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► **To cite this version:**

A. Laszcz, J. Ratajczak, A. Czerwinski, J. Katcki, V. Srot, et al.. Transmission electron microscopy study of the platinum germanide formation process in the Ge/Pt/SiO₂/Si structure. *Materials Science and Engineering: B*, 2008, 154-155, pp.175-178. 10.1016/j.mseb.2008.10.002 . hal-00356977

HAL Id: hal-00356977

<https://hal.science/hal-00356977v1>

Submitted on 26 Sep 2024

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Transmission electron microscopy study of the platinum germanide formation process in the Ge/Pt/Ge/SiO₂/Si structure

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A B S T R A C T

The mechanisms of the platinum germanide formation by RTA processes in the Ge/Pt/Ge/SiO₂/Si structure in the temperature range from 200 °C to 600 °C were investigated by means of transmission electron microscopy (TEM) techniques. The studies were focused on the observations of the layer microstructure and of Ge/Pt/Ge interfaces at an atomic scale by high resolution TEM (HRTEM), as well as on the identification of formed phases using analytical TEM and diffraction techniques. The formation of platinum germanides in the Ge/Pt/Ge/SiO₂/Si structure is visible at 200 °C. However, at this temperature only a part of Ge reacted with the whole Pt during annealing. The whole Ge layer reacted with the Pt layer at 300 °C. The formed Pt–Ge layer is not a mono-layer but consists of two platinum germanides layers. The results of the annealing of Ge/Pt/Ge/SiO₂/Si structure at higher temperatures are very similar to the results obtained at 300 °C. Various Pt–Ge phases have been found in the samples studied. The PtGe phase in the germanide layer of the sample annealed at 200 °C was found by means of TEM diffraction analysis and the energy-dispersive X-ray spectroscopy (EDXS) in scanning TEM. At 300 °C the diffraction pattern reveals the reflections corresponding to PtGe and Pt₂Ge₃ phases. Analytical TEM studies showed that the phase composition depends on annealing temperature and that the Ge content in the Pt–Ge phases increases with temperature.

Keywords:

Transmission electron microscopy (TEM)

EDX spectroscopy

TEM diffraction

Platinum germanides

1. Introduction

Platinum silicide is a very attractive material as a band-edge source/drain for *p*-type metal-oxide-semiconductor field-effect transistors (MOSFET) [1]. Platinum silicide is formed at relatively low temperatures and reduces the consumption of silicon during the silicidation process. However, during the silicidation of platinum, not entire metal layer is transformed into silicide. The excessive Pt should be removed, without affecting the already formed silicide. Since the only existing selective etchant – aqua regia – etches also silicide, an alternative solution has been proposed. This solution consists in the transformation of the excessive Pt into more reactive Pt–Ge phases, which are easily etched in a sulfuric peroxide mixture [2]. Hence, the mechanisms of the platinum germanide formation in the Ge/Pt/Ge/SiO₂/Si structure are studied in this paper. Metal-germanides can be formed

very easily by the solid-state reaction at the metal/Ge interface in a similar mechanism of the formation as metal-silicides [3–5].

2. Experimental

Platinum (20 nm) and germanium (45 nm) layers were deposited consecutively by e-gun evaporation, on the so-called pseudo-Ge substrate (3 nm thick Ge layer) laying on SiO₂/silicon substrate. Platinum germanide was formed by solid-state reaction between Ge and Pt layers during RTA process for 5 min at one temperature within a range of temperatures from 200 °C to 600 °C. For the investigation of the mechanisms of the platinum germanide formation in the Ge/Pt/Ge/SiO₂/Si structure the transmission electron microscopy (TEM) specimens were prepared by the conventional cross-section method using low-temperature argon ion milling process. The studies were focused on the observations of the layer microstructure by TEM (JEM-200CX) and of Ge/Pt/Ge interfaces at an atomic scale by HRTEM (JEOL-4000FX), as well as on the identification of formed phases using a scanning TEM (STEM –

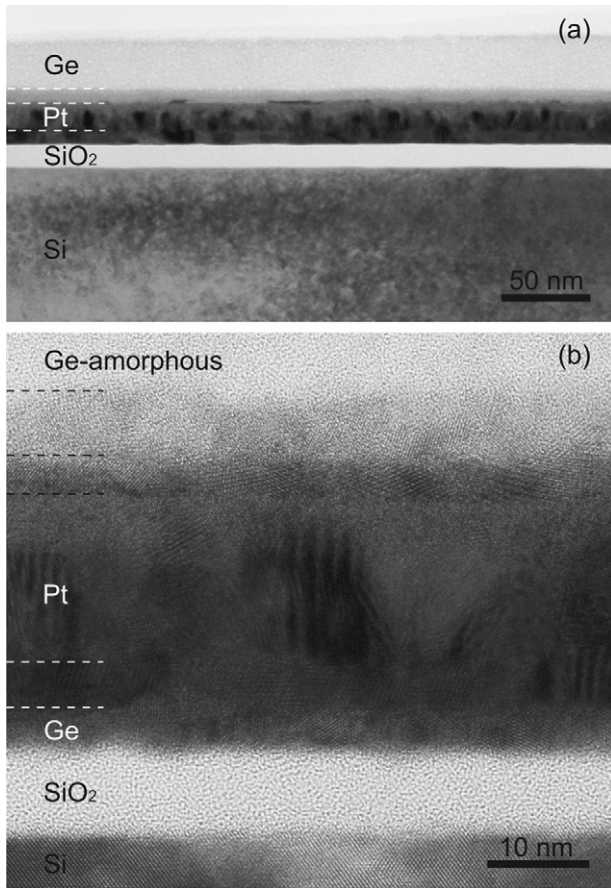


Fig. 1. TEM (a) and HRTEM (b) images of as-deposited Ge/Pt/Ge/SiO₂/Si structure.

VG HB-501UX) and selected area electron diffraction (SAED) technique.

3. Results and discussion

The TEM micrographs (both TEM and HRTEM) of as-deposited Ge/Pt/Ge/SiO₂/Si structure are shown in Fig. 1. The HRTEM image reveals that the atoms of Ge and Pt layers react already during deposition, forming several thin layers at their interfaces (marked by dashed lines in Fig. 1b). Two crystalline Ge layers (about 6 nm and 4 nm thick) with a small concentration of Pt atoms are formed at the upper interface. We expect that the Ge layer located close to the Pt layer contains more Pt atoms than the upper Ge layer. Also, an about 4 nm thick Pt layer with a small concentration of Ge is formed between the deposited Pt layer and the so-called pseudo-Ge substrate laying on SiO₂. The fact that the measured thickness of so-called pseudo-Ge substrate reaches about 4 nm (while part of Ge atoms migrated to the intermediate layer), can be explained by the fact that either this deposited layer was thicker than its desired thickness (3 nm) or this layer also contains Pt atoms, which migrated into this layer during deposition.

During annealing of the Ge/Pt/Ge/SiO₂/Si structure at 200 °C the whole Pt layer reacted with a part of the Ge layer. As a result, an about 35–40 nm thick crystalline platinum germanide layer is formed directly on the oxide (Fig. 2a). The grains in this layer have various shapes. The rest of the unreacted Ge layer (about 10–15 nm thick) is visible at the top of the structure. During annealing at 300 °C the whole Ge reacted with Pt, forming platinum germanide layer consisting of two phases in the form of continuous layers: an upper (thicker) Pt_xGe_y(1) phase and a very thin second Pt_xGe_y(2)

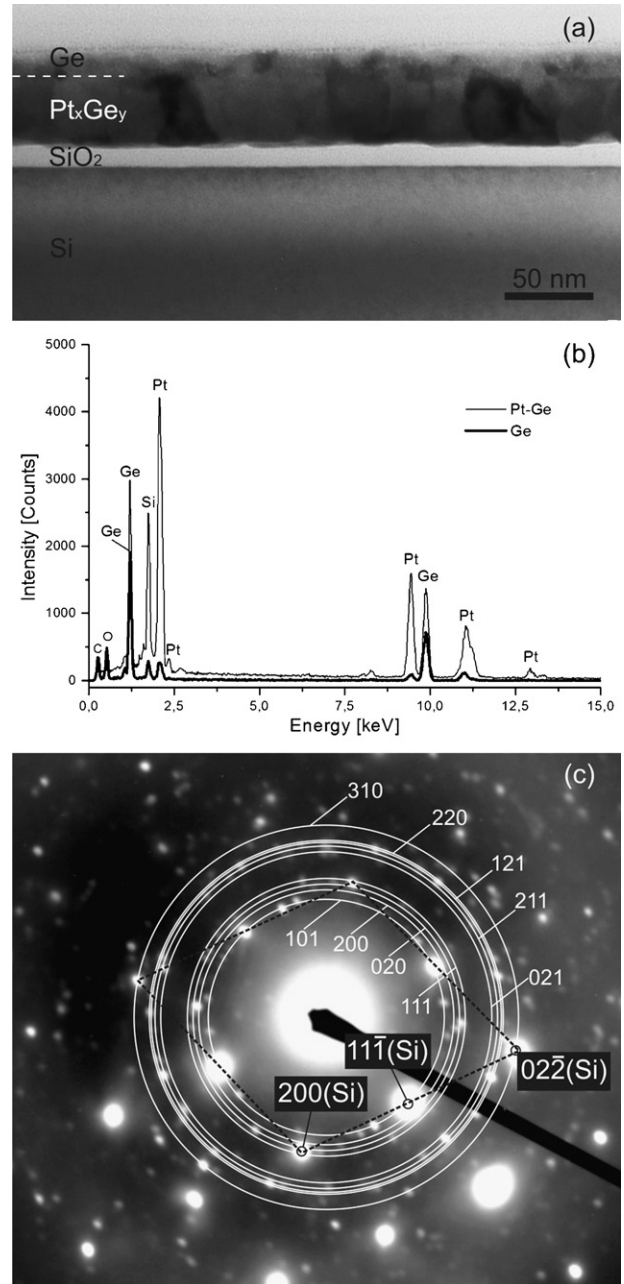


Fig. 2. Ge/Pt/Ge/SiO₂/Si structure annealed at 200 °C: (a) TEM image of cross-sectional specimen, (b) EDX spectra obtained from Ge and Pt_xGe_y layer, and (c) diffraction pattern of the structure. [0 1 1]-orientated Si reflections and poly-rings of the PtGe phase are marked in the diffraction pattern. The presence of the Si peak in the Pt–Ge spectrum results from the silicon contamination of the platinum germanide layer caused by the ion milling process. Due to the fact that the SiO₂ layer is relatively thin, most of the sputtered material comes from Si substrate. The appearance of C and O peaks in the Ge spectrum result from the contamination and oxidation of the Ge top surface.

phase located directly on the oxide (Fig. 3a). HRTEM image reveals a difference in lattice parameters of these phases, and an indistinct and very rough interface between them (Fig. 3b). The results of the annealing of the structure at 400 °C and 500 °C are very similar to the results obtained at 300 °C. The thicker upper layer consists of large columnar grains and the layer below is composed of elongated grains (Fig. 4a and b). The top surface of the thicker Pt_xGe_y(1) layer formed at higher temperature (500 °C) is more irregular than the one obtained at 400 °C, and the one formed at 600 °C is very

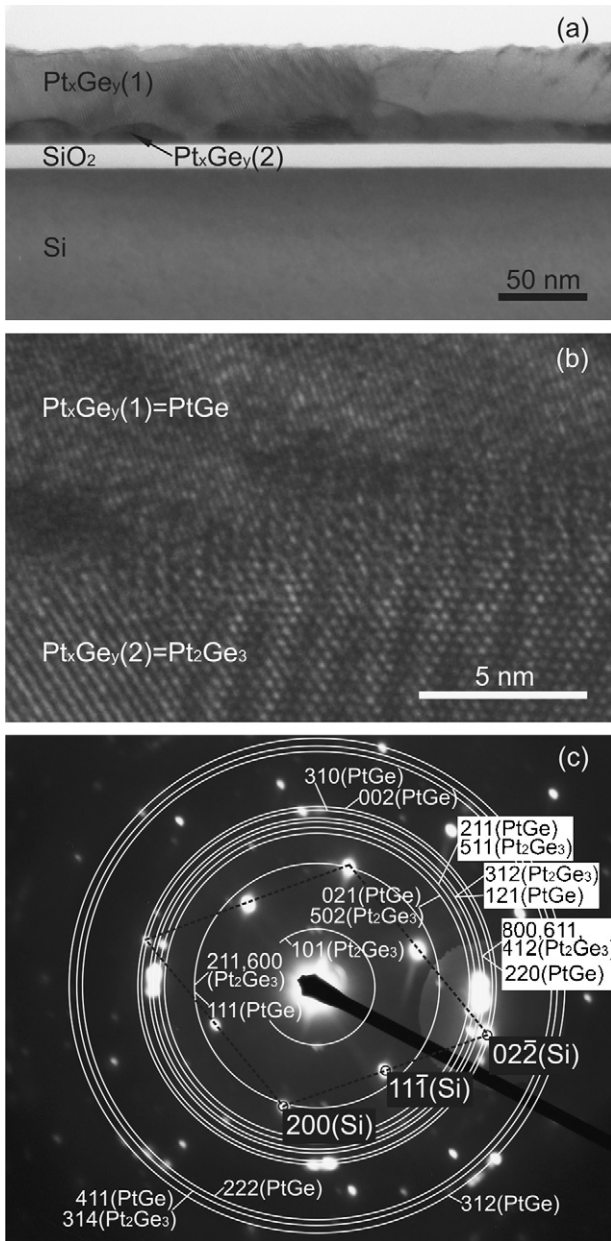


Fig. 3. Ge/Pt/Ge/SiO₂/Si structure annealed at 300 °C: (a) TEM image of cross-sectional specimen, (b) HRTEM image of the Pt_xGe_y(1)/Pt_xGe_y(2) interface and (c) diffraction pattern of the structure. [0 1 1]-orientated Si reflections and poly-rings of PtGe and Pt₂Ge₃ phases are visible in the diffraction pattern.

irregular. Even for 600 °C elongated grains of the thinner Pt_xGe_y(2) phase are still observed, but they already do not form a continuous layer (Fig. 4c).

EDXS experiments and SAED technique were used for the identification of Pt-Ge phases. They were identified by energy-dispersive X-ray spectroscopy (EDXS) in a scanning TEM (STEM, with the electron beam size about 0.7 nm – full width at half maximum) as corresponding to PtGe and Pt₃Ge₂ at 200 °C (Fig. 2b). The results obtained from the remaining Ge layer show that this layer is not pure but contains up to 11% of Pt atoms (Fig. 2b). Probably, it results from a sputtering of the materials during ion milling. Analysis of the diffraction pattern shows that the product of the annealing at 200 °C gives poly-rings corresponding only to the PtGe phase (Fig. 2c), which crystallographic structure is described in [6], while for 300 °C the reflections correspond to both PtGe and Pt₂Ge₃ (Fig. 3c), which

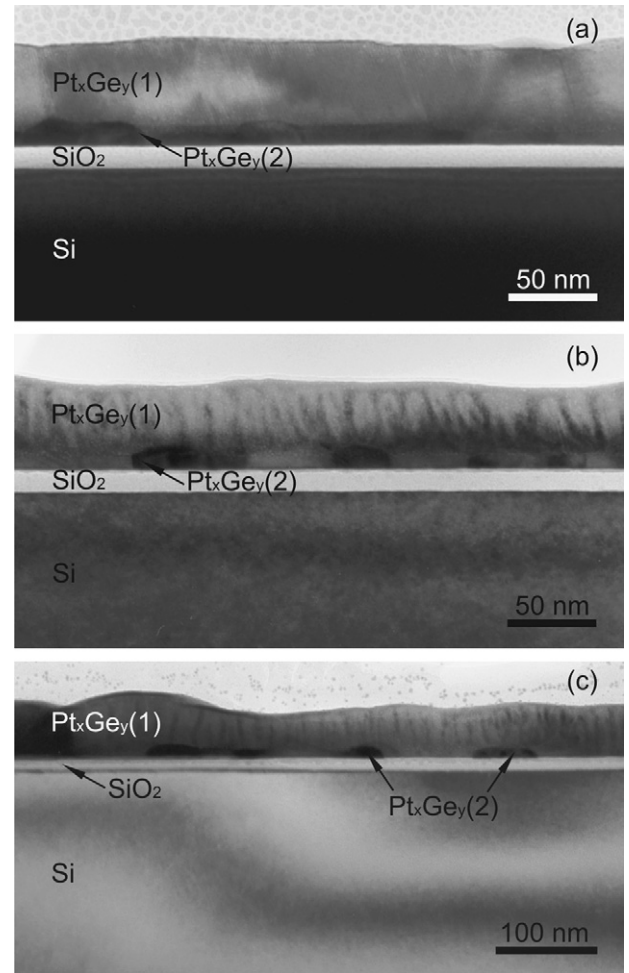


Fig. 4. TEM images of cross-sectional Ge/Pt/Ge/SiO₂/Si specimen annealed at: (a) 400 °C, (b) 500 °C and (c) 600 °C.

structure is described in [7]. The EDXS measurements are susceptible to the sample preparation. Atoms sputtered during ion milling contaminate the specimen as an amorphous phase. However, the SAED pattern reveals the crystal structure of phases, and therefore this method is less sensitive to such contamination. Oppositely, EDXS measurements show only the content of atoms and do not differentiate between crystalline and amorphous phases, therefore they are less reliable in the case of such contamination. Because the diffraction pattern does not confirm the presence of Pt₃Ge₂, therefore this presence seems dubious and probably only PtGe phase exists in the sample annealed at 200 °C.

It was mentioned above that at 200 °C, only a part of Ge reacted with the whole Pt during annealing, while the whole Ge layer reacted with the Pt layer at 300 °C. Fig. 3a shows that the Pt-Ge layer consists of two platinum germanides layers, which contain more Ge than the phases formed at 200 °C. The very thin Pt_xGe_y(2) phase located directly on the oxide, with the composition different from that of the dominant upper Pt_xGe_y(1) phase, probably results from deposition on the pseudo-Ge substrate. Such a clearly distinguished second germanide layer laying on the oxide is not observed in TEM image for 200 °C.

When the 30 nm thick Pt layer is deposited directly on the Ge (001) substrate, so that an unlimited amount of Ge atoms is supplied to the reaction by diffusion from the substrate during annealing, then the composition of Pt-Ge phases depends on the annealing temperature [8]. The Ge content in these phases

increases then with temperature, from PtGe at 300 °C and Pt₂Ge₃ at 400 °C to PtGe₂ at 500 °C. However, in the case of a limited amount of Ge, three different systems are listed in [5]: (1) a PtGe mono-layer structure, (2) a double-layer structure consisting of Pt₂Ge and Pt₃Ge phases, or (3) a double-layer composed only of the Pt₃Ge phase, as found for the 500–600 °C temperature range and thicknesses of Ge and Pt in the ranges from 19 to 43.7 nm and from 14.8 to 39 nm, respectively. In such a case the phase composition depends on the thickness ratio of Pt and Ge layers before annealing.

The structures studied in this paper were also examined by means of XRD grazing angle analysis [2]. It showed that the sample annealed at the 200 °C was composed of the PtGe phase. For 300 °C the Pt₂Ge₃ phase also appeared. The presence of two phases (the dominant upper PtGe phase and the thin bottom Pt₂Ge₃ phase) at 300 °C and 400 °C was confirmed by TEM images and TEM diffraction. The XRD results for samples annealed above 400 °C show the existence of only Pt₂Ge₃. However, our TEM images reveal two different phases still existing at 500 °C and 600 °C, although at 600 °C the thinner bottom phase in certain areas is consumed by the dominant upper phase.

4. Conclusions

The mechanisms of the platinum germanide formation by RTA processes in the Ge/Pt/Ge/SiO₂/Si structure at 200–600 °C range were investigated by means of different TEM techniques. During annealing of the structure at 200 °C the whole Pt layer has reacted with a part of the Ge layer. When the structure was annealed at 300 °C, then the whole Ge reacted with Pt. The application of so-called pseudo-Ge substrate laying on SiO₂ before deposition of Pt

layer caused the formation of double-layered structure of the germanide. The analytical TEM studies showed that the composition of Pt–Ge phases depends on annealing temperature with the Ge content increasing with temperature. TEM images showed that the results of annealing of the structure in the 300–500 °C range are very similar and stable, while annealing above 500 °C unfavorably influences its top surface.

Acknowledgements

This publication is based on the research partly supported by the European Commission under the projects: “Metallic Source/Drain Architecture for Advanced MOS Technology” (IST-016677 METAMOS). Support from the European Union under the Sixth Framework Programme under the contract for an Integrated Infrastructure Initiative, Reference 026019 ESTEEM, Transnational Access (TA7) to MPI-MF is gratefully acknowledged.

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