Investigation of the phase formation from Ni-modified nanostructured silicon

O V Volovlikova, Y I Shilyaeva*, A Y Berezkina, D I Smirnov and S A Gavrilov
National Research University of Electronic Technology - MIET, 1 Shokin Square, Zelenograd, Moscow, 124498, Russia

*shyliaeva@gmail.com

Abstract. The phase formation behavior during the thermally induced solid-state reaction of the Ni-modified nanostructured Si has been investigated using a combination of differential scanning calorimetry and x-ray diffraction analysis. The effect of nanostructured interface on the silicides formation temperatures is discussed. Special attention is paid to the methodical aspects of the characterization of the thermal behavior of the Ni-modified nanostructured Si. The role of the thermal instability of nanostructured Si in the calorimetric studies of the silicides formation is also reviewed.

1. Introduction
Transition metal silicides are widely used as metal contact materials for multilayer metallization in modern silicon microelectronics. As the trend of device-miniaturization continues, the nanostructured silicides come into use in different applications such as field emitters, nanoscale interconnects, biomedical cell separation systems, as high-performance catalysts and others [1-3]. A preferred use of Ni silicides is explained by several reasons, in particular, relatively low formation temperatures, low specific resistivity and a small amount of silicon consumed during silicidation.

The formation process of the nickel silicide by solid-state interaction usually involves applying metal coating to the silicon surface using various techniques (evaporation, sputtering, and electrochemical deposition) and subsequent heat treatment. Mechanism of silicide growth during solid-state interaction have been fairly well studied for thin-film systems. Studies [4-6] devoted to questions of phase identification, stability and formation sequence during the solid-state reaction at the metal/Si interface. The influence of nature of alloy components and impurities on silicidation mechanism is discussed in [7]. Formation of Mn, Fe and Co silicides in thin-film systems are reviewed in [8-10], etc.

The key challenge in this research area is to reduce the temperature of silicide formation. Realization of solid-state synthesis in nanoscale is a promising solution that could significantly reduce the silicide formation temperature. However, as is known according to classical thermodynamic concepts, the role of the Si/metal interface increases in the case of nanostructured systems. In this regard, changes in thermal behavior can be observed. In particular, the temperature characteristics of silicidation processes, stability of phases and the phase formation sequence during solid-state reaction can change. The use of nanostructured Si as templates (matrices) for the synthesis of Si/metal nanocomposites allows to vary the geometric parameters of structures and opens new possibilities for
studying the silicide formation processes. In addition, in this case, nanostructured Si is an active matrix directly involved in the solid-state interaction.

In this work, the phase formation behavior during the thermally induced solid-state reaction of the Ni-modified nanostructured Si has been investigated using a combination of differential scanning calorimetry and x-ray diffraction analysis. The effect of nanostructured interface on the silicides formation temperatures is discussed. Special attention is paid to the methodical aspects of the characterization of the thermal behavior of the Ni-modified nanostructured Si. The role of the thermal instability of nanostructured Si in the calorimetric studies of the silicides formation is also reviewed.

2. Experimental details

2.1. Sample preparation

Single crystal silicon wafers (n-type) of (111) orientation and 0.001 Ω⋅cm resistivity were used for fabricating Si/Ni samples. Si wafers were pre-treated consistently in a mixture of H₂SO₄ and H₂O₂ (1:1) and HF:H₂O (1:4), rinsed with deionized water and isopropyl alcohol.

Figure 1 shows the flowchart of the fabrication of membrane-based and thinned substrate-supported Si/Ni samples. Nanostructured porous Si layers were prepared by electrochemical anodizing [11] of pre-treated Si wafers in a polytetrafluoroethylene (PTFE) cell in a mixture of HF and CH₃COOH (7:4) in the galvanostatic mode, the cathode material – Pt. The current density was 15 mA/cm² and the anodizing time – 2 hours. In order to obtain Si membrane the separation of the porous Si layer was performed by gradually increasing the current density of the anodizing by 10-15 mA/cm² every 3-5 min. The maximum current density at detachment was 62.2 mA/cm². The conductive Ni layer on the backside of Si membranes was applied by deposition of a 200 nm thick Ni layer using magnetron sputtering. Thinned Si substrates after membrane detachment were reused to form substrate-supported nanostructured porous Si layers (Figure 1).

Figure 1. Schema of the fabrication of membrane-based and thinned substrate-supported Si/Ni samples.

Si membranes with conductive layer and substrate-supported nanostructured porous Si were subjected to Ni electrodeposition after etching a possible thin native oxide layer for 10 s in diluted HF solution. Cathodic Ni deposition was carried out from an aqueous solution containing 213 g/l NiSO₄·7H₂O, 25 g/l NiCl₂·6H₂O, 25 g/l H₃BO₃ and 3 g/l of saccharin (pH = 2 – 3). The current density was 3.5 mA/cm². Ni was used as the anode. The deposition time was about 2 hours.

2.2. Structural characterization

The structure of the samples was characterized by means of x-ray diffraction analysis (XRD). Measurements were carried out using the "RIKOR-8" x-ray measuring system ("IRO", Moscow, Russia). Samples were studied in the 2θ scan mode with a wavelength λ(CuKα) = 1,541 Å using Bragg–Brentano focusing. A Ni filter was used for the Kβ-line stripping, scanning time of 800 s in a point. The investigation of the samples’ morphology was carried out by means of scanning electron microscope (SEM), JEOL JSM-6010PLUS/LA.
2.3. Differential scanning calorimetry

The investigation of the thermal behaviour of samples was carried out using the precalibrated differential scanning calorimeter Netzsch DSC 204 F1 Phoenix (Netzsch-Geratebau GmbH, Germany). The heating of the samples of 10 – 15 mg was conducted in press-fitted aluminium crucibles in an argon atmosphere with four different heating rates (5, 10, 20, and 30 °C/min). The lid of the crucible was punched before sealing. Empty aluminium crucible was used as a reference. A sample fragment was cut in the shape of a disc and placed on the bottom of the crucible, then pressed with the lid with the upturned convex side down to provide good contact between the material and the bottom of the crucible.

3. Results and discussion

From the point of view of calorimetric investigations, it is important to limit the influence of the substrate on the DSC signal. For this purpose, membrane-based and thinned substrate-supported Si/Ni samples were prepared for DSC analysis. Porous Si layer prepared according to the procedure described in [11] has nanometer-sized pores and when coated with Ni it allows to fabricate a nanostructured Si/Ni interface. The results of electron microscopy (Figure 2) reveal that the thickness of nanostructured porous Si layer was of the order of 80 μm. A SEM images of the membrane-based Si/Ni sample illustrate a dense Ni film on the surface of nanostructured porous Si layer.

![Figure 2. SEM image of membrane-based Si/Ni samples: (a) cross-section and (b) top view.](image)

Also, it is important to distinguish which effects relate to the Si/Ni composite structure as a whole and which are due to the nature of their components taken separately. It is therefore necessary to have reliable information about the thermal behavior of the nanostructured porous Si layer. It is known that porous silicon is unstable during heat treatment and is prone to oxidation. Figure 3a shows the DSC scans of Si membrane. During the first heating up to 500 °C, two thermal effects are observed that are not reproducible upon cooling and reheating. Weakly expressed endothermic effect displayed at 80 – 110 °C is caused by loss of residual water and alcohol used in the fabrication process. This is evidenced by the fact that the loss of the samples’ weight after the first heating was 1 – 3%.

In the range of 250 – 400 °C, the exothermic effect of a complex shape is observed, presumably because of the low-temperature oxidation (preoxidation) [12] in an atmosphere of non-dehydrated argon. This effect is also weakly expressed due to a small amount of oxidizing agents in the purge gas and is observed only at relatively high heating rates (30 °C/min).

Figure 3b presents DSC signal of Si membrane with 200 nm thick conductive Ni layer deposited using magnetron sputtering. In the range of 80 – 110 °C, the distinctive nonlinearity of the DSC signal is observed, because of loss of residual water and alcohol. The exothermic bend of the DSC curve in the range of 150 – 450 °C can be explained by the low-temperature oxidation of Si membrane and by
the solid-state reaction between Si membrane and conductive Ni layer. This fact should be taken into account when analyzing membrane-based Si/Ni samples.

Figure 3. DSC scans of as-prepared Si membrane (a) and Si membrane with conductive Ni layer (b).

Figure 4 presents DSC curves, showing similar behavior of the membrane-based and thinned substrate-supported Si/Ni samples at the specified temperature range. In the range of 80 – 110 °C, the distinctive nonlinearity of the DSC signal is observed, because of loss of residual water and alcohol. Also, in both cases the exothermic effect is observed in the range of 200 – 300 °C non-reproducible upon cooling and reheating. Evidently, this exo-effect relates to the Si/Ni nanocomposite structure as a whole.

Figure 4. DSC scans of the membrane-based (a) and thinned substrate-supported (b) Si/Ni samples.

Combining both XRD (Figure 5) and DSC measurements it was established that this effect is caused by solid-state interaction at the nanostructured Si/Ni interface. According to the data obtained earlier, Ni$_3$Si and NiSi reflections appears on XRD spectra after heat treatment at 200 °C [13]. After heat treatment at 500 °C, XRD shows the presence of Ni and NiSi phase. It is also necessary to note, that exo-effect is more clear and intensive in the case of Si/Ni sample on thinned Si substrate, while the DSC signal of membrane-based Si/Ni sample has a complicated shape presumably due to a contribute of reaction between Si membrane and Ni conductive layer.
Figure 5. X-ray diffractograms of thinned substrate-supported Si/Ni samples before (a) and after (b) heating up to 500 °C.

Endothermic effect on the DSC curve of the thinned substrate-supported Si/Ni sample can be caused by the loss of surface hydrogen from porous silicon. [14].

Figure 6a exemplifies the DSC curves of the thinned substrate-supported Si/Ni samples corresponding to different heating rates. As it follows from the data in this figure, the extrapolated peak onset temperature ($T_{\text{onset}}$) of the solid-state reaction at the nanostructured Si/Ni interface decreased with decreasing heating rate.

Figure 6. Set of DSC curves of the thinned substrate-supported Si/Ni samples for different heating rates (a) and (b) observed values of $T_{\text{onset}}$ as a function of heating rate.

The true temperature of the solid-state reaction at the nanostructured Si/Ni interface estimated by the extrapolation of observed values of $T_{\text{onset}}$ to zero heating rate (Figure 6b) is 188.7 °C. This temperature is lower than that for similar thin-film systems [15] and is much lower than the equilibrium temperatures of the formation of silicide phases on the Ni-Si phase diagram [16].

4. Conclusions
In our work, the membrane-based and thinned substrate-supported Si/Ni samples with nanostructured interface have been electrochemically prepared and investigated using a combination of DSC and XRD analysis. DSC analysis in combination with XRD reveal that the thermal behavior of Ni-modified nanostructured Si is caused both by instability of nanostructured Si during heating and solid-state interaction at the nanostructured Si/Ni interface. The estimated true temperature of the solid-state
reaction at the nanostructured Si/Ni interface (188.7 °C) is lower than that for similar thin-film systems and is much lower than the equilibrium temperatures of the silicides formation on the Ni-Si phase diagram. It was experimentally shown, that the atmosphere as well as presence of secondary components (such as metal conductive layer) contribute to the DSC signal and this fact should be taken into account when analyzing nanostructured Si-based systems.

**Acknowledgment**
The reported study was funded by RFBR according to the research project No. 16-33-00712 мол.а.

**References**

[1] Lin J-Y, Hsu H-M and Lu K-C 2015 Cryst. Eng. Comm. 17 1911–6
[2] Kim D-J, Seol J-K, Lee M-R, Hyung J-H, Kim G-S, Ohgai T and Lee S-K 2012 Appl. Phys. Lett. 100 163703
[3] Zhao A, Zhang X, Chen X, Guan J and Liang C 2010 J. Phys. Chem. 114 3962–7
[4] Beyers R and Sinclair R 1985 J. Appl. Phys. 57 5240–5
[5] Gromov D G, Mochalov A I, Pugachevich V P, Sorokin I N 2000 Appl. Phys. A 70 333–40
[6] Baglin J E, d’Heurle F M, Petersson C S 1980 Appl. Phys. Lett. 36 594–6
[7] Mangelinck D, Hoummada K, Panciera F, Kousseifi M E, Blum I, Descoings M, Bertoglio M, Portavoce A, Perrin C and Putero M 2014 Phys. Status Solidi A 211 152–65
[8] Gomoyunova M V, Malygin D E, Pronin I I 2006 Phys. Solid State 48 2016-20
[9] Varnakov S N, Zabluda V N, Ovchinnikov S G, Gomoyunova M V, Grebenyuk G S, Pronin I I 2014 Phys. Solid State 56 812-5
[10] Gomoyunova M V, Grebenyuk G S, Pronin I I 2014 Tech. Phys.: The Russian Journal of Applied Physics 59 1492-8
[11] Solanki C S, Bilyalov R R, Poortmans J, Celis J P, Nijs J and Mertens R 2004 J. Electrochem. Soc. 151 C307-14
[12] Herino R, Perio A, Barla K and Bomchil G 1984 Materials Lett. 2 519–23
[13] Shilyaeva Y I, Pyatilova O V, Berezkina A Y, Sysa A V, Dudin A A, Smirnov D I and Gavrilo S A 2016 Proc. SPIE. 10224, Int. Conf. on Micro- and Nano-Electronics 102240E
[14] Bomchil G, Halimaoui A and Herino R 1988 Microelectron. eng. 8 293-310
[15] Liew K P, Li Y, Yeadon M, Bernstein R, Thompson C V 2003 Adv. Mater. for Micro- and Nano-Systems 2003-01
[16] Lyakishev N P 1996 Phase Diagrams of Binary Metallic Systems: reference book in 3 vol. (Moscow: Mashinostroenie) 1 89-90