Fabrication of Nanoporous Silicon By Ag^+ -Ion Implantation

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Abstract A new nanotechnology approach to create a nanoporous silicon layers by low-energy high-dose metal-ion implantation is demonstrated. Ag-ion implantation into monocrystalline silicon substrate at energy 30 keV with doses from 7.5×10^{16} to 1.5×10^{17} ion/cm² was carried out. Surface nanoporous structures were studied by scanning electron microscope imaging and energy-dispersive X-ray analysis. For the first time it is shown that nanoporous silicon were formed by Ag-ion implantation. The average sizes of porous holes and thickness of walls between porous are about 110-130 and 30-60 nm, respectively. The formation of silver nanoparticles with average size of 5-10 nm inside porous silicon structures was detected. Thus, ion implantation is suggested to be used for a fabrication of nanoporous layer structure, which could be easily combined with the silicon matrix for various applications.

Keywords Nanoporous Silicon, Silver Nanoparticles, Ion Implantation

1. Introduction

Nanoporous materials have attracted remarkable concerns and found tremendous importance widespread in both fundamental research and industrial applications. Such materials could be widely used for variety applications as absorbents, lightings, catalysts, and for biological molecular filtration and isolation.

At present time nanoporous silicon (p-Si) is considering as a key material in many industrial sectors as electronics, sensors and photonics. Such p-Si layer was first obtained in the mid-1950s at Bell Labs [1], but it was not seriously used until the discovery of its strong luminescent properties in 1990 [2]. Prior to this discovery, p-Si was almost exclusively considered as insulating layer devices in the microelectronics industry [3]. The detail advantages of p-Si vs. silicon are observed in a literature very well [4, 5].

In past there were only two main technological methods for production of p-Si structures: electrochemical etching

and chemical stain etching. Thus, p-Si could be chemically created on silicon under the appropriate conditions with typical feature porous sizes in the order of a few nanometers [3, 6]. Both the porosity and the pore morphology of p-Si are greatly influenced by the electrochemical and chemical stain etching parameters. As it will be discussed here, the metal-ion implantation physical technique was not used before in practice for fabrication of p-Si [7].

Additionally, the interest to silicon nanostructures containing noble metal nanoparticles was recently found. It was initiated because metal nanoparticles with localized surface plasmon modes demonstrate a specific option to enhance the recombination rate of the light silicon emitter to increase the efficiency of photoluminescence and internal quantum effectively [6, 8]. Silver nanoparticles (AgNPs) are the subject of specific increasing interests due to their strongest plasmon resonance in the visible spectrum [9, 10]. For example, p-Si samples coated with a layer of AgNPs after their electrochemical etching showed that a photoluminescence intensity becomes remarkably increased [11] or the reflection of incident light with wavelength below 1100 nm could be reduced to use them for antireflection devices [12].

Instead of using simple silicon as the substrate for the AgNPs deposition on the top of a sample, the ion implantation technique can be used to form AgNPs in a volume of silicon as in the case of ion-irradiated silica glass or polymers [10, 13]. In experiments of the works [14, 15] Ag-ion implantation into crystalline silicon wafers and silicon nanocrystal layers at energy of 30-35 keV and rather lower dose of 5.0×10^{15} ion/cm² was performed. Then AgNPs in silicon matrix were synthesized after thermal annealing at 500°C of implanted samples. In another work [16] Ag^+ -ion implantation of silicon using a conventional metal vapor vacuum arc - MEVVA ion source, which produced a mixture of Ag^{n+} ions, was applied at higher dose of 2.0×10^{17} ion/cm² to create AgNPs. However, it has to be mentioned that p-Si structures in these publications has never been observed after implantation [16, 17].

At the present work a novel technological way based on low energy ion implantation was suggested and realized to

create p-Si layers on the crystalline surface of Si wafers. It is also demonstrated that using a high-dose (more than 1.0×10^{16} ion/cm²) Ag-ion implantation of silicon with the energy of 30 keV various p-Si structures with AgNPs can be successfully fabricated.

2. Materials and Methods

A p-type (100)-oriented single crystalline silicon wafers as the substrate were used for Ag-ion implantation to create p-Si structures. The substrates were cleaned in a wet chemical etching process. The silicon wafers were implanted with Ag⁺ ions at 30 keV and the ion current density of 4 μ A/cm² with doses in the range between 7.5×10^{16} and 1.5×10^{17} ion/cm² using the ion beam implanter “ILU-3” at residual vacuum of 10^{-5} Torr and room temperature of the irradiated samples.

Some silicon substrates were implanted through a mask consisting of a mesh nickel grid with square holes and the bar width of 40 μ m. In this way, selectively implanted regions next to unimplanted ones were prepared in order to perform the step-height profilimetry.

Depth distribution profiles of Ag atoms and the damage level in implanted silicon were modeled using the simulation-program the Stopping and Range of Ions in Matter (SRIM-2013) [18]. The morphology of the implanted samples were characterized in plan-view by scanning electron microscopy (SEM) using microscope Merlin Zeiss combined with ASB (Angle Selective Backscattering) and ESB InLens (Energy selective Backscattering) detectors, which was also equipped for energy-dispersive X-ray spectroscopy (EDX) analysis with AZtec X-MAX device from Oxford Instruments.

Pore size estimation was determined from SEM micrographs with an Axio Vision software similar to algorithm used in the work [19].

3. Results and Discussions

According to the SRIM simulations, during ion bombardment an excess vacancy-rich region and accumulation of implanted ions can be formed close to the surface in irradiated matrix (Figure 1). A mean penetration range (R_p^{Ag}) of 30 keV accelerated Ag⁺-ions into silicon substrate is about 26 nm with a longitudinal straggling (ΔR_p^{Ag}) of 8 nm in the Gaussian depth distribution. Thus, the assumed thickness of the modified silicon surface layer ($R_p + 2\Delta R_p$) is about 42 nm. It was assumed [20] that during ion implantation various porous semiconductor structures can be resulted from nucleation of small voids in the irradiated materials by vacancy generations. Therefore the vacancy depth distribution for silicon implanted with Ag⁺ ions was also simulated by the SRIM, which showed similar profile to ion distribution for such low accelerating energies. Analyzing SRIM modeling, however it should be taking in

account that obtained depth distribution of Ag ions and vacancies are corresponded to implantation process of uniform silicon matrix before a nucleation and growth (for ion dose less than 1.0×10^{16} ion/cm²) of p-Si.

Figure 1. Depth ion distribution of Ag-ions implanted in silicon with energy of 30 keV calculated using the SRIM Ag code.

Figure 2 shows a plane-view SEM image of unimplanted silicon, which looks like as very smooth without any surface structural inhomogeneity.

Figure 2. SEM image of unimplanted silicon surface.

The results of porosification of the silicon samples are observed by plan-view SEM images (Figures 3). In contrast to unimplanted silicon (Figure 2) the characteristic p-Si surface structures show the black hole appearance in the implanted silicon region. They are consisting of near cellular features partitioned by rather thin walls with thicknesses about 30-60 nm. Such features are clearly resolved in all samples formed by various Ag-ion dose irradiations: 7.5×10^{16} , 1.0×10^{17} and 1.5×10^{17} ion/cm². Uniform pore distributions with distinguished sharp holes over all

implanted surfaces on silicon-implanted samples were observed. The size of pores were measured by counting the number of holes in several micrographs, taking into account all visible holes boundaries and subtracting those holes that intersects an edge of the SEM image. From this, the size of the pores was estimated. It is seen that mean size of pores (black holes) increasing in magnitude with an increasing of Ag-ion doses with estimated average range 100 to 130 nm. A white spots in these SEM figures corresponds to material with higher density against to silicon that suggests them to be AgNPs.

Figure 3. SEM images and EDX characteristic spectrum of p-Si fabricated at various doses: (a) 7.5×10^{16} ; (b) 1.0×10^{17} and 1.5×10^{17} ion/cm².

In Figure 4 it is shown an EDX spectrum recorded on the examined p-Si structure with AgNPs fabricated at highest ion dose. Such EDX spectra measurements were done in the area on surface sample outside black holes of the silicon pores. In contrast to EDX data for unimplanted silicon, in the middle part of the presented spectra of p-Si it is clear seen

four peaks located between 2.5 and 3.5 keV. Those maxima are directly related to the Ag characteristic lines. It was observed that the intensity of Ag EDX peaks was increasing with increasing of ion implantation dose that means a growing of Ag concentrations in the silicon samples. Appearance of Ag peaks is in consistence with white sports in SEM images of the p-Si (Figure 3), which are corresponding to AgNPs synthesized in p-Si during ion implantation.

Figure 4. EDX characteristic spectrum of p-Si fabricated at ion dose of 1.5×10^{17} ion/cm². Visible EDX peaks confirm the presence of Ag in the synthesized p-Si structures.

The SEM images with different scales show the same sample implanted at highest dose of 1.5×10^{17} ion/cm² (Figure 5) where white sports are AgNPs with a size in the range of 5-10 nm. Thus, as demonstrated at present study, using selected conditions for low-energy Ag-ion implantation of silicon, AgNPs can be easily fabricated without post-implantation thermal annealing as it was forcibly used in the work [16].

The Figure 6 presents the step-height data for silicon implanted with a dose of 1.5×10^{17} ion/cm² and which was carried out on the sample selectively implanted through the nickel grid. The image of unimplanted silicon region corresponds to dark area whereas implanted p-Si structures are presented as a light gray squares (Figures 6a and 6b). The spattering of the implanted part of the sample with respect of the unimplanted region is determined (Figure 7). In first approximation, it could be speculated that the volume expansion is related to a mechanism simply governed by the nuclear energy deposition, which is usually measured in displacement per atom [20].

It is known that for a critical rather-low implantation dose, silicon undergoes a crystalline to amorphous phase transition [21, 22]. As seen in present experiments at higher doses the amorphous silicon layer transforms to a porous structure with AgNPs. Thus, as the first time in practice, it is demonstrated by present experiment that p-Si growth was stimulated by high-dose metal-ion implantation. This new result for silicon could be considered in consistence with published data for porous germanium fabricated during ion implantation process [7, 23, 24] and a similar suited possible

mechanism for p-Si structuring could also be assumed.

Figure 5. SEM images of p-Si structure fabricated at a dose of 1.5×10^{17} ion/cm² presented with different scales.

Despite p-Si creation by metal-ion implantation of silicon, in case of germanium over the past 30 years there was much debate as to what mechanism governs the formation of the porous semiconductor structure in ion implanted germanium [25]. Currently, there are two main theories of void formation for germanium: vacancy clustering and so-called “microexplosions”. The vacancy clustering theory invokes the inefficient recombination of germanium point defects during ion-implantation, where once a critical point defect population is created by ion-implantation, excess vacancies cluster into pores in order to minimize the dangling bond density. In contrast, the microexplosion theory is based on the creation of voids through pressure waves and thermal

spikes caused by the overlap of ion cascades [25]. Therefore, in principle, it is possible to determine which theory better models void and porous formation in silicon by selecting appropriate implant conditions and observing the resulting microstructure after implantation. Thus, additional experimental study of p-Si fabrication by high-dose ion implantation of silicon is necessary and such work will be continued.

Figure 6. (a) and (b) SEM image (different scales) of structures with p-Si (light gray) fabricated at a Ag^+ -ion dose of 1.5×10^{17} ion/cm² through a mesh nickel mask used to analyze the step-height between unimplanted silicon (dark gray) covered during irradiation with the mask and implanted regions with P-Si (light area).

Figure 7. 3D SEM reconstruction of step area that demonstrates a sputtering of the silicon surface during Ag^+ -ion implantation.

4. Conclusion

The first data on a novel technique for p-Si fabrication on silicon wafers combined with AgNPs, which are nucleated and growth inside P-Si walls, using low energy high dose ion implantation was presented. Formation of porous material with AgNPs for various ion doses was directly evident by SEM and EDX analysis. The novel developed nanostructuring porous semiconductor material with metal nanopartilces is a subject for following study of optical plasmonic, photoluminescence, antireflection, nonlinear-optical and biosensor perspective properties.

Acknowledgements

This work was partly supported by the Russian Foundation for Basic Research (Nos. 12-02-97029, 12-02-00528 and 13-02-12012) and NIR KFU 13-56. A.L.S. grateful to the Alexander von Humboldt Foundation and the DAAD (Germany).

REFERENCES

- [1] A. Uglir, Electrolytic shaping of germanium and silicon, *Bell Syst. Tech. J.*, 1956, Vol. 35, 333-347.
- [2] L.T. Canham, Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers, *Appl. Phys. Lett.*, 1990, Vol. 57, 1046-1048.
- [3] V. Torres-Costa, R.J. Martin-Palma, Application of nanostructured porous silicon in the field of optics. A review. *J. Mater. Sci.*, 2010, Vol. 45, 2823-2830.
- [4] Z.C. Feng, R. Tsu, *Porous silicon*, World Scientific Publ., New York, 1994.
- [5] M.J. Sallor, *Porous Silicon in Practice. Properties, Characterization and Applications*, Willey-VCH, Weinheim, 2011.
- [6] G. Oskam, J.G. Long, A. Natarajan, P.C. Searson, Electrochemical deposition of metals onto silicon. *J. Phys. D: Appl. Phys.*, 1998, 31, 1927-1949.
- [7] L. Romano, G. Impellizzeri, L. Bosco, F. Ruffino, M. Miritello, G. Grimaldi, Nanoporosity induced by ion implantation in deposited amorphous Ge thin film, *J. Appl. Phys.*, 2012, Vol. 111, 113515-0 – 113515-5.
- [8] T.S. Amran, M.R. Hashim, N.K. Al-Obaidi, H. Yazid, R. Adnan, Optical absorption and photoluminescence studies of gold nanoparticles deposited on porous silicon, *Nanoscale Research Lett.*, 2013, Vol. 8, 35-39.
- [9] U. Kreibig, M. Vollmer, *Optical properties of metal clusters*, Springer, Berlin, 1995.
- [10] A.L. Stepanov, Ion-synthesis of silver nanoparticles and their optical properties. *Nova Sci. Publ.*, New York, 2010.
- [11] D.T. Cao, L.T.Q. Ngan, C.T. Anh, Enhancement and stabilization of the photoluminescence from porous silicon prepared by Ag-assisted electrochemical etching, *Surf. Interface Anal.*, 2013, Vol. 45, 762-771.
- [12] Y. Wang, Y.P. Liu, H.L. Liang, Z.X. Mei, X.L. Du, Broadband antireflection on the silicon surface realized by Ag nanoparticle-patterned black silicon, *Phys. Chem. Chem. Phys.*, 2013, Vol.15, 2345-2350.
- [13] A.L. Stepanov, Optical properties of metal nanoparticles synthesized in polymer by ion implantation: A review, *Tech. Phys.*, 2004, Vol. 49, 143-153.
- [14] A.K. Sing, K.G. Gryczynski, F.D. McDaniel, S.Y. Park, S.Y. M. Kim, A. Neogi, Localized surface plasmon polariton enhanced radiative recombination in ion-implanted silicon emitters, *Appl. Phys. Express*, 2010, Vol. 3, 102201-102204.
- [15] A.K. Sing, K.G. Gryczynski, A. Neogi, Origin of room temperature broadband light emission and carrier dynamics in Ag ion implanted silicon nanocrystals, *Opt. Mater. Express*, 2012, Vol. 2, 501-508.
- [16] H.W. Seo, Q.Y. Chen, I.A. Rusakova, Z.H. Zhang, D. Wijesundera, S.W. Yeh, X.M. Wang, L.W. Tu, N.J. Ho, Y.G. Wu, H.X. Zhang, W.K. Chu, Formation of silver nanoparticles in silicon by metal vapor vacuum arc ion implantation, *Nucl. Instr. Meth. Phys. Res. B*, 2012, Vol. 292, 50-54.
- [17] L. Romano, G. Impellizzeri, M.V. Tomasello, F. Giannazzo, C. Spinella, M.G. Grimaldi, Nanostructuring in Ge by self-ion implantation, *J. Appl. Phys.*, 2010, Vol. 107, 84310-1 – 84310-5.
- [18] J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon Press, New York, 1985.
- [19] J. Peckham, G.T. Andrews, Effect of anodization current density on pore geometry in macroporous silicon, *Semicond. Sci. Technol.*, 2013, Vol. 28, 105027-1 – 105027-5.
- [20] L.M. Wang, R.C. Birtcher, Radiation-induced formation of cavities in amorphous germanium, *Appl. Phys. Lett.*, 1989, Vol. 55, 2494-2496.
- [21] E. Chason, S.T. Picraux, J.M. Poate, J.O. Borland, M.I. Current, T. Diaz de la Rubia, D.J. Eaglesham, O.W. Holland, M.E. Law, C.W. Mayer, J. Melngails, A.F. Tasch, Ionbeams in silicon processing and characterization, *J. Appl. Phys.*, 1997, Vol. 81, 6513-6561.
- [22] J.S. Williams, Ion implantation of semiconductors, *Mater. Sci. Eng. A*, 1998, Vol. 253, 8-14.
- [23] T.M. Donovan, K. Heinemann, High-resolution electron microscopy observation of voids in amorphous Ge, *Phys. Rev. Lett.*, 1971, Vol. 27, 1794-1799.
- [24] T. Steinbach, J. Wemcke, P. Kluth, M.C. Ridgway, W. Wesch, Structural modifications of low-energy heavy-ion irradiated germanium, *Phys. Rev. B*, 1987, Vol. 35, 104108-1 – 104108-15.
- [25] B.L. Darby, B.R. Yates, N.G. Rudawski, K.S. Jones, A. Kontos, R.G. Elliman, Insights for void formation in ion-implanted, *Thin Solid Films*, 2011, Vol. 519, 5962-5965.