One-step electrochemical synthesis of Ag/por-Si composite from monocrystalline Si

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Abstract. The technique of obtaining Ag/por-Si composite material with homogeneously distributed silver nanoparticles over the surface of porous silicon by one cycle of electrochemical treatment of single-crystalline silicon. The effect is achieved by using an electrolyte to produce porous silicon with a special composition containing silver ions. During the electrochemical anode treatment of single-crystalline silicon in Ag-containing electrolyte a layer of porous silicon and silver islets are formed on the sample surface simultaneously. It is shown that the controlling the conditions of electrochemical processing provide an opportunity to form homogeneously distributed on the surface silver nanoparticles with a narrow-size distribution.

1. Introduction

Hybrid nanostructures based on porous silicon and silver nanoclusters are promising for photovoltaic device structures [1-3], for novel nanoelectronic and plasma energy systems [4-6], for biosensors, including based on Giant Raman scattering [7], for optical filters [8]. Many of these applications require the creation of well-ordered arrays of silver nanoclusters on the substrates. For example, arrays of noble metal nanoclusters in demand in metal-assisted chemical etching (MACE) technology [9-13]. MACE technology is applied for silicon nanowires formation. Si nanowires parameters (diameter of the wire, distance between wires) are primarily determined by the size and location of metal nanoclusters on the surface of single-crystal silicon [14].

Currently, ordered arrays of silicon nanowires (SiNWs) are promising for hybrid functional elements integrated on a single silicon substrate with processing electronics. The possibility of creating gas sensors on hybrid materials is shown on the example of resistors based on SiNWs as gas sensors for ammonia (NH\textsubscript{3}) and smoke detection [12]. A hybrid material based on SiNWs (TiO\textsubscript{2}(SiNWs/TiO\textsubscript{2}) with a core-shell nanostructure demonstrated excellent sensibility for CH\textsubscript{4} detection at a room temperature [13]. The sensor has a linear response to CH\textsubscript{4} gas in the range of 30-120 ppm with a detection limit of 20 ppm which is significantly lower than most previously reported CH\textsubscript{4} sensors. A new method was reported in [15], which allows one to significantly improve the sensibility of SiNWs to C\textsubscript{6}H\textsubscript{6} by combining TeO\textsubscript{2} branches and sensibility with palladium Pd. Therefore, unique properties dependent on the size, the ability to control the morphology of the surface by varying the conditions of its obtaining, compatibility with the modern microelectronics
industry provide SiNWs-based structures successful application in various fields where the most interesting is gas sensory [16-17]. The combination of nanowires and branched gas-sensitive materials could help to improve the sensitivity and operating parameters of gas sensors.

Despite active publications in this area over the past 10-15 years, the technology for industrial production of nanowires requires significant improvement. The deposition of metal nanodots are still quite expensive and needs sophisticated equipment, which prevent the application of the MACE method for commercial production.

Therefore, this paper is devoted to the development of technique for Ag/Por-Si composite material with uniformly distributed silver nanoparticles on the surface of porous silicon in one cycle of electrochemical processing of single-crystal silicon.

2. Experiment

Samples were obtained by electrochemical anodic etching of single-crystalline n-Si (111). For the simultaneous selective dissolution of silicon with the formation of pore channels and deposition of silver, a special electrolyte composition containing silver ions was used. The electrolyte consisted of an aqueous solution of hydrogen fluoride, isopropanol and silver nitrate. Varying parameter was concentration of AgNO₃. Technological parameters for obtaining the composite are presented in Table 1.

| Concentrations of aqueous solution AgNO₃ (M) | Current density (mA/sm²) | Anodizing time (min) |
|---------------------------------------------|--------------------------|----------------------|
| 0.005                                       | 15                       | 5                    |
| 0.5                                         | 15                       | 5                    |

3. Result and discussion

Visually, the samples differed in color: at a higher concentration of silver nitrate, the samples had a metallic luster and had a silver tint, and at a concentration of 0.005 mol/L, they were yellowish.

Figures 1 and 2 demonstrate surface morphology and cross-section of obtained Ag/por-Si composite by means of SEM at different AgNO₃ concentrations. As one can observe on Figure 1, a, b a homogeneous island layer formed on the sample surface consisting of uniform spherical-like silver particles with average size of 30-60 nm. The cross-section (Figure 1, c) confirms that spherical metal islands do not contact each other. As salt concentration in the electrolyte increases (Figure 2, a, b), a continuous metal layer is formed. It is also seen that higher concentration of silver salt leads to the dendrite formation on the surface. Moreover, the formation of pore channels in n-Si (111) could be observed on cross-sections with a typical morphology for the (111) crystallographic orientation of the substrate [14, 17].

Solid (granular) silver films can be formed on the surface of porous silicon, varying the concentration of AgNO₃. In one cycle, porous silicon with a contact layer can be produced and (0D) layers can be synthesized with homogeneous distribution of metal islets over the porous silicon surface.
Figure 1. AgNO$_3$ concentration – 0.005 mol/g, anodizing time – 5 min, $j=15$ mA/cm$^2$: (a) and (b) sample surface at different magnifications, (c) – cross-section. The size of clusters is 30-60 nm.

Figure 2. AgNO$_3$ concentration – 0.5 mol/g, anodizing time – 5 min, $j=15$ mA/cm$^2$: (a) and (b) sample surface at different magnifications, (c) – cross-section. The size of clusters is 50-100 nm.

Table 2 shows the EDX spectra which indicates that elements such as deposited silver, oxygen and carbon are detected on the silicon wafer surface. The last two elements on the spectrum are explained by natural processes of oxidation and carbonization of Si influenced by the environment. In the investigation of the inner surface of pores it was found that during electrochemical deposition silver does not go deep into pores and prevents the process of oxidation of their surface.

Table 2. EDX spectra obtained from Ag/Por-Si composite surface.

| Material | Composite surface | Pore surface |
|----------|-------------------|--------------|
|          | Intensity (arb.u.)| Energy (keV) | Intensity (arb.u.)| Energy (keV) |
| C        | 2                 | 0.3          | –              | –           |
| O        | 2                 | 0.5          | –              | –           |
| Si       | 39                | 1.8          | 100            | 1.75        |
| Ag       | 57                | 3            | –              | –           |

4. Conclusions

Morphological characteristics of Ag/Por-Si allow being the composite perspective for application in many fields of electronics and medicine, and also revealing new possibilities for obtaining silicon nanostructures used in solar energy, gas sensory and so on.

The results show that it is possible to form Ag/Por-Si composite by one technological cycle. The parameters of the obtained composite can vary by changing the technological conditions, in particular the concentration of AgNO$_3$, anodizing current density and anodizing time. In the condition of low concentrations of silver nitrate solution a small amount of silver is deposited on the por-Si
surface, and at higher concentrations of AgNO\textsubscript{3} practically solid films are formed on the Si surface which can be used as conductive contacts to the porous layer. The results of EDX confirm that silver nanoparticles serve as a catalyst for the process of pore formation in single crystalline silicon and in the process of electrochemical etching does not go deep into the pores.

References

[1] Martín-Palma R J, McAtee P D, Ramadan R and Lakhtakia A 2019 Scientific reports \textbf{9} 1-8

[2] Ramadan R, Manso-Silván M and Martín-Palma R J 2020 \textit{Journal of Materials Science} \textbf{55} 5458-70

[3] Smerdov R S, Mustafaev A S, Soukhomlinov V S, Spivak Y M and Moshnikov V A 2019 \textit{IEEE Conf. of Russian Young Researchers in Electrical and Electronic Engineering} (IEEE) pp 786-90

[4] Spivak Y M 2018 \textit{Int. Conf. EExPolytech} (IEEE) pp 244-8

[5] Smerdov R S, Mustafaev A S, Spivak Y M and Moshnikov V A 2018 \textit{Proc. of the Int. Forum-Contest of Young Researchers} (St. Petersburg: CRC Press) p 439

[6] Smerdov R S, Mustafaev A S, Spivak Y M and Moshnikov V A 2019 \textit{Proc. of the XV Int. Forum-Contest of Students and Young Researchers under the auspices of UNESCO} (St. Petersburg: CRC Press) p 434

[7] Graham D, Faulds K and Smith W E 2006 \textit{Chemical communications} \textbf{42} 4363-437

[8] Smerdov R S, Spivak Y M, Garcev K G, Pschelko N S and Moshnikov V A 2017 \textit{Smart Nanocomposites} \textbf{8} 311-4

[9] Werner P, Geyer N, Gösele U, Huang Z and Boor K J 2011 \textit{Advanced Materials} (Deerfield Beach, Fla.) \textbf{22} 285-308

[10] Lischchuk P, Isaiev M, Osminkina L, Burbelo R, Nychyporuk T and Timoshenko V 2019 \textit{Physica E: Low-dimensional Systems and Nanostructures} \textbf{107} 131-6

[11] Sivakov V A, Bronstrup G, Pecz B, Berger A, Radnocy G Z, Krause M and Christiansen S H 2010 \textit{The Journal of Physical Chemistry C} \textbf{114} 3798-803

[12] Georgobiani V A, Gonchar K A, Zvereva E A and Osminkina L A 2018 \textit{Physica status solidi (a)} \textbf{215} 1700565

[13] Liu D, Lin L, Chen Q, Zhou H and Wu J 2017 \textit{ACS sensors} \textbf{2} 1491-7

[14] Korotcenkov G and Cho B K 2010 \textit{Critical Reviews in Solid State and Materials Sciences} \textbf{35} 153-260

[15] Chen S, Tang Y, Zhan K, Sun D and Hou X 2018 \textit{Nano Today} \textbf{20} 84-100

[16] Moshnikov V A, Gracheva I, Lenshin A S, Spivak Y M, Anchkov M G, Kuznetsov V V and Olchowik J M 2012 \textit{Journal of non-crystalline solids} \textbf{358} 590-95

[17] Spivak Y M, Mjakin S V, Moshnikov V A, Panov M F, Belorus A O and Bobkov A A 2016 \textit{Journal of Nanomaterials} \textbf{2016} 1-8