Structure, optical properties and resistance to laser radiation of thin barium disilicide films grown on silicon

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Abstract. Polycrystalline and oriented films of barium disilicide (BaSi₂) with a thickness of up to 100 nm were formed on silicon (111) substrates by high-temperature (800 °C) solid-phase (single-stage and two-stage) annealing. The single phase of barium disilicide films and their semiconductor nature have been proven to be below 1.25 eV according to X-ray and optical spectroscopic methods. Two preferential orientations of the BaSi₂ crystallites were detected and their orientation was determined in the films formed by two-stage annealing. According to the calculations of the parameters of the crystal structure of BaSi₂ films, a compression of the unit cell volume from 2.7% to 5.13% was found, depending on the cooling time to room temperature. The stability of the films to laser radiation was studied by registering the Raman spectra with a variable power of laser radiation. The maximum power density of the laser beam (3·10⁹ W/m²), which does not lead to the beginning of the destruction of these films, was determined.

1. Introduction

Silicon is currently the most common material for solar energy. However, semiconductor compounds based on silicon and metals - semiconductor silicides are often used to expand the spectral range of silicon solar cells [1]. The most actively considered silicides with a width of the energy gap greater than that of silicon. In this series, one of the main materials is orthorhombic barium disilicide (BaSi2), whose band gap is at least 1.3 eV [2]. This interest is caused by the fact that this material also has a high density of electronic states and a high absorption coefficient of up to 3·10⁴ cm⁻¹ at photon energy of about 1.5 eV [3]. In the epitaxial BaSi₂ films grown by MBE method, the following were also found: a large diffusion length of minority carriers (up to 10 μm [4]); a long lifetime of minority carriers (up to 10 μs [5]) and high carrier mobility at room temperature (electrons about 800 cm²/V·s and holes 200-300 cm²/V·s [6]).

Based on BaSi₂/Si hetero diodes, the photo conversion efficiency of at least 9 % was obtained [7]. MBE method is quite expensive, so in recent years, work has been launched on the growth and study of the properties of BaSi₂ films grown by cheaper methods: magnetron sputtering [8] and vacuum thermal evaporation of BaSi₂ at substrate temperatures up to 550 °C [9]. To improve the properties of grown BaSi₂ films by the indicated methods, as a rule, short-term annealing at 1000 °C was used [10]. However, such annealing was performed after growth in separate chambers containing an inert gas.
and required protection against oxidation. The combination of growth procedures with high temperature regimes during solid-phase epitaxy began to be investigated in [11,12], where the range of growth temperatures was extended from 600 °C to 800 °C. However, in the obtained films there was no oriented growth of BaSi$_2$ crystallites.

This article is devoted to the study of the effect of annealing temperature and a preformed template on the possibility of orderly growth of BaSi$_2$ on silicon substrates with (111) orientation, and also on the effect of the cooling rate after high-temperature annealing on the formation of microcracks and the stability of the grown films to high-intensity laser radiation and on the possibility of their use to create solar cells with solar concentrators.

2. Experimental

The growth of BaSi$_2$ films on silicon substrates was carried out in a VARIAN PHI-590 ultrahigh-vacuum (UHV) chamber with a base vacuum of 2·10$^{-10}$ Torr, equipped with a two-span Auger analyzer (PHI Model 15-255G), a holder for three samples, a quartz thickness sensor, as well as sources of silicon and barium. The substrates for the samples were cut with dimensions of 15 × 5 mm$^2$ from a Si(111) n-type industrial wafer with a specific resistance of 5–7.5 Ω cm. A silicon source with dimensions of 15 x 5 mm$^2$ was cut from an FZN100 Si(111) wafer with a resistivity of 50-75 Ohm cm and subjected to the same cleaning procedure as the substrates for the samples. After all the samples and the source of silicon were loaded, the barium (Ba, 99.96%), purified from oxide, and defatted was loaded into a tantalum tube, which was immediately placed in the UHV chamber and pumped to a pressure of 10$^{-4}$ Torr with an oil-free system pumping and further magnetic pump.

In the UHV chamber, silicon substrates were subjected to prolonged degassing at a temperature of 600 °C for 6 hours, after which 3-4 short-term (3 sec.) Annealing was performed at 1250 °C with pauses of 10 minutes. Calibration of the deposition rates of Ba and Si was carried out using a Sycon Instrument piezoelectric deposition sensor. The following deposition rates were established: 0.6 nm/min for barium and 0.4 nm/min for silicon.

As a result of growth experiments, three samples were formed. Sample #1 at room temperature was co-deposited with Ba and Si for 100 minutes, after which it was subjected to crystallization at $T = 800$ °C for 60 minutes. The formation of samples #2 and #3 began with the growth of the template, which was obtained by co-deposition of 20 nm of Ba and Si at a temperature of 600 °C. Next, both samples were co-deposited with 80 nm of Ba and Si at room temperature. The crystallization of the grown mixture’s layers was carried out in two stages. At the first stage, the mixture crystallized at 600 °C for 60 minutes. The annealing temperature $T = 600$ °C was chosen on the basis of the conditions for minimizing the desorption of Ba from the mixture and the conditions for complete silicide formation [3]. Then both samples (#2 and #3) were recrystallized at $T = 800$ °C for 60 minutes. To reduce the cracking of films [9, 10] the temperature in samples was slowly reduced. Sample #2 was cooled for 10 minutes by incrementally decreasing the current through the sample, and for sample # 3 this time was increased to 30 minutes.

After unloading samples from the UHV camera, the surface morphology of the barium disilicide films, as well as the structure and optical properties of the films, were investigated using the methods described in [11, 12].

3. Results and discussion

Studies of the surface morphology of samples using scanning electron microscopy showed that there is a strong roughness of the films and there is a network of microcracks. The maximum density of microcracks was observed for sample #1, which, after annealing at 800 °C, was subjected to an abrupt current shutdown for 1 minute, which led to stresses in the barium disilicide film with such rapid cooling. For samples #2 and #3, the cooling was slower, which led to a corresponding decrease in the density of microcracks with an increase in the cooling time. In all three cases, the average grain size was 0.1–0.3 µm, which are quasi-uniformly distributed over the surface, but for sample #1 this distribution is less uniform than for the other two samples. In the first sample, the surface density of
the observed micropores is minimal, and for the second and third samples it increases. The increase in micropore density with sizes in micron units for the second and third samples can be attributed to the two-step annealing procedure at two temperatures of 600 °C and 800 °C. At the first stage of annealing, silicide formation occurred, and a polycrystalline BaSi₂ film was formed, which was previously established in our work according to X-ray diffraction data at annealing temperatures of 600 °C and 700 °C [12]. An increase in the annealing temperature to 800 °C ensured the recrystallization of crystallites with the release of preferential directions of barium disilicide on the Si(111) surface according to the data of [12]. Barium disilicide crystallites with other directions in relation to silicon could begin to coalesce with the crystallites of the selected directions, which could lead to an increase in the diffusion mass transfer and an increase in the film roughness. An increase in the cooling time to 30 minutes after annealing at a temperature of 800 °C actually led to an increase in the effective annealing time and, as a result, to a decrease in the density of micropores.

Figure 1. X-ray diffraction spectra of thin BaSi₂ films of (# 1, # 2 and # 3) on Si(111) substrates. Dotted lines indicate tabulated values for various interplanar distances in orthorhombic BaSi₂ [14].

X-ray diffraction studies of the crystal structure of the grown films (figure 1) confirmed the best orientation of BaSi₂ crystallites in films on samples # 2 and # 3. These groups are characterized by 2 groups of similar crystallite orientations relative to the substrate: (211) and (411), (301) and (601). The dominant orientations are (301) and (601), which provide the most advantageous lattice mating with the Si(111) plane. The remaining two (211) and (411) are less profitable, but also noticeable. The remaining orientations are suppressed during recrystallization due to association with small crystallites of other orientations. In contrast, for sample #1 (Figure 1), additional peaks are observed, which indicates a greater number of crystallites with different orientations in this film and correlates with the lack of large mass transfer and pronounced pores according to SEM. The ratio of the intensities of the BaSi₂ peaks to the intensities of the Si(111) peak make it possible to state about a thicker formed film in sample #3. Further, with decreasing thickness, there are samples #1 and #2. Calculations using the Scherrer formula [13] allowed us to determine crystallite sizes: 43 nm - for sample #1 and 29 nm - for samples #2 and #3 (Table 1). Based on the obtained crystallite size estimation, it can be argued that during the first high-temperature annealing for sample #1, crystallite coalescence occurs in parallel with silicide formation, but the annealing time is not enough to separate the preferred orientation of the grains relative to the Si substrate. The template for samples #2 and #3 leads to the formation of crystallites of two preferential orientations with a silicon substrate, which during solid annealing of the deposited Ba-Si mixture compete with each other, as a result of which the growth rate of crystallites is limited and their size is smaller than that of crystallites sample #1. For all three samples, it was found that the X-ray diffraction peaks are shifted toward smaller angles compared with the tabular data for
bulk BaSi$_2$ [14], which indicates compression of the BaSi$_2$ unit cell in the film after its high-temperature and long-term annealing.

**Table 1.** The lattice constants of the orthorhombic BaSi$_2$ calculated for the interplanar distances [14] for the reference polycrystalline sample and films in samples # 1, # 2 and # 3.

| Sample     | $a$, nm | $b$, nm | $c$, nm | $V$, nm$^3$ | ε[%] |
|------------|---------|---------|---------|-------------|------|
| etalon     | 0.892   | 0.680   | 1.158   | 0.702       | -    |
| BaSi$_2$   |         |         |         |             |      |
| #1         | 0.889   | 0.667   | 1.152   | 0.683       | -2.70|
| #2         | 0.890   | 0.664   | 1.132   | 0.670       | -4.67|
| #3         | 0.887   | 0.667   | 1.127   | 0.666       | -5.13|

Similar compression was found in our samples, formed at temperatures of 600 °C and 700 °C [12]. The greatest compression of the BaSi$_2$ unit cell volume is observed for sample #3, the effective annealing time of which at 800 °C is maximal, taking into account slow cooling for 30 minutes. The method used to determine the parameters of the crystal lattice [15] according to X-ray diffraction analysis is intended primarily for polycrystalline or powder samples with a large number of grain orientations, which increases the accuracy of determining interplanar distances and constant gratings. In our case, for samples #2 and #3, the number of directions of crystallites decreased to 4-6, which led to an increase in the error of the crystal constant in the calculations to 0.5 %. However, this error is significantly less than the calculated amount of compression relative to the available tabular data for bulk BaSi$_2$ [14].

![Figure 2.](image-url) Optical transmission (a) and specular reflection (b) spectra in the near and far infrared for thin BaSi$_2$ films on Si substrates in samples # 1, # 2 and # 3 and for single-crystal Si substrate.

The study of grown samples by optical transmission spectroscopy in the near-IR range (figure 2(a)) showed that the transmittance increases with two maxima in the range from 1.2 to 0.6 eV and approaches the transmittance of the silicon substrate. The specular reflection spectra are shown in figure 2(b). It can be seen that in the region of partial transparency of BaSi$_2$ films up to 0.7 eV, the reflection coefficient of the films varies from 0.37 for sample #2 to 0.42 for sample #1. In this case, the sum of the reflection coefficient and the transmittance should be close to 1 [16]. However, in our case, this value changes from 0.83 (sample #2) to 0.92 (sample #1) at 0.7 eV. At a photon energy of 1.0 eV, the above sum is in the range of 0.70 - 0.82, which corresponds to a large scattering (from 18 % to 30 %) and does not allow with sufficient accuracy to calculate optical constant films near the boundary of their fundamental absorption 1.0 - 1.25 eV. At the same time, the contribution of BaSi$_2$ films in transmission spectra at photon energies of 0.6–1.0 eV is noticeable with respect to the silicon.
Figure 3. Raman intensity for samples #1 (a), #2 (b) and #3 (c) versus the Raman shift. The Raman spectra were recorded at 6 laser beam powers: 0.014, 0.1, 0.92, 2.4, 4.3 and 9.7 mW. The Raman spectra are shifted by an arbitrary value along the Intensity axis for ease of perception.

substrate, therefore, taking into account the thickness of BaSi$_2$ films (at least 100 nm, due to the presence of interference in the films in the region of full transparency of the silicon substrate [16]) the absorption coefficient in them in this region can vary from $1\times10^3$ to $1\times10^4$ cm$^{-1}$. Such a high improper absorption is a consequence of the high density of defect levels, which are distributed in the BaSi$_2$ band gap and on which intense photon absorption occurs. Defect levels arise due to dangling bonds
between nanocrystals, as well as due to impurity atoms embedded in the BaSi$_2$ lattice or in its interstitials. However, the absorption of light in the BaSi$_2$/Si system (figure 2(a)) at photon energies of 1.1–1.25 eV is slightly higher than in the Si substrate. This allows you to qualitatively estimate the fundamental absorption edge in BaSi$_2$, which is at least 1.25 eV.

It is known that, despite the resistance of barium disilicide films to oxidation, it can undergo destruction with desorption (evaporation) of Ba during high-temperature treatment or irradiation with focused laser radiation in any atmosphere. Studies of the method of combination scattering of light in films of orthorhombic barium disilicide, on the one hand, allow us to establish the nature of the observed active modes, which belong to the internal and external oscillation modes of silicon clusters in the lattice, and on the other hand, it allows to determine the stability limit of the films to laser probing radiation and to control the appearance of additional phases in the process of destruction of barium disilicide films. Figure 3 shows the Raman spectra of BaSi$_2$ films in samples #1, #2, and #3, recorded at different powers of the probing radiation. It has been established that all peaks of lattice characteristic of barium disilicide are observed only with a minimum of 0.1 mW of laser power. They correspond to the F$_2$, E$_2$, and A$_1$ modes, which correspond to the internal and external oscillation modes in orthorhombic barium disilicide [17]. The detected small shifts (2–4 cm$^{-1}$) in our data (figure 3) can be explained by the choice of the laser wavelength (488 nm) instead of 532 nm, which was used in [17]. Such shifts were detected in [14], in which laser radiation with a wavelength of 488 nm was also used when recording the Raman spectra from BaSi$_2$ films. An additional factor affecting the Raman shifts of peaks can be stresses in the BaSi$_2$ lattice, which were determined according to X-ray diffraction data and calculations of the lattice constants in the grown BaSi$_2$ films (Table 1). It was found (figure 3(a)) that with the laser beam power starting from 0.92 mW, the cattle peaks of barium disilicide in sample #1 begin to broaden and decrease in amplitude. This corresponds to the beginning of the process of BaSi$_2$ softening under the beam and changing the width of the lines of the vibrational modes. With a laser power of 2.4 mW for sample #1, the process of decomposition of BaSi$_2$, evaporation of Ba from the surface, and segregation of silicon on the under the laser beam began. The decomposition of BaSi$_2$ is confirmed by the appearance of a wide shoulder in the Raman spectrum of about 470 cm$^{-1}$ and an intense peak at 507 cm$^{-1}$, which correspond to amorphous and nanocrystalline silicon [18], respectively. For sample #2, the laser radiation power of 2.4 mW (figure 3(b)) became the threshold energy for softening the BaSi$_2$ film, and the power surface of 4.3 mW for the sample #3 (figure 3(c)). At 4.3 mW laser power a contribution from nanocrystalline Si was already observed for sample #2, which determines the limit of laser power stability. Sample #3 has the maximum resistance to laser radiation, in which the destruction of BaSi$_2$. Ba desorption from the surface and the formation of nanocrystalline Si under the beam begins to occur only at a radiation power of 9.7 mW. That is, the maximum resistance to radiation was found in BaSi$_2$ films with the best crystal structure and two types of oriented BaSi$_2$ crystallites.

An analysis of the micro images of the film surfaces showed that the diameter of the destroyed section under the action of the laser beam is no more than 1 μm. Estimation of the power density of laser radiation, which is guaranteed not to lead to the destruction of BaSi$_2$ film in air, led to values of power density of $3 \times 10^9$ W/m$^2$. This proves that oriented BaSi$_2$ films on silicon can be successfully used to develop designs of solar cells with solar concentrators.

4. Conclusion
Three films of barium disilicide (BaSi$_2$) with a thickness of about 100 nm were formed on Si(111) substrates with orientation (111) by solid-phase epitaxy (SPE), including the room temperature deposition and long-term (60 minutes) high-temperature single-stage annealing at 800 °C and two-stage (600 °C and 800 °C) annealing under UHV conditions. In the films with a two-stage annealing the BaSi$_2$ template was firstly formed with a thickness of 20 nm, using the method of co-deposition of Ba and Si atoms on the atomically-clean substrate at 600 °C, followed by 80 nm deposition of a Ba-Si mixture at room temperature and two-stage annealing. It was found that the films are single phase and consist of orthorhombic BaSi$_2$ crystallites according to X-ray diffraction data. This is confirmed by the
data of optical and Raman spectroscopies. It was established that single-stage annealing at 800 °C leads to the formation of polycrystalline BaSi$_2$ film with an average crystallite size of 43 nm and the lattice volume is reduced by 2.7%. Co-deposition of Ba and Si atoms on the template and two-stage annealing leads to the formation of BaSi$_2$ films with mainly two orientations of crystallites [(301), (601)] and [(211), (411)], which are epitaxially oriented with respect to the Si(111) substrate. Oriented crystallite growth occurs at the recrystallization stage at 800 °C as a result of diffusive transfer of barium disilicide during the coalescence of crystallites. This forms a high density of pinholes with dimensions of 1-2 microns. With an increase in the effective cooling time of samples from 10 to 30 minutes, the density of such pinholes decreases, the density and linear dimensions of microcracks decrease, the volume of the BaSi$_2$ unit cell decreases by 4.67% at 10 minutes and 5.13% at 30 minutes of the cooling time. The study of the BaSi$_2$ film's stability when exposed to intense laser radiation with variable power during the registration of the Raman spectra showed that films formed by double annealing and slow cooling have the greatest stability. It was established that the maximum power of the laser beam during registration of the Raman spectra without destruction of BaSi$_2$ varies from 0.92 mW to 4.3 mW depending on the degree of the crystallite orientation in the film. This proves that oriented BaSi$_2$ films on Si can be successfully used to develop solar cells with solar concentrators.

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