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Electronic structure and optical properties of Ca_2Si films grown on silicon different oriented substrates and calculated from first principles

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Abstract. The work considered the growth, optical properties and emerging interband transitions in Ca_2Si films grown on silicon substrates with (111), (001), and (110) orientations at two temperatures (250 °C and 300 °C) using the sacrificial-template method. The optimum temperature for MBE single-phase growth of Ca_2Si is 250 °C. Calculations of optical functions from the transmission and reflection spectra were carried out within the framework of a two-layer model and by the Kramers–Kronig method. It is shown that the main peaks in the experimental reflection spectra and the optical conductivity calculated according to Kramers–Kronig are in good agreement with each other. Comparison of *ab initio* calculations of the energy band structure and optical properties of a Ca_2Si single crystal and two-dimensional Ca_2Si layers with experimental data in the region of high-energy transitions showed good coincidence.

Keywords: Ca_2Si films, silicon, growth method, optical functions, energy band structure, *ab initio* calculations

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Материалы конференции
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Электронная структура и оптические свойства пленок Ca_2Si, выращенных кремниевых подложках с различной ориентацией и рассчитанных из первых принципов

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Аннотация. В работе исследованы рост, оптические свойства и возникающие межзонные переходы в пленках Ca_2Si, выращенных на кремниевых подложках с ориентациями (111), (001) и (110) при двух температурах (250°C и 300°C) с использованием метода расходуемого шаблона. Показано, что основные пики в экспериментальных спектрах отражения и оптической проводимости, рассчитанной по Крамерсу-Кронигу, хорошо согласуются друг с другом. Сравнение первопринципных расчетов зонной энергетической структуры и оптических свойств монокристалла Ca_2Si и двумерных слоев Ca_2Si с экспериментальными данными в области высокоэнергетических переходов показало хорошее совпадение.

Ключевые слова: пленки Ca_2Si, кремний, метод выращивания, оптические функции, зонная структура, первопринципные расчеты

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Introduction

At least six silicides are formed in the calcium-silicon system [1], including calcium semi-silicide (Ca_2Si), which has semiconductor properties [2]. Since calcium silicides are formed from environmentally friendly and widely distributed elements in the Earth's crust [3], they are of considerable interest for silicon electronics and optoelectronics. Ca_2Si, the most well-known and obtained in the form of films, has been mainly studied on silicon with the (111) orientation [4], while studies of its structure and optical properties on other surfaces (Si(100) and Si(110)) have not yet been carried out.

The goal of this work is to investigate experimentally and theoretically the parameters of the energy band structure and optical functions for Ca_2Si epitaxial films on silicon substrates with different orientations.

Experimental

Ca_2Si films were grown in an ultrahigh vacuum (UHV) chamber of an OMICRON Compact setup with a base vacuum of $2 \cdot 10^{-11}$ Torr, equipped with a LEED and AES/EELS analyzer, a block of molecular beam sources of silicon (Si), magnesium (Mg), and calcium (Ca) by carrying out the deposition of Mg, Ca and Si on the Si(111), Si(001) and Si(110) substrates. The deposition rates (Ca, Mg, and Si) were calibrated using a quartz thickness sensor. Sources of Ca, Mg, and Si and film growth techniques are described in [4].

The reflection spectra (R-spectra) and transmission spectra (T-spectra) of the grown samples were recorded within one day after unloading at room temperature in the photon energy range of 0.05–6.5 eV on a Hitachi U-3010 spectrophotometer with an integrating sphere and Fourier spectrometer Bruker Vertex 80 v. The optical functions were calculated in the transparency region from the T- and R-spectra in the frame of the two-layer model [5] as well as from the integral Kramers–Kronig relations over the entire range of photon energies.

Calculations of the electronic band structure and optical functions of Ca_2Si were also performed using the method of self-consistent full-potential linearized augmented plane waves (FLAPW) in its scalar-relativistic version using the WIEN2k package [6].

Results and Discussion

The morphology of the grown films was studied by AFM. Most of them for samples C423 and C424 on Si(111), C419 on Si(100) and C422 on Si(110) substrates consist of nanograins with sizes of 50–150 nm. Only the film in sample C425 consists of rectangular grains 200–400 nm in size, what it says about their epitaxial ordering.

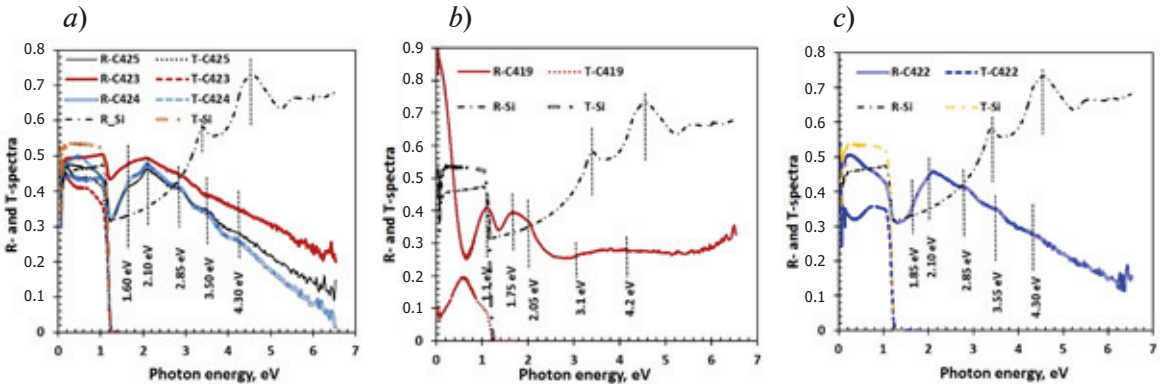

Fig. 1. Reflection and transmission spectra of Ca_2Si films on Si(111) (samples C423, C424, C425) (*a*), Si(001) (sample C419) (*b*) and Si(110) (sample C422) (*c*) substrates

The main features for the selected samples with Ca_2Si films were transparency in the photon energy range of 0.05–1.2 eV. The shape of the reflection spectra (Fig. 1) and the position of the peaks at energies from 1.3 eV to 4.5 eV for Ca_2Si films not covered by silicon are retained also taking into account Ca_2Si films on silicon [4].

Furthermore, absorption coefficient spectra were calculated (Fig. 2, *a*). It can be seen that a high level of the absorption coefficient $(1.0–1.5)\cdot10^4$ cm^{-1} is maintained from 1.0 eV to 0.4 eV, which corresponds to a high density of states in the Ca_2Si band gap. Fundamental absorption of light begins at photon energies above 1.0 eV, which is confirmed by the spectra of the squared absorption coefficient versus photon energy (Fig. 2, *b*). Extrapolation of the linear portions of this dependence for the grown films gives a certain spread in the values of the direct interband transition from 1.02 eV to 1.09 eV, which are close to the values of $E_{1d} = 1.095 \pm 0.15$ eV [4]. The maximum value of the direct interband transition was obtained for a film with a minimum thickness and grown at a temperature of 250 °C.

Comparison with the data of ab initio theoretical calculations of the absorption coefficient spectra (Fig. 3 left panel) and reflection spectra (Fig. 3, right panel) for three light polarizations in $Ca_2Si(100)$ thin films shows a good agreement in terms of peaks in Ca_2Si, which corresponds to the main interband transitions in Ca_2Si single crystals [7] and experimental spectra (Fig. 1).

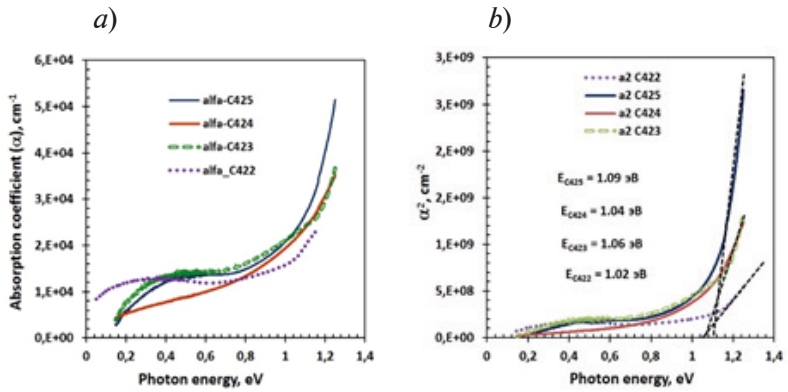

Fig. 2. Spectra for absorption coefficient (*a*) and square of absorption coefficient versus photon energy (*b*) for Ca_2Si films on Si(111) (samples C423, C424, C425) and Si(110) (sample C422) substrates

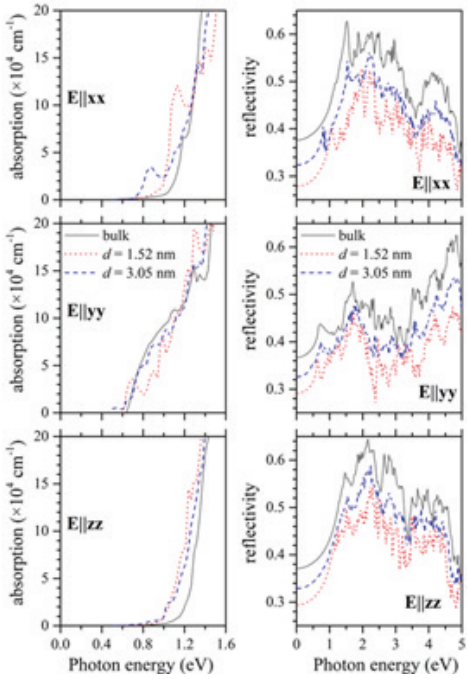

Fig. 3. Dependence of optical absorption (left panel) and reflection (right panel) coefficients on the energy of photons for thin $Ca_2Si(100)$ films in comparison with bulk Ca_2Si material

The absorption edge, according to the calculation data, is at an energy of about 0.72–0.82 eV (Fig. 3, left panel), depending on the polarization of the incident radiation (*xx*, *yy*, *zz*). The strongest interband transition begins at energy of about 1.2 eV. The latter value is in good agreement with the experimental data (E_g = 1.095 eV) [4].

Calculations from the reflection spectra by the Kramers–Kronig method showed the presence in Ca_2Si films on silicon of strong absorption at energies higher than 1.5–2.0 eV, depending on the presence of an additional phase, for example, CaSi (sample C419) (Fig. 4, *a*). This absorption is associated with direct interband transitions occurring with a strong oscillator far enough from the fundamental absorption edge in Ca_2Si (0.88 eV). Calculation of the optical absorption value showed that it starts at energies above 1.5 eV with a peak above 2.1 eV (Fig. 4, *b*) regardless of the crystalline quality of the films and the presence of the calcium monosilicide phase.

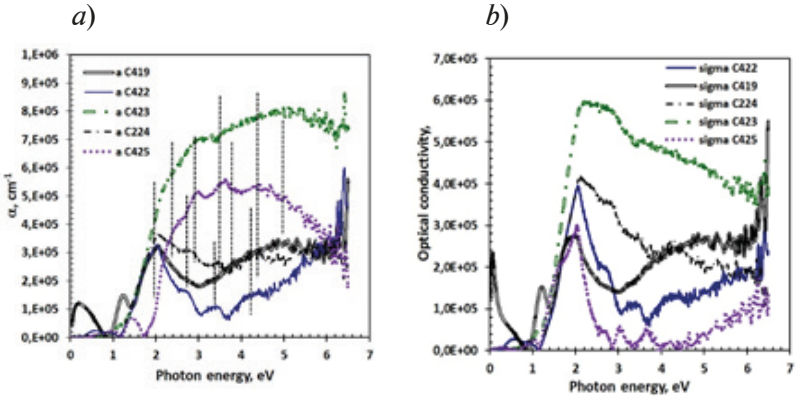

Fig. 4. Spectra for absorption coefficient (*a*) and optical conductivity (*b*) for Ca_2Si films on Si(111), Si(001) and Si(110) substrates in samples C419, C422, C423, C424 and C425

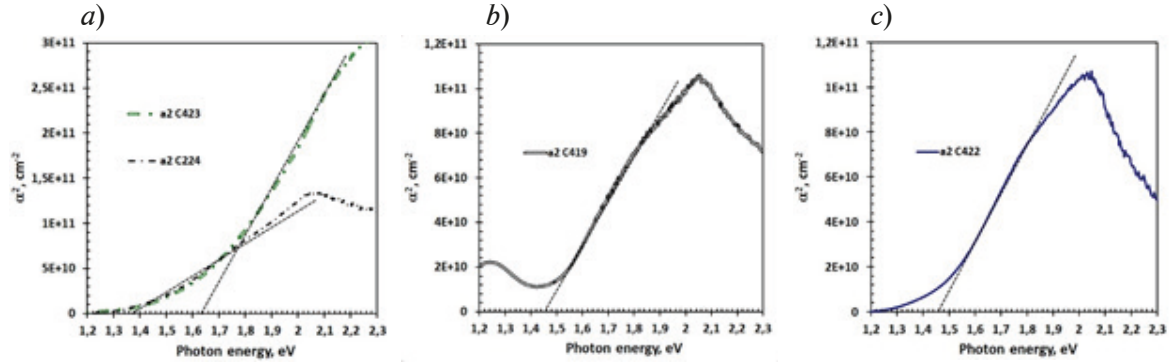

Fig. 5. Spectral dependences of the square of the absorption coefficient versus photon energy for Ca_2Si films on Si(111) (*a*), Si(001) (*b*) and Si(110) (*c*) substrates in samples C423, C424, C419 and C422

The values of interband transitions were determined by the standard procedure for straightening the dependence of the square of the absorption coefficient on the photon energy [9] (Fig. 5). For Ca_2Si films on a Si(111) substrate (samples C423 and C424), two direct interband transitions with energies of 1.37 eV and 1.64 eV were determined (Fig. 5, *a*). For the sample C419 on the Si(001) substrate, which contains the main Ca_2Si phase and an additional CaSi phase, one direct interband transition with an energy of 1.46 eV is observed (Fig. 5, *b*). The same value is observed for the Ca_2Si film on the Si(110) substrate (Fig. 5,*c*, sample C422). For grains of Ca_2Si in the sample C425 the main interband transition is observed at 1.98 eV, and the first one is observed at about 1.27 eV.

Using the rules of integral sums [8] for samples with Ca_2Si films on silicon substrates with (111), (001) and (110) orientations, effective values of the number of electrons per unit cell (n_{eff}) (Fig. 6, *a*) and effective permittivity (ε_{eff}) (Fig. 6, *b*) were calculated. The value of n_{eff} begins to increase at energies above 1.6 eV, which corresponds to the calculated reflectance spectra (Fig. 4). The initial contribution to the effective permittivity (ε_{eff}) (Fig. 6, *b*) is also made by interband transitions with energies from 0.4 eV to 1.4 eV, which is associated with their low oscillator strength according to the theoretical data [7]. This contribution increases with increasing density of states and transition probabilities at energies above 1.6 eV.

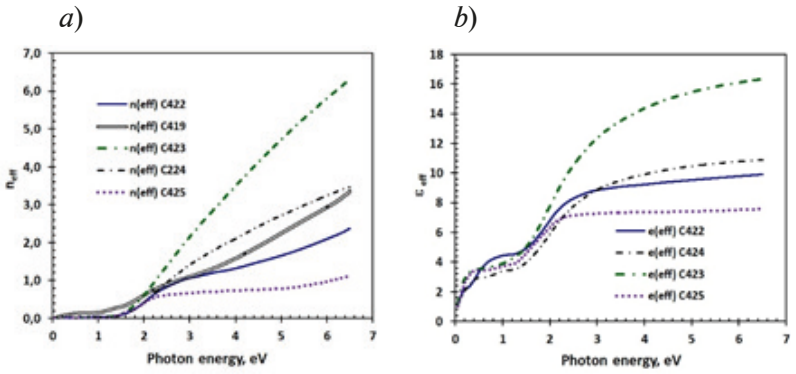

Fig. 6. Spectral dependences of the effective values of the number of electrons per unit cell (n_{eff}) (Fig. 4, *a*) and effective permittivity (e_{eff}) versus photon energy for Ca_2Si films on the Si(111) (*a*), Si(001) (*b*) and Si(110) (*c*) substrates in samples C423, C424, C419 and C422

Conclusion

An analysis of the structure, phase composition, optical and phonon properties of films grown by MBE on silicon surfaces with (111), (100), and (110) orientations showed that the optimum temperature for single-phase formation of Ca_2Si is 250 °C. An increase in the substrate temperature to 300 °C during growth on a template leads to an increase in the contribution of the CaSi phase and blocking the growth of Ca_2Si, regardless of the ratio of the rates of Ca and Si deposition. From Kramers–Kronig calculations it was shown that the main peaks in the optical conductivity spectrum with energies of 1.60, 2.0, 2.67, 3.25 and 4.05 eV repeat the peaks in the reflection spectrum. The absorption coefficient spectrum shows a major increase above 1.6 eV, which corresponds to the contribution from high-energy interband transitions in the Ca_2Si film. The contribution of transitions with lower energies is poorly reproduced due to the contradictions between the idealized two-layer model with a sharp boundary and a film with a developed surface and interface. A comparison of ab initio calculations of the band energy structure and optical properties for a bulk Ca_2Si and 2D Ca_2Si layers with experimental data in the region of high-energy transitions showed good agreement between the main maxima in the theoretical and experimental reflection spectra.

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