Analysis of nanostructured cobalt ion beam-modified Ge surface for high capacity Li-ion battery anodes by X-ray photoelectron spectroscopy

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Abstract. The results of the study of nanostructured germanium (Ge), intended for its subsequent use as electrodes of lithium-ion batteries are presented. Single-crystal germanium plate was irradiated by cobalt ions with an energy of 40 keV in the dose $4 \times 10^{16}$ Co$^+$/cm$^2$ for the nanostructuring. The changes in the elemental composition occurring during the electrochemical lithiation of manufactured germanium electrode were investigated by X-ray photoelectron spectroscopy (XPS).

1. Introduction
It is well known that the high-dose ion-implantation doping of Ge leads to the formation of a porous surface layer that is several times thicker than the implanted ion range [1-4]. In recent years, the possibility of creating a nanoporous structure on the Ge surface has stimulated a trend toward using this material in new applications such as anode material in lithium ion batteries [5]. A porous layer appears upon the bombardment of germanium by a broad spectrum of heavy ions with energies in the range from a few to several hundred keV with a threshold implantation dose of $10^{16}$ ion/cm$^2$ [2].

Here we present the investigations of single crystal germanium plates nanostructured by the irradiation of Co ions and subjected to the electrochemical lithiation using XPS method.

2. Materials and methods
The investigation was performed on (111)-oriented c-Ge plates (GDG-45 grade) implanted with 40-keV Co$^+$ ions in the dose of $4 \times 10^{16}$ ion/cm$^2$ at an ion beam current density of $\sim 4$ μA/cm$^2$ (Fig. 1).
Figure 1. SEM - image of the surface of a Ge plate implanted with cobalt ions, dose $= 4 \times 10^{16}$ Co$^+$ /cm$^2$. Images obtained at an angle of 70°

The experiments on lithiation / delithiation of implanted germanium with a nanostructured surface layer were performed using a CR2032 electrochemical cell on a 5-channel potentiostat/galvanostat BIOLOGIC VSP. This cell consisted of two electrodes: a lithium metal plate separated by a special separator from another electrode — a Ge plate modified by ion irradiation. The test cell was lithiated up to a charge of 16 mAh. It was observed that the surface of the germanium crystal was coated with an electrolyte salt after lithiation. Therefore, part of the surface was wiped with a lint-free paper napkin moistened with distilled water. After that the elemental composition of lithiated and lithiated/wiped Ge plate surface was investigated using XPS. In order to determine the possible effect of cleaning on modified layer, the lithiated and cleansed samples were separately analyzed.

XPS measurements were carried out in a high-vacuum setup SPECS (Germany) equipped with an Al Kα X-ray source and a Phoibos 150 hemispherical electron energy analyzer. The size of the analyzed region was $\sim 2 \times 4$ mm$^2$. The samples were attached to carbon tape, so lines both from carbon and oxygen existing in the tape can be observed in the spectrum. Before measurements, both samples were etched in the analytical chamber by an Ar$^+$ ion beam (with an energy of 2 keV) for 2 minutes to remove adsorbed gases [6]. The overview spectrum was recorded with a step of 1 eV and a transmission energy of 100 eV. Detailed spectra were recorded with a step of 0.1 eV and a transmission energy of 20 eV with the accumulation of 20 spectra. The decomposition into components was carried out with the shape of the Gauss-Lorentz line using the Shirley background. The quantitative composition was determined from the lines of Li 1s, O 1s, Ge 3d.

3. Results and discussions
3.1 Analysis of the sample coated with an electrolyte salt
Elemental analysis of the sample coated with an electrolyte salt (Fig. 2-5) showed the presence of lithium, germanium, oxygen, and carbon. Two chemical states of germanium were observed (Fig. 3-4), both in the Ge$^0$ phase and in oxidized to GeO$_2$ (lines 2p3 / 2 1220 eV and 3d 32.5 eV [6]), which are typical for crystals coated with a thin oxide film. The ratio of Ge$^{4+}$ / Ge$^0 = 1.6$. Lithium and oxygen dominate by the amount of element in the surface layer. Perhaps the most (or all) of lithium is located in salt.
Figure 2. Overview XPS spectrum of the surface of a Ge crystal coated with an electrolyte salt.

Figure 3. Detailed XPS spectrum of the surface of a Ge crystal coated with an electrolyte salt in the region of Li 1s. The Ge 3d signal was decomposed into two: one - from the oxide, the second - from a pure element.
Figure 4. Detailed XPS spectrum of the surface of a Ge crystal coated with an electrolyte salt in the Ge 2p region.

Figure 5. Detailed XPS spectrum of the surface of a Ge crystal coated with an electrolyte salt in the region of O 1s.
3.2 Analysis of the wiped sample

The XPS spectra of lithiated/wiped Ge plate surface are presented on Figs. 6-9. As one can see, the signal from lithium is not detected after purification (Table 1, Fig. 6). The ratio Ge$^{4+}$ / Ge$^0 = 0.73$ is reduced compared to the initial sample (Fig. 7–8), which indicates that part of the oxide was mechanically removed from the salt during wiping. At the same time, a significant part of oxide remains in the sample. This cannot be a newly formed oxide, since immediately after cleaning the sample was loaded into the airlock for pumping. During this time, a substantial oxide layer should not form (by analogy with the cleaning of silicon oxide from the surface). Therefore, we can assume that a sufficiently large surface of the Ge crystal remained intact as a result of cleaning (Fig. 6).

Figure 6. Overview XPS spectrum of the surface of a Ge crystal wiped from an electrolyte salt.
Figure 7. Detailed XPS spectrum of the surface of a Ge crystal wiped from an electrolyte salt in the region of Li 1s. The Ge 3d signal was decomposed into two: one from oxide, the second from a pure element.

Figure 8. Detailed XPS spectrum of the surface of a Ge crystal wiped from an electrolyte salt in the Ge 2p region.
Figure 9. Detailed XPS spectrum of the surface of a Ge crystal wiped from an electrolyte salt in the region of O 1s.

4. Conclusions
Ion beam-modified Ge plate subjected to lithiation were investigated using XPS. Elemental analysis of the lithiated and lithiated/wiped samples was established (Table 1). It was found that purification leaded to the disappearance of the signal from lithium. Considering that implantation leaded to the formation of caverns with depths of about 150 nm, it can be assumed that after lithiation a significant amount of lithium is located at a depth exceeding the probing depth of the XPS (3 nm) and cannot be determined.

| Table 1. The composition of the analyzed surface in at. % (analysis depth ~ 3 nm). |
|---------------------------------------------------------------|
| Ge<sup>0</sup> | Ge<sup>4+</sup> | O | Li |
|-----------------|----------------|---|----|
| with salt       | 2.4            | 3.9 | 47.7 | 46 |
| wiped           | 23.8           | 17.3 | 58.9 | below the sensitivity limit |

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