Materials Letters 313 (2022) 131802

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

A new approach for producing of film structures based on $Si_{1-x}Ge_x$

I.M. Gavrilin [a,*], N.L. Grevtsov [b], A.V. Pavlikov [c], A.A. Dronov [a], E.B. Chubenko [b], V. P. Bondarenko [b], S.A. Gavrilov [a]

[a] *National Research University of Electronic Technology – MIET, Bld. 1, Shokin Square, Zelenograd, Moscow 124498, Russia*
[b] *Belarusian State University of Informatics and Radioelectronics, P. Brovki str. 6, Minsk 220013, Belarus*
[c] *Physics Department, M.V. Lomonosov Moscow State University, Leninskie Gory 1-2, Moscow 119991, Russia*

ARTICLE INFO

Keywords:
Electrodeposition
$Si_{1-x}Ge_x$ films
Germanium nanowires
Porous silicon

ABSTRACT

In this work, we propose a new, previously unpresented in the literature, approach to the formation of $Si_{1-x}Ge_x$ films. This approach includes electrochemical processes of the formation of porous silicon, electrochemical deposition of low-melting metals and Ge. Post-heat treatment is made possible to synthesize film structures based on $Si_{1-x}Ge_x$ solid solutions. Using this approach an alloy of the composition $Si_{0.4}Ge_{0.6}$ has been obtained at a lower formation temperature than predicted by the phase diagram for the Si-Ge system.

1. Introduction

Film structures based on $Si_{1-x}Ge_x$ are widely used in high-temperature thermoelectric converters, which have high stability and high efficiency in the temperature range 800–1100 °C, which provides a wide range of their application from the utilization of heat removed during various high-temperature processes to equipment for the study of outer space [1]. Also, $Si_{1-x}Ge_x$ films are used in optoelectronic devices [2].

Currently, film structures based on $Si_{1-x}Ge_x$ solid solutions are obtained by various chemical vapor deposition methods, for example: plasma chemical deposition [3], low pressure deposition (LPCVD) [4], thermal evaporation [5]. Magnetron or electron beam evaporation, either of individual Si and Ge targets, or of the finished $Si_{1-x}Ge_x$ alloy, is also used [6,7]. However, despite the progress made in recent years, many unsolved problems remain in this area that impede the widespread practical use of $Si_{1-x}Ge_x$. This is mainly due to the high cost of crystalline Ge and its toxic gaseous precursors. A promising solution to the problem is the use of technologically simple electrochemical methods for producing $Si_{1-x}Ge_x$ films. However, intensive hydrolysis of liquid precursors ($SiCl_4$ and $GeCl_4$) used for the electrochemical deposition of Si and Ge layers requires applying of non-aqueous solvents with a high degree of purification and carrying out the process in an inert atmosphere [8].

Recently, a new approach to the electrochemical synthesis of Ge from aqueous solutions of GeO_2 [9] has been demonstrated. GeO_2 is an intermediate in the production of Ge and its cost is significantly less than the cost of crystalline Ge or its liquid and gaseous precursors. A feature of this method is the use of metal with low melting point as a medium for the dissolution and crystallization of Ge. The metal serves as an electrode for the reduction of ions containing Ge to Ge in the atomic state, followed by the formation of a melt of eutectic composition. A continuous cathodic reduction reaction provides concentration supersaturation of the melt with Ge atoms; as a result, Ge crystallizes in the melt at the interface with the substrate, by analogy with the growth of crystals from the gas phase by the well-known vapor–liquid-solid (VLS) mechanism [10].

However, in the case of Si, using same approach we can't reject non-aqueous electrolytes due to the lack of available water-soluble precursors. In this work it is proposed to use porous Si (por-Si) as a source of silicon for the synthesis of $Si_{1-x}Ge_x$ alloy, which will directly participate in the formation of $Si_{1-x}Ge_x$ solid solution. The methods for producing por-Si (anodic etching of Si) are technologically simple and also allow obtaining structures with a wide range of geometric parameters. When pores are filled with germanium at a given porosity, por-Si allows to control the ratio of Ge and Si in the initial Si/Ge nanocomposite and, as a consequence, the Ge concentration in the final $Si_{1-x}Ge_x$ alloy after heat treatment.

2. Experimental.

A schematically proposed approach for obtaining $Si_{1-x}Ge_x$ films is shown in Fig. 1. This approach consists of the following stages: 1) anodic

---

* Corresponding author.
E-mail address: u002209@edu.miet.ru (I.M. Gavrilin).

https://doi.org/10.1016/j.matlet.2022.131802
Received 17 November 2021; Received in revised form 17 January 2022; Accepted 23 January 2022

etching of a single-crystal plate to obtain porous silicon, 2) electrochemical deposition of In nanoparticles (which are germanium crystallization centers) into a porous Si matrix, 3) electrochemical deposition of Ge from an aqueous solution of GeO_2 into porous Si, 4) Heat treatment of porous Si with deposited Ge nanowires in order to obtain an $Si_{1-x}Ge_x$ alloy.

The details of synthesis and characterizations are displayed in electronic Supplementary information.

3. Results and discussions

Fig. 2 shows SEM images of the sample morphology after various stages of $Si_{1-x}Ge_x$ film formation. As you can see, after anodic etching of the Si plate, pores with an average size of ≈ 80 nm have been formed (Fig. 2 a). After the electrochemical deposition of In on the surface and in the pores of silicon, particles have been formed (Fig. 2b), which subsequently served as crystallization centers during the subsequent deposition of Ge (Fig. 2 c). After heat treatment of the obtained por-Si/GeNWs composite a film with globules has been formed (Fig. 2d). The nanowire structures haven't been observed. This fact indicates that the GeNWs array has been melted.

In order to investigate the structure of the obtained film Raman measurements have been performed (Fig. 3).

The Raman spectrum (Fig. 3) shows peaks at ~ 291 cm^{-1}, 403 cm^{-1}, 489 cm^{-1}. These peaks correspond to the vibration modes of the Ge-Ge, Si-Ge, and Si-Si bonds in the $Si_{1-x}Ge_x$ film, respectively [11]. The ratio of Si and Ge in the obtained $Si_{1-x}Ge_x$ alloy has been determined from the obtained Raman spectra (in electronic Supplementary information).

The Ge fraction of the analyzed sample in Fig. 3 has been found about 0,6. As a result, an alloy of the composition ~ $Si_{0.4}Ge_{0.6}$ has been obtained.

The formation of the alloy can be explained as follows. To obtain a $Si_{1-x}Ge_x$ alloy of various compositions, it is necessary to activate the mutual diffusion of Si and Ge atoms through the por-Si/GeNW interface. The solid-phase diffusion coefficients of Si atoms in Ge and Ge atoms in Si are significant only at high temperatures. [12]. In turn, the diffusion coefficient of Ge atoms in Si is much lower and, as a consequence, it will be predominantly diffusion of Si atoms in Ge [13]. At the melting point of bulk Ge (as in this work), the diffusion coefficient of Si atoms in Ge becomes much higher. As soon as Ge melts upon heating, the diffusion of Si atoms in Ge from por-Si increases sharply, forming $Si_{1-x}Ge_x$ melt. It is known that Si and Ge, dissolving indefinitely in each other, form a continuous series of solid solutions. According to the phase diagram of the Si-Ge binary system [14] at a temperature of 950 °C (which has been used in this work), a melt with the composition $Si_{0.005}Ge_{0.995}$ and crystals of a solid solution with the composition $Si_{0.05}Ge_{0.95}$ have been formed. When cooling the system, the liquid changes along the liquidus curve, the composition of the solid solution - along the solidus curve. When the composition of the solid solution coincides with the initial composition of the $Si_{0.005}Ge_{0.995}$ melt, crystallization will end. Further cooling of the system will no longer lead to a significant change in the alloy composition. However, in our case, the alloy has been obtained of the composition $Si_{0.4}Ge_{0.6}$. This is a significantly higher concentration of Si atoms in the alloy. According to the phase diagram, such composition of the final alloy can be obtained under the condition of the onset of crystallization at a temperature of ≈1230 °C, which is much higher than the annealing temperature in this work. This means that GeNWs have been melted at a temperature significantly lower than bulk Ge (≈940 °C). This difference can be explained by the nanoscale effect. It is known that with a decrease in the size of the material, the melting point decreases [15]. Moreover, it has been shown in [16] that, with a decrease in size, there is a shift to the region of lower temperatures and a transformation of the entire phase diagram of the system. As a result, crystallization of a melt with a higher Si concentration can occur at lower temperatures.

4. Conclusion

Thus, in this work, we propose a new, previously unpresented in the literature, approach to the formation of $Si_{1-x}Ge_x$ films. This approach includes electrochemical processes of the formation of porous silicon, electrochemical deposition of low-melting metals and Ge. Post-heat treatment is made possible to synthesize film structures based on $Si_{1-x}Ge_x$ solid solutions. Using this approach in this work, an alloy of the composition $Si_{0.4}Ge_{0.6}$ has been obtained at a lower formation temperature than predicted by the phase diagram for the Si-Ge system. The obtained results will contribute not only to the development of technologies for creating thermoelectric converters, but also optoelectronic devices, including those integrated with silicon circuitry, photodetectors, photocells and components of semiconductor devices based on heterojunctions.

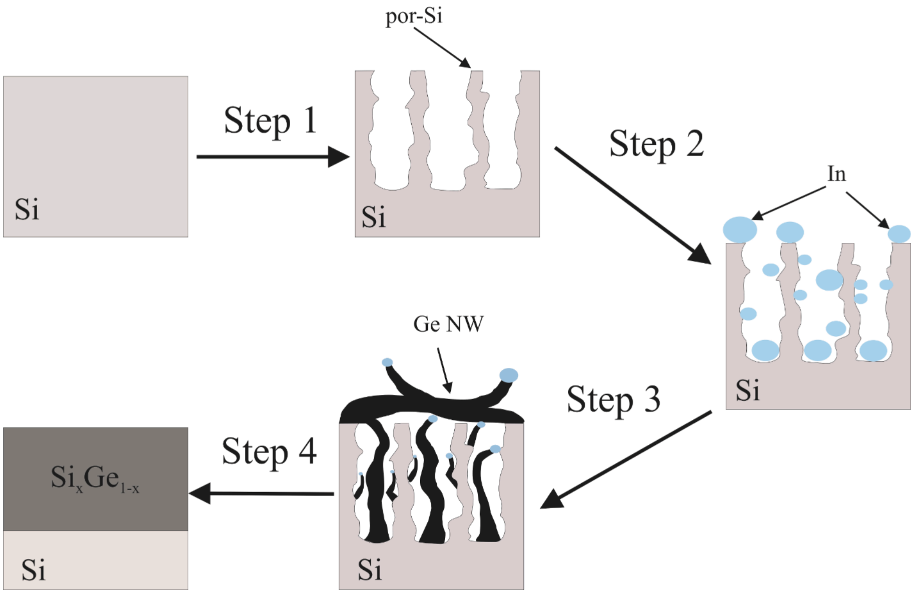

Fig. 1. Schematic illustration of $Si_{1-x}Ge_x$ film fabrication.

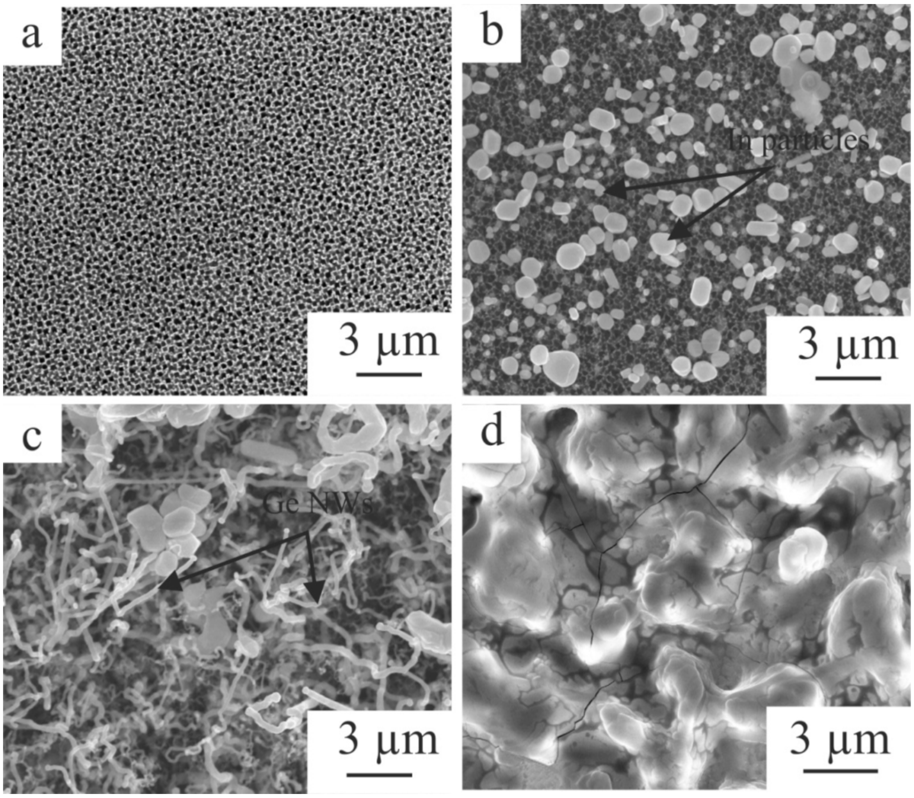

Fig. 2. SEM images of sample morphology at different stages of $Si_{1-x}Ge_x$ film formation: $Si_{1-x}Ge_x$. a) por-Si, b) In particles, c) GeNWs, d) $Si_{1-x}Ge_x$ film.

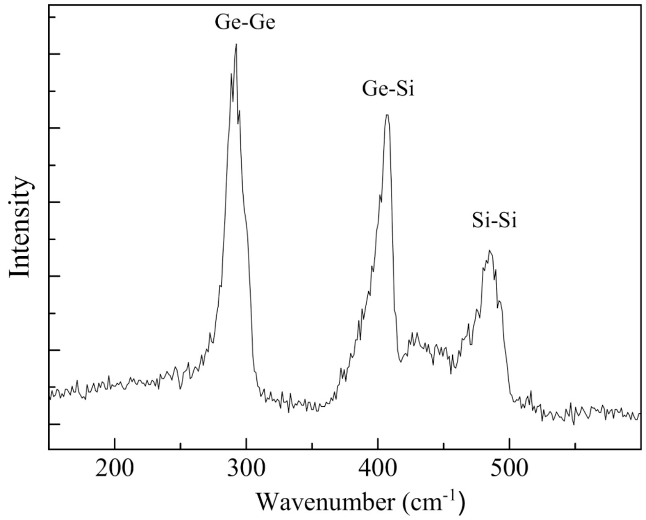

Fig. 3. Raman spectra for $Si_{1-x}Ge_x$ film.

CRediT authorship contribution statement

I.M. Gavrilin: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **N.L. Grevtsov:** Investigation, Methodology. **A.V. Pavlikov:** Formal analysis, Writing – review & editing. **A.A. Dronov:** Conceptualization, Writing – review & editing. **E.B. Chubenko:** Methodology, Visualization. **V.P. Bondarenko:** Conceptualization, Supervision. **S.A. Gavrilov:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was financially supported by the Russian Science Foundation (Project no. 20-19-00720).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2022.131802.

References

[1] J. Yang, T. Caillat, Thermoelectric Materials for Space and Automotive Power Generation, MRS Bull. 31 (3) (2006) 224–229, https://doi.org/10.1557/mrs2006.49.

[2] C. Kriso, F. Triozon, C. Delerue, L. Schneider, F. Abbate, E. Nolot, D. Rideau, Y.-M. Niquet, G. Mugny, C. Tavernier, Modeled optical properties of SiGe and Si layers compared to spectroscopic ellipsometry measurements, Solid-State Electron. 129 (2017) 93–96, https://doi.org/10.1016/j.sse.2016.12.011.

[3] R. Xu, W. Li, J. He, Y. Sun, Y.-D. Jiang, Boron-doped nanocrystalline silicon germanium thin films for uncooled infrared bolometer applications, Infrared Phys. Technol. 58 (2013) 32–35, https://doi.org/10.1016/j.infrared.2013.01.005.

[4] J. Lu, R. Guo, W. Dai, B. Huang, Enhanced in-plane thermoelectric figure of merit in p-type SiGe thin films by nanograin boundaries, Nanoscale 7 (16) (2015) 7331–7339, https://doi.org/10.1039/C5NR00181A.

[5] T. Mizoguchi, T. Imajo, J. Chen, T. Sekiguchi, T. Suemasu, K. Toko, Composition dependent properties of p- and n-type polycrystalline group-IV alloy thin films, 161306-1–161306-6, J. Alloy. Compd. 887 (2021), https://doi.org/10.1016/j.jallcom.2021.161306.

[6] A. Hamdoh, T. Kaneko, M. Isomura, Formation of crystalline silicon-germanium thin films on silicon substrates by solid phase crystallization, Thin Solid Films 645 (2018) 203–208, https://doi.org/10.1016/j.tsf.2017.10.002.

[7] K. Toko, K. Kusano, M. Nakata, T. Suemasu, Low temperature synthesis of highly oriented p-type $Si_{1-x}Ge_x$ (x: 0–1) on an insulator by Al-induced layer exchange, 155305-1–155305-5, J. Appl. Phys. 122 (2017), https://doi.org/10.1063/1.4996373.

[8] M. Wu, G. Vanhoutte, N.R. Brooks, K. Binnemans, J. Fransaer, Electrodeposition of germanium at elevated temperatures and pressures from ionic liquids, PCCP 17 (2015) 12080–12089, https://doi.org/10.1039/C4CP06076H.

[9] J. Gu, S.M. Collins, A.I. Carim, X. Hao, B.M. Bartlett, S. Maldonado, Template-Free Preparation of Crystalline Ge Nanowire Film Electrodes via an Electrochemical Liquid–Liquid–Solid Process in Water at Ambient Pressure and Temperature for Energy Storage, Nano Lett. 12 (9) (2012) 4617–4623, https://doi.org/10.1021/nl301912f.

[10] V. Schmidt, U. Gösele, How Nanowires Grow, Science 316 (2007) 698–699, https://doi.org/10.1126/science.1142951.

[11] V.A. Volodin, M.D. Efremov, A.S. Deryabin, L.V. Sokolov, Determination of the Composition and Stresses in $Ge_xSi_{(1-x)}$ Heterostructures from Raman Spectroscopy Data: Refinement of Model Parameters, Semiconductors 40 (2006) 1314–1320, https://doi.org/10.1134/s106378260611011x.

[12] H.H. Silvestri, H. Bracht, J.L. Hansen, A.N. Larsen, E.E. Haller, Diffusion of silicon in crystalline germanium, Semicond. Sci. Technol. 21 (6) (2006) 758–762, https://doi.org/10.1088/0268-1242/21/6/008.

[13] J. Räisänen, J. Hirvonen, A. Anttila, The diffusion of silicon in germanium, Solid-State Electron. 24 (1981) 333–336, https://doi.org/10.1016/0038-1101(81)90027-7.

[14] R.W. Olesinski, G.J. Abbaschian, The Ge–Si (Germanium-Silicon) system, Bulletin of Alloy Phase Diagrams 5 (1984) 180–183, https://doi.org/10.1007/bf02868957.

[15] D.G. Gromov, S.A. Gavrilov, Manifestation of the heterogeneous mechanism upon melting of low-dimensional systems, Phys. Solid State 51 (2009) 2135–2144, https://doi.org/10.1134/S1063783409100242.

[16] M. Wautelet, J.P. Dauchot, M. Hecq, Phase diagrams of small particles of binary systems: a theoretical approach, Nanotechnology 11 (2000) 6–9, https://doi.org/10.1088/0957-4484/11/1/302.