Formation of the $\beta$-FeSi$_2$ phase by pulsed laser deposition

Yu M Kuznetsov$^{1,2}$, M V Dorokhin$^1$, A V Nezhdanov, D A Zdoroveichev$^{1,2}$, V P Lesnikov$^1$ and M V Ved$^1$

$^1$Research Institute for Physics and Technology of Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, 603950 Russia
$^2$Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, 603950 Russia

E-mail: yurakz94@list.ru

Abstract. This paper presents a method for the formation of the $\beta$-FeSi$_2$ phase on silicon and sapphire substrates by pulsed laser deposition in vacuum. The analysis of the phase composition of the films, based on the identification of Raman peaks, is presented. The magnetic properties of the samples were studied by measuring the magnetic field dependence of the Hall resistance. The presence of a magnetic $FeSi$ phase on a silicon substrate was shown.

1. Introduction
Iron silicide is a complex compound with a large number of different phases characterized by a wide range of physical properties. This stimulates great interest in their study. For example, the $\beta$-FeSi$_2$ compound is a direct-gap semiconductor with a band gap of 0.83 - 0.87 eV, which makes it attractive as a source of light emission at 1.54 $\mu$m [1-3]. Since this compound is based on silicon, it can be used in silicon optoelectronics and is easily incorporated into silicon technology. Also, according to [4], the formation of FeSi$_2$ nanoclusters in a semiconductor matrix can significantly reduce the thermal conductivity, which makes it possible to consider the $\beta$-FeSi$_2$/Si composite system promising in the field of thermoelectric energy converters. Finally, it has been shown earlier that the single-phase $\beta$-FeSi$_2$ has a high Seebeck coefficient in the low-temperature range. For example, a value of 2 mV/K was obtained in [5] at an average temperature of 160 K, which allows considering the $\beta$-FeSi$_2$ phase as a potential thermoelectric material with an increased thermoelectric efficiency, operating at low temperatures. The latter is important, for example, in space. Mentioning some other applications, one should note that there is very little information on the magnetic properties of the $\beta$-FeSi$_2$ phase; moreover, the presented results do not agree with each other. In [6,7], the "ferromagnet-paramagnet" phase transition was not detected, but a nonlinear magnetic field dependence of the Hall resistance in a $\beta$-FeSi$_2$ thin film was observed at low temperatures. In [8], the presence of paramagnetic centers in the $\beta$-FeSi$_2$ phase was proved by the electron paramagnetic resonance method. In [9,10], it was shown that the magnetism can be associated with a transition layer between the $\beta$-FeSi$_2$ phase and the silicon substrate. This area was enriched with iron, which promotes the formation of iron silicide phases that have magnetic properties.

All of the above allows us to conclude that the study of various properties of $\beta$-FeSi$_2$ films is an interesting task. The literature contains studies of such films formed on silicon substrates by ion implantation. This method has a significant drawback, which consists in the introduction of many
additional iron silicide phases along with the desired $\beta$-FeSi$_2$ one. These phases have undesired properties that complicate the analysis of experimental results. For this reason, the development of methods for the formation of a single-phase $\beta$-FeSi$_2$ film is an urgent task. In this paper, a method for the formation of the $\beta$-FeSi$_2$ phase by pulsed laser deposition is presented.

2. Studied structures
Silicon wafers were used as a substrate to obtain a single-phase $\beta$-FeSi$_2$ layer. Such structures have a significant drawback, which consists in the diffusion of iron into the silicon bulk [9-11]. It was shown in [11] that a transition layer of a Si-Fe solid solution was formed at the interface. Upon reaching the critical thickness (of about 5 monolayers), this layer was rearranged into the magnetic phase of iron silicide, Fe$_3$Si, which, in particular, changes the optoelectronic properties of the film. Thus, there is a problem in the formation of a single-phase $\beta$-FeSi$_2$ film. For that reason, we have also chosen dielectric substrates that are not affected by the diffusion of iron during film growth.

Silicon (100) and sapphire (1102) substrates were chosen to analyze the effect of iron diffusion on the properties of iron silicide films. The structures were formed by pulsed laser deposition in vacuum (PLD). Sputtering of a composite target from the Si and Fe sectors was performed by a pulsed YAG:Nd laser with a pulse duration of 10 ns. The ratio of the Si and Fe components in the target was 2:1. Sputtering was carried out at a temperature of 500 °C for 60 minutes. The thickness of the films was about 100 nm.

3. Experimental technique
The phase analysis of the structures obtained was carried out by recording the spectra of Raman light scattering using an INTEGRA SPECTRA system (NT-MDT). The laser wavelength was 473 nm. The radiation was focused by a 100x objective with an aperture NA = 0.95 into a spot of 1 μm in diameter. The laser radiation power was 0.5 mW.

The magnetic properties were studied by measuring the magnetic field dependence of the Hall resistance, which is proportional to the magnetization of the film. The measurements were carried out at room temperature in the magnetic field range of ± 2.8 T. The Hall voltage was measured using a KEITHLEY-2401 voltage meter.

4. Results and discussion
Raman spectra were recorded for three structures: an initial substrate (Si) and films grown on silicon (on-Si) and sapphire (on-Al$_2$O$_3$) substrates. The spectra are shown in figure 1. The position and value of the relative intensity of the peaks are shown in table 1.

![Figure 1. Raman spectra of Si-substrate (c-Si), films grown on silicon (on-Si) and sapphire (on-Al$_2$O$_3$).](image-url)
For clarity of display, the Raman intensities from the on-Si and on-Al₂O₃ structures were multiplied by 4.

It can be seen from the obtained Raman spectra that four peaks (at 178, 194, 248, and 340) cm⁻¹ are clearly resolved on the structures formed on both substrates. These peaks correspond to the Fe-Fe and Fe-Si bonds of the β-FeSi₂ phase (see table 1). The combination of the peaks suggests that the β-FeSi₂ phase was formed regardless of the chosen substrate and, as a consequence, the lattice parameter mismatch. It is also important to note the presence of a 525 cm⁻¹ peak in the spectra. This peak corresponds to the Si-Si bond in the pure silicon phase (see the Raman spectrum of a silicon substrate). Since the thickness of the films is large (about 100 nm), we can confidently assert that the presence of this peak is explained by the formation of the main polycrystalline silicon phase (poly-Si) in addition to the β-FeSi₂ phase. Convincing evidence for the formation of the silicon phase in the film is the presence of this peak in the Raman spectrum of the on-Al₂O₃ structure.

### Table 1. Position of peaks in the Raman spectrum of the structures under study

| №  | Peak position, cm⁻¹ | I (on-Si) | I (on-Al₂O₃) | I (c-Si) | Phase               | References |
|----|---------------------|-----------|--------------|---------|---------------------|------------|
| 1  | 178                 | 323       | 315          | 0       | β-FeSi₂ (Fe-Fe)     | [13,14]    |
| 2  | 194                 | 349       | 342          | 0       | β-FeSi₂ (Fe-Fe)     | [12-14]    |
| 3  | 248                 | 374       | 368          | 0       | β-FeSi₂ (Fe-Fe)     | [12-15]    |
| 4  | 268                 | 337       | 0            | 0       | Fe₃Si (Si-Fe)       | [16]       |
| 5  | 291                 | 1038      | 0            | 0       | Fe₃Si (Si-Fe)       | [16]       |
| 6  | 340                 | 320       | 320          | 0       | β-FeSi₂ (Si-Fe)     | [12-15]    |
| 7  | 525                 | 546       | 557          | 1833    | Si (Si-Si)          | [12,16]    |

It is noteworthy that the Raman spectrum of the on-Si structure contains two additional peaks at 268 and 291 cm⁻¹, which are not observed in the spectrum of the on-Al₂O₃ structure. The positions of the peaks do not coincide with the literature data on the positions of the peaks of Raman scattering of bonds in the β-FeSi₂ phase. To identify these peaks, it is necessary to consider other phases of the iron silicide compound that could have formed on the silicon substrate simultaneously with the β-FeSi₂ and poly-Si phases.

It is known from the phase diagrams of Fe-Si-based compounds [2,17] that only three stable phases of iron silicide can exist at room temperature: β-FeSi₂, Fe₃Si₁₇, and Fe₃Si. As mentioned above, there are few published data on the presence of magnetic properties in the β-FeSi₂ phase, while the magnetic properties of the Fe₃Si₁₇ and Fe₃Si phases have been studied in detail. For example, it was indicated in [16,18] that Fe₃Si₁₇ and Fe₃Si compounds are ferromagnetic with a Curie point of 373 K and 823 K, respectively. We believe that the main reason for the formation of the Fe₃Si phase (as considered above) is the diffusion of iron atoms into the silicon substrate during the growth of the structure with the formation of a Fe-rich solid solution, which, after reaching the critical thickness, transforms into two phases [11,19]: metastable Fe₃Si₁₇ and stable Fe₃Si. These structural phases are characterized by a low Seebeck coefficient (20-50 μV/K) [5], therefore, they are not of interest in the field of thermoelectricity. However, their magnetic properties with a high Curie point (especially for the Fe₃Si compound) are of great interest for practical use in spintronic devices.

In [16], the Raman peaks corresponding to the Si-Fe bond in the Fe₃Si phase were revealed at 268 cm⁻¹ and 291 cm⁻¹, which is in good agreement with the experimentally obtained Raman spectrum of the on-Si structure. Based on the ratio of the peak intensities, it can be argued that the concentration of the Fe₃Si phase is even higher than the concentration of the β-FeSi₂ phase in the on-Si structure. Based on the phase diagram of iron silicides [17], we can also suggest that a decrease in the growth temperature in the PLD-method will lead to an increase in the Fe₃Si phase concentration and a greater decrease in the β-FeSi₂ phase concentration. On the contrary, an increase in temperature will not lead to the opposite effect due to the fact that the high-temperature diffusion of iron into the silicon
substrate during the growth process should lead to a decrease in the total Fe content in the film. For this reason, in order to form a single \( \beta \)-FeSi\(_2\) phase, it is necessary to use substrates with a low diffusion coefficient of iron.

Further evidence for the formation of the third Fe\(_3\)Si phase, in addition to the \( \beta \)-FeSi\(_2\) and poly-Si phases for the on-Si structure, may be the presence of magnetic properties in the studied film. Figure 2 shows the magnetic field dependences of the Hall resistance of the films.

Figure 2. Magnetic-field dependences of the Hall resistance of the films formed on silicon (on-Si) and sapphire (on-Al\(_2\)O\(_3\)).

It can be seen that the Hall resistance curve for the on-Si structure has a nonlinear form, which is associated with the presence of magnetic properties, presumably, of the Fe\(_3\)Si phase. It is impossible to state unequivocally which phase leads to a deviation from the linear dependence. We failed to register the Hall effect for the on-Al\(_2\)O\(_3\) structure, which indirectly indicates that it is the Fe\(_3\)Si phase that is the source of the nonlinear effect. The absence of a linear Hall effect is explained by the low mobility of free charge carriers in polycrystalline silicon.

The subject of discussion is the growth of iron-rich phases on Si substrates, despite the obvious diffusion of iron into Si. We suggest that the total Fe incorporation into the film depends on the used substrate. For the Si substrate, as compared with the Al\(_2\)O\(_3\) one, the Fe dissociation should be compensated for by greater Fe incorporation into the film, which actually leads to the formation of the Fe\(_3\)Si phase with a higher iron content.

5. Conclusions
The paper shows a method for the formation of the \( \beta \)-FeSi\(_2\) phase by pulsed laser deposition in vacuum. The formation of additional phases of iron silicide on a silicon substrate due to the diffusion of iron atoms into the substrate during the growth of the structure was confirmed. The presence of magnetic properties due to additional phases was shown. It has been established that the use of dielectric substrates with low diffusion penetration of iron during the growth makes it possible to obtain a single phase of \( \beta \)-FeSi\(_2\) iron silicide without the formation of additional iron silicide phases.

Acknowledgments
This work was supported by a grant of the President of the Russian Federation (MD-1708.2019.2), as well as by the RFBR projects (20-38-70063, 20-32-90032).

References
[1] Liu Z et al 2007 J. Cryst. Growth 307 82
[2] Wan Q, Wang T H and Lin C L 2003 Appl. Phys. Lett. 82 3224
[3] Han Y P et al 2012 Mod. Phys. Lett. B 26 1250097
[4] Chena Z G et al 2012 Progress in Natural Science: Materials International 22 6 535
[5] Behr G et al 1997 Phys. Stat. Sol. A 160 549
[6] Arushanov E et al 1994 *J. Appl. Phys.* **75** 5106
[7] Brehme S, Behr G and Heinrich A 2001 *J. Appl. Phys.* **89** 3798
[8] Irmscher K et al 1997 *Phys. Rev. B* **55** 4417
[9] Berling D et al 2001 *JMMM* **237** 181
[10] Klaesges R et al 1997 *Phys. Rev. B* **56** 10801
[11] Liu Z 2004 et al *J. Appl. Phys.* **95** 4019
[12] Schuller B, Carius R and Manti S 2003 *J. App. Phys.* **94** 207
[13] Terai Y et al 2018 *AIP Adv.* **8** 105028
[14] Maeda Y et al 2001 *Thin Solid Films* **381** 219
[15] Terai Y 2015 *JJAP Conf. Proc.* **3** 011109
[16] Zhengxin L et al 2007 *Journal of Crystal Growth* **307** 82
[17] Kubaschewski O 1982 *Iron-Binary Phase Diagrams* (Berlin: Springer) p 138
[18] Skomski R et al 2018 *JMMM* **460** 438
[19] Chu W K et al 1975 *Thin Solid Films* **25** 393