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Ca_5Si_3 film MBE growth on Si(111) substrate: structure and optical properties

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Abstract. In this work calcium silicide films grown by MBE method on a Si(111) substrate at a temperature of 500 °C with deposition flux ratios NCa : NSi = 3.49, 3.98, the formation of a epitaxial Ca_5Si_3 film with a thickness of up to 40 nm was detected, which was proven by XRD method. Reflection peaks in the region of interband transitions at 2.2, 2.75, 3.57 and 4.4 eV, a semi-metallic character of reflection at energies less than 0.5 eV, partial transmittance at 0.4–1.25 eV and a unique phonon structure with Raman shifts at 102, 110, 124, 160, 190, 220, 241, 344 and 379 cm^{-1} were detected for the first time in the reflection and Raman spectra of the Ca_5Si_3 film.

Keywords: silicon, Ca_5Si_3, MBE growth, film, crystal structure, optical functions, IR transparency, free carrier absorption

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Рост пленок Ca_5Si_3 методом МЛЭ на подложке Si(111): структура и оптические свойства

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Аннотация. В данной работе на пленках силицида кальция, выращенных методом молекулярно-лучевой эпитаксии на подложке Si(111) при температуре 500 °C с соотношениями потоков осаждения NCa : NSi = 3,49, 3,98, обнаружено образование эпитаксиальной пленки Ca_5Si_3 толщиной до 40 нм, что подтверждено методом рентгеновской дифракции. Впервые в спектрах отражения и комбинационного рассеяния пленки Ca_5Si_3 обнаружены пики отражения в области межзонных переходов при 2,2, 2,75, 3,57 и 4,4 эВ, полуметаллический характер отражения при энергиях менее 0,5 эВ, частичное пропускание при 0,4–1,25 эВ и уникальная фононная структура с КРС сдвигами при 102, 110, 124, 160, 190, 220, 241, 344 и 379 $см^{-1}$.

Ключевые слова: кремний, Ca_5Si_3, МЛЭ рост, пленка, кристаллическая структура, оптические функции, ИК прозрачность, поглощение на свободных носителях

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Introduction

Among calcium silicides $CaSi_2$, Ca_2Si and CaSi are most common displaying interesting optical and electrical properties and they have been grown as single-phase films on silicon [1–4]. However, the other calcium silicide Ca_5Si_3 has not been easily grown as films and powders [5–7], because of the peritectic reactions during its formation in addition to close energies of formation of silicides in the Ca-Si system [8]. In paper [4] it was decided to follow the two-step method previously used for the formation of magnesium silicide. At the first stage, a CaSi layer was formed on the atomically clean silicon surface with the (001) orientation by the MBE (molecular beam epitaxy) method with an average Ca supersaturation (NCa : NSi = 3.2) at a temperature of 400 °C, and then, with additional step-by-step reactive deposition of calcium at temperatures of 490 °C, 600 °C and 700 °C, the transformation of the CaSi lattice into the Ca_5Si_3 lattice was ensured. However, according to the XRD (X-ray diffraction) data [4], the resulting film consisted of the contribution of Ca_5Si_3 grains (small narrow peaks) and a bigger contribution of CaSi grains (broadened peaks). The presence of two phases in the film did not allow analyzing the structure and determining their optical functions as well as the nature of optical conductivity.

In this work, we study the growth of the film by the MBE method with an increased ratio of Ca to Si deposition rates at a temperature of 500 °C with the following identification of the structure of the Ca_5Si_3 film by the XRD method and investigation the its optical and phonon properties, including the calculations of the optical functions.

Materials and Methods

Experiments on the formation of Ca_5Si_3 films on Si(111) substrate were carried out in an OMICRON Compact ultrahigh vacuum setup with a base vacuum of 1×10^{-10} Torr, as well as a block of Si and Ca molecular beam sources and a quartz thickness gauge. A rectangular strip of *n*-type silicon (4×17 mm^2) with a resistivity of 1000 Ohm × cm (Si(111)-FZ1000) served as a sublimation silicon source and a silicon substrate. The Knudsen cell made of pyrolytic boron nitride heated with direct current was used as a Ca source. For the grown samples, the deposition rates of Ca and Si were (7.3–8.4) nm min^{-1} and (0.9–0.95) nm min^{-1}, respectively, in different experiments. The morphology of the films was examined using a SPM Solver P47 in the tapping mode. The transmission and reflectance spectra were recorded at room temperature using Hitachi U-3010 spectrophotometers and a Bruker Vertex 80v Fourier transform spectrometer in the photon energy range of 0.05–6.50 eV. Calculations of optical functions were done in the frame of a two-layer optical model of the film-substrate system [9]. Raman spectra excited by light with wavelengths of 473 and 633 nm were recorded at room temperature using an NTEGRA SPECTRA II setup. The crystal structure of the grown films was examined by X-ray diffraction on a RIGAKU SmartLab diffractometer (ICH FEB RAS) in the 2θ angle range from 5° to 80° with a step of $2\theta = 0.01°$.

Results and Discussion

Two samples (A and B) were respectively grown at different calcium to silicon flux ratios ($N_{Ca} : N_{Si} = 3.49$ and 3.98) and the same deposition time. After reloading of samples the morphology of grown films were studied. At the minimal ratio of Ca to Si atom flows in samples A (Fig. 1, *a*), the small number of islands on the film surfaces and the film root mean square roughness

(σ_{rms}) 3.7 nm is observed. At the maximum ratio of Ca/Si atomic flow (sample B, Fig. 1, *b*), a certain density of rectangular elongated nanocrystals (NC) on the film surface with $\sigma_{rms} = 4.23$ nm is observed.

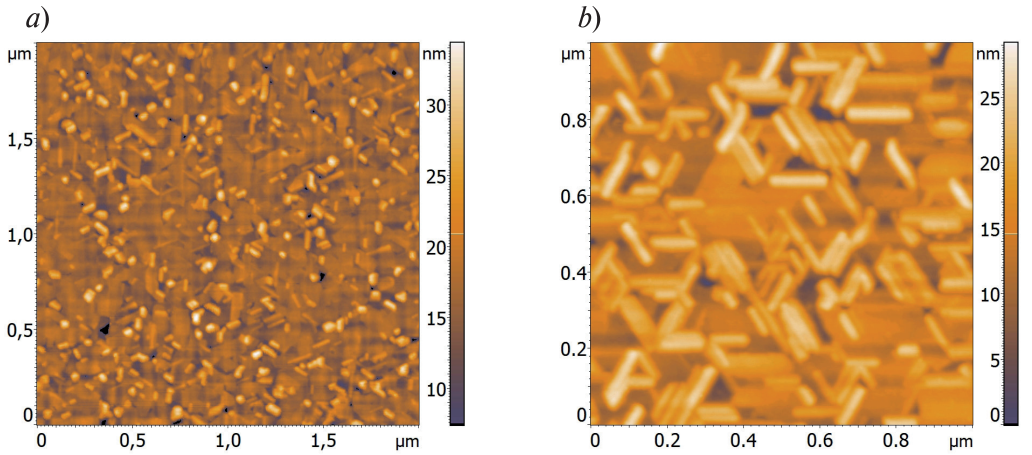

Fig. 1. AFM images of the surface of the Ca silicide films in samples A (*a*) and B (*b*)

The XRD spectrum was recorded immediately after unloading from the chamber for sample B. The XRD spectrum (Fig. 2) shows contributions from the Si substrate on which the film was grown at 28.45° and 58.86°, corresponding to diffraction from the Si(111) and Si(222) planes. In addition, it shows peaks from the film at several angles 2Θ: 16.1°, 32.5°, 40.16°, 44.5°, 49.6° and 75.6°. The first peak corresponds to trigonal-rhombohedral $CaSi_2$ polymorphs (space group $R\bar{3}m$) of the $CaSi_2$-3R(003) [10] plane. The second peak can be attributed to two silicides: $CaSi_2$-3R(006) and tetragonal Ca_5Si_3(220) (space group I4/mcm) [11]. According to databases, the intensities of these peaks are approximately the same, so it is difficult to unambiguously interpret which silicide a given peak belongs to. The third peak is in good agreement with the Ca_5Si_3(125). The other three peaks are characterized by an intensity less than 1% of the intensity of the peak $2\Theta = 32.5°$ and correspond to Ca_5Si_3 with planes (134), (141) and (12 11), respectively.

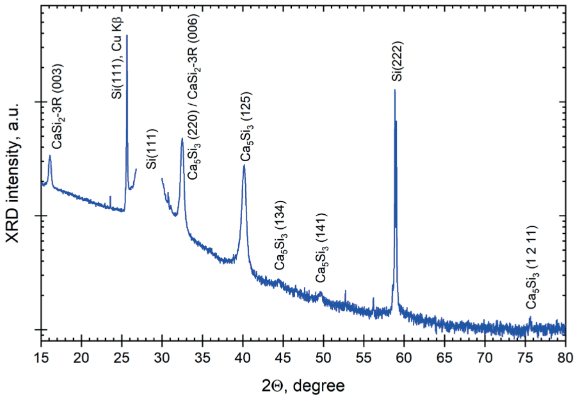

Fig. 2. XRD spectrum of the film Ca_5Si_3 film in the sample B

Studies of the optical transmission and reflection spectra of Ca_5Si_3 showed (Fig. 3) that the highest velocity ratio (3.95, sample B) provides a larger reflectivity amplitude in the 0.1–1.2 eV range and narrower peaks, indicating better crystalline film quality. In addition, in the reflection spectra for samples A and B in the region of photon energies greater than 2 eV, peaks with energies of 2.20, 2.75, 3.57 and 4.4 eV are observed, which almost do not coincide with the peaks CaSi (1.95, 2.6, 3.5 and 4.4 eV) and $CaSi_2$ (1.9, 3.2, 3.9 and 5.0) [4]. According to the XRD data (Fig. 2) in the sample B there is an admixture of the $CaSi_2$ phase on the film surface. Calculations of the true reflectance spectrum of the calcium silicide film for sample B from the two-layer model [9] in the energy range of 0.1–1.2 eV showed (Fig. 3, curve R_0_B) that at energies below

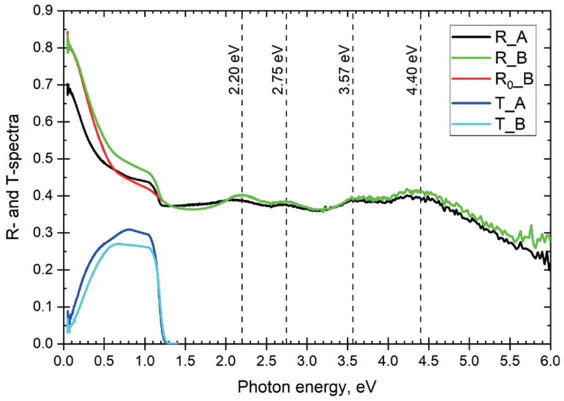

Fig. 3. Reflectance (R) and transmittance (T) spectra for samples A and B

1 eV a weak minimum with an energy of about 0.6 eV is observed [4]. Reflectance in all films below 0.5 eV increases to 0.6–0.8 indicating a metallic character in the films. Registration of transmission spectra in the far IR region (50–700 cm^{-1}) showed that Ca_5Si_3 films are characterized by the absence of IR-active phonon modes.

From the reflection and transmission spectra, within the framework of the two-layer model [9], calculations of the optical functions for the Ca_5Si_3 film were performed. The spectra of the refractive index (n) and extinction (k) are shown in Fig. 4, *a*. Sample B is characterized by higher values of the refractive index and extinction coefficient than sample A, which is due to less scattering at grain boundaries, i.e. better crystalline quality in comparison. Calculations of the absorption coefficient in films (Fig. 4, *b*) showed the relative transparency of the films in the photon energy range of 0.4–1.25 eV and a smooth increase at lower energies, which is determined by the absorption on free carriers in them [12].

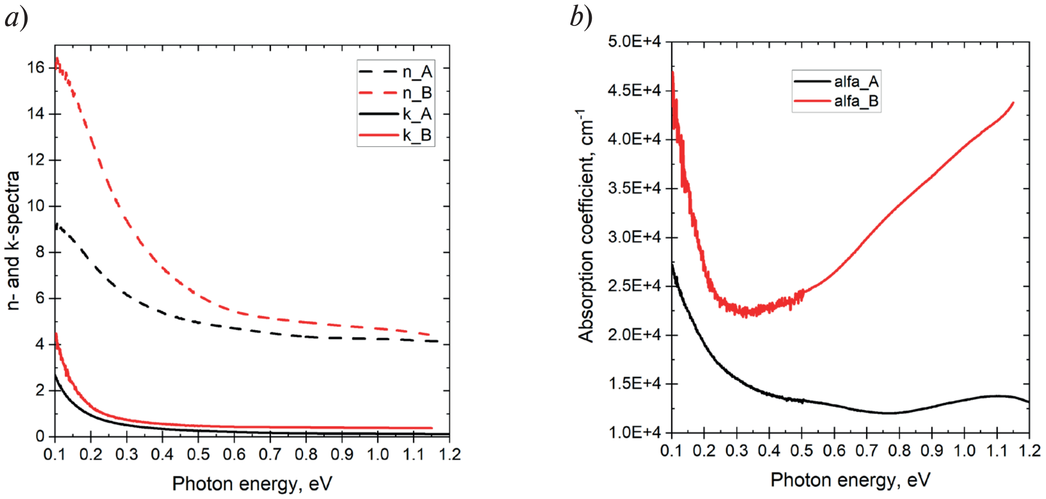

Fig. 4. Spectra of refraction index (n) and extinction coefficient (k) (*a*) and spectra of absorption coefficient for films in the samples A and B (*b*)

The studies of the Raman spectrum of the film in sample B upon excitation by a laser with a wavelength of 633 nm showed the appearance of a pronounced structure of 14 peaks with Raman shifts (102, 110, 124, 160, 190, 220, 241, 304, 344, 379, 387, 416, 449 and 521 cm^{-1}). When the laser wavelength is reduced to 473 nm, some of the peaks below 190 cm^{-1} and the peak at 304 cm^{-1} disappear from the spectrum, but the rest repeat the peaks with large Raman shifts. The peaks at 304 and 521 cm^{-1} are attributed to the silicon substrate phonons (2TA and TO s, respectively). It is known [4, 10] that a peaks at 387, 416 and 449 cm^{-1} is observed in the $CaSi_2$ film, which confirms the presence of the $CaSi_2$ phase detected according to the XRD data in the grown film. The remaining 9 peaks 102, 110, 124, 160, 190, 220, 241, 344 and 379 cm^{-1}correspond to the

Ca_5Si_3 phase, for which there are currently no data on active Raman phonons in the literature. These calculations are planned to be carried out together with first-principles calculations of the electronic structure and presented in the next article.

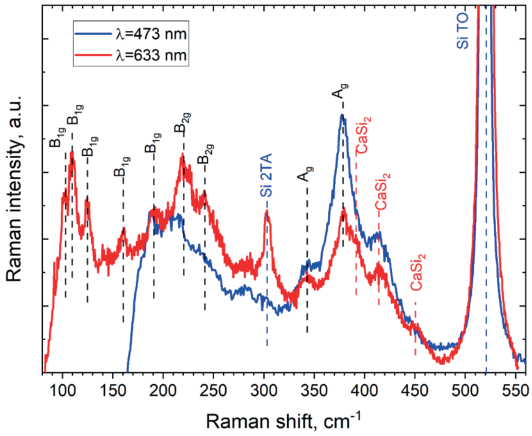

Fig. 5. Raman spectra of the Ca_5Si_3 film in the sample *C* on the Si substrate

Conclusion

A technique for growing Ca_5Si_3 films by molecular beam epitaxy with a variable calcium-to-silicon flux ratio at a substrate temperature of $T = 500$ °C has been developed. According to X-ray diffraction and morphology studies, it has been established that the maximum single-phase state of the Ca_5Si_3 film is achieved with a calcium-to-silicon flux ratio of 3.98. A study of the optical reflection and transmission spectra, as well as the Raman spectra of calcium silicide films, has shown that the polycrystalline Ca_5Si_3 film is characterized by a reflection spectrum with unique peaks at 2.20, 2.75, 3.57, and 4.4 eV and a reflection coefficient of 0.38–0.43 with an increase in the reflection coefficient to $R = 0.8$ in the far IR range. It was found that the Ca_5Si_3 film has a unique phonon structure with 9 peaks in the Raman shift range from 102 to 379 cm^{-1}. Calculations of the optical functions of the Ca_5Si_3 films showed that it exhibits semi-metallic properties with transparency in the photon energy range of 0.4–1.1 eV and absorption on free carriers at phonon energies of 0.1–0.4 eV.

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