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Review Article

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Silver Nanoparticles in Porous Germanium

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Abstract

Recent experiments on fabrication of nanoporous Si and Ge layers with Ag nanoparticles by low-energy high-dose ion implantation are discussed. Ag+-ion implantation of single-crystal c-Si and c-Ge at low-energy (E = 30 keV) high-doses (D = $1.25\cdot10^{15}$ - $1.5\cdot10^{17}$ ion/cm^2) and current density (J = 2-15 μA/cm^2) was carried out for this purpose. The changes of Si and Ge surface morphology after ion implantation were studied by scanning electron and atom-force microscopy. The near surface area of samples was also analyzed by diffraction of the backscattered electrons and energy-dispersive X-ray microanalysis. Amorphization of near-surface layer was observed at the lowest implantation doses of c-Si. Ag nanoparticles were synthesized and uniformly distributed over the near Si surface when the threshold dose of $3.1\cdot10^{15}$ ion/cm^2 exceeded. At a dose of more than 10^{17} ion/cm^2, the formation of a surface nanoporous PSi structure was detected. Ag nanoparticle size distribution function became bimodal and the largest particles were localized along Si-pore walls. In the case of Ge substrates, as a result of the implantation on the c-Ge surface, a porous amorphous PGe layer of a spongy structure was formed consisting of a network of intersecting Ge nanowires with an average diameter of ~ 10-20 nm. At the ends of the nanowires, the synthesis of Ag nanoparticles was observed. It was found that the formation of pores during Ag$^+$-ion implantation was accompanied by efficient spattering of the Si and Ge surface. Thus, ion implantation is suggested to be used for the formation of nanoporous semiconductor thin layers for industry, which could be easily combined with the crystalline matrix for various applications.

Keywords: Porous Germanium, Silver nanoparticles

Introduction

Porous germanium (PGe), discovered experimentally by the first time in 1971 is now widely used in optoelectronics to create solar cell elements as is the case of Si. Several technologies have been developed to create PGe layers, such as electrochemical treatment of single-crystal *c*-Ge in highly concentrated electrolytes plasma-stimulated chemical vapour deposition spark discharge method thermal annealing of GeO$_2$ ceramic films in a hydrogen atmosphere and others [1-6].

A high-dose implantation by various ions in vacuum is a specific effective nonchemical technique for nanoscale fabrication of thin PGe layers on the *c*-Ge surface. The first direct evidence of the PGe formation by such technological approach was obtained by the electron-microscopic observations, while *c*-Ge was irradiated by Ge$^+$-ions at 50 keV [7]. Subsequently, the porous structure was recorded, as shown in the review [8], as amorphous (a-Ge) and as *c*-Ge substrates by low-energy high-dose (> 1 MeV) implantation with variety of ions: Ga$^+$, Ge$^+$, Mn$^+$, Ni$^+$, In$^+$, Sn$^+$, Sb$^+$, I$^+$, Au$^+$ and Bi$^+$. It should be mentioned some publications in which the Ag$^+$-ion implantation at high energies of 100 MeV, but rather small doses in the range of $5.0\cdot10^{12}$ - $2.0\cdot10^{14}$ ion/cm^2, was used to create PGe layers and to produce their crystallization [8,9].

The present paragraph also addresses to the creation of PGe layers by the ion implantation method, but the main goal is to synthesize Ag nanoparticles simultaneously with the PGe structure (Ag:PGi). For this purpose, the low-energy (<100 keV) high-dose (> $1.0\cdot10^{17}$ ion/cm^2) Ag$^+$ -ion implantation of *c*-Ge was applied, similar to the fabrication of porous Si layers with Ag nanoparticles by ion irradiation of c-Si. The special interest in porous semiconductor structures with noble metal nanoparticles showing Plasmon resonance properties was drawn due to their multiple prospective uses: to increase the absorptivity in solar cells, to improve photoconductivity, to generate electron-hole pairs, etc.

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 and irradiation dose of $1.5\cdot10^{17}$ ion/cm^2 , current density of 5 μA/cm^2 with the ion accelerator ILU-3 at room temperature.

Due to the peculiarities of ion implantation, the distribution of implanted ions in the irradiated material is not homogeneous along the sample depth. Therefore, using the computer program SRIM-2013 for modelling the implanted ions profile and generated vacancies in depth of irradiated matrices, the corresponding distributions for the case of Ag^+-ion implantation with an energy of 30 keV into Ge were calculated (Figure 1a)). It is found that in the initial period of irradiation in the near-surface region of Ge there is an accumulation of Ag atoms with a maximum of the statistical Gaussian concentration distribution in the sample depth given by $R_p \sim 14.6$ nm, and the straggle of the ion range from Rp is $\Delta Rp \sim 6.9$ nm (Figure 1a). The effective thickness of the implanted layer is estimated as $Rp + 2\Delta R_p = 28.4$ nm. However, as will be shown below, prolonged ion irradiation of *c*-Ge, simultaneously with the formation of PGe and the segregation of Ag at the sample surface, leads to an effective Ge sputtering. The profile of the generated vacancies in Ge during Ag^+-ion implantation has the same Gaussian shape and practically coincides with the distribution of Ag^+ ions in the depth of the sample (Figure 1b).

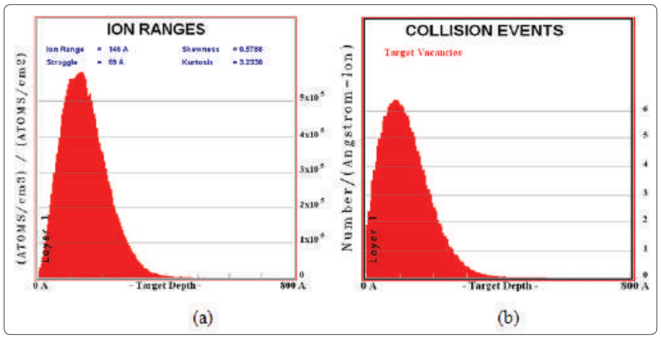
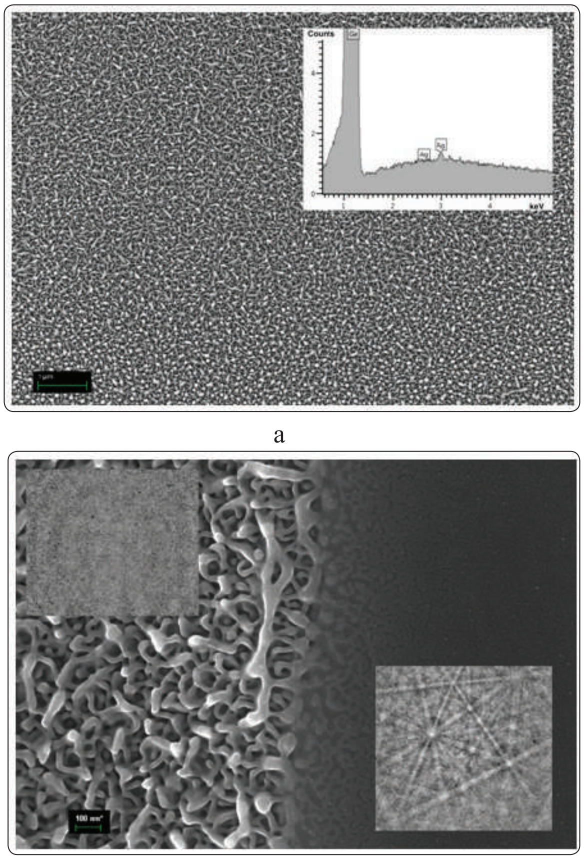


Figure 1: Simulated depth distribution profiles of implanted Ag+-ions (a) and generated vacancies (b) in irradiated Ge.

SEM images of the Ge surface implanted with Ag^+ ions presented with various scales are shown in Figures 2 and 3. Unlike the virgin polished *c*-Ge substrate (the right-hand side in Figure 2b), the morphology of the irradiated surface is the highly developed open porous spongy structure (the left-hand side in Figure 2b). It should be noted that a similar spongy structure of PGe was formed by implantation of *c*-Ge, for example, by Bi^+-ion with an energy of 30 keV [8]. However, it significantly differs from the columnar type PGe formed by implantation with a lighter Ge^+ ion at low energies [11, 12]. In principal, the possibility of creating pores by implantation with Ge^+ self-ions indicates that the formation of pores takes place not due to impurity, but because of some specific energy conditions during the irradiation process, which could be either assumed also for our case Ag:PGi, although heavy implants such as Ag could stimulate the appearance of a generally spongy structure [13].

The morphological homogeneity of the Ag: PGe surface observed over a rather large area of the sample in tens of microns (Figure 2a) indicates that the porous structure is not a random local artifact of surface change during implantation, and could be characterized by the concept of scalability important for certain technological applications. EDX microanalysis of the implanted *c*-Ge surface is characterized by a spectrum with Ag peaks in the energy range of 2.5-3.5 keV (insert in Figure 2a, which were not observed in the spectrum of unirradiated c-Ge. As the scale of the surface fragment increases (Figures 2b), a pore structure consisting of interlacing Ge nanowires (gray color) with average diameter of about 10-20 nm could be seen more clearly. At the ends of Ge nanowires, close to spherical ion-synthesized nano fragments - nanoparticles (bright spots) with sizes of ~ 20-30 nm were observed. To make it clear, some of these nanoparticles are marked in Figure 3a by circles.Since heavier chemical elements detected by the backscattered electron detector are shown in SEM images in a brighter tone color, for a composite material consisting only of Ge atoms and implanted Ag one, it can be assumed that the circled bright spots are determined as the ion-synthesized metallic Ag in the form of nanoparticles Figure 3a. It should be noted that the solubility of Ag in Ge is extremely small (~ 10^{16} at/cm^{-3}), and for the dose of $1.5 \cdot 10^{17}$ ion/cm^2 used in this study, by analogy with various implanted dielectrics, the generation of Ag nanoparticles in Ge is quite realistic. Here with, atoms of Ag and Ge do not form any chemical compounds.



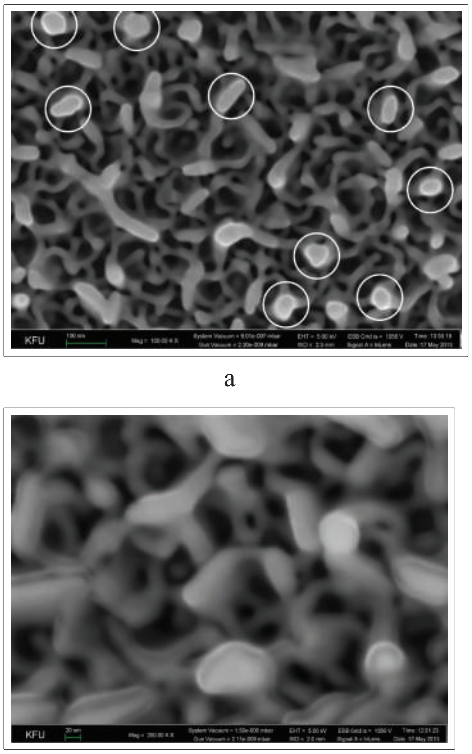
a

b

Figure 2: SEM images, shown at different scales, of the Ag:PGe surface obtained by low-energy high-dose Ag^+-ion implantation into *c*-Ge.

The inset in Figure 1a shows the EDX spectrum. The right-hand side of Figure 1b demonstrates the non-irradiated area of the virgin *c*-Ge substrate, and the left corresponds to implanted Ag:PGe region. Corresponding inserts are represented by the EBSD patterns.

The inset in Figure 2b (on the right side) shows the experimentally observed EBSD picture of the Kikuchi diffraction from the virgin *c*-G. It means that the c-Ge substrate used in this work is characterized by a single-crystal cubic structure with the parameters $a = b = c = 5.66$ Å and $\alpha = \beta = \gamma = 90°$. For the implanted region of the Ag:PGe sample, unlike the Kikuchi diffraction in the form of parallel lines to the planes of the crystal lattice bands, a EBSD pattern is observed from the wide diffuse rings (the insert on the left in Figure 2b of the amorphous layer PGe.

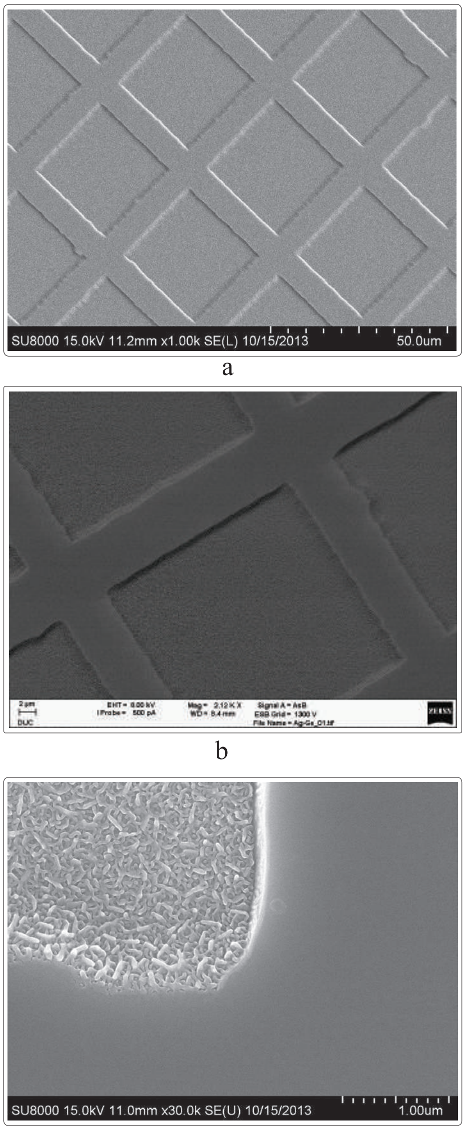

a

b

Figure 3: SEM images, shown at different scales, of the Ag:PGe surface with ion-synthesized Ag nanoparticles.

The morphological homogeneity of the Ag: PGe surface observed over a large enough area of the sample in tens of microns (Figure 2a) indicates that the porous structure is not a random local artifact of the surface change during implantation, and could be characterized by scalability important for certain technological applications. EDX microanalysis of the implanted *c*-Ge surface is characterized by a spectrum with Ag peaks in the energy range of 2.5-3.5 keV (insert in Fig. 2a, which were not observed in the spectrum of unirradiated *c*-Ge. As the scale of the surface fragment increases (Figures 2b), a pore structure consisting of interlacing Ge nano wires (gray colour) with average diameter sizes of about 10-20nm could be seen more clearly. At the ends of Ge nanowires, close to spherical ion-synthesized nanofragments - nanoparticles (bright spots) with sizes of ~ 20-30 nm are observed.For clarity, some of these nanoparticles are marked in Figure 3a by circles.Since heavier chemical elements detected by the backscattered electron detector are shown in SEM images in a brighter tone colour, for a composite material consisting only of Ge atoms and implanted Ag one, it can be assumed that the circled bright spots are determined as the ion-synthesized metallic Ag in the form of nanoparticles (Figure 3a). It should be noted that the solubility of Ag in Ge is extremely small (~ 10^{16} at/cm^{-3}), and for the dose of $1.5 \cdot 10^{17}$ ion/cm^2 used in this study, by analogy with various implanted dielectrics, the generation of Ag nanoparticles in Ge is quite realistic.Herewith, atoms of Ag and Ge do not form any chemical compounds.

Implantation through a mask is traditionally used in order to evaluate the emerging step on the boundary between the irradiated and non-irradiated regions of a sample, due to sputtering or swelling of the surface, in particular when creating pores in semiconductors, for example, when Ge is irradiated with Ge$^+$ self-ion, implantation through a mask is traditionally used [8, 14]. The SEM images of the Ge surface containing fragments of PGe microstructures formed by Ag$^+$-ion implantation through a mask are shown in Figure 4.



a

b

c

Figure 4: SEM images, shown at different scales, of periodic microstructures on the *c*-Ge surface with PGe areas obtained by Ag$^+$ ion implantation through a mask.

For the purpose of an independent evaluation of the topology of the surface after implantation, observations were made at different scales and with two different electron microscopes SU 8000 (Figures 4a and 4c) and Merlin (Figure 4b). As it can be seen from these images, implantation on the *c*-Ge surface results in the formation of square immersed areas of PGe, bounded by the walls of the unirradiated c-Ge, which indicates the effective sputtering of the Ge surface rather than its swelling. The SEM image, with a largest magnification at the corner of the square cell (Figure 4c) clearly demonstrates the formation of spongy PGe in the implanted area of the cell.

A fragment of the sample, covering a region of several square mask cells, represented in the 3D projection of AFM image of an implanted Ag:PGe, is shown in Figure 5. As seen from this figure, during the

Ag$^+$-ion implantation of c-Ge simultaneously with the formation of the porous structure, an effective sputtering of the surface of the *c*-Ge substrate occurs, which confirms the SEM results (Figure 4).

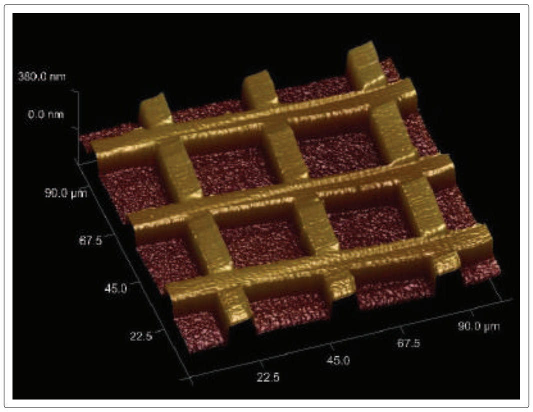


Figure 5: 3D fragment of the AFM image of the *c*-Ge surface in the mask region, demonstrating Ge sputtering during implantation In this case, a step on the boundary between *c*-Ge walls and sputtered PGe area are formed. According to the AFM profile measurement the depth of sputtering sample sections is estimated to be ~ 200 nm.

From the mass ratios of Ge and Ag atoms for case of low implantation energy (30 keV), it could be assumed that the nuclear collisions of Ag$^+$ ions with the substrate Ge atoms dominate, and as a result, the latter are sputtered by the direct knockout mechanism from the target. This fact is important from the point of view of determining the pathways for the formation of PGe, and it turns out to be somewhat unexpected, because of, as it was previously shown, the formation of pores in *c*-Ge implanted with Ge$^+$ self-ions was accompanied by the opposite phenomenon, surface swelling. Therefore, the mechanism for the formation of pores in implanted *c*-Ge, based on the generation and unification of vacancies in an irradiated semiconductor, proposed for example in could not be simply transferred to the case of implantation of *c*-Ge with heavy Ag$^+$ ions, as in the present study [8].

Thus, in this paragraph, a technique for obtaining PGe layers with Ag nanoparticles on the *c*-Ge surface using low-energy high-dose implantation was demonstrated. It was found that Ag$^+$-ion implantation leads to the sputtering of the surface on which a spongy amorphous porous structure with metal nanoparticles is formed. Ion implantation technology is currently one of the main techniques used in industrial semiconductor microelectronics to form various types of Ge nano- and micro-devices. Therefore, the suggested method of obtaining PGe by irradiation with Ag$^+$ ions, unlike chemical approaches, has advantages as it can be easily integrated into the modern industrial process to improve the manufacturing microchips technology.

Conclusion

The study presents the novel data that refers to the technique of porous fabrication on Si and Ge wafers combined with Ag NPs, which are nucleated and growth inside PSi walls, using low energy high dose ion implantation. The advantage of the presented technology is that it suggests a physical preparation method of semiconductor porous structures without any chemical solution, which is almost not used for microelectronics and chip preparation. Additionally, nowadays ion implantation is widely used in modern microprocessor preparation industry. Therefore, suggested technology of PSi a PGe fabrication can be easily integrated into practice and combined with implantation technique.

Acknowledgment

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