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# Structural features and surface composition of epitaxial α-$FeSi_2$ films obtained by CVD

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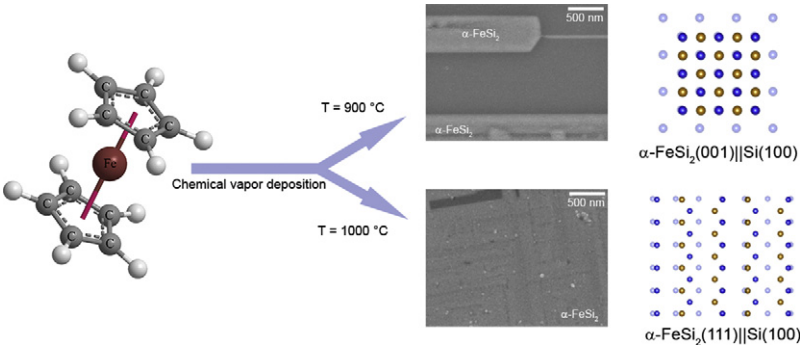
## HIGHLIGHTS

- Epitaxial α-$FeSi_2$ self-assembled structures were deposited from ferrocene using chemical vapor deposition technique.
- The epitaxial orientation of α-$FeSi_2$ structures depends on the deposition temperature.
- Morphology of the films changes from nanocrystallites to dense film depending on the deposition conditions.
- The surface of self-assembled structures is covered with thin layer of $Fe_2O_3$.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Iron disilicide (α-$FeSi_2$) is one of the promising materials for building ohmic contacts over silicon substrates. Complex approaches have been used to synthesize this material resulting in the insufficient control of the film surface and interface structure. The morphology of the α-$FeSi_2$ films synthesized in this work by one-step CVD technique from ferrocene varies from the highly-oriented self-assembled crystallites to the dense film of α-$FeSi_2$. The orientation of the material could be changed from α-$FeSi_2$(001)||Si(100) to α-$FeSi_2$(111)||Si(100) by raising the deposition temperature from 900 to 1000 °C. The epitaxial relationships $FeSi_2$(001)||Si(100), α-$FeSi_2$(010)||Si(001), and α-$FeSi_2$(111)||Si(100), α-$FeSi_2$($1\bar{1}0$)||Si(011) were determined for both orientations by a pole figure technique. It was found the surface of the material has an iron oxide admixture. Both the surface and interface structure might have a great impact on the properties of the α-$FeSi_2$/Si structures.



## 1. Introduction

Low-dimensional (1D, 2D) nanoscale materials, such as transition-metal silicides, have attracted much attention due to the potential applicability in the field of electronic, optoelectronic and spintronic devices. The special interest in the silicide materials is due to their compatibility with existing silicon technology.

The structure and properties of silicides of different metals, such as Fe, Re, Cr, Mn, Ni, Ti, Co, and Pt, were studied in detail elsewhere [1–29]. Some of these materials found the application as a good ohmic contact material to silicon. One of the major issues preventing these materials from finding wide application in technology is a complex formation mechanism. Different scientific groups have shown that epitaxial

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growth mechanism dictates the orientation and texture of the structures obtained, while the Detavernier et al. [1,10] have shown that another mechanism, so-called "axiotaxy growth" is possible. It may be the reason for the formation of self-assembled oriented nanostructures.

Fe-based silicides have several advantages comparing to other Si-based materials: iron and silicon are eco-friendly elements, and iron is much cheaper than platinum-group metals. At the same time, the properties of iron silicides match all the modern technology requirements. The wide variety of silicides with different composition and crystal structure also may be considered as a merit. Various silicides ($Fe_5Si_3$, $Fe_3Si$, FeSi, α-$FeSi_2$, and β-$FeSi_2$) may possess ferromagnetic/superparamagnetic/nonmagnetic and semiconducting/conducting properties [3–8,11,21,23,30]. Among the above-mentioned compounds, β-$FeSi_2$ is the most studied one. This material is a semiconductor with the direct band gap of 0.85 eV. β-$FeSi_2$ was synthesized by various deposition techniques, such as molecular-beam epitaxy [31,32], solid-state epitaxy [32], reactive deposition epitaxy [8] and chemical vapor deposition [11,33]. The structure of the material and its properties highly depend on the deposition method being used. The CVD experiments resulted in the formation of the nanowires with aspect ratio about 500, while the synthesis by other techniques results in the formation of films with epitaxial [32] and non-epitaxial [11,31] growth.

Comparing to β-$FeSi_2$, α-$FeSi_2$ is not sufficiently studied due to the fact, that this phase is metastable at room temperature, and becomes stable at temperatures above 937 °C. Despite this fact, α-$FeSi_2$ is a very promising material for building ohmic contact to silicon [5,22,23] and as a good candidate for spintronic device basis [6,16]. α-$FeSi_2$ was obtained by means of a wide range of deposition techniques: pulse laser deposition [16], solid-state epitaxy [6], molecular-beam epitaxy [22,23], reactive epitaxy [4], and magnetron sputtering [8]. These techniques provide a possibility to synthesize a material with different structures: either highly-oriented or non-oriented. Is most cases, the epitaxial or endotaxial formation mechanism are considered as the reason of oriented growth. These above-mentioned methods allow one to synthesize high-quality α-$FeSi_2$, but are complex and require multi-step approach (for example, subsequent annealing at elevated temperatures). The CVD technique is faster and more versatile (different precursor, excitation sources) [34]. Nevertheless, the CVD deposition process of α-$FeSi_2$ requires additional characterization in order to determine the quality and structure of this material.

In this paper, we used ferrocene as a precursor for the synthesis of α-$FeSi_2$ oriented self-assembled nanostructures by the low-pressure CVD technique. The ferrocene was chosen as a conventional Fe-containing precursor. Additionally, $H_2$ was used as a reducing gas. FTIR and Raman spectroscopies were used to determine the admixture composition of the product. The morphology of the structures was observed by SEM. XPS and XRD were used in order to confirm the formation of α-$FeSi_2$ and as the additional tools to study the composition of the product. The epitaxial relationships and preferred orientation of self-assembled disicilide nanocrystallites were determined by the pole figure technique.

## 2. Experimental

### 2.1. Deposition process

α-$FeSi_2$ thin films were synthesized using a conventional chemical vapor deposition technique by the thermal decomposition of ferrocene and hydrogen gas mixture described in detail elsewhere [35,36]. The deposition procedure was carried out at low pressure ($10^{-1} - 10^{-2}$ Torr) in a horizontal-type flow reactor. Fore vacuum pump was used to maintain this pressure. Helium or hydrogen was supplied into the reactor through a valve system. The temperature of the ferrocene source (65 °C) and growth zone was controlled with two heat controllers equipped with chromel-alumel and platinum platinum rhodium thermocouples, respectively. The total pressure in the reactor was varying from $4 \times 10^{-2}$ to $6 \times 10^{-2}$ Torr. The scheme of CVD setup is depicted in Fig. 1.

Hydrogen was chosen as a reducing gas. Si(100) wafers were used as a substrate for the film deposition. The wafers were subjected to treatment in HF acid in order to remove the surface oxide layer. The deposition conditions are presented in Table 1.

The experiments at temperatures higher than 900 °C in the first experimental series resulted in the material containing a high concentration of carbon admixture, while the samples obtained below 900 °C contain a small amount of carbon or no carbon at all. Two different approaches (2 and 3 experimental series) were taken in order to reduce the carbon content in the films obtained above 900 °C: the first one is to conduct longer experiments at deposition temperature 900 °C and the second one is to elevate the hydrogen pressure to reduce carbon concentration in the films deposited at 1000 °C.

### 2.2. Material characterization

The morphology of the films was studied by scanning electron microscopy using a JSM-6700F microscope with a resolution of 1 nm. The microscope is equipped with an EX-23000VU detector for energy-dispersive spectroscopy (EDS) analysis. Apart from surface analysis, SEM was used for the film thickness determination through the cross-section observation.

The IR absorption spectra of the films were recorded on an FTIR SCIMITAR FTS 2000 spectrometer in the range 300—4000 $cm^{-1}$. For comparison, the FTIR spectra were normalized to the film thickness. The Raman spectra were recorded using the argon laser wavelength of 488 nm of PHILIPS PU-95 and Triplemate, Spex spectrometers.

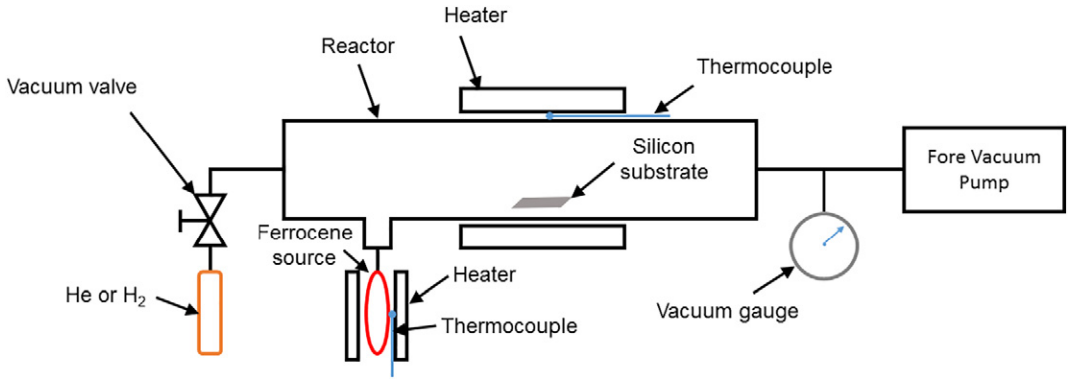


**Fig. 1.** CVD setup scheme.