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Mg_2Si synthesis on silicon crystals with different aspect ratio

E.Yu. Subbotin[1]✉, A.G. Kozlov[2], D.L. Goroshko[1],
I.M. Chernev[1], D.A. Khoroshilov [1], O.E. Lisenkov [1],
A.Yu. Zhizhchenko[1], S.A. Kitan'[1], N.G.Galkin[1]

[1] Institute of Automation and Control Processes FEB RAS, Vladivostok, Russia;

[2] Far Eastern Federal University, Vladivostok, Russia

✉ jons712@mail.ru

Abstract. In the paper synthesis of magnesium silicide (Mg_2Si) features on silicon crystal with different aspect ratio were observed. These crystals were etched from monocrystalline borondoped silicon wafers with (100) orientation by metal-assisted chemical etching. The synthesis was occurred in ultra-high vacuum condition by a solid phase epitaxy and the modified reactive epitaxy with ultrafast Mg deposition. The substrate temperature range in both methods was 340—390 °C. As result co-axial core-shell Si/Mg_2Si heterostructures with magnesium silicide thickness 500—1200 nm were produced.

Keywords: silicon, magnesium silicide, Mg_2Si, epitaxy, metal-assisted chemical etching, MACE, Raman, SEM

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Синтез Mg_2Si на кремниевых кристаллах с различным аспектным соотношением

Е.Ю. Субботин[1]✉, А.Г. Козлов[2], Д.Л. Горошко[1],
И.М. Чернев[1], Д.А. Хорошилов[1], О.Е. Лисенков[1],
А.Ю. Жижченко[1], С.А. Китань[1], Н.Г. Галкин[1]

[1] Институт автоматики и процессов управления ДВО РАН, г. Владивосток, Россия;

[2] Дальневосточный федеральный университет, г. Владивосток, Россия

✉ jons712@mail.ru

Аннотация. В данной работе были рассмотрены особенности синтеза силицида магния (Mg_2Si) на кремниевых кристаллах с различным аспектным соотношением. Получение кристаллов кремния с различным сечением осуществлялось методом металлстимулированного химического травления кремниевых монокристаллических подложек, легированных бором, с ориентацией (100). Синтез осуществлялся в условиях сверхвысокого вакуума методами модифицированной реактивной эпитаксией со сверхбыстрым осаждением магния и твердофазной эпитаксией. Температура формирования лежала в пределах 390—340 °С. В результате получились коаксиальные гетероструктуры типа «ядро-оболочка» Si/Mg_2Si с толщиной покрытия Mg_2Si 500—1200 нм в зависимости от метода формирования.

Ключевые слова: кремний, силицид магния, Mg_2Si, эпитаксия, металлстимулированное химическое травление, МСХТ, Raman, СЭМ, эпитаксия

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Introduction

Recently research and development of micrometer-size thermoelectric devices (μ-TED) were in a focus of many science groups [1, 2]. The important feature of such devices is high surface density of thermocouples (> 10^6 cm^{-2}) [3] that allows to generate relatively high output voltage at low temperature gradient (less than 10 K) and to work with fast cooling response. Such devices can be used for power supplying wearable electronic, wireless sensors and Internet of Things.

Such high-density arrays of semiconductor crystals with controllable lateral size, length and surface density can be produced by metal-assisted chemical etching (MACE) combined with high-resolution lithography [4]. As a thermoelectrical material magnesium silicide (Mg_2Si) was chosen due to it perspective thermoelectric performance [5], Mg and Si are ecology-friendly and relatively cheap elements and Mg_2Si is well-developed and matured in thermoelectrical terms [6, 7]. The research of core-shell heterostructures based on silicon and magnesium silicide is interesting also for solar energy [8] and infra-red photodetectors [9].

Materials and methods

Applying the mask was occurred by a high-resolution electron lithography on scanning electron microscope (SEM) ThermoFisher Scios 2 DualBeam. Taking SEM images and energy dispersive X-ray spectroscopy (EDX) analysis were occurred by this microscope. The mask is stripes with 1 – 2 μm thickness separated for 1 – 5 μm to each other. A 30 nm gold film with 1.5 – 3 nm adhesive titanium film were used as a catalytic layer. The deposition of Ti/Au films was occurred by electron beam sputtering with pretreatment surface by Ar^+ ions. The metal-assisted chemical etching was used for etching silicon substrates and producing silicon crystals with different aspect ratio. The solution consists 4.6 M HF (40%) and 0.23 or 0.44 M H_2O_2 (31%). Substrates are boron-doped monocrystalline silicon with (100) orientation and resistivity 1–10 Ω×cm. SEM and atomic force microscope NT-MDT Solver P47 were used for control of etching process.

The growth of Mg_2Si on the etched silicon was occurred in ultrahigh vacuum (UHV) chamber with basic pressure 2×10^{-9} Torr. Before loading in the chamber samples were pre-cleaned in Piranha solution, rinsed is deionized water, ethyl alcohol and dried. Then samples were annealed at 650 °C for 10 hours for degassing and remove oxide at 950 C for 40 minutes (high aspect ratio structures) or at 1160 °C during 5 minutes (for low aspect ratio structures). As a magnesium source was used tantalum tube with Mg pillars 5N purity. Work features of Mg source for reactive epitaxy with ultrafast Mg deposition described in [10, 11]. Mg flow was calibrated by quartz microbalance. Mg_2Si was synthesized by solid phase epitaxy and reactive epitaxy with ultrafast Mg flow at substrate temperature of 340–390 °C. The temperature was controlled by infra-red pyrometer PhotriX with working range of 300–1400 °C.

By Raman (NT-MDT Ntegra Spectra II) was used for control the synthesize process. An estimation of silicide thickness was carried out with cross-section of samples by focused ion beam (Ga^+) in the SEM. EDX was used for mapping of chemical elements.

Result and discussion

Mg_2Si growth on silicon structure with low aspect ratio (height ~1.5 µm, width ~1 µm, Fig. 1, *a*) was conducted by reactive epitaxy with ultrafast Mg deposition at 340 °C [10]. The deposited portion was ~1200 nm. As a result, the magnesium silicide film with ~500 nm thickness was synthesized (Fig. 1, *b*). The peak at 267.1 cm^{-1} on Raman spectra (Fig. 1, *c*) indicates on Mg_2Si [12].

It can be seen that reaction with high-intense but short Mg deposition appropriately leak on the flat surface of crystals that normal to Mg flow. But there is no film on sidewalls such silicon crystals. Taking into account this fact and the growth of the thick film on a monocrystalline substrate case [11] it can be summarized that the growth method works for low aspect ratio structures: planar µ-TED [13], thin film thermoelectric converters.

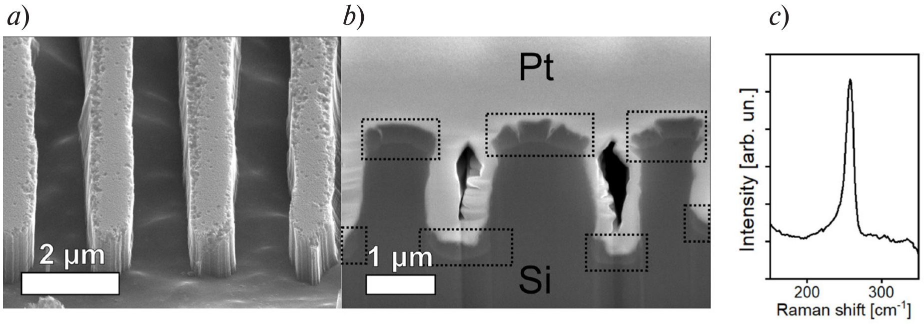

Fig. 1. SEM images of etched silicon crystals used as substrate for Mg_2Si layer growth (*a*) and cross-section of Mg_2Si/Si heterostructure (*b*) (silicide selected in dotted frames). Raman spectra with the peak at 267.1 cm^{-1} agree the silicide successful growth [12] (*c*)

Synthesis of the magnesium silicide on silicon patterns with high aspect ratio (width ≥ 290 nm, length > 20 µm, Fig. 2, *a*) was carried out by a solid phase epitaxy with step by step increasing recrystallization annealing temperature for 10 °C from 340 °C to 390 °C. The deposited portion was increased to ~5 µm.

By the method the Mg_2Si layer with maximum thickness ~1.2 µm was formed (Fig. 2, *b*, *c*). It is important to note that the method provide the silicide growths on sidewalls of crystals. Also, the silicide thickness was significantly increased. But the Mg_2Si growth on hidden (shaded) areas is not occurred. The difference in the deposited Mg portion and the film thickness is due to an intensive Mg desorption.

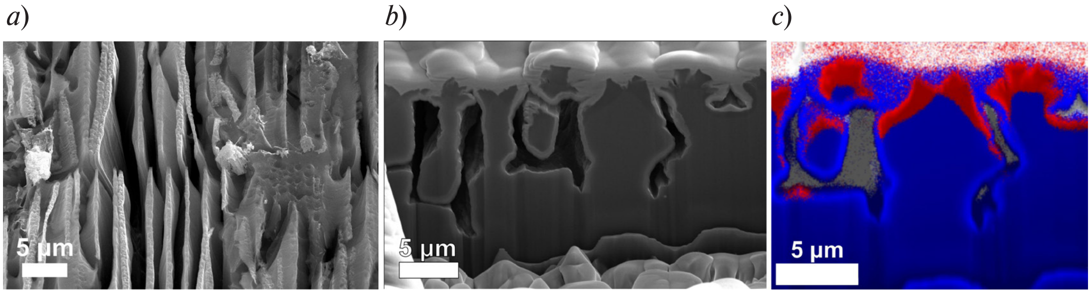

Fig. 2. SEM images of high aspect-ratio silicon crystals (*a*) and cross-section of Mg_2Si layers formed on the top of these crystals (*b*). EDX mapping of the chemical element's distribution (blue is silicon, red is Mg/Si mixture) (*c*)

For the next sample it was decided to modify the solid phase epitaxy method and to conduct the recrystallization annealing in the intensive magnesium flow (≥ 200 nm/min). The annealing was conduct for 40 minutes at fixed temperature 360 °C. The aspect ratio of silicon crystals of the sample is close to that shown on Fig. 1, *a*.

As can be seen, the method allows to growth the silicide shell both on sidewalls and shaded areas. The Mg_2Si layer thickness is ~1 µm.

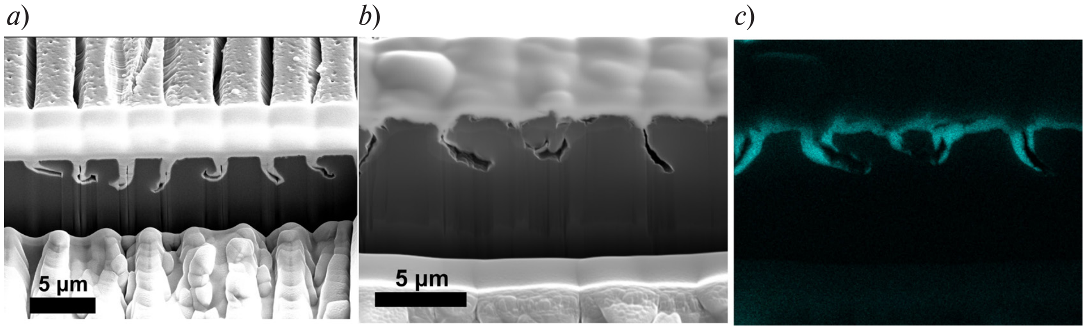

Fig. 3. SEM images of silicon crystals (*a*) and cross-section of Mg_2Si layers formed on the top of these crystals (*b*). EDX mapping of the chemical element's distribution (blue is a Mg/Si mixture) (*c*)

Conclusion

Using a solid phase epitaxy and reactive epitaxy with ultrafast magnesium deposition core-shell Mg_2Si/Si heterostructures were synthesized. It was showed that modified regime of reactive epitaxy is useful in cases of low aspect ratio structures, planar or thin film μ-TEDs. A solid phase epitaxy allows to increase the film thickness and to growth a shell around a silicon core.

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THE AUTHORS

SUBBOTIN Evgenii Yu.
jons712@mail.ru
ORCID: 0000-0001-9531-3867

KOZLOV Alexey G.
kozlov.ag@dvfu.ru
ORCID: 0000-0001-8774-0631

GOROSHKO Dmitry L.
goroshko@iacp.dvo.ru
ORCID: 0000-0002-1250-3372

CHERNEV Igor M.
igor_chernev7@mail.ru
ORCID: 0000-0002-8726-9832

KHOROSHILOV Dmitry A.
khoroshilov.20092003@mail.ru
ORCID: 0009-0007-4827-2653

LISENKOV Oleg E.
oleglis2003@mail.ru
ORCID: 0009-0007-5206-5753

ZHIZHCHENKO Alexey Yu.
g89leksig@mail.ru
ORCID: 0000-0001-6878-679X

KITAN' Sergei A.
kitansa1981@gmail.com
ORCID: 0000-0003-3377-1912

GALKIN Nikolay G.
galkin@iacp.dvo.ru
ORCID: 0000-0003-4127-2988

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