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Formation and properties of crystalline $BaSi_2$ thin films obtained by solid phase epitaxy on Si(111)

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Barium disilicide may be considered to be a promising material for solar cells. Thin films of $BaSi_2$ can be developed in various ways. In this paper, we discuss the properties of a barium silicide film obtained by a solid phase epitaxy. GIXRD method showed the presence of $BaSi_2$ in the film which was obtained at the temperature T = 600, 750 and T = 800 ° C. We hypothesize that the co-precipitation of Ba and Si can solve this problem and find that the increase of the annealing temperature results in better film crystallization (for the selected temperature).

1. Introduction

Annually, the world community expresses an increasing interest in renewable energy sources. This concern is growing due to the reduction of hydrocarbon raw materials, financial and energy crisis. The greatest interest today is connected with the production of solar cells, which find application both on earth and in space. The direct conversion of solar radiation into electrical energy requires efficient solar cells production. Therefore, the search of new and cheap materials for them has become an important task at present. In a number of theoretical and practical works [1-5] the barium disilicide ($BaSi_2$) is referred to as a suitable material for solar cells.
According to the literature, the basic properties of $BaSi_2$ are as follows. The band gap of $BaSi_2$ is E_g = 1.3 eV (optimal for photovoltaic conversion) [1, 6]. The carrier concentration ($5 \cdot 10^{15}$ cm^{-3}) and majority carrier mobility (820 $cm^2/V \cdot sec$) are determined for $BaSi_2$ film with a thickness of 250 nm. The absorption starts at 1.3 eV and reaches a maximum at 1.5 eV. For a film thickness of 900 nm the absorption starts also at 1.3 eV, reaching a maximum at 1.7 eV [7]. In most cases, a molecular beam epitaxy was used to obtain $BaSi_2$. The formation mechanisms of the $BaSi_2$ thin film on the Si substrate during the process of vacuum sputtering of $BaSi_2$ granules as starting materials were proposed [8].
Barium silicide formation is not an easy task, since it is necessary to take into account various factors affecting the process. First, in the Ba / Si system, there are several different phases in barium silicide properties, characterized by different ratios of barium and silicon atoms, and their formation temperature is different too [9]. Second, the alkaline earth metal is barium which rapidly oxidizes in the air. Virtually, all forms of barium silicide, except $BaSi_2$, are quick enough to oxidize in the air [10]. Minor amounts of impurities formed in the samples may produce additional compounds (e.g., oxygen), which adversely affect properties of barium disilicide. Third, at the

moment, there are 4 detected and allotropic forms of $BaSi_2$ which special conditions of growth are indicated in [11-13].
In our work we use the method of solid-phase epitaxy (SPE). It is the simplest and much cheaper method. $BaSi_2$ gained by this method will make the research of this promising material more accessible for the majority of scholars. We have not found the works of other researchers, who used SPE method for forming silicide barium. In most cases, barium silicide is obtained using the method of molecular-beam epitaxy. The research novelty involves the first film produced by SPE $BaSi_2$ and further steps to improve it.
In this paper, we generalized the results of our researches related to the $BaSi_2$ thin films formation by SPE method.

2. Experimental

$BaSi_2$ films on Si(111) substrates were formed in the ultra-high vacuum (UHV) chamber of PHI model 590 device equipped with a two-span Auger-type cylindrical mirror analyzer. The base pressure in UHV chamber was $1 \cdot 10^{-9}$ Torr. Barium deposition was carried out from the evaporator constructed as a tantalum tube loaded with chemically clean (99.94%) barium. Silicon deposition was carried out from the second evaporator with a rectangular Si plate. The 5x15 mm Si plate size with the (111) surface orientation and resistivity of between 45 and 75 Ω·cm was used as a substrate. Si substrates were subjected to a standard cleaning procedure, namely, heating to the temperature of 600°C by constant current for 5 hours, cooling to room temperature, and, then, annealing at the temperature of 1250°C for few seconds. The purity of Si surface and the process of each layer deposition were controlled by Auger electron spectroscopy (AES). Calibration of the deposition rates of Ba and Si was carried out by quartz sensors using industrial film thickness gauge from Sycon Instruments.
$BaSi_2$ films with a thickness of about 100 nm were formed on an atomically clean silicon surface Si(111)7x7 by SPE with the use of the template technology (alternate deposition of layers of Ba and Si at room temperature). For the first pair of samples generated and researched earlier, the last stage was subjected to thermal annealing at T= 600 and 750°C for 15 min. The second pair of samples generated at present are obtained by thermal annealing at T= 700 and 800°C for 60 min.
The samples obtained *in-situ* were investigated by AES. After the discharge from the growth chamber the samples were investigated with the methods of atomic force microscopy (AFM) and grazing incidence x-ray diffraction (GIXRD).

3. Results and discussion

We have an opportunity to demonstrate the AES only sample formed at an annealing temperature T= 800°C. It provides an understanding of how to monitor the process of layer deposition of thin layers of barium and silicon and the estimated final result. Figure 1 on the lower chart shows the Auger electron spectrum of substrates. High-intensity peak 90 eV corresponds to Si. The absence of other peaks indicates good pre-cleaning of the substrate. Curve 1 in Figure 1 was obtained after the precipitation of barium on the cleaned silicon substrate. There are twin peaks in the vicinity of 580 eV, belonging to barium. Curve 2, the same figure, was obtained after the deposition of silicon layer on top of barium. And curve 3 was obtained after thermal annealing and forming $BaSi_2$ films.

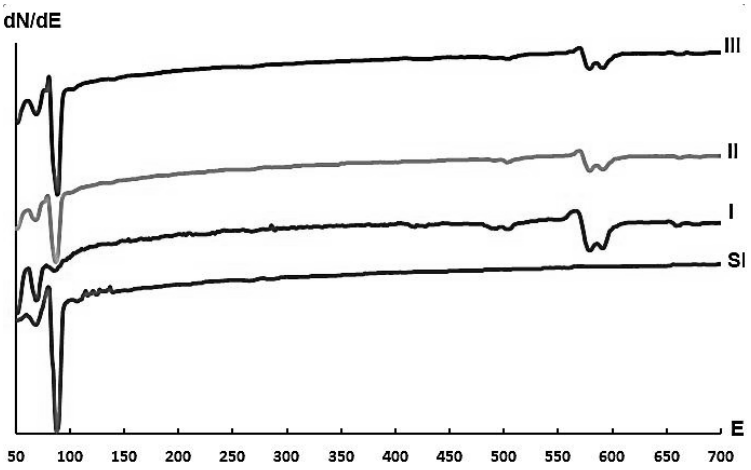

Fig. 1. AES spectra for the samples deposited at 300 K and annealed at 800 °C

AES method does not give a precise answer to the question whether the barium disilicide is formed or not. Thus, crystal structure of the SPE grown films was studied by the GIXRD method. Figure 1 shows the spectra measured at φ=2° with step of 0.05° in the range of 2Θ from 15° to 80° for the samples, which were classified as $BaSi_2$. It should be noted that the research of samples obtained at annealing temperatures T = 600 and 750°C, and samples obtained at T = 700 and 800°C were performed using different diffractive devices.

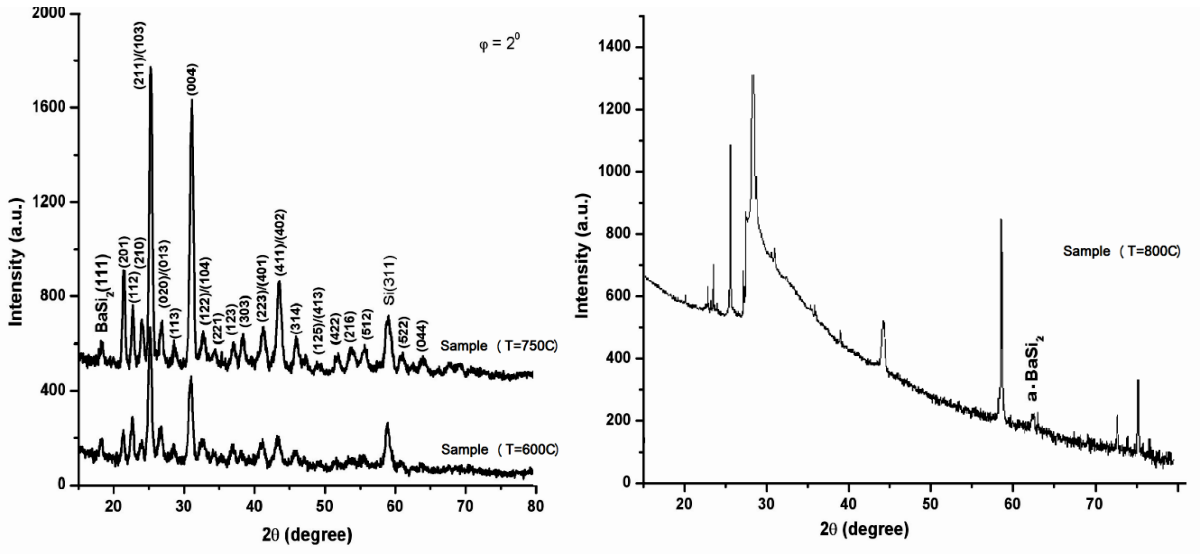

Fig. 2. GIXRD spectra for the samples deposited at 300 K and annealed at 600, 750 and 800 °C and measured at incidence angle φ = 2°.

In the first case, the thermal annealing at 600°C led to the formation of single-phase polycrystalline film with orthorhombic $BaSi_2$ structure. Phase identification was carried out by the comparison of experimental spectrum with crystallography data for Ba_2Si_4 sample (#8103005) [14]. The increase of annealing temperature up to 750°C resulted in the enhancement of all $BaSi_2$ diffraction peak intensities. This fact indicates higher crystalline fraction in this film compared to the sample annealed at T= 600°C [15].

We compared with spectra obtained by the data presented in [16], where it is shown that the peak (62,8 °) belongs $BaSi_2$ (600). In addition, in Figure 2, we see that the pattern formed at a temperature of 800 ° C, has a small peak (62.8 °) corresponding oriented barium disilicide (a-BaSi2 (600)). In the [17] we find confirmation of this result. As soon as the sample formed at T = 700°C did not show the peak, we did not make its further exploration.
The sample formed by the layered solid-phase epitaxy recrystallization at T = 800° C has a weak peak $BaSi_2$ (600) on the radiograph, while the samples of barium disilicide thin films formed by molecular beam epitaxy [16] have peaks of high intensity (Figure 3). It follows that the amount of barium in the test disilicide film is much less. We assume that this is due to a low barium diffusion coefficient in silicon, and layered solid-phase epitaxy barium disilicide is formed mainly on the boundary layers of barium and silicon.
The surface roughness determined by AFM also increases from 6.9 nm (T=600°C) and 18.4 nm (T=750°C) [15] to 20.52 nm (T=800°C) with temperature increase. It is comparable with the roughness of thin film samples $BaSi_2$, grown by molecular beam epitaxy in other studies [16].

4. Conclusion

GIXRD showed the presence of $BaSi_2$ in the film which was obtained at temperatures of T=600, 750 and T=800°C. It can be concluded that the barium disilicide film can be obtained by SPE. However, a comparison with the samples formed by MBE indicates that the method used needs to be improved. This problem can be solved by coprecipitation Si and Ba on a silicon substrate, as was done in another way in [6]. Annealing temperature increase leads to a better crystallization at the specified temperature. The surface roughness, determined by AFM, also increases from 6.9 nm (T=600°C) and 18.4 nm (T=750°C) to 20.52 nm (T=800°C) with the temperature increase.

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