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Optical, phononic and semiconductor properties of magnesium silicide films formed on silicon by layer-by-layer (Mg+Si) reactive epitaxy

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Abstract. Magnesium silicide films were formed on *n*-type Si (111) substrates with resistivities ranging from 2 to 15 Ohm·cm (samples 1 and 2) and from 0.1 to 0.5 Ohm·cm (samples 3 and 4) using reactive epitaxy with layer-by-layer deposition of magnesium and silicon layers at a temperature of 250 °C. The article presents the results of a study of the morphology, optical and phononic properties, and the band gap of samples containing magnesium silicide films with thicknesses of 496, 682, 1143, and 414 nm, according to SEM data on a cross section. Atomic force microscopy showed that the films of all samples were formed by the Volmer-Weber mechanism, with the islands coalescing into clusters and grains. The island area of the film of the first sample ranges from 0.12 to 0.48 μm^2, the second − from 0.02 to 0.06 μm^2, the third − from 0.01 to 0.04 μm^2, and the fourth − from 0.04 to 0.09 μm^2. The islands coalesce into clusters and grains. In all grown films, Raman scattering (RS) peaks were detected at 258, 348, and 693 cm^{-1}, which correspond to the formation of Mg_2Si. In the IR spectra, the minimum transmittance at a wavenumber of 270 cm^{-1} varies from 0.04 to 0.01, which corresponds to an increase in the absorption of IR photons with an increase in the thickness of the Mg_2Si films in the grown samples. The reflection and transmission spectra of the grown films revealed both interference peaks (below 1.5 eV) and a peak with an energy of 2.2−2.3 eV, corresponding to the interband transition in Mg_2Si. Based on the infrared absorption spectra, the indirect band gap width was calculated for each film: 0.80 and 0.86 eV for samples 1 and 2; 0.77 and 0.79 eV for samples 3 and 4.

Keywords: magnesium silicide, nanofilms, optical spectra, band gap, surface morphology

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Материалы конференции
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Оптические, фононные и полупроводниковые свойства пленок силицида магния, сформированных на кремнии методом послойной (Mg+Si) реактивной эпитаксии

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Аннотация. Формирование пленок силицида магния осуществлялось на подложках *n*-типа Si (111) с удельным сопротивлением от 2 до 15 Ом·см (образцы 1, 2) и от 0,1 до 0,5 Ом·см (образцы 3 и 4) способом реактивной эпитаксии при послойном осаждении слоев магния и кремния при температуре 250 °C. В статье представлены результаты исследования морфологии, оптических, фононных свойств и ширины запрещенной зоны образцов, содержащих пленки силицида магния с толщинами 496, 682, 1143 и 414 нм по данным СЭМ на поперечном срезе. Методом атомно-силовой микроскопии показано, что пленки всех образцов формировались по механизму Вольмера-Вебера, при этом островки коалесцируют в кластеры и зерна. Во всех выращенных пленках обнаружены пики комбинационного рассеяния света (КРС) 258, 348, 693 см$^{-1}$, которые соответствуют формированию Mg_2Si. В ИК-спектрах минимальное пропускание при волновом числе 270 см$^{-1}$ изменяется от 0,04 до 0,01, что соответствует увеличению поглощения ИК-фотонов с ростом толщины пленок Mg_2Si в выращенных образцах. В спектрах отражения и пропускания выращенных пленок обнаружены как интерференционные пики (ниже 1,5 эВ), так и пик с энергией 2,2–2,3 эВ, соответствующий межзонному переходу в Mg_2Si. По данным инфракрасных спектров поглощения, рассчитана непрямая ширина запрещенной зоны для каждой пленки: 0,80 и 0,86 эВ – образцы 1 и 2; 0,77 и 0,79 эВ – образцы 3 и 4.

Ключевые слова: силицид магния, нанопленки, оптические спектры, запрещенная зона, морфология поверхности

Финансирование: Рост пленок Mg_2Si и расчеты их оптических констант проводили в рамках госзадания АмГУ (внутренний грант АмГУ на 2025-2026 гг.). Исследования оптических и фононных свойств образцов выполнены при поддержке государственного задания ИАПУ ДВО РАН (Тема FWFW-2026-0008).

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Introduction

Currently, areas related to nano- and microelectronics are being widely developed in science and technology. Many modern researchers in the field of photovoltaics are searching for promising materials with new properties in order to increase the conversion rate of light energy into electrical energy. One of these materials is Mg_2Si nanofilms [1–3]. This material is a narrow-band semiconductor with an indirect band gap (from 0.6 to 0.8 eV) [1, 2]. Mg_2Si films have a wide spectral photostability range (200–1800 nm) and a high maximum absorption coefficient (95%) in this wavelength range [3]. The epitaxial growth of magnesium silicide in the film form is complicated by the high degree of Mg atom desorption from the silicon substrate at temperatures

above 300 °C [5]. Therefore, one of the main tasks of modern researchers is also to find an effective method for their formation. This paper discusses the optical, electronic properties, and surface morphology of Mg_2Si films formed on silicon.

Materials and Methods

The formation of Mg_2Si films was carried out in the surface physics laboratory of AmSU in a Varian vacuum chamber, a PHI-590 device, with a base pressure of 10^{-7} Pa. Two experiments were conducted to grow Mg_2Si films on *n*-type Si (111) substrates. The first experiment used substrates with a resistivity of 2 to 15 Ohm·cm, while the second experiment used substrates with a resistivity of 0.1 to 0.5 Ohm·cm. In both cases, the deposition of silicon and magnesium on the substrates was performed using the following thermal sources: *n*-type Si (111) with a resistivity of 50 to 85 Ohm·cm and Mg with a purity of 99.999%. Before the films were grown, the substrates and sources were chemically and thermally cleaned.

All samples with films were formed by the reactive epitaxy method at the substrate heating temperature of 250 °C. A Si (60 nm) buffer layer was formed on the substrates beforehand, the successive deposition of portions of Mg and Si was carried out.

In the first experiment, Mg and Si layers were deposited three times in a thickness ratio of 2.75:1 (sample 1) and 3:1 (sample 2). The deposition rates of magnesium and silicon were 9.4 and 1.1 nm/min, respectively. In the second experiment, Mg and Si layers were deposited in a thickness ratio of 3:1, three times (sample 3) and four times (sample 4). The deposition rates of magnesium and silicon were 10.7 and 1.7 nm/min, respectively.

The thickness of the formed films was determined using scanning electron microscopy (SEM), their optical properties were researched using Raman, infrared, and visible spectroscopy, and their surface morphology was researched using atomic force microscopy.

Results and Discussion

The AFM images of the samples (Fig. 1 and 2) were obtained using the Solver P47 microscope in semi-contact mode.

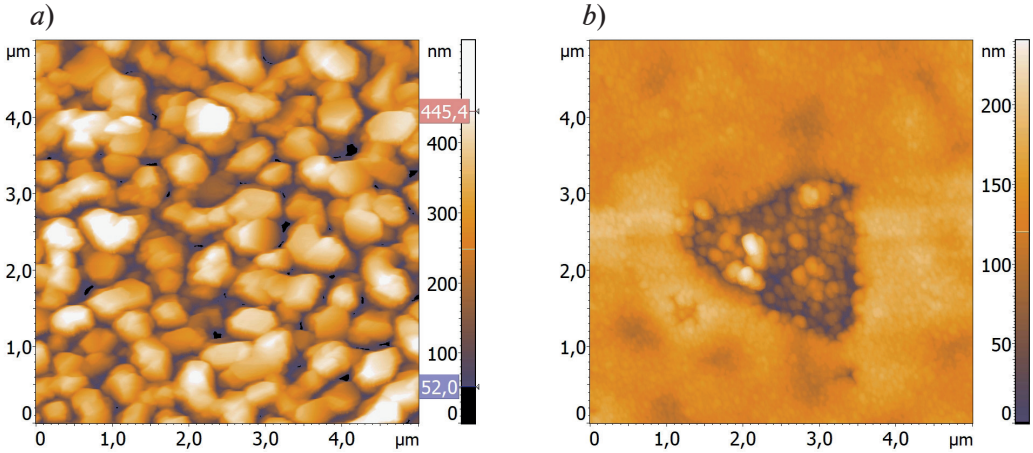

Fig. 1. AFM images of the surface of the first (*a*) and second (*b*) samples

Analysis of the AFM images of the film surface (Fig. 1) showed that both the first and the second sample have a Volmer-Weber island growth mechanism [6, 7]. The lateral dimensions of the particles are in the following ranges: length from 0.4 to 0.8 μm (sample 1) and from 0.2 to 0.3 μm (sample 2), and width from 0.3 to 0.6 μm (sample 1) and from 0.1 to 0.2 μm (sample 2). Based on the geometric measurements, the area of the islands for the first sample ranges from 0.12 to 0.48 μm^2, and for the second sample, it ranges from 0.02 to 0.06 μm^2. Visualization of the AFM images showed that the islands did not completely fuse in sample 1, but in sample 2, they coalesced and formed clusters. The cluster sizes of the second sample in the XY plane are as follows: length from 1.4 to 1.8 μm, and width from 0.7 to 1.4 μm. Their area ranged from 0.98 to 2.52 μm^2. In addition to the islands, a triangular step with a depth of 30 nm is clearly visible in the surface relief. Based on the above, the first sample has a more developed surface relief than the second.

By analyzing the AFM images of samples 3 and 4 (Fig. 2), it was found that the growth of the films also followed the Volmer-Weber mechanism [6, 7]. In the third sample, the size of the islands ranges from 0.1 to 0.2 μm, and in the fourth sample, it ranges from 0.2 to 0.3 μm. The area of the islands ranges from 0.01 to 0.04 μm^2 (sample 3) and from 0.04 to 0.09 μm^2 (sample 4). The islands coalesce into larger grains of about 0.5 μm, with an area of 0.25 μm^2, in sample 3. In sample 4, the coalescence of the islands is less pronounced. There is heterogeneity due to the presence of punctures with a depth of about 20 nm in the surface relief of the third sample. The fourth sample has almost no punctures. Based on the above, it can be concluded that sample 4, compared to sample 3, contains a film with a less developed surface relief.

The thickness of the grown films was determined from the analysis of the SEM images of the cross-sections of the samples obtained using a Hitachi S-3400N electron microscope (Fig. 3). Based on the image analysis results, the film thickness of sample 1 is 496 nm, sample 2 is 682 nm, sample 3 is 1143 nm, and sample 4 is 414 nm.

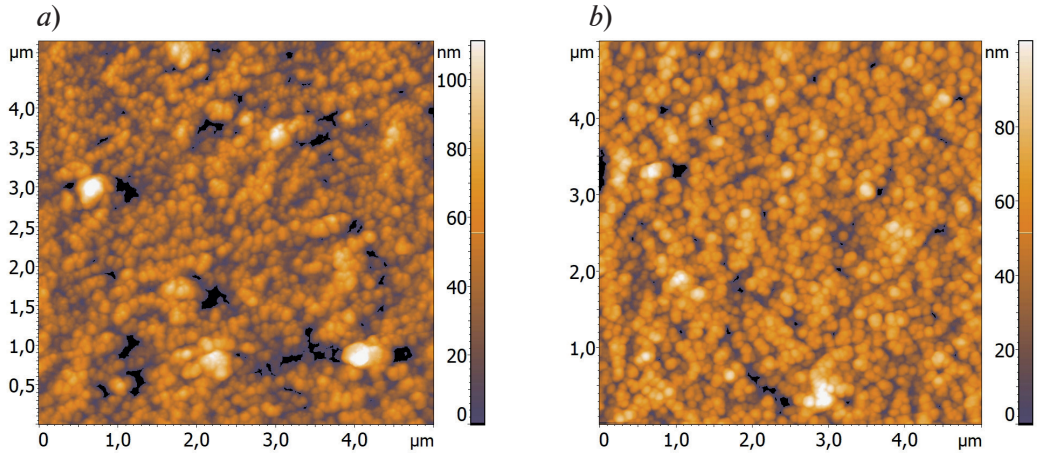

Fig. 2. AFM images of the surface of the third (*a*) and fourth (*b*) samples

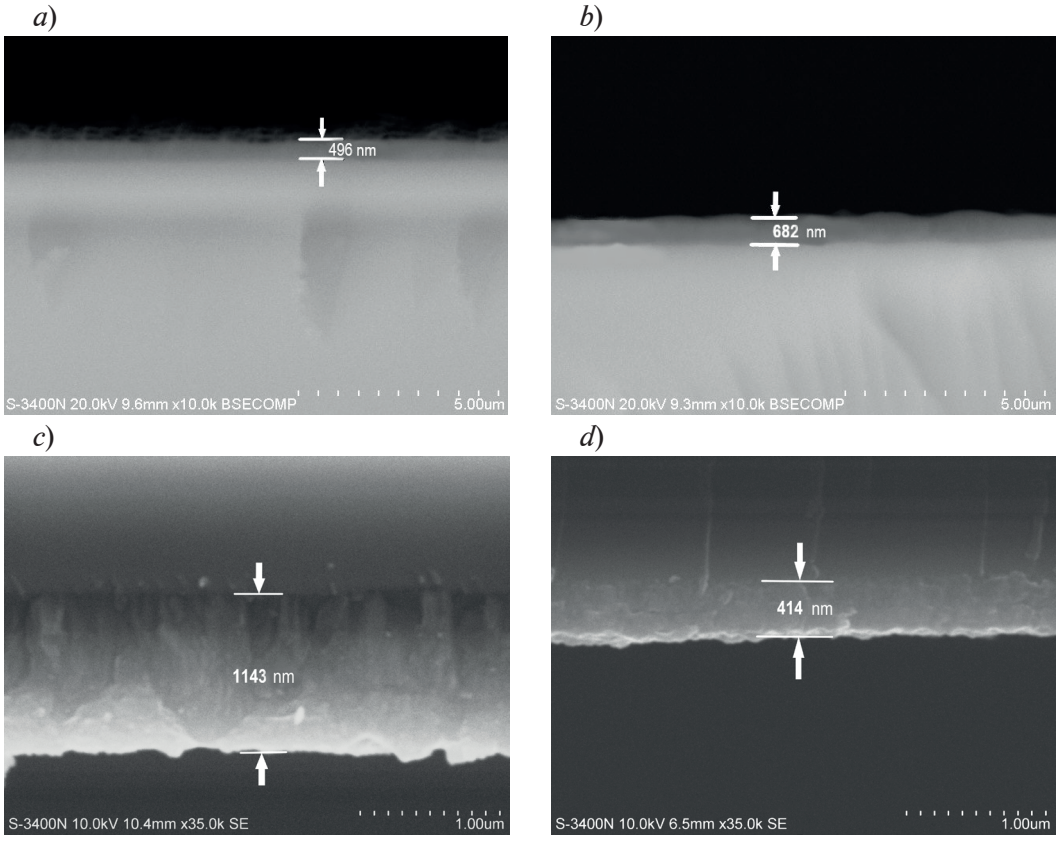

Fig. 3. SEM images of samples 1 (*a*), 2 (*b*), 3 (*c*), and 4 (*d*)

The samples were examined by Raman spectroscopy using an NTEGRA Spectra II (NT-MDT) spectrophotometer at a laser wavelength of 473 nm. Raman spectra are shown in Figure 4.

The spectra have all the peaks characteristic of Mg_2Si at raman shifts of 259, 349, and 693 cm^{-1} [4, 8, 9]. These maxima indicate the excitation of longitudinal optical phonons (F_{2g}, LO, 2LO, respectively) in this film material. The graphs (Fig. 4) show a low-amplitude peak at 480 cm^{-1}, which is consistent with amorphous silicon according to [4, 8].

The far-infrared transmission vibrational spectra (Fig. 5) were obtained using a Bruker VERTEX 80v Fourier spectrophotometer.

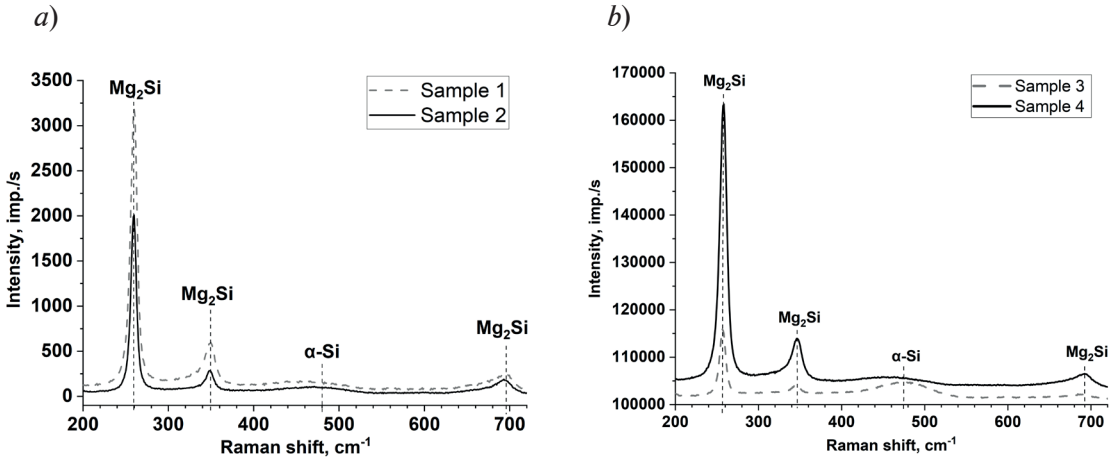

Fig. 4. Raman scattering spectra for samples 1 and 2 (*a*), 3 and 4 (*b*)

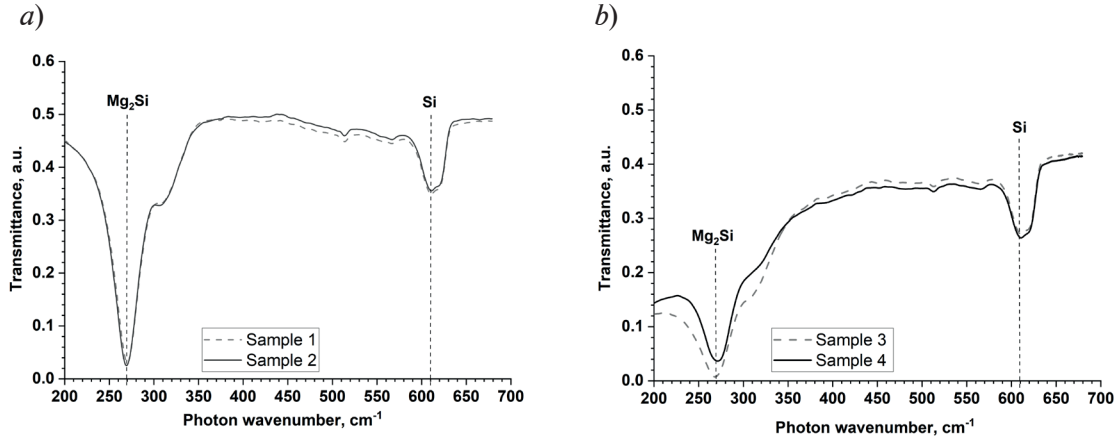

Fig. 5. Infrared transmission spectra for samples 1 and 2 (*a*), 3 and 4 (*b*)

The light transmission spectra through the samples (Fig. 5) show a minimum at a photon wave number of 610 cm^{-1}. According to sources [8, 10], this peak corresponds to the excitation of a phonon in Si. At the same time, the graphs show a minimum in the transmission coefficient at 270 cm^{-1}, which, according to [8, 10, 11], corresponds to the fact that the formed films contain Mg_2Si. The presence of a peak at 270 cm^{-1} is due to the excitation of the transverse optical phonon TO, which is responsible for the absorption in the silicide films of all samples. The minimum transmission value corresponding to Mg_2Si for the formed films is 0.03 (sample 1), 0.02 (sample 2), 0.01 (sample 3), and 0.04 (sample 4). This is due to the fact that thicker films transmit less of the incident light. The above results are consistent with the SEM data presented in Figure 3.

The IR-UV transmission spectra (Fig. 6) and reflection spectra (Fig. 7) were obtained using the following spectrometers: Bruker VERTEX 80v and Spectrophotometer U-3010.

From the graphs of the transmission coefficient as a function of photon energy (Fig. 6), it can be seen that there is an alternation of minima and maxima in the range from 0.2 to 1.1 eV.

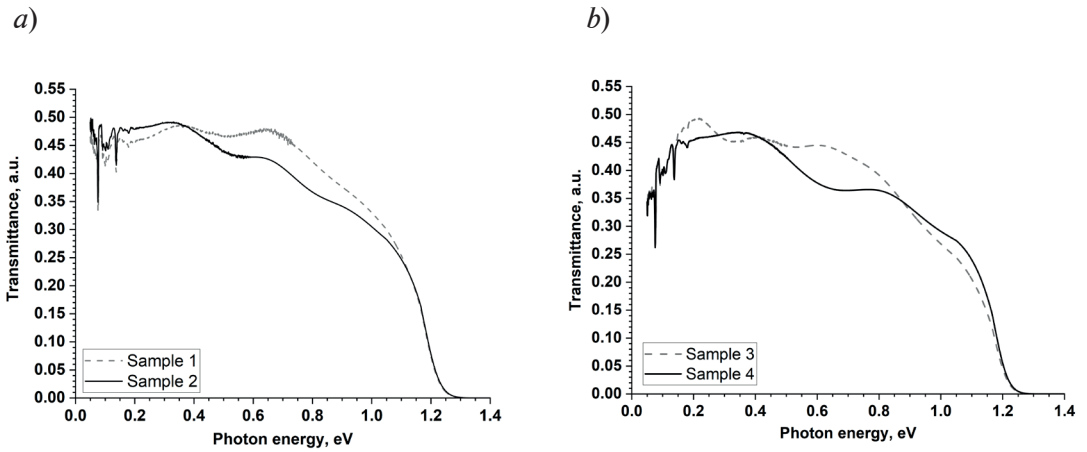

Fig. 6. Near- and mid-infrared transmission spectra for samples 1 and 2 (*a*), 3 and 4 (*b*)

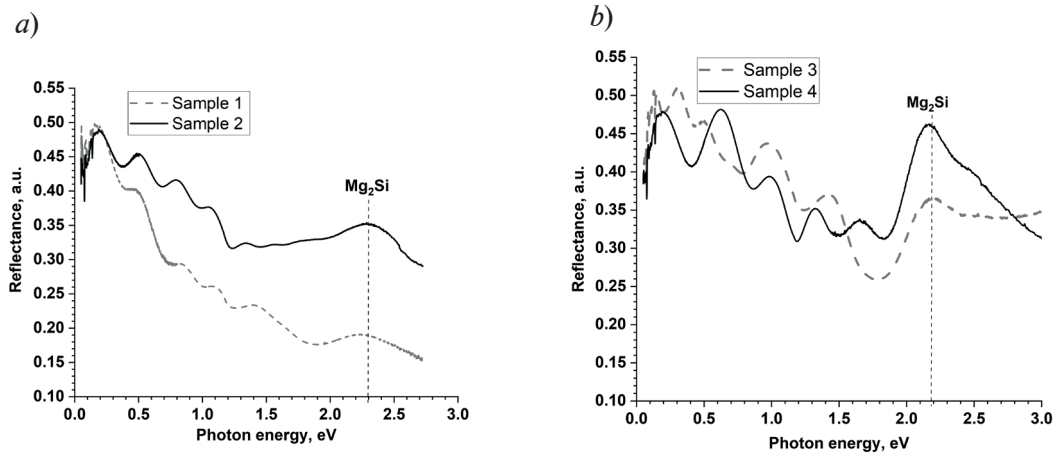

Fig. 7. Reflection spectra for samples 1 and 2 (*a*), 3 and 4 (*b*)

This, according to [1, 2], indicates the interference features of the films. In the energy range of 1.1 to 1.3 eV, there is a significant decrease in the transmission value. This is due to absorption, both in silicon [12] and partially in magnesium silicide [3], which is related to the specific electronic structure of magnesium silicide films in the samples. At energies above 1.3 eV, the absorption coefficient of silicon increases significantly, and the transmission of the film-substrate system approaches zero. The absorption coefficient in magnesium silicide also increases due to interband transitions, which is characteristic of the semiconductor Mg_2Si [10].

The reflection spectra in the IR region of the spectrum in the energy ranges from 0.2 to 1.8 eV (Fig. 7) show alternating maxima and minima of interference, as well as peaks in the visible region at 2.3 (samples 1, 2) and 2.2 eV (samples 3, 4), which are attributed to indirect band Mg_2Si according to [6, 8, 10]. Due to the relatively small thickness, the transmission of Mg_2Si films is still noticeable at photon energies in the range of 1.2–1.5 eV [3]. This leads to the appearance of the first interference maximum in the reflection spectrum at a photon energy of about 1.5 eV (Fig. 7) when light is reflected from the film-opaque silicon substrate system at these energies. The intensity of the maxima increases smoothly with decreasing photon energy, which is due to a decrease in the absorption coefficient in the transparency region, but not to zero. The latter is determined by the absorption on defects [12] in the grown films. The increase in the intensity of the peaks at 2.3 and 2.2 eV is associated with a decrease in grain scattering in the films in samples 3 and 4, as well as with an improvement in their crystalline quality. The latter is confirmed not only by an increase in intensity, but also by a decrease in the half-width of the reflection peaks. In samples 1 and 2, an increase in light scattering on the film grains reduces the reflection coefficient due to multiple reflections on the grains and partial loss of light during absorption in the grains.

To calculate the indirect band gap of the formed Mg_2Si semiconductor films, we plotted the dependence of the square root of the absorption coefficient on the photon energy (Fig. 8).

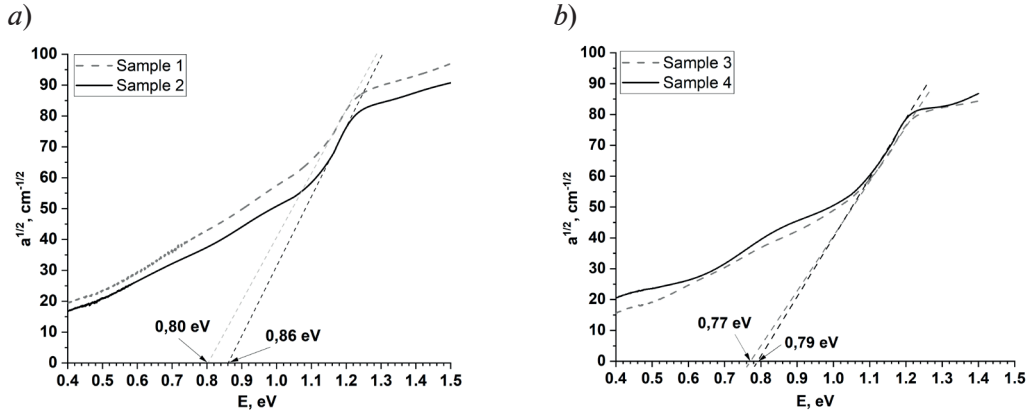

Fig. 8. Absorption coefficient spectra for samples 1 and 2 (*a*), 3 and 4 (*b*)

According to the results of geometric calculation of the indirect band gap from absorption spectra, according to the method described in [6, 7], the following values of this parameter were obtained: 0.80 and 0.86 eV for the first and second samples; 0.77 and 0.79 eV for the third and fourth samples. These values are close to the reference values (0.6–0.8 eV) [1, 2]. Higher values of the indirect band gap in Mg_2Si films in samples 1 and 2 compared to samples 3 and 4 may be due to increased uncontrolled scattering of light on numerous grains and increased errors in extrapolating experimental data.

Conclusion

Thus, this work presents the results of Mg_2Si film formation on Si (111) by reactive epitaxy with layer-by-layer deposition of magnesium and silicon at a substrate heating temperature of 250 °C. The film thicknesses in the samples were 496, 682, 1143, and 414 nm for the first, second, third, and fourth samples, respectively. The island growth mechanism of films was revealed using atomic force microscopy. The area of the film islands varies in the following ranges: from 0.12 to 0.48 μm^2 (sample 1), from 0.02 to 0.06 μm^2 (sample 2), from 0.01 to 0.04 μm^2 (sample 3), and from 0.04 to 0.09 μm^2 (sample 4). The surface morphology of the films is also characterized by the presence of grains and clusters caused by the coalescence of islands. Using the Raman spectroscopy method, silicide formation was detected in all samples based on the peaks corresponding to Mg_2Si phonons: F_{2g} (259 cm^{-1}), LO (349 cm^{-1}), and 2LO (693 cm^{-1}). The formation of Mg_2Si in the films of all samples was confirmed by IR vibrational spectroscopy, based on the presence of a strong absorption peak for the 270 cm^{-1} phonon in the transmission spectrum, whose amplitude correlates with the thickness of the grown films. The reflection spectra of the grown films show a peak at an energy of 2.2–2.3 eV, which also confirms the formation of Mg_2Si in all the films. However, the best crystal quality of the films and the maximum amplitudes of the reflection peak at 2.3 eV are observed for samples grown with an increased ratio of magnesium deposition rates to silicon, which provides a more uniform surface with minimal roughness. Based on the results of geometric calculations of the band gap width of Mg_2Si films, it was found that the band gap width for the first sample is 0.80 eV, for the second sample it is 0.86 eV, for the third sample it is 0.77 eV, and for the fourth sample it is 0.79 eV. Based on the above, it can be concluded that the reactive epitaxy method, with the sequential deposition of magnesium and silicon portions, allows for the formation of magnesium silicide films with specified properties by changing the deposition rate ratio towards magnesium enrichment.

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