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Formation, structure, and optical properties of single-phase CaSi and $CaSi_2$ films on Si substrates

N. G. Galkin [1,2] ✉, K. N. Galkin [1], O. V. Kropachev [1], I. M. Chernev [1],
S. A. Dotsenko [1], D. L. Goroshko [1,2], E. Yu. Subbotin [1], A. Yu. Alekseev [3], D. B. Migas [3]

[1] Institute of Automation and Control Processes FEB RAS, Vladivostok, Russia;
[2] Far Eastern Federal University, Vladivostok, Russia;
[3] Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus

✉ galkin@iacp.dvo.ru

Abstract: In this paper, we report on optimizing the conditions for subsequently growing single-phase films of calcium monosilicide (CaSi) and calcium disilicide ($CaSi_2$) on single-crystal silicon by reactive deposition epitaxy (RDE) and molecular beam epitaxy (MBE). The temperature range for the growth of CaSi films (400–500 °C) was determined, as well as the temperature range (600–680 °C) for the growth of $CaSi_2$ films on silicon with three orientations: (111), (100) and (110). The minimum temperatures for the epitaxial growth of CaSi films by the RDE method and $CaSi_2$ films by the MBE method were determined, amounting to, respectively, T = 475 °C and T = 640 °C. An increase in the ratio of Ca to Si deposition rates to 26 made it possible to grow a large-block $CaSi_2$ epitaxial film with the hR6 structure by the MBE method at T = 680 °C. Raman spectra and reflection spectra from single-phase epitaxial CaSi and $CaSi_2$ films on silicon were recorded and identified for the first time. The correspondence between the experimental reflection spectra and the theoretically calculated reflection spectra in terms of amplitude and peak positions at photon energies of 0.1–6.5 eV has been established. Single-phase CaSi and $CaSi_2$ films retain transparency in the photon energy range 0.4–1.2 eV.

Keywords: CaSi films, $CaSi_2$ films, silicon, single-phase growth, optical functions, energy band structure, ab initio calculations

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Формирование, структура и оптические свойства однофазных пленок CaSi И $CaSi_2$ на Si подложках

Н. Г. Галкин [1,2] ✉, К. Н. Галкин [1], О. В. Кропачев [1], И. М. Чернев [1],
С. А. Доценко [1], Д. Л. Горошко [1,2], Е. Ю. Субботин [1], А. Ю. Алексеев [3], Д. Б. Мигас [3]

[1] Институт автоматики и процессов управления ДВО РАН, г. Владивосток, Россия;
[2] Дальневосточный федеральный университет, Владивосток, Россия;
[3] Белорусский государственный университет информатики и радиоэлектроники, г. Минск, Беларусь

✉ galkin@iacp.dvo.ru

Аннотация. В работе оптимизированы условия и выращены однофазные пленки моносилицида кальция (CaSi) и дисилицида кальция ($CaSi_2$) на монокристаллическом кремнии с тремя ориентациями: (111), (100) и (110). Определена минимальная температура эпитаксиального роста пленок CaSi методом РДЭ: T = 475 °C и пленок $CaSi_2$ методом МЛЭ: T = 640 °C, выращена крупноблочная эпитаксиальная пленка $CaSi_2$ со структурой hR6. Впервые зарегистрированы и идентифицированы спектры КР и спектры отражения от однофазных эпитаксиальных пленок CaSi и $CaSi_2$ на кремнии. Установлено соответствие между экспериментальными спектрами отражения и теоретически рассчитанными спектрами отражения при энергиях фотонов 0,1 – 6,5 эВ. Однофазные пленки CaSi и $CaSi_2$ сохраняют прозрачность в диапазоне энергий фотонов 0,4–1,2 эВ.

Ключевые слова: пленки CaSi и $CaSi_2$, кремний, однофазный рост, оптические функции, зонная структура, первопринципные расчеты

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Introduction

Calcium silicides are environmentally friendly materials, taking a special place among alkaline earth metal silicides. This is primarily due to a wide range of properties of calcium silicides from semiconducting [1] to semimetallic [2]. This shows promise for their widespread use in various fields of technology and electronics. However, growing single-phase films of semimetallic monosilicide (CaSi) and calcium disilicide ($CaSi_2$) on silicon and studying their optical properties are challenging tasks due to the presence of at least 6 silicides of different compositions in the Ca-Si system [3] and the lack of methods for separating the preferred orientation during growth silicon silicides.

The purpose of this work is to grow single-phase CaSi and $CaSi_2$ epitaxial films on silicon with different orientations and to determine the features of their band structure and optical properties by experimental and theoretical methods.

Experimental

The growth of CaSi and $CaSi_2$ films was carried out in an ultra-high vacuum (UHV) chamber of the OMICRON Compact setup (2×10^{-11} Torr) equipped with a LEED analytic equipment and different sources of Si and metals (Mg, Ca) [4]. The deposition of Ca (RDE method) or Ca and Si (MBE method) was carried out on an atomically clean Si(111)-7x7 surface in two temperature ranges: 400–500 °C and 600–680 °C. The deposition rates of Si and Ca were calibrated using a quartz thickness gauge. Data on growth regimes and structures of grown Ca silicide films are presented in Table 1.

Experimental equipment for optical and Raman spectroscopy and conditions for recording transmission (T) and reflection (R) spectra are described in [4]. The crystal structure of the grown films was studied by X-ray diffraction (XRD) using the equipment presented in [5]. The analysis of the optical characteristics of the grown films was carried out in the framework of a two-layer model [6]. Methods for the first-principle calculation of the band structure of CaSi and $CaSi_2$ in bulk form and the form of films are presented in [7].

Table 1

Growth regimes and structures of CaSi and CaSi2 films on silicon substrates

Sample	Substrate	Growth method	V_{Ca}/V_{Si}	Substrate temperature, °C	Film thickness, nm	XRD data
C440	Si(111)	MBE	8.7	500	40	CaSi(010)‖Si(111) CaSi(100)‖-Si(111)
V688	Si(111)	RDE	–	400	100	CaSi (010)/Si(111)
V691	Si(111)	RDE	–	475	90	CaSi (100)/Si(111)
C317	Si(001)	MBE	26	680	400	hR6-$CaSi_2$[100]‖Si[10] hR6-$CaSi_2$(01)‖Si(002)
C446	Si(001)	MBE	29.3	640	120	hR6-$CaSi_2$(01)‖Si(111), hR6-$CaSi_2$(012)‖Si(111)
V694	Si(111)	RDE	–	625	80	hR6-$CaSi_2$(001)/Si(111) hR3-$CaSi_2$(001)/Si(111)
V699	Si(110)	RDE	–	600	140	hR3-$CaSi_2$(001)/Si(110)

Results and Discussion

Studies of the morphology and structure of films formed by the RDE method at temperatures of 400–475 °C showed that there is a temperature limit (475 °C) when CaSi grains crystallize in the form of rectangular nanocrystals with dimensions 30–50 nm wide and 200–300 nm long. Application of the MBE method for film growth at a temperature of 500°C made it possible to form a single-phase CaSi film (Fig. 1,*a*), which also consisted of ordered rectangular nanocrystals (Fig. 1,*a*, inset). The formation of $CaSi_2$ films was detected during Ca RDE method in the temperature range of 600–625 °C on two types of substrates: Si(111) (V694, Table 1) and Si(110) (V699, Table 1). Regardless of the substrate orientation, the growth of grains with the hR3-$CaSi_2$(001)/Si(111) epitaxial orientation was observed. However, in the case of growth on a Si(111) substrate at a temperature of 625°C, the appearance of a polymorphic $CaSi_2$ phase with the hR6-$CaSi_2$(001)/Si(111) epitaxial orientation was also observed. During the growth of $CaSi_2$ films, the orientation of the formed grains depended on the substrate temperature and the ratio of calcium to silicon deposition rates. An increase in the ratio of the Ca to Si deposition rate to 26 at a temperature of 680°C led to the formation by MBE method of a thick (400 nm) large-block $CaSi_2$ film (sample C317) with epitaxial relationships: hR6-$CaSi_2$[100]‖Si[$1\bar{1}0$] and hR6-$CaSi_2$($01\bar{1}$)‖Si(002) (Table 1). With a decrease in the substrate temperature and an approximate preservation of the ratio of rates, the formation of epitaxial grains with two epitaxial orientations was observed: hR6-$CaSi_2$(01)‖Si(111) and hR6-$CaSi_2$(012)‖Si(111) (Fig. 1, *b*).

After the samples were unloaded from the growth chambers, the transmission and reflection spectra were recorded in the photon energy range from 0.05 eV to 6.5 eV. The main features for

a) *b*)

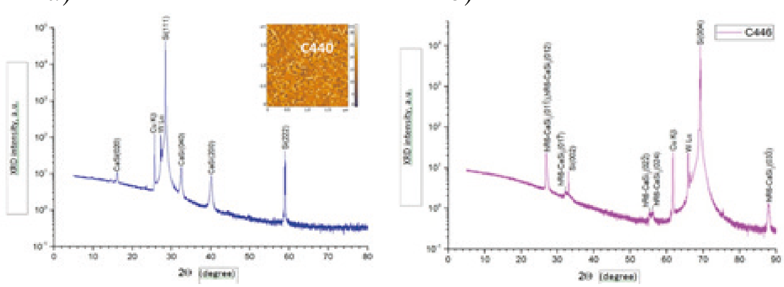

Fig. 1. XRD spectra for a single-phase CaSi film grown by MBE at T = 500 °C (*a*) and a single-phase CaSi2 film (MBE, T = 640 °C, sample C446) (*b*)
The inset in (*a*) shows the AFM image of the CaSi film (sample C440)

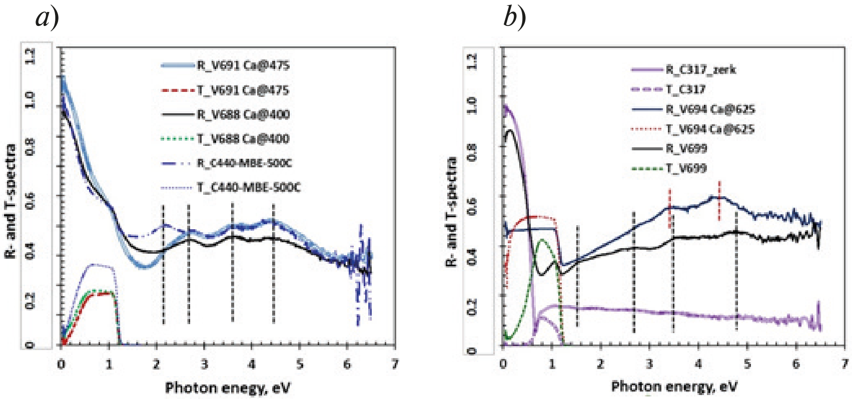

Fig. 2. Reflectance and transmittance spectra for CaSi (*a*) (samples V688, V691, C440) and $CaSi_2$ (*b*) (samples V694, V699, C317) films on Si substrates

the CaSi and $CaSi_2$ films were the partial transparency of both films in the photon energy range of 0.2–1.1 eV and the plasma minimum in reflection, which was previously observed for $CaSi_2$ films [8] with semimetallic properties. The transparency of $CaSi_2$ films (Fig. 2, *b*) is slightly higher than the transparency of CaSi (Fig. 2, *a*).

Registration of Raman spectra showed that single-phase CaSi and $CaSi_2$ films have several individual peaks, which are in good agreement with the data of theoretical calculations [8] and preliminary experimental studies for nanocrystalline and non-single-phase films [9, 10]. Therefore, Raman spectroscopy data can be used to identify the elemental composition and its single-phase nature.

Comparison with the data of theoretical reflection spectra for three planes of a single crystal of CaSi (Fig. 4, *a*) and $CaSi_2$ (Fig. 4, *b*) shows good agreement in the position of the plasma minimum for both silicides, which is associated with the contribution of two types of carriers, according to the calculations performed in this work. The reflection spectra also agree in magnitude and position of the main peaks in the photon energy range of 1.5–6.5 eV, which corresponds to the main interband transitions in CaSi and $CaSi_2$ single crystals.

Calculations of the optical functions of CaSi films from the reflection and transmission spectra (Fig. 2, *a*) within the two-layer model [6], taking into account multiple reflection and absorption, made it possible to obtain the spectral dependences of the refractive index and extinction coefficient (Fig. 5, *a*), absorption coefficient spectra (Fig. 5, *b*) and optical conductivity spectrum (Fig. 5, *c*) for CaSi films on silicon in the photon energy range of 0.1–1.2 eV. CaSi films in both samples (V691 and V688) have an almost constant absorption coefficient $(4–5)\cdot10^4$ cm^{-1} at energies of 0.4–1.2 eV and increasing absorption on free carriers at energies less than 0.4 eV, which is consistent with the plasma minimum in the reflection spectrum (Fig. 2, *a*). An increase in the concentration of free carriers correlates with an increase in optical conductivity (Fig. 5, *c*).

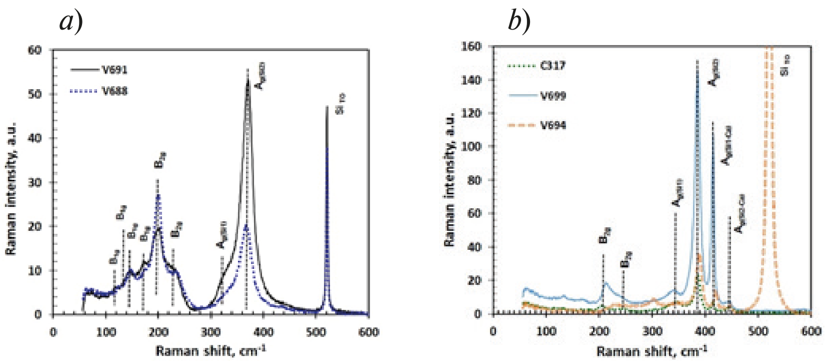

Fig. 3. Raman spectra for CaSi (*a*) (samples V688, V691, C440) and $CaSi_2$ (*b*) (samples V694, V699, C317) films on Si substrates

Calculations of the optical functions of $CaSi_2$ films from the reflection and transmission spectra (Fig. 2, *a*) within the two-layer model, taking into account multiple reflection and absorption, made it possible to obtain the spectral dependences of the refractive index and extinction coefficient (Fig. 6, *a*), absorption coefficient spectra (Fig. 6, *b*) and optical conductivity spectrum (Fig. 6, *c*) for $CaSi_2$ films on silicon in the photon energy range of 0.1–1.2 eV. $CaSi_2$ film in the sample V699 has a slightly variable absorption coefficient (3–4)·10^4 cm^{-1} at energies of 0.1–1.2 eV. The film in the V694 sample has a small thickness and may not be continuous, so the calculations showed underestimated values of the absorption coefficient (Fig. 6, *c*). The increase in optical conductivity in the sample V699 (Fig. 6, *c*) is also associated with plasma reflection on free carriers of two signs, typical for semimetals [2, 5].

a) *b*)

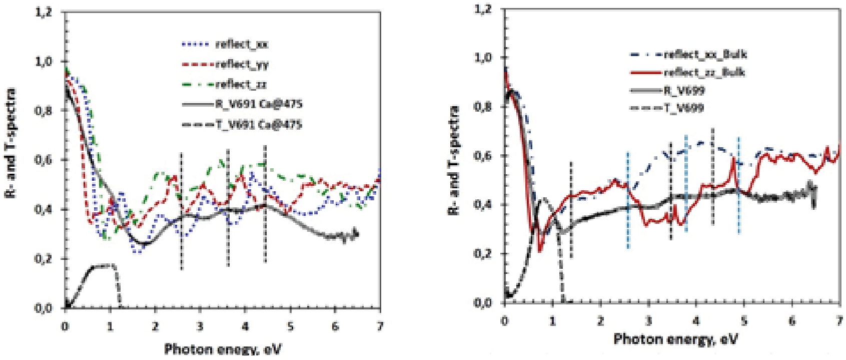

Fig. 4. Comparison of the theoretical (*xx*, *yy*, *zz* correspond to polarizations) and experimental reflection and transmission spectra of CaSi (*a*) (samples V688, V691, C440) and $CaSi_2$ (*b*) (samples V694, V699, C317) films on Si substrates

a) *b*) *c*)

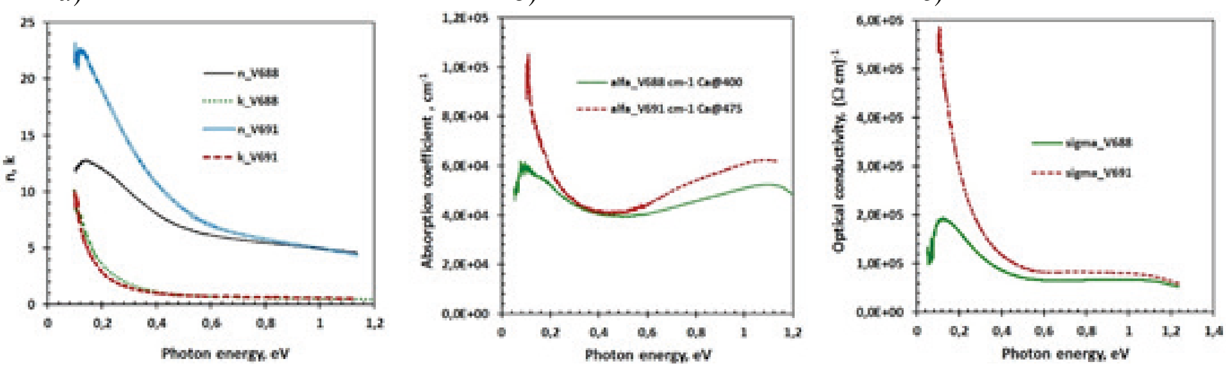

Fig. 5. Spectra for refractive index n and extinction coefficient *k* (*a*), absorption coefficient (*b*) and optical conductivity (*c*) for CaSi films on Si(111) substrates (samples V688 and V691)

a) *b*) *c*)

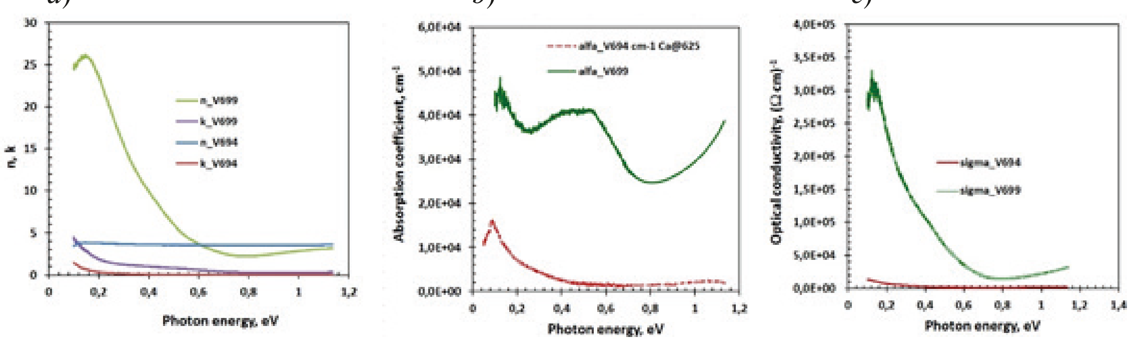

Fig. 6. Spectra for refractive index n and extinction coefficient *k* (*a*), absorption coefficient (*b*) and optical conductivity (*c*) for $CaSi_2$ films on Si(111) substrates (samples V694 and V699)

Conclusion

Methods for growing single-phase films of calcium monosilicide and disilicide on single-crystal silicon in the temperature range 400–680 °C are analyzed. It has been established that a CaSi film with grains without faceting is formed under RDE at a temperature of 400 °C. The faceting of CaSi grains was found at T = 475 oC. Single-phase growth of the CaSi film with epitaxial grain orientation was observed during MBE growth at T = 500 °C. The formation of epitaxial $CaSi_2$ on Si with (111), (100), and (110) orientations was detected in the temperature range 600–680 °C by RDE and MBE methods. During the growth by the RDE method, the formation of two isomorphic phases was observed hR3-$CaSi_2$ and hR6-$CaSi_2$. At the same time, during MBE growth the increase in the ratio of Ca to Si deposition rates up to 26 makes it possible to increase the substrate temperature to 680 °C and grow a large-block epitaxial film with hR6-$CaSi_2$ modification. Raman spectra and reflection spectra from single-phase CaSi and $CaSi_2$ films were recorded and identified, and their correspondence in amplitude and peak positions at 0.1–6.5 eV with the theoretically calculated reflection spectra, as well as with the available theoretical data on Raman spectra, was established. Calculations of the optical functions of single-phase CaSi and $CaSi_2$ films, including the spectra of the absorption coefficient and optical conductivity, showed the retention of high transparency and high conductivity in the energy range of 0.4–1.2 eV and the determining effect of absorption on free carriers on the loss of transparency at energies below 0.4 eV.

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THE AUTHORS

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

KROPACHEV Oleg V.
chernobez@gmail.com
ORCID: 0000-0003-4300-0070

GALKIN Konstantin N.
galkinkn@iacp.dvo.ru
ORCID: 0000-0001-5386-1013

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

DOTSENKO Sergei A.
docenko@iacp.dvo.ru
ORCID: 0000-0002-0052-7465

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

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

ALEKSEEV Aleksey Yu.
lucky.alexey94@gmail.com
ORCID: 0000-0001-5102-6647

MIGAS Dmitry B.
migas@bsuir.by
ORCID: 0000-0003-3004-7996

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