Conference materials
UDC 539.23+539.25+539.26+537.32+537.9
DOI: https://doi.org/10.18721/JPM.163.119

Mg_2Si film on Si(111) prepared by Ultra-Fast Mg reactive deposition: crystal structure and thermoelectric properties

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Abstract. The Mg_2Si film (~ 800 nm thick) was grown by pulsed reactive deposition of Mg on Si(111) at 340 °C in UHV. Structural investigations by XRD, SEM and cross-sectional x-HR-TEM demonstrate high crystal quality and 100% texture of the film. Thermoelectric properties of the Mg_2Si film are characterized within 290–470 K. The film conductivity changes from p-type below 309 K to n-type at higher temperatures. The power factor is 0.27 mW/m×K^2 at 470 K. The p-type conductivity can be associated with presence of oxygen or/and vacancies (V_{Mg}, V_{Mg2Si}).

Keywords: magnesium silicide, silicon, films, epitaxy, reactive epitaxy, pulsed deposition, crystal structure, microscopy, transport properties, Seebeck coefficient, power factor

Funding: This study was funded by the state budget “Physics of low-dimensional structures and semiconductor nanomaterials” No. [0202-2021-0002]. A.G. K. acknowledges the Russian Ministry of Science and Higher Education for state support of scientific research (State Assignment No. FZNS-2023-0012). M.V. P. acknowledges the Russian Science Foundation, grant No. 20-13-00277 P.

Citation: Chernev I.M., Subbotin E.Yu., Argunov E.V., Kozlov A.G., Gerasimenko A.V., Galkin N.G., Poliakov M.V., Volkova L.S., Dudin A.A., Gouralnik A.S., Mg_2Si film on Si(111) prepared by Ultra-Fast Mg reactive deposition: crystal structure and thermoelectric properties, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 106–111. DOI: https://doi.org/10.18721/JPM.163.119

Материалы конференции
УДК 539.23+539.25+539.26+537.32+537.9
DOI: https://doi.org/10.18721/JPM.163.119

Пленка Mg_2Si на Si(111), полученная методом сверхбыстрого реактивного осаждения Mg: структура и термоэлектрические свойства

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Аннотация. Пленка Mg_2Si толщиной ~ 800 нм была выращена методом импульсного реактивного осаждения Mg на Si(111) при 340 °C в условиях сверхвысокого вакуума. Структурные исследования с помощью рентгеновской дифракции, сканирующей электронной микроскопии и высокоразрешающей просвечивающей микроскопии поперечного сечения образца демонстрируют высокое кристаллическое качество и 100% текстуру пленки. Термоэлектрические свойства пленки Mg_2Si были исследованы в диапазоне температур от 290 K до 470 K. Тип проводимости пленки меняется с p-типа проводимости при температурах ниже 309 K на n-тип при более высоких температурах. Фактор мощности составляет 0,27 мВт/м×K² при 470 K. Проводимость p-типа может быть связана с наличием кислорода, и/или вакансиями Mg и тройными вакансиями Mg_2Si.

Ключевые слова: силицид магния, кремний, пленки, эпитаксия, реактивная эпитаксия, импульсное осаждение, кристаллическая структура, микроскопия, транспортные свойства, коэффициент Зеебека, фактор мощности

Финансирование: Государственный бюджет «Физика низкоразмерных структур и полупроводниковых наноматериалов» № [0202-2021-0002], А.Г. Козлов благодарит Министерство науки и высшего образования Российской Федерации за государственную поддержку научных исследований (гос.задание № ФЗНС-2023-0012), М.В. Поляков благодарит Российский научный фонд, грант No. 20-13-00277 P.

Ссылка при цитировании: Чернев И.М., Субботин Е.Ю., Аргунов Е.В., Козлов А.Г., Герасименко А.В., Галкин Н.Г., Поляков М.В., Волкова Л.С., Дудин А.А., Гуральник А.С. Пленка Mg_2Si на Si(111), полученная методом сверхбыстрого реактивного осаждения Mg: структура и термоэлектрические свойства // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 106–111. DOI: https://doi.org/10.18721/JPM.163.119

Introduction

The narrow band (E_g ~ 0.6–0.8 eV) semiconductor Mg_2Si is a promising material for SWIR detectors and solar cells [1] and thermoelectric (TE) energy conversion [2]. Usually, Mg_2Si is an n-type semiconductor, almost irrespective to a synthesis method. The p-type Mg_2Si is highly required for preparing p-Mg_2Si/n-Si heterojunction SWIR sensors and p-type legs for thermoelectric (TE) double leg generators based on n- and p-Mg_2Si. Mg_2Si of the p-type has been obtained by overcompensation with impurities, e.g. Ag, but this resulted in a significant decrease in carrier mobility [3]. As well, the p-type conductivity can be caused by vacancies (VMg, VMg_2Si) or oxygen interstitials which represent acceptors [4–6]. Synthesis of high crystal quality Mg_2Si is a difficult task. The Mg_2Si films grown on Si substrates at ≈ 200 °C [7, 8] have rather poor crystal quality, irrespective of the growth technique. For typical deposition rates ~ 10^{-1} – 10 nm/min and substrate temperatures (T) above ≳ 300 °C, Mg re-evaporates without formation of Mg_2Si. We showed [10] that this problem can be avoided by radical increase of the deposition rate. In our works [9, 10] ~ 10–100 nm thick perfect Mg_2Si films were grown on Si(111) and Si(100) substrates at 360–480 °C by pulsed UHV deposition of Mg at the rates of 10^2–10^4 nm/sec. Since the temperature of this exothermic process is in large extent determined by the reaction heat release (≈ 0.8 eV per a formula unit) we concluded that the initial temperature of ≈ 340 °C can be optimal for Mg_2Si film growth. In this work we present the growth and TE properties of a ~ 800 nm thick crystalline Mg_2Si film prepared on Si(111) by ultra-fast Mg deposition (≈ 10^4 nm/s) at the substrate temperature 340 °C.

Materials and Methods

The experiment was carried out in the Ultra High Vacuum (UHV) chamber Varian with the base vacuum of ~ 2×10^{-9} Torr. The substrate, Si(111) $\rho > 1000$ Ohm×cm was degassed in UHV by DC heating at ~ 650 °C for 6 hours and cleaned by multiple high temperature (*T*) flashes at *T* ~ 1120 °C just before the growth experiment. The magnesium source was well degassed during several hours at high *T* in UHV as well. The pyrometer PhotriX was used for *T* measuring. The calibration and pulse deposition procedures are described in our previous works [5, 6]. The Mg portion (≈ 650 nm) was deposited onto the substrate during ≈ 200 msec. Some small part of the deposited dose re-evaporated from the hot substrate (340 °C) but most of Mg atoms reacted with Si and finally a ~ 800 nm thick Mg_2Si film was synthesized. The XRD spectrum was obtained with a RIGAKU SmartLab diffractometer using a 9 kW rotating anode, CuKα radiation. The diffraction patterns were recorded within the 2θ range of 22° – 61° with the 2θ step of 0.01°. The thickness of the grown Mg_2Si film was studied with the ThermoFisher Scios 2 DualBeam scanning electron microscope (SEM). For preparing a hole with a smooth flat surface a focused Ga^+ ion beam (FIB) was used. The Cross-sectional High-Resolution Transmission Electron Microscopy (x-HRTEM) image was obtained with an electron microscope JEM-2100 Plus JEOL operating at 200 kV. The thermoelectrical measurements (Seebeck coefficient and electrical conductivity) were carried out in He atmosphere in the temperaturee range 290–470 K in a Cryotel laboratory setup (MISIS).

Results and Discussion

Fig. 1 demonstrates Raman spectroscopy data for the grown Mg_2Si film. The strong F_{2g} Raman peak at 257 cm^{-1} and absence of the peak at 520 cm^{-1} attributed to crystalline Si indicate a rather thick Mg_2Si film. Some other Mg_2Si Raman modes are also clearly seen in Fig 1. Raman spectra demonstrate that the positions of all the peaks are slightly shifted to low wavenumbers as compared to the literature data [11, 12] (see Table). We suggest that this indicates some compressive stresses inside the Mg_2Si film. The stress could occur during the very short heating-cooling cycle due to the large difference in the thermal expansion factors; as well it could be caused by the lattice mismatch.

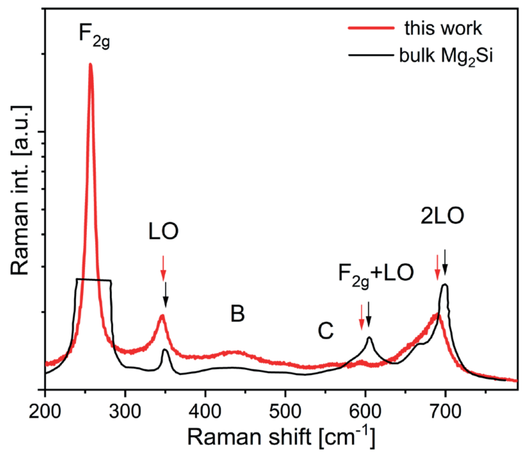

Fig. 1. Raman scattering spectrum for Mg_2Si film on Si(111) substrate (red curve) and reference [11] data for bulk Mg_2Si (black curve)

Table

The positions of the peaks of the Raman spectrum

Mode	Raman shift[cm^{-1}]	
	this work	Bulk Mg_2Si [11]
F_{2g}	257	258.5 [12]
LO	346	360
B	433	433
F_{2g} + LO	568	604
2LO	689	699

Fig. 2, *a* shows the XRD data of the Mg_2Si/Si(111) sample. The spectrum demonstrates only peaks from silicon substrate (111) and Mg_2Si features corresponding to (111) and (222) planes at 2θ angles 24.28°, 49.79° respectively. No other magnesium silicide phases (Mg_5S_6, Mg_9Si_5, Mg_3Si) are observed. The Mg_2Si lattice parameter (6.346 Å) obtained from our data is ~ 0.08% smaller than that accepted in [13] (6.351 Å). This supports the above suggestion on some compression stress in the film material. This result is in correspondence with the Raman investigations data discussed above.

By SEM data, the film has the thickness ≈ 800 nm (see insertion in Fig. 2, *a*). The cross-sectional HRTEM image is presented in Fig. 2, *b*. The interface Mg_2Si/Si is sharp. The typical columnar structure [5] is clearly seen. The column lateral size varies within 100–170 nm. The upper surface of the film is naturally oxidized.

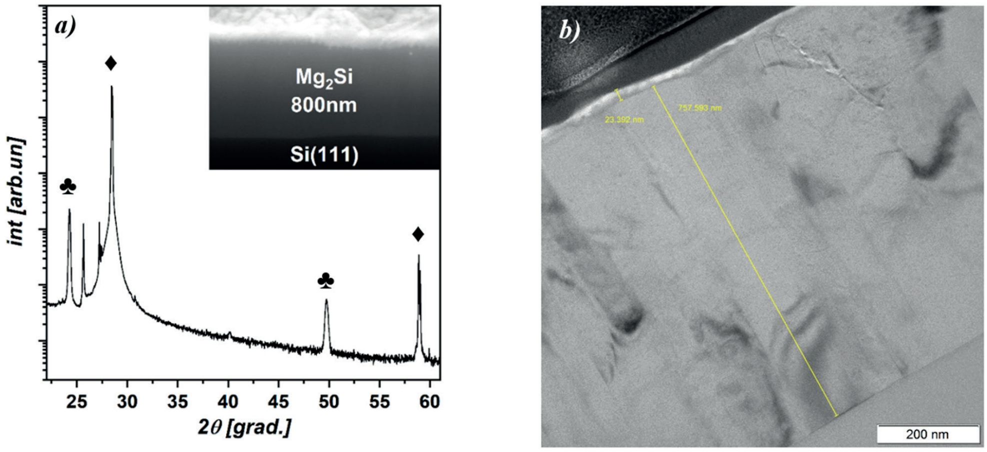

Fig. 2. The XRD spectrum of the Mg_2Si/Si(111) sample and the SEM cross-section profile in insertion, ≈ 800 nm Mg_2Si film demonstrates high crystal quality and perfect texture (111). Mg_2Si and Si(111) peaks are indicated with ♣ and ♦ marks, respectively (*a*). The cross-section HRTEM image, the 760 nm thickness and columnar structure are clearly seen (*b*)

The temperature dependencies of the thermoelectric properties of the Mg_2Si film in the range of 290–470 K are shown in Fig. 3. The Seebeck coefficient is +478 $\mu V \times K^{-1}$ at 290 K (see Fig. 3, *a*), it decreases with *T* and changes the sign at 309 K. In the range of 350–470 K its dependence on T is linear. At 470 K it gets the value of –605 $\mu V \times K^{-1}$. The Seebeck coefficient sign change corresponds to the compensation between p- and n-type carriers. At 309 K the intrinsic n-type conductivity of the Mg_2Si film is activated and the electron contribution becomes larger than the hole contribution. The nature of the p-type conductivity in Mg_2Si is under investigation now. Theoretical calculations show that Mg vacancies, Mg_2Si triple vacancies and oxygen interstitials represent acceptors in Mg_2Si [8–10].

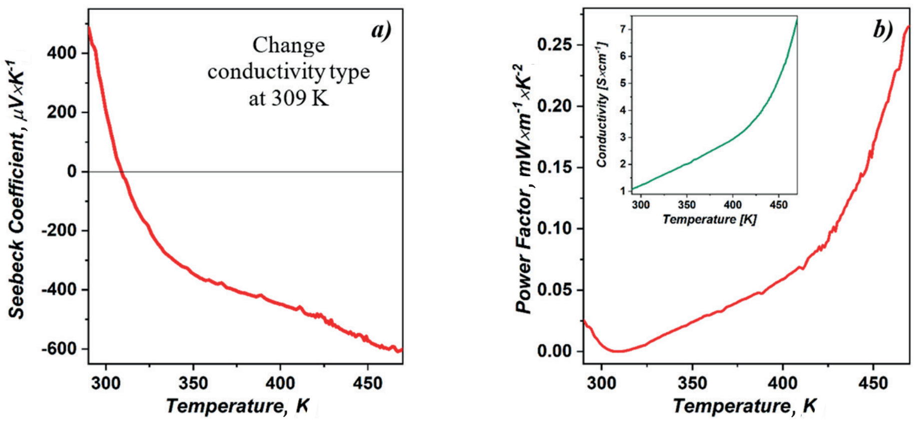

Fig. 3. Temperature dependance of Seebeck coefficient (*a*), Power Factor (*b*) and conductivity (insertion on *b*) for Mg_2Si film on Si substrate

The conductivity of the Mg_2Si film increases with temperature (see insertion in Fig. 3, *b*) and reaches 7.4 S×cm^{-1} at 470 K. As seen in Fig. 3, *b*, the Power Factor (PF) maximum is 0.27 mW/m×K^2 at 470 K. The PF is rather small at 290 K (25 μW/m×K^2), decreases almost to zero at 309 K and then increases with T. This behavior and the PF value around 309 K are due to carrier compensation. Further investigations of the thermal conductivity and effect of impurities on thermoelectric properties are planned for our future researches.

Conclusions

High crystal quality ~ 800 nm thick Mg_2Si film with ≈ 100% texture (111) was formed by pulsed Mg deposition onto Si(111) at 340 °C. Some compressive stress of ≈ 0.08% is present in the film material. The film conductivity is of the p-type at T < 309 K and n-type at T > 309 C. The p-type could be attributed to Mg vacancies, M_2Si triple vacancies and oxygen interstitials. The power factor is 0.27 mW/m×K^2 at 470 K.

Acknowledgments

This study was funded by the state budget "Physics of low-dimensional structures and semiconductor nanomaterials" No. [0202-2021-0002]. A.G. K. acknowledges the Russian Ministry of Science and Higher Education for state support of scientific research (State Assignment No. FZNS-2023-0012). M.V. P. acknowledges the Russian Science Foundation, grant No. 20-13-00277 P. We thank the Far Eastern Federal University, Institute of Chemistry FEB RAS, Institute of Nanotechnology of Microelectronics of the RAS and National Research Technological University for the opportunities to carry out SEM, XRD, HRTEM and thermoelectric studies on their experimental equipment.

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Received 10.07.2023. Approved after reviewing 31.07.2023. Accepted 02.08.2023.