and incorporation of Li is started. The anode part of the curve demonstrates the process of Li extraction from p-Ge.

As can be seen from Fig. 2, the sample demonstrates the high Coulomb efficiency (over 97%) after the first cycle and keeps 79.5% of its capacity after 1000 cycles. It should be noted that the real capacity of the electrode in is considerably higher, if we take into account that only the thin implanted layer is involved in the lithiation/delithiation processe, which requires further investigation.

It is known from literature, that there are several methods to reduce the degree of mechanical destruction of LIB anodes and improve the cyclicity in the process of charging/discharging [13]. In addition to the use of various nanostructured materials to produce anodes (for example, nanoparticles, nanotubes, nanopores, etc.), it turns to be relevant to use of amorphous phases instead of crystalline structures. Efficiency of the use of the produced by electrodeposition in solution amorphous p-Ge to increase the number of electrode working cycles was demonstrated in the work [14]. The investigated in this work spongy layers of p-Ge were formed by the implantation with Ag^+ ions and composed of amorphous nanowires as well [9] in contrast to the majority the synthesized by chemical and electrochemical methods Ge samples consisted of nanowires with a crystalline structure [15]. Therefore, one can suggest that the low degradation of the investigated electrode in the charging/discharging process up to 1000 cycles is related to the formation of the amorphous layers of Ag:p-Ge in the process of ion implantation. On the other hand, it is known from literature that the longer mechanical stability and cyclic operability of the chemically produced p-Ge are observed in Ag-containing samples (as compared with pure p-Ge) because Ag prevents agglomeration and adhesion of nanowires of the Ge active material when it expands in the process of lithiation [1]. Thus, the low degradation of the investigated in this work sample can be related to the presence of Ag^+ ions as well.

Thus, in this work we have shown the principle possibility of producing LIB anodes based on spongy layers of Ag:p-Ge composed of Ge nanowires formed on a c-Ge substrate implanted with Ag^+ ions. The electrochemical investigations of lithiation/delithiation processes demonstrate the efficiency of the obtained electrode without significant mechanical destructions through 1000 cycles of charging/discharging.

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Conflict of interest

The authors declare that they have no conflict of interest.

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