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Synthesis of Mg_2Si-based core-shell nanowires

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Abstract. In this work, we proposed the method for synthesis of nanowires with Mg_2Si/Si-based core-shell heterostructure. Silicon nanowires acting as a source of silicon for the silicification reaction were obtained by well-studied metal-stimulated chemical etching of silicon with orientation (100) doped with boron, with a resistivity of 1–10 Ω×cm. A 30 nm thick gold film with an adhesive titanium sublayer 1.5 nm thick was used as the catalytic metal. The etched nanowires had a height of ~10 microns and a diameter of 1.5 microns. The Mg_2Si shell was formed using the solid-phase epitaxy method under ultrahigh vacuum conditions. The thickness of the silicide shell was 400–600 nm on the side surfaces of the nanowires.

Keywords: silicon, magnesium silicide, epitaxy, nanowires, core-shell, thermoelectricity, MACE, SEM, EDX, TEM

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Синтез нанопроволок типа ядро-оболочка на основе Mg_2Si

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Аннотация. В данной работе был предложен метод синтеза нанопроволок с гетероструктурой типа ядро-оболочка на основе Mg_2Si/Si. Нанопроволоки кремния, выступающие в качестве источника кремния для реакции силицидообразования, были получены хорошо изученным металл-стимулированным химическим травлением кремния с ориентацией (100), легированного бором, с удельным сопротивлением 1–10 Ω×см. В качестве каталитического металла использовалась пленка золота толщиной 30 нм с адгезионным подслоем титана толщиной 1,5 нм. Вытравленные нанопроволоки имели высоту ~10 мкм и диаметр 1,5 мкм. Оболочка Mg_2Si была сформирована с помощью метода твердофазной эпитаксии в условиях сверхвысокого вакуума. Толщина силицидной оболочки составляла 400–600 нм на боковых поверхностях нанопроволок.

Ключевые слова: кремний, силицид магния, эпитаксия, нанопроволоки, ядро-оболочка, термоэлектричество, МСХТ, СЭМ, ЭДС, ПЭМ

Финансирование: Данная работа была поддержана Российским научным фондом, грант №23-72-01128. Исследования с помощью сканирующей электронной микроскопии и энергодисперсионной рентгеновской спектроскопии были выполнены при поддержке Министерства науки и образования Российской Федерации, Государственное задание №FZNS-2023-0012.

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Introduction

Micrometer-size thermoelectric converters (μ-TEC) [1] are at the cutting edge of science and technology due to their potential of both development and application. These converters could be used as a power source of microelectromechanical systems and micro-watt devices. Surface density of micrometer-size thermocouples (nanowires, for example) arrangement is higher than standard modules for two-three order (10^6 vs 10^3–10^4 cm^{-2}). Such density provides a number of advantages like high cooling response [2] and ability of μ-TECs to work at low temperature gradient [3]. However, traditional production methods (cutting and assembling) are complicated in this size range. So, it is required to find some new approaches. Among them, a reactive ion etching and an anisotropic wet chemical etching combined with a high-resolution lithography or a laser nanofabrication are the most popular. There are many works using these methods of treatment the silicon. Unfortunately, this material has poor thermoelectric properties due to its large thermal conductivity. There is worth considering the Mg_2Si as a more perspective Si-based thermoelectric material [4] that could be synthesized directly on etched silicon nanowires as a substrate. We should note that the using of nanowires in thermoelectricity is the promising idea because these objects have both the same power factor and much less thermal conductivity as compared with bulk ones [5].

Materials and methods

Silicon nanowires with controllable size and arrangement were etched by the well-known metal-assisted chemical etching (MACE) of a monocrystalline boron doped silicon wafer with (100) orientation and 1–10 Ω×cm resistivity. A 30 nm thick gold film with an adhesive titanium sublayer 1.5 nm thick was used as the catalytic metal, which was deposited by electron beam evaporation on silicon surface pre-cleaned with isopropanol and Ar^+ ion beam. The sample was etched in solution of HF (48%, 5.7M), H_2O_2 (37%, 1M) and deionized water with 12:4:34 volume ratio, respectively, for one hour at room temperature.

The etched silicon nanowires were cleaned in *aqua regia* for Au film removing, Piranha solution and rinsed in isopropanol and deionized water before loading into ultra-high vacuum (UHV) chamber. After the loading, outgassing was carried out at 600 °C for 12 hours and 850 °C for 20 minutes for SiO_x removing. Mg_2Si was grown by solid phase epitaxy (SPE) in UHV conditions (10^{-9} Torr). Mg amorphous film was deposited onto the cleaned nanowire's surface at room temperature and then there recrystallization annealing was carried out with consequently increasing temperature, at 300, 330 and 360 °C. Size of nanowires was estimated by scanning electron microscope (SEM, Scios 2 DualBeam Thermofisher) combined with X-ray energy dispersive spectroscopy (EDX) to establish chemical element distribution. Structural analysis was carried out by high-resolution transmission electron microscopy (TEM, JEOL JEM-2100 Plus).

Results and discussion

As a result, anisotropic MACE silicon nanowires with 10 μm height and 1.5 μm diameter were etched (Fig. 1, *a*). Mg_2Si shell was grown on the surface of these crystals (core) (Fig. 1, *b*, *c* and Fig. 2, *a*) with 400–600 nm thickness on sidewalls and ~1 μm on the top (Fig. 1, *c*). The stoichiometric ratio estimated by EDX is 2:1 (Fig. 1, *c*).

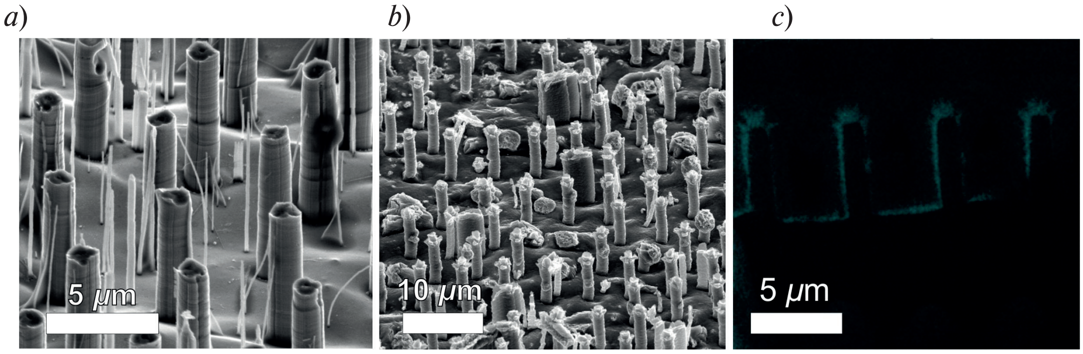

Fig 1. SEM images of etched silicon nanowires (*a*) and synthesized Mg_2Si/Si core-shell nanowires (*b*). Magnesium (blue) distribution on Mg_2Si "shell" (*c*)

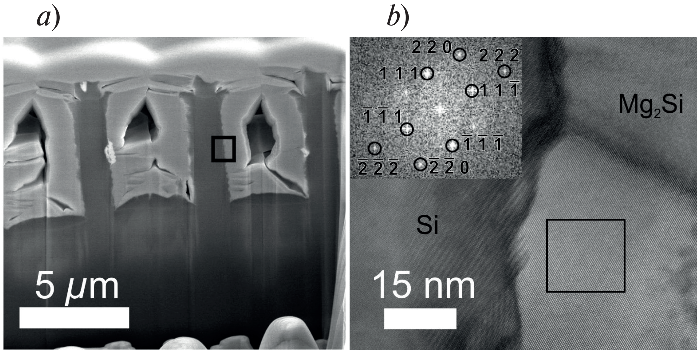

Fig 2. SEM image of Mg_2Si/Si cross-section (*a*) with highlighted section that used for TEM analysis (*b*). On the insert of TEM scan (B) was shown the Fast Fourier Transformation image of selected area with Mg_2Si plane reflexes

The analysis of Mg_2Si/Si structure was carried out by the high-resolution TEM (Fig. 2). Mg_2Si layer has been formed epitaxially with the relation $Mg_2Si(111)\|Si(111)$ (Fig. 2, *b*). According to peak analysis of FFT image (Fig. 2, *b*) Mg_2Si lattice is stretched for 2.7% along [111] and 7.6% along [220].

Conclusion

The Mg_2Si/Si core-shell nanowires were synthesized by the SPE at UHV condition. Silicon nanowires array played the role of a substrate, and a core was etched by MACE. The etched nanowires had a height of ~10 microns and a diameter of 1.5 microns, and the thickness of the silicide shell was 400–600 nm on the side surfaces of nanowires. Mg_2Si was formed by epitaxy with the epitaxial relationship $Mg_2Si(111)\|Si(111)$. The Mg_2Si lattice is found to be stretched by 2.7% along [111] and 7.6% along [220].

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