Study of the electrophysical properties of nanostructured porous germanium as a promising material for electrodes of electrochemical capacitors

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Abstract. Electrochemical capacitors (ECC) are a fast charging devices, with high power density, capacity and increased life time. Nanostructured semiconductors are now considered as the promising materials for electrodes of such devices due to its conductive properties and effective surface. One of such materials is the porous germanium which can be used as an electrode in electrochemical capacitors. In this article the novel approach based on the method of ion implantation was developed to grow these structures. This method allows to obtain structures up to 1 μm thick. The object of this work was the investigation of the electrophysical characteristics of samples of nanostructured porous germanium (Ge) depending on the implantation dose and surface morphology. The scientific novelty of this research lies in the search the structures with the highest effective surface area and electronic conductivity, capable of multiplying the energy capacity and specific power of ECC. Methods: The samples of amorphous Ge were grown on dielectric single-crystal substrates of Al2O3. The thickness of samples was 600 and 1000 nm. The magnetron sputtering and ion implantation methods were used to grow these structures. The irradiation with Ge+ ions produced with an energy of 40 keV and the range of implantation doses varied from 2 x 1016 to 12 x 1016 ion / cm2. The study of electrical properties was carried out on the Hall installation HL55PC at the NPP KVANT in Moscow. The following parameters were measured: the sheet concentration of carriers in the near-surface layer, electrical resistance, mobility of the charge carriers, Hall coefficient. As a result, the dependences of carriers concentration and their mobility as the function of the implantation dose and thickness of the samples of nanostructured porous germanium were determined, and the results were analyzed. Results: It was found that ion implantation of single-crystal germanium leads to an increase in the carrier concentration in the near-surface layer. To sum up, the most suitable material as an electrode for ECC is the porous germanium with the maximum dose of ion implantation and the largest thickness. The maximum sheet carrier concentration that was obtained in the study for Ge is 1017 cm2.

1 Introduction

Electrochemical capacitors (supercapacitors) by their properties are located between electrochemical batteries and ordinary electric capacitors [1, 2]. The main requirements for these energy sources are the high specific power, energy capacity, service life (number of charge-discharge cycles).

In hybrid electrochemical capacitors the accumulation of charge is carried out by two processes: accumulation of Faraday charge as a result of redox reactions on one electrode and the appearance of the capacity of the electric double layer (DES) on the other electrode [3]. ECC are the fast-charging devices with high power density. The decisive factor for achieving a high specific energy content are the surface area of the electrodes and availability of active components for the redox reactions. In this regard, highly porous conducting materials are essential for the manufacture of electrodes of ECCs [4]. All of the above requirements and characteristics of ECCs indicate the need to search of new semiconductor and carbon materials with high electrophysical characteristics. Therefore, the research of new promising materials for electrodes of supercapacitors is an urgent task.

The main task of this study is to find the most optimal morphology of the porous germanium structure, with the best electrophysical characteristics as an electrode in ECC: with a high sheet concentration and mobility of charge carriers.

2 Literature Review

The nanostructured semiconductor materials based on germanium (Ge) are considered as the most promising materials for electrodes, along with carbon nanosystems. In this regard, special attention is attracted to approaches based on the development of methods for obtaining...
nanostructured porous germanium, with a large number of voids and pores, providing a high effective surface with high electronic conductivity. The high electronic conductivity of porous germanium is due to the small band gap of Ge ($E_g = 0.66$ eV at 300 K). For comparison, this value for silicon (Si) is 1.12 eV at 300 K.

There are several methods to growing porous layers of germanium: thermal deposition (resistive thermal evaporation, electron beam evaporation, etc.), gas deposition methods, deposition from liquid solutions (electrochemical etching) [6].

In treatise [7] are provided a new design of germanium electrodes containing three-dimensional spherical formations of crystalline nanowires on strong one-dimensional nanostructures. These structures were directly grown on a metal current collector by thermal evaporation of germanium.

It is known that high-dose ion implantation into germanium, as a rule, leads to intensive nanopore formation. Implantation of heavy chemically active elements ($m_{ion} > m_{Ge}$) leads to the formation of an amorphous layer. Implantation [13]. In this case, nanopores on the surface near-surface region of amorphous Ge-films are formed (disordered regions in the lattice). After irradiation, in the primary places, which leads to the appearance of active radiation defects arising from ion implantation [16].

The saturation of the concentration of charge carriers in the structure occurs at certain doses of implanted ions, depending on their mass. It was shown in [17], that when the concentration of electrons in layers saturates with an increase of the ion dose, the mobility of carriers remains constant value at the level $\mu_{n} = (3-5) \cdot 10^{2}$ cm$^2$V$^{-1}$s$^{-1}$ (higher electron mobility for small doses). In [18] was established the opposite fact – with an increasing the dose implantation of B$^+$ ions, the effective electron mobility decreased to the value $\mu_{n} = 1.1 \cdot 10^{5}$ cm$^2$V$^{-1}$s$^{-1}$. In [16] and [18], the electron mobility differs from the almost an order of magnitude. Thus, the clear dependence of the mobility of charge carriers on the implantation dose wasn’t found in many experiments. This dependence is multifactorial and specific for each of the materials.

3 Materials and methods

Six (6) samples with dimensions of 10x10 mm were prepared for the study (fig. 4). A single-crystal germanium substrate GDG-45 with orientation (111) with thickness 500 μm was taken as a zero reference sample, which was not subsequently subjected to ion implantation. This sample is called “reference sample” for subsequent comparison of the results of ion implantation other samples.

The other five (5) samples were grown by magnetron sputtering: the amorphous Ge layers with different thicknesses (600 nm and 1000 nm) were obtained on single-crystal dielectric substrates Al$_2$O$_3$. At the next stage of preparation, these samples were irradiated with Ge$^+$ ions with an energy of 40 keV in the range of implantation doses: $2 \cdot 10^{16} \div 12 \cdot 10^{16}$ ion/cm$^2$. A dielectric substrate was used to exclude an unnecessary contribution to the conductivity of investigated layer during measurements of the study. As already indicated, a single-crystal sapphire plates Al$_2$O$_3$ with orientation (012) were used as a substrates. The substrates were cleaned before growth in several stages: on the first stage the chemical solvents with ultrasound were used, and at the final stage the cleaning in a vacuum chamber by ion etching was provided.

The initial α-Ge films with a thickness of 600 nm and 1000 nm were obtained by magnetron sputtering of a germanium target (99.95% purity, OOO Girmet) in an ultrahigh vacuum setup (SPECS / BESTEC, Germany) at room temperature in an argon atmosphere. The base pressure in the magnetron chamber was no more than $5 \times 10^{-4}$ mbar, the working pressure of argon was $6 \times 10^{-3}$ mbar. The magnetron power during deposition was 50
The germanium deposition rate was 8.33 nm/min and was controlled by a quartz thickness gauge. The thickness of the films was measured with a stylus nanoprofilometer BRUKER Dektak XT [13].

Implantation with Ge⁺ ions was carried out in the dose range (2–12)·10¹⁶ ion/cm² with an energy of E=40 keV and a current density in the ion beam of 4–5 μA /cm² on an ILU-3 ion accelerator at a residual vacuum of 10⁻⁵ Torr.

The structure of the five (5) investigated samples, which were subjected on ion implantation, is shown in Table 1:

| Investigated layer | Number of sample, № | Thickness of porous Ge, nm | Dose of implantation, 10¹⁶ ion/cm² |
|--------------------|----------------------|----------------------------|-----------------------------------|
| Substrate          |                      |                            |                                   |

Substrate Single crystal dielectric substrate (500 μm) Al₂O₃

Each of the samples was measured several times: in 4-5 different positions (after each measurement, the sample was rotated by 90 °). The total result of Hall measurements is given as the average of 4-5 measurements.

4 Results and discussion

In the Table 3 the results of measurements of electrophysical characteristics of the nanostructured porous germanium samples are presented. Since germanium belongs to semiconductors of mixed type of conductivity, the modulus (absolute value) of the layer concentration of the charge carriers and Hall coefficient are given in the resulting table.

According to the data in Table 3 the sheet concentration of the charge carriers in the "reference" sample is tens times less than in the samples that were subjected to ion implantation and on the contrary, the mobility and Hall coefficient are several times higher. Based on the obtained data were plotted the following dependences: sheet concentration and mobility of free charge carriers in the studied layers of porous Ge depending on the implantation dose (Fig. 3 and 4) and the thickness of the samples (Fig. 5).
Analyzing the graphs in Figures 3 and 5, it should be noted that the maximum sheet concentration of charge carriers $(10^{16} \div 10^{17} \text{ cm}^{-2})$ is achieved in sample No. 5 which was grown with the maximum implantation dose $(12\cdot10^{16} \text{ ion / cm}^2)$ and having the maximum thickness (1000 nm). Since amorphous Ge after ion implantation becomes porous with a large number of defects that increase the electron layer conductivity [9]. The thickness of the sample also affects its properties, albeit to a lesser extent, which we can see in Fig.5: with increasing thickness of the samples, the concentration of charge carriers growing too.

Investigating the experimental data of mobility charge carries, according to the graph in Fig. 4, it should be noted: with an increasing the implantation dose, the values of mobility first increased (samples No. 2 and No. 4) from 1.64 to $3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and then decreased to the minimum value $0.16 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (sample No. 5).

The obtained dependences of the sheet concentration of charge carriers in the layers under study is in agreement with the results of [20], in which it was found that the concentration of charge carriers increases with an increase in the implantation dose. At the same time, in [14] and [15], it was found that the layer concentration of electrons $N_s$ does not depend on either the type or the dose of implanted ions. Note that in the cited works, various ions with different masses were used.

Similar to the results of our research, in [13] it was shown that as a result of ion implantation, the irradiated
material gradually becomes porous and the pore size increases with increasing doses. As noted in the literature review, ion implantation with large doses leads to the appearance of a large number of point, linear, and bulk crystal defects ( pores, channels). In addition to pores and vacancies, dislocations, grain boundaries, channels and their associations arise in the material.

Ions of Ge are considered heavy and in accordance with [20], and upon hitting the Ge surface form dislocation defects in porous germanium even at low implantation doses. The increasing the electron concentration in such structures may be connected with appearance of defects, as claimed the authors of [21]. They assumed that the presence of radiation defects leads to n-type conductivity of irradiated materials. Thus, it was concluded that samples with a higher implantation dose have a greater number of radiation defects, which enhance the surface conductivity of the layer.

Undoubtedly, there is a possibility that in this study we did not “catch” the range of implantation doses where concentration of radiation defects saturates, as shown in [22–25]. So, for samples No. 1 and No. 2 with a thickness of 600 nm, the expected change in the layer concentration did not occur when the implantation dose was changed. In this regard, it can be assumed that the saturation of the concentrations of charge carriers for different thicknesses of the samples will occur at different doses of implantation.

Comparing the values of the mobility of charge carriers with other works it can be noted that the value of mobility obtained by measuring our samples is less than that in treatises [16] and [18]. This fact can also be associated with the presence of a large number of defects in the structure, which “absorb” free electrons and holes.

5 Conclusions

1. The measurements of the electrophysical characteristics of porous amorphous Ge (obtained by the method of ion implantation) is carried out: with different doses of Ge⁺ ion implantation and the thickness of the working layer.

2. It was found that ion implantation of single-crystal germanium leads to the amorphization and an increase in the concentration of carriers in the surface layer.

3. The maximum concentration of carriers is observed at the maximum sample thickness (1000 nm) and implantation dose is $1.2 \times 10^{16}$ ion/cm² and consist 1.5-10¹⁷ cm⁻².

4. It has been suggested that at a certain dose of implantation, the surface layer is saturated with charge carriers, but this value may differ for layers of different thicknesses - this requires additional research.

5. It has been established that one of the possible reasons for the increased concentration of carriers and low mobility in the material under study, can be structural defects which was appeared during irradiation materials with Ge⁺ ions.

6. A large effective surface area and the maximum charge carrier concentration is expected for the samples of porous germanium with the maximum dose of ion implantation and the largest thickness as an electrode for ECC.

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