The 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 studied the growth, optical propertie sand 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 band energy 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 agreement.

Introduction

In the calcium-silicon system, at least ***six silicides*** are formed [**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.

[**1**] P. Manfrinetti, et.al. Intermetallics. **8** (2000) 223.

[**2**] S. Lebegue, et.al. Phys. Rev. B **72** (2005) 085103.

[**3**] F.W. Clarke, Phil. Soc. Washington Bull. **11** (1889) 135.

[**4**] N.G. Galkin, et.al. Mat. Sci. in Sem. Proc. **113** (2020) 105036.

1. Experimental

The growth of Ca_2Si films was carried out in an ultrahigh vacuum (UHV) chamber of an OMICRON Compact setup with a base vacuum of 2×10^{-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.

In all growth experiments, Knudsen cells were used as evaporative sources of **Mg** and **Ca** with direct current passing through a resistive heating element. **Ca_2Si** films were grown on all substrates by co-deposition of **Si** and **Ca** at a temperature of **250°C** or **300 °C** on a preliminarily formed ***Mg_2Si sacrificial layer***, which was transformed into **Ca_2Si** upon deposition of **Ca** atoms on the substrate at **250°C**. The deposition rates (**Ca**, **Mg**, and **Si**) were calibrated using a quartz thickness sensor.

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 **0.05-6.20 eV** on a ***Hitachi U-3010 spectrophotometer*** with an integrating sphere and ***Fourier spectrometer Bruker Vertex 80v***. The optical functions were calculated in the transparency region from the transmission and reflection 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**].

[**5**] Galkin, N.G.; Maslov A.M.; Konchenko, A.V., *Thin Solid Films* **311** (1997**)** 230-238.

[6] P. Blaha, et.al. (Karlheinz Schwarz, Tech. Universität Wien, Vienna, 2001).

2. Results and Discussion

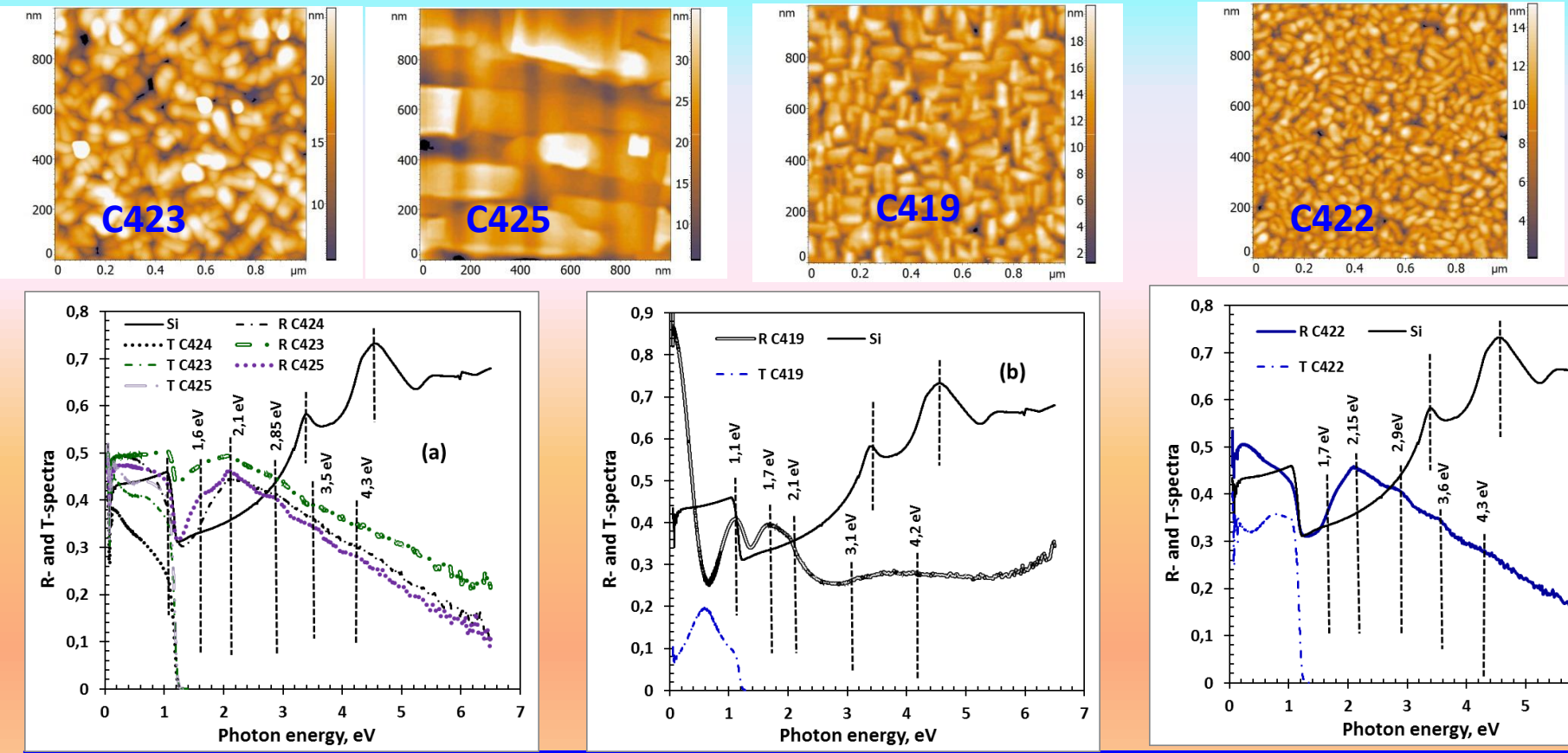
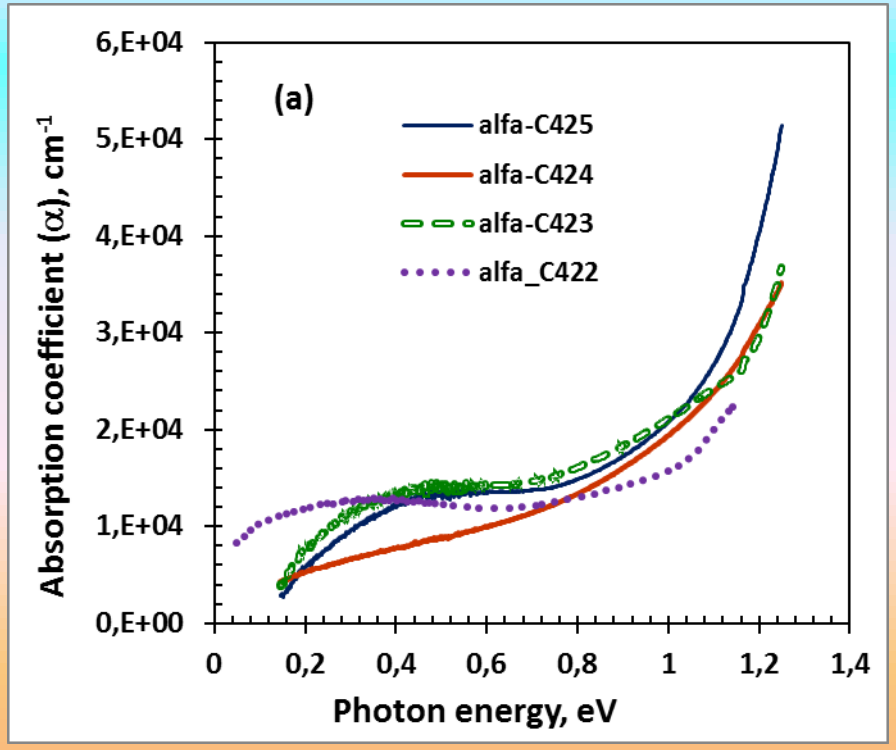


Fig. 1. AFM images and Reflectance and transmittance spectra of Ca_2Si films on *Si(111)* (samples C423, C424, C425) (a), *Si(001)* (sample C419) (b) and *Si(110)* (sample C422) (c) substrates).

The **morphology** of the grown films was studied by **AFM**. Most of them consist of nanograins with sizes of 5–150 nm. Only the film in sample **C425** consists of rectangular grains ***200–400 nm*** in size.

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** 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**].



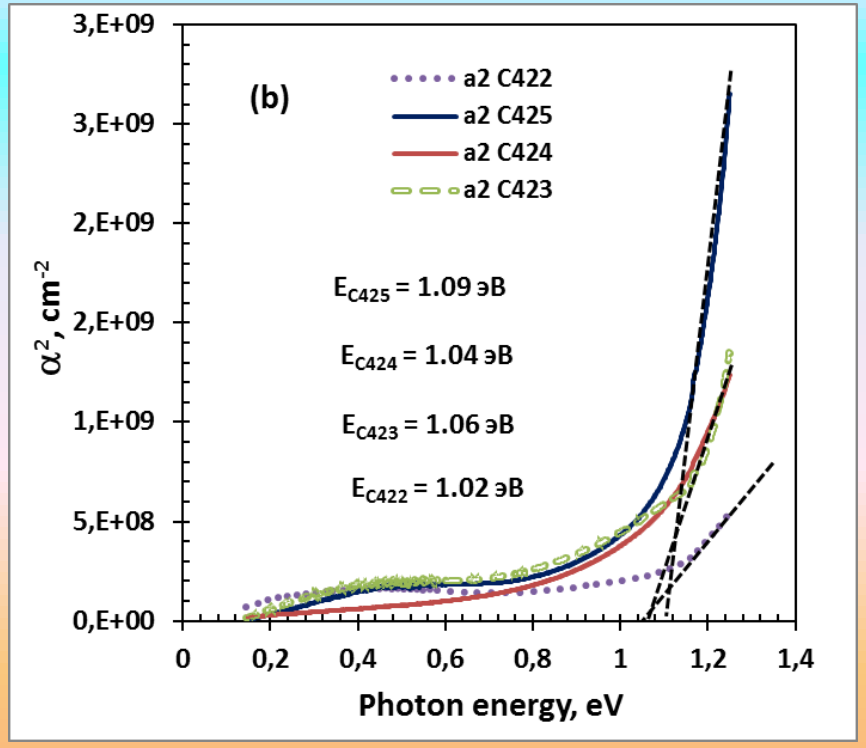
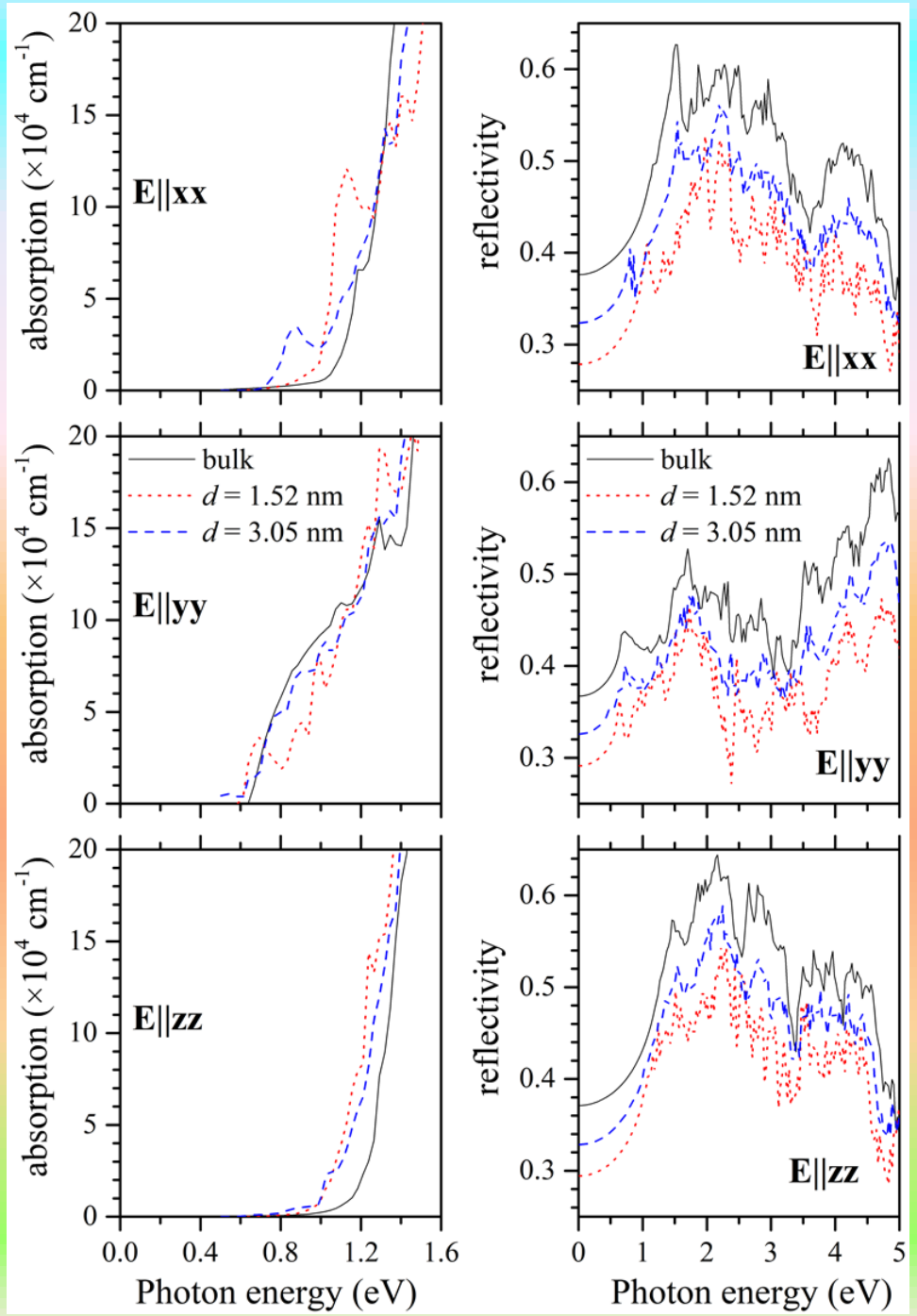


Fig. 2. Spectra of the absorption coefficient (a) and the square of the absorption coefficient versus photon energy (b) for Ca_2Si films on *Si(111)* (samples C423, C424, C425) and *Si(110)* (sample C422) substrates .

Absorption coefficient spectra were calculated (**Fig. 2a**). It can be seen that from **1.0 eV** to **0.4 eV**, a high level of the absorption coefficient **$(1.5 – 1.0) \times 10^4$ cm^{-1}** is maintained, 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. 2b**). 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 ± 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**.

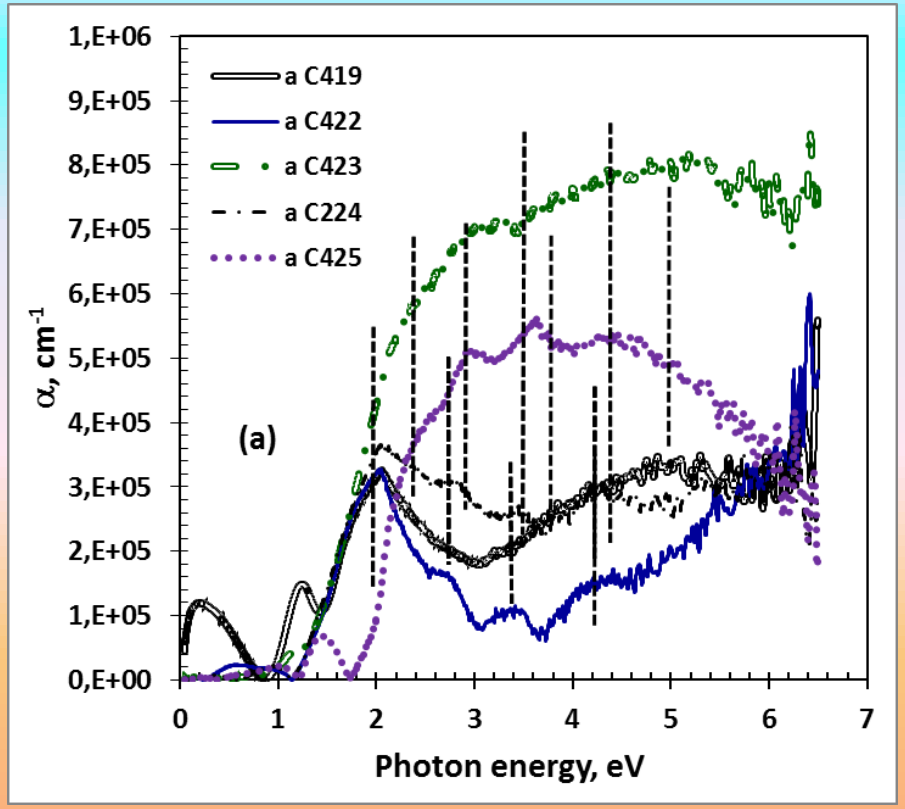


Comparison with the data of ***ab initio*** theoretical calculations of the absorption coefficient spectra (**Fig. 3 left**) and reflection spectra (**Fig. 3, right**) for three polarizations of light in **Ca_2Si (100) thin films** shows a good agreement in terms of peaks in **Ca_2Si**, which corresponds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

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

[7] Migas, D.B.; Miglio, L.; Shaposhnikov V.L.; Borisenko V.E., Physical Review B 2003, 67, 205203.

Fig. 3. The dependence of the coefficients of optical absorption and reflection depending on the energy of photons for ***thin* Ca_2Si(100) *films*** in comparison with bulk material.



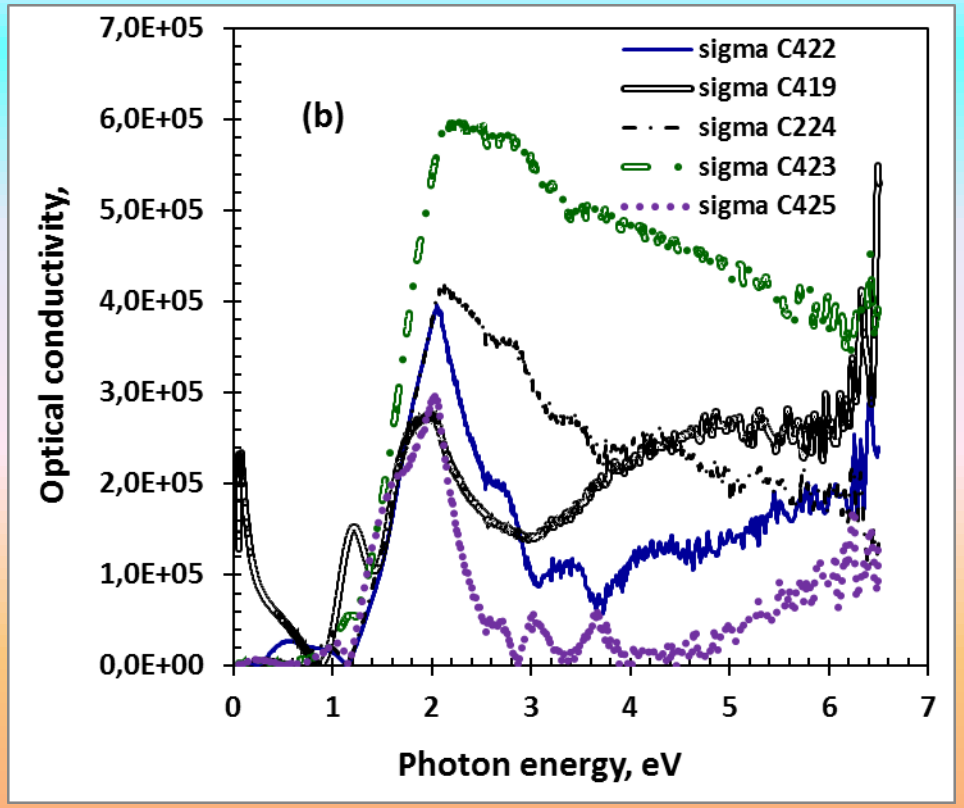
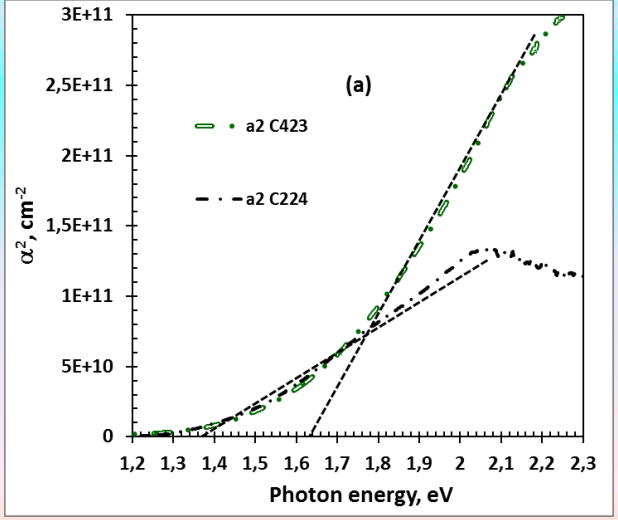
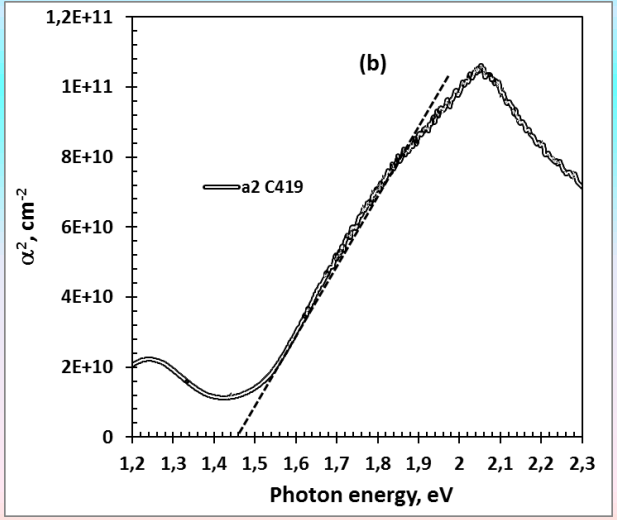


Figure 5. Spectra of absorption coefficient (**a**) and optical conductivity (**b**) for **Ca_2Si** films on the ***Si(111), Si(001)*** and **Si(110)** ***substrates*** in samples ***C419, C422, C423, C424*** and ***C425***.

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. 5a**). This absorption is associated with the realization of direct interband transitions 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. 5b**) regardless of the crystalline quality of the films and the presence of the calcium monosilicide phase.





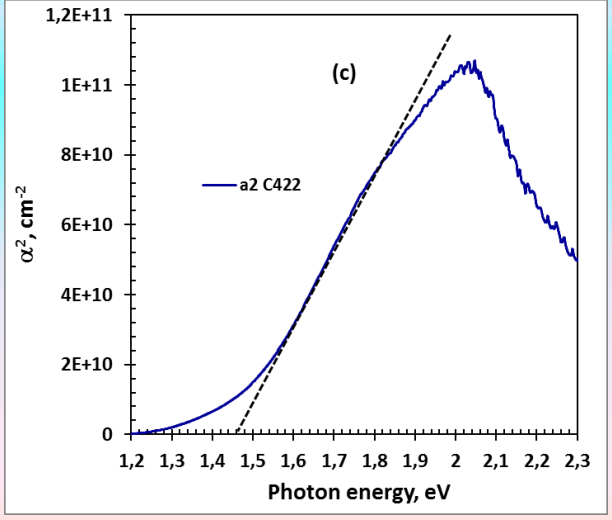


Figure 6. Spectral dependences of the square of the absorption coefficient versus photon energy for **Ca_2Si** films on the ***Si(111) (a), Si(001) (b)*** and **Si(110) (c)** ***substrates*** in samples ***C423, C424, C419*** and ***C422***.

To determine the values of interband transitions, the standard procedure for straightening the dependence of the square of the absorption coefficient on the photon energy [9] was used (**Fig. 6**). 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. 6a**). 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. 6b**). The same value is observed for the **Ca_2Si** film on the ***Si(110)*** substrate (**Fig. 6c**, 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**.

[9] J.I. Pankov, Optical Processes in Semiconductors, 2nd Revised ed. edition, Dover Books on Physics, New York, 2010; pp. 22-448.

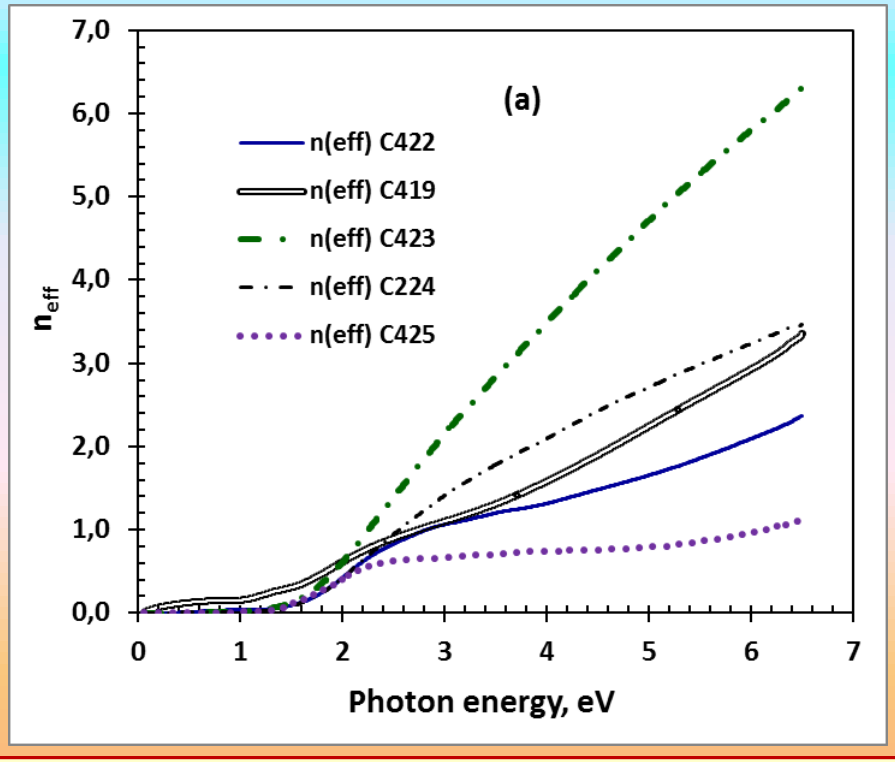


Figure7. Spectral dependences of the effective values of the number of electrons per unit cell (n_{eff}) (Fig. 5a) and effective permittivity (ε_{eff}) versus photon energy for **Ca_2Si** films on the ***Si(111) (a), Si(001) (b)*** and **Si(110) (c)** ***substrates*** in samples ***C423, C424, C419*** and ***C422***.

Using the rules of integral sums [**9**] 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. 5a**) and ***effective permittivity (ε_{eff})*** (**Fig. 7b**) were calculated. The value of n_{eff} begins to increase at energies above **1.6 eV**, which corresponds to the calculated reflectance spectra (**Fig. 5**). The initial contribution to the effective permittivity (ε_{eff}) (**Fig. 7b**) 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**.

Conclusions

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 seed layer 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. For **Ca_2Si** films with different crystalline quality, calculations were carried out using the Kramers-Kronig method. It is shown that the main peaks in the optical conductivity spectrum with energies of ***1.60 eV, 2.0 eV, 2.67 eV, 3.25 eV*** 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 morphology. A comparison of ***ab initio*** calculations of the band energy structure and optical properties for a **Ca_2Si** single crystal and two-dimensional **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***. However, the calculated values of the absorption coefficient for a **Ca_2Si** single crystal and ***thin Ca_2Si films*** at photon energies of **0.8–1.2 eV** are approximately **10–12 times** lower than the values of the absorption coefficient calculated from the experimentally observed transmission and reflection spectra for the **Ca_2Si** films, which correspond to an increase in absorption on free carriers by dispersionless region.