Phase Composition Evolution of Iron Silicide Nanocrystals in the Course of Embedding into Monocrystalline Silicon

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Phase composition of iron silicide nanocrystals (NCs) in the course of formation by solid phase epitaxy (SPE) method, and embedding into silicon was studied. It was found that SPE of 0.4-nm-thick Fe film at 630 °C resulted in formation of small (less than 29.5 nm) and big (more than 42.6 nm) NCs. The former contained only β-FeSi₂ phase and the latter consisted of β-FeSi₂ and ε-FeSi phases. Annealing of these NCs at 750 °C for 90 min led to transformation of β-FeSi₂ and ε-FeSi into α-FeSi₂ NCs. However, when the as-grown NCs have been covered with silicon layer with thickness of 25 – 380 nm at 750 °C, they turned into β-FeSi₂ NC. Epitaxial relationship and crystal lattice deformation obtained for β-FeSi₂ NCs covered by Si layer is favorable for indirect to direct band gap transition.

1. Introduction

For the last 20-35 years the processes of heteroepitaxial growth of different materials (III-V, silicides, etc.) on silicon have been extensively studied, both from theoretical and from practical points of view [1]. The development of an effective light source and detector, which operates in transparency windows of quartz optical fibers (1.26 – 1.67 μm) and can be formed by means of commercial silicon technology, was among the aims of the undertaken studies. The semiconductor iron disilicide (β-FeSi₂) is one of the promising materials for the light source operated in quartz transparency window as its thin films grown on Si substrate demonstrate RT electroluminescence at 1.56 μm [2]. Furthermore, the β-FeSi₂/Si structure can be used as infrared (IR) photodetector with a high photovoltaic sensitivity [3]. One of the main problem one encountered during the heteroepitaxial growth of β-FeSi₂ on Si is a great number of structural defects in the β-FeSi₂ layer and in Si cap layer, in the case of double heterostructure Si/β-FeSi₂ film/Si [4]. The defects origin is a crystal lattice mismatch between the Si and β-FeSi₂ [5]. The simplest and the most effective way to prevent this issue is to form on the silicon surface nanosized objects, such as nanocrystals (quantum dots) [6] or nanowires [7], instead of a continuous film. Owing to a small size, β-FeSi₂ nanocrystals (NCs) can be embedded into the silicon matrix almost without defects [8]. Recently, for diode structure $p^+\text{Si}/p\text{Si}_{\text{with} \beta\text{-FeSi}_2} \text{NCs/n-Si}(111)$ we obtained a photoresponse of 20 mA/W. The main feature of the diode were 7 layers of SPE formed β-FeSi₂ NCs, embedded into the diode depletion region ($p\text{-Si}$). A nominal thickness of Fe layer in each NC layer was 0.4 nm, the total thickness of β-FeSi₂ was just 10 nm [8,9]. The photoresponse value is close to that obtained for prospective $n$-type $\beta\text{-FeSi}_2$ film/$p\text{-Si}(111)$ diode structure (16.6 mA/A), where the film thickness was 300 nm [10]. However, in the course of embedding into the silicon a phase transitions can occur inside the...
iron silicide NCs due to deformation and interaction with Si atoms [11,12], which requires detailed study. Therefore, the evolution of the phase composition of β-FeSi$_2$ NCs formed by SPE of 0.4-nm-thick Fe film on Si(111) in the process of their embedding into the silicon cap layer was studied in this paper.

2. Experiment

The samples were formed on n-type silicon substrates with (111) orientation and a resistivity of 2 – 15 Ohm-cm. Growth procedure took place in Omicron ultrahigh vacuum chamber with a base pressure of 5×10$^{-10}$ Torr. The deposition rate of Fe and Si was calibrated by quartz thickness sensor. The substrate temperature was monitored by IR pyrometer. Iron silicide NCs were formed by SPE of 0.4 nm Fe at 630 °C, as these growth conditions are suitable for β-FeSi$_2$ NCs formation [13]. Covering silicon layer was deposited over the NCs at a temperature of 750 °C since this temperature is high enough to grow single-crystal Si film on Si(111) surface [14]. To study the effect of annealing on uncovered NCs sample $B$ with as-grown NCs was subjected to an additional annealing at 750 °C. The main parameters of the samples are shown in Table I.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Additional annealing, °C, duration</th>
<th>Si layer thickness, nm</th>
<th>NCs height ±, nm</th>
<th>NCs width ±, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>750, 90 min</td>
<td>–</td>
<td>9 ± 3</td>
<td>21 ± 8</td>
</tr>
<tr>
<td>$C$</td>
<td>–</td>
<td>25</td>
<td>11 ± 3</td>
<td>24 ± 6</td>
</tr>
<tr>
<td>$D$</td>
<td>–</td>
<td>65</td>
<td>15 ± 2</td>
<td>26 ± 6</td>
</tr>
<tr>
<td>$E$</td>
<td>–</td>
<td>380</td>
<td>24 ± 10</td>
<td>22 ± 5</td>
</tr>
</tbody>
</table>

*NCs height and width was measured on HRTEM images.*

The structure of the as-grown sample surface was studied ex-situ using an atomic force microscope Solver P47 (NT-MDT). Atomic force microscopy (AFM) images were analyzed with “Calculating of Average Parameters of Objects on Surface” software [15]. A cross-sectional images of the samples were obtained by high-resolution transmission electron microscopy (HRTEM) with a microscope JEM 4000EX and JEM 2200FS. To determine phase composition of observed NCs fast Fourier transformation (FFT) patterns of HRTEM images were obtained by ImageJ software and analyzed with SingleCrystalTM and CrystalMaker® software [16].

3. Results and discussion

Typical HRTEM images obtained for the grown samples and corresponding FFT patterns are shown in Fig. 1. It is known that after room-temperature deposition of 0.4-nm-thick Fe film a non-continuous FeSi layer is formed [17]. After annealing of the layer at 630 °C (sample $A$), NCs strongly stretched along the surface were formed. The most part of NCs is big (more than 42.6 nm) and consists of two phases: $\beta$-FeSi$_2$ at NC/substrate interface and $\varepsilon$-FeSi on top of $\beta$-FeSi$_2$ (Fig. 1 a, b), while another part is small (less than 29.5 nm) and consists of $\beta$-FeSi$_2$ only (not shown). The observed transformation of FeSi from layer to $\varepsilon$-FeSi NCs is favorable due to reducing of internal energy [18]. However, bulk and grain-boundary diffusion of Si atoms from substrate into $\varepsilon$-FeSi NCs at 630 °C results in increasing of internal energy of $\varepsilon$-FeSi due to stress. To reduce internal energy reaction $\varepsilon$-FeSi + Si = $\beta$-FeSi$_2$ takes place in NCs [19]. This phase transition is observed in small NCs, while in big ones $\beta$-FeSi$_2$ is formed only at the NC/substrate interface and blocks silicon diffusion inside the $\varepsilon$-FeSi part of the NC [20].

After annealing at 750 °C for 90 minute (sample $B$), all NCs turned into $\alpha$-FeSi$_2$ phase and their...
shape became semispherical (not shown). Taking into account that Si diffusion into the NCs at 750 °C is higher than that at 630 °C [20], one can suggest that this transformation results from reactions $\beta$-FeSi$_2 = \alpha$-FeSi$_2 + \varepsilon$-FeSi and $\varepsilon$-FeSi + Si = $\alpha$-FeSi$_2$ [21], since Si-rich $\alpha$-FeSi$_2$ phase has lower internal energy than $\beta$-FeSi$_2$ and $\varepsilon$-FeSi at 750 °C. In large ion beam synthesized $\beta$-FeSi$_2$ grains (up to 150 µm), $\beta$-FeSi$_2$ to $\alpha$-FeSi$_2$ phase transition occur at a temperature higher than 950 °C [21, 22]. The observed difference in phase transition temperature (200 °C) is higher than deviation of IR pyrometer we used (about 10 °C). Lattice mismatch between the Si substrate and $\beta$-FeSi$_2$ NCs results in deformation of these NCs, and strain energy has noticeable contribution in internal energy of $\beta$-FeSi$_2$ NCs, while crystal structure of the large grains is close to relaxed $\beta$-FeSi$_2$, therefore strain energy has small contribution. This additional energy (strain energy in NCs) facilitates $\beta$-FeSi$_2$ to $\alpha$-FeSi$_2$ phase transition in NCs, and results in reduction of the phase transition temperature. Although crystal lattice of $\alpha$-FeSi$_2$ is deformed (sample B, Table II), internal energy of $\alpha$-FeSi$_2$ is lower than that for $\beta$-FeSi$_2$ at 750 °C. The observed decrease of the phase transition temperature is

![HRTEM images](image)

**Fig. 1.** HRTEM images and fast Fourier transformation patterns: (a, b) – sample A; (c, d) – sample C; (e, f) – sample E; (g) – dependence of $\beta$-FeSi$_2$ (220) interplanar distance increase and nanocrystal aspect ratio vs. thickness of silicon coverage layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Epitaxial relationship</th>
<th>$\Delta a$, %</th>
<th>$\Delta b$, %</th>
<th>$\Delta c$, %</th>
</tr>
</thead>
</table>
| B      | $\alpha$-FeSi$_2$ (112)$||\text{Si}(11\bar{1})$  
$\alpha$-FeSi$_2$ (021)$||\text{Si}(1\bar{1}0)$ | -1.12 | -1.12 | 12.97 |
| C      | $\beta$-FeSi$_2$ (220)$||\text{Si}(1\bar{1}\bar{1})$  
$\beta$-FeSi$_2$ (11\bar{1})$||\text{Si}(1\bar{1}0)$ | 3.76 | -5.67 | 0.19 |
| D      | $\beta$-FeSi$_2$ (220)$||\text{Si}(111)$  
$\beta$-FeSi$_2$ (11\bar{1})$||\text{Si}(1\bar{1}0)$ | 10.30 | -3.49 | -1.44 |
| E      | $\beta$-FeSi$_2$ (220)$||\text{Si}(11\bar{1})$  
$\beta$-FeSi$_2$ (11\bar{1})$||\text{Si}(1\bar{1}0)$ | 9.83 | -2.60 | -3.99 |

*a in comparison with relaxed bulk $\beta$-FeSi$_2$: “+” means tension, “−” means compression.
not unique, a similar result was obtained in [23] for $\beta$-FeSi$_2$ to $\gamma$-FeSi$_2$ transition: when Fe coverage decrease from 20 to 5 monolayer, the phase transition temperature decrease by about 200 °C.

However, when NCs grown by SPE at 630 °C have been covered with silicon layer at 750 °C (the growth duration was about 90 minute) (sample E), they turned into $\beta$-FeSi$_2$ (Fig. 1 e). Since the only difference in growth techniques (sample B and E) is silicon layer deposition, an interaction of NCs and silicon layer results in $\beta$-FeSi$_2$ NCs formation rather than $\alpha$-FeSi$_2$ ones. Voids and misfit dislocations were not found at NC/Si interface in Fig. 1 e, because lateral faces of $\beta$-FeSi$_2$ NC well matched with Si planes (Table II). This well matching of crystal lattices resulted in reducing of strain energy of $\beta$-FeSi$_2$ and internal energy of $\beta$-FeSi$_2$ became lower than that for $\alpha$-FeSi$_2$ at 750 °C. In this case reaction $\epsilon$-FeSi + Si = $\beta$-FeSi$_2$ instead of $\beta$-FeSi$_2$ = $\alpha$-FeSi$_2$ + $\epsilon$-FeSi or $\epsilon$-FeSi + Si = $\alpha$-FeSi$_2$ took place. The result of this reaction was also observed for lower thickness of silicon layer (sample C), when NCs was not fully capped by Si layer (Fig. 1 c). One can see that shape of uncovered NC is different from that of capped NC. It means that shape of NCs is changed during embedding in silicon to obtain well matching of crystal lattices and low strain energy. Therefore, $\beta$-FeSi$_2$ phase remains more suitable than $\alpha$-FeSi$_2$, and phase transition from $\beta$-FeSi$_2$ to $\alpha$-FeSi$_2$ does not occur even when we increase the Si layer thickness. To show phase transformations we observed during NCs growth and embedding into Si, a simple scheme was proposed:

$$\text{Fe @ RT on Si } \rightarrow \text{FeSi } \xrightarrow{630 ^\circ C} \epsilon\text{-FeSi+} \beta\text{-FeSi}_2 \xrightarrow{750 ^\circ C} \alpha\text{-FeSi}_2$$

(1)

$$\epsilon\text{-FeSi+} \beta\text{-FeSi}_2 \xrightarrow{750 ^\circ C+Si} \beta\text{-FeSi}_2$$

(2)

It is clear that the relationships we obtain for all the imbedded NCs (samples C – D), in terms of plane position, correspond to $\beta$-FeSi$_2$ (110) || Si (111) with $\beta$-FeSi$_2$ [001] || Si (110) (Table II, Fig. 1 b, d, f). It is so called C(110) relation [24] which was proved to be favorable for efficient light-emission owing direct interband transition at Y point as a result of band structure rearrangement under stress condition. A compression of axis c for sample E is about 4%, which should cause a direct interband transition in $\beta$-FeSi$_2$, as it was shown after the theoretical calculation of band-gap value under uniaxial strain condition in [24].

To obtain sizes of NC, height and width of NCs were measured at HRTEM images. Since in the HRTEM image we can see only one projection of NCs, we cannot judge about NCs volume. It is worth noting that when the shape of NCs becomes closer to ellipse (Fig. 1 c, e), measurable sizes of $\beta$-FeSi$_2$ NCs slightly increase (samples C, D, and E) with the increasing of thickness of the covering silicon layer (Table I). This increasing of NCs sizes could results from $\beta$-FeSi$_2$ NCs coalescence.

With the increase of silicon layer thickness, NC aspect ratio significantly increase from 0.46 to 1.1 (Fig. 1 g) and NC shape became elongated in direction perpendicular to the surface (Fig. 1 e). It is important to note that we could not achieve full NC embedding in silicon even after deposition of 380 nm of Si at 750 °C (Fig. 1 e). We assume that the reason is that the silicon grows not only around, but also under the NCs due to grain-boundary Si diffusion [25]. One can suggest that $\beta$-FeSi$_2$ NCs extrusion from silicon crystal lattice takes place during Si growth. A possible mechanism of this phenomenon is diffusive motion of the nanocrystal with lattice parameter are very different from that of matrix. At sufficient temperature and a low silicon growth rate, due to a high energy at interface island/matrix, the nanocrystal extruded as a bubble on a surface. During the NCs embedding process a distance between $\beta$-FeSi$_2$ (220) planes, which are parallel to the surface, increase from 1.86 % when embedding just began up to 8.65 % when almost all the NC was inside silicon (Fig. 1 g). Further increase of the silicon layer resulted in decrease of the interplanar distance as a consequence of relaxation under influence of temperature and the pressure from silicon lattice.

4. Conclusion

As a result of solid-phase epitaxy of thin iron layers (0.4 nm at 630 °C) NCs of $\epsilon$-FeSi and $\beta$-FeSi$_2$
are formed, and these phases often co-exist within the one and the same NCs. A lack of silicon prevents a full transition of ε-FeSi NCs into β-FeSi2. Additional annealing at 750 °C for 90 minutes leads to transformation of ε-FeSi and β-FeSi2 NCs into α-FeSi2. In the process of NCs covering with silicon layer at 750 °C, all ε-FeSi NCs turns into β-FeSi2 and NCs coalescence takes place. Moreover, the crystal lattice deformation of partially embedded into the silicon β-FeSi2 NCs (sample C, Table II) is less than that of uncovered α-FeSi2 NCs. A better matching of β-FeSi2 lattice with silicon can cause predominantly β phase formation. During β-FeSi2 NC embedding into the silicon, the increase of β-FeSi2(220) interplanar distance takes place having the maximum of 8.65 %, when almost all the NC was inside the silicon lattice. The epitaxial relation of β-FeSi2 NCs with silicon matrix observed along with appropriate NCs deformation promises an indirect to direct β-FeSi2 band gap transition.

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References