Porous germanium with Ag nanoparticles formed by ion implantation

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Abstract. A novel approach is proposed and tested for the synthesis of thin porous PGe layers with Ag nanoparticles based on low-energy high-dose ion implantation of single-crystal c-Ge. To demonstrate a successes of this technique, an Ag⁺-ion implantation of a polished c-Ge substrates with an energy of 30 keV at various doses of 1.0×10¹⁶-1.5×10¹⁷ ion/cm² and a current density of 5 μA/cm² was performed. Various analytical methods such as scanning electron and probe microscopy, as well as EDX analysis and electron backscattered diffraction were applied for observation of PGe formation of a spongy structure consisting of a network of intersecting Ge nanowires. At the ends of the nanowires, the synthesis of Ag nanoparticles were detected. It was also found that the formation of pores during Ag⁺-ion implantation was accompanied by efficient spattering of the Ge surface.

Introduction

Porous germanium (PGe), which for first time was mentioned in the work [1], is widely used nowadays in optoelectronics and in the field of solar cell elements creation [2] as alongside with porous silicon (PSi). Multiple technologies for the creation of PGe layers were developed, for example the electrochemical treatment of single-crystal c-Ge in highly concentrated electrolytes [3], plasma-stimulated chemical vapor deposition [4], spark discharge method [5], thermal annealing of GeO₂ ceramic films in a hydrogen atmosphere [6] and others.

An effective nonchemical method of fabrication of nanoscale thin PGe layers on the c-Ge surface is a high-dose implantation with various ions in a vacuum. The first direct evidence of the PGe formation by such technological approach was obtained by electron-microscopic observations, while c-Ge was irradiated by Ge⁺-ions at energy of 50 keV [7]. The porous structure was recorded, as shown in the review [8], for as amorphous (a-Ge) as c-Ge substrates by low-energy high-dose (> 1 MeV) implantation with variety of ions. It should also be mentioned some publications [9, 10] in which the Ag⁺-ion implantation at high energies (100 MeV) and low doses in the range of 5.0×10¹² - 2.0×10¹⁴ ion/cm², was used to create PGe layers.

This paper is also devoted to the creation of PGe layers by the ion implantation, but the aim is to synthesize Ag nanoparticles simultaneously with the PGe structure (Ag:PGi). For this purpose, the low-energy (<100 keV) in dose range (1.0×10¹⁶ -1.5×10¹⁷ ion/cm²) Ag⁺-ion implantation of c-Ge was applied. Interest in PGe structures with noble metal nanoparticles showing plasmon resonance properties is due to their possible use in various applications: to increase the absorptivity in solar cells [11], to improve photoconductivity [12], to generate electron-hole pairs [13] and so on.
Experimental

Polished c-Ge substrate with thickness of 0.5 mm was used to obtain a structured surface Ag:PGe layer. For this purpose the implantation of c-Ge was carried out by Ag$^+$ ions with an energy of 30 keV at various irradiation doses of $1.0 \times 10^{16} - 1.5 \times 10^{17}$ ion/cm$^2$ and a current density of 5 μA/cm$^2$ with the ion accelerator ILU-3 at the room temperature of the substrate. Observation of morphology of the sample surface and energy-dispersive X-ray (EDX) spectral microanalysis of implanted Ge was carried out with a self-emission high-resolution scanning electron microscope (SEM) Merlin (Carl Zeiss) and which was equipped with Aztec X-Max spectrometer (Oxford Instruments). Structure of surface sample layer was characterized by electron backscattered diffraction (EBSD) patterns using HKL NordLys detector (Oxford Instruments).

In order to obtain the distribution of Ag nanoparticle we used scanning probe microscope (SPM) Dimension FastScan (Bruker) was used. This microscope is known for quantitative nanomechanical mapping feature which allows to obtain information on mechanical properties of the sample surface, such as adhesion, Young’s modulus etc, alongside with classic atomic force measurements in a single-pass scanning.

Results and discussion

SEM images of the Ge surface implanted with Ag$^+$ ions presented with various scales are shown in Fig. 1 and 2. Unlike the virgin polished c-Ge substrate, the morphology of the irradiated surface is seen as the highly developed open porous spongy structure (Fig. 1). It’s also important to note that similar structure of PGe was formed by implantation of c-Ge, for example, by Bi$^+$-ion with an energy of 30 keV [8], but it differs significantly from the columnar type PGe formed by implantation with a lighter Ge$^+$ ion at low energies [13, 14]. In principal, the possibility of creating pores by implantation with Ge$^+$ self-ions indicates that the formation of pores is happened not due the presence of an impurity, but because of some specific energy conditions during irradiation [18], which could be assumed also for our case Ag:PGi too, although heavy implants such as Ag could stimulate the appearance of a generally spongy structure.

Based on the SEM and SPM microphotographs (fig. 1,2,3), we also assume the following mechanism of distribution of Ag in PGe: small dose of $1.0 \times 10^{16}$ ion/cm$^2$ is characterized with small Ag nanoparticles (bright dots on fig 2a and 3a) but not a very effective spattering of Ge, the increase of the dose leads to better spattering and formation of spongy structure and at the same time the size of Ge nanowires in this structure also increases and starting from the dose range of around $1.0 \times 10^{16}$ ion/cm$^2$ these nanowires are decorated with Ag nanoparticles (fig 2b and 3b). The effect of the rise if the size of the nanowires can be explained in terms of covering initial Ge nanowires with Ag “film”.

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Fig. 1 SEM image of the Ge surface implanted with Ag+ ions

Fig. 2 SEM images of the Ge surface implanted with Ag+ ions a. dose 1.0 \times 10^6 \text{ ion/cm}^2; \text{ b. dose } 1.5 \times 10^7 \text{ ion/cm}^2
Fig. 3 AFM images of the Ge surface implanted with Ag+ ions a. dose 1.0 \times 10^6 \text{ ion/cm}^2; b. dose 1.5 \times 10^7 \text{ ion/cm}^2