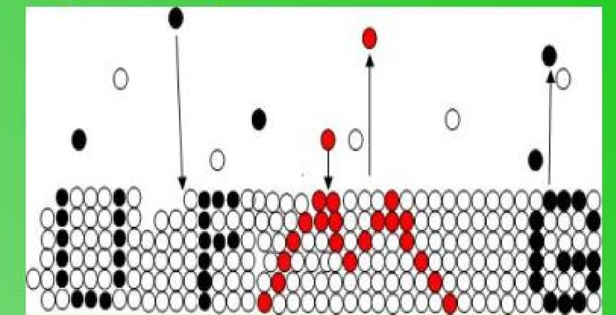
Morphology and crystal phases of iron silicide layer grown on Si (111)

D. R. Miquita*, J. C. González, M. I. N. da Silva, R. Paniago, W. N. Rodrigues, M. V. B. Moreira, H-D. Pfannes, and A. G. de Oliveira

Departamento de Física, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, CP 702, CEP 30123-970, Belo Horizonte, Minas Gerais, Brazil

Laboratório de Epitaxia por Feixe Molecular



Introduction

Since silicon is an indirect band gap semiconductor the development of integrated optoelectronic devices based on this material is hindered. This problem motivated numerous attempts to develop structures and materials based on silicon with good light emission characteristics. Some silicides of transition metals present basic properties that qualify them for optoelectronics. The beta phase of FeSi2 is especially important due to its direct gap (0.85 – 0.89 eV), close to the absorption minimum of the optical fibers. The demonstration of light emission at 1.5 Am in a device based on β-FeSi2 confirmed this expectative. However the production of good quality β-$FeSi_2$ layers is a challenge to overcome in order to allow the spreading of technologies based in this material. The complexity of the phase diagram and kinetics of the growth processes makes the properties of iron silicide films strongly dependent on the deposition methods, such as Solid Phase Epitaxy (SPE) and Reactive Deposition Epitaxy (RDE) among others.

In this work we investigate the growth of iron silicide thin films by both, SPE and RDE methods under different conditions of growth temperature, annealing temperature, and annealing time. Special attention is given to the formation of pure β-$FeSi_2$ layers.

X-ray Photoelectron Spectroscopy (XPS) was used to determine the chemical composition and phases formed at various growth conditions. In order to obtain more specific information on the iron-silicon interaction, Conversion Electron Mössbauer Spectroscopy (CEMS) studies were performed. Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Magnetic Force Microscopy (MFM) were used to study the morphology, and the iron silicide phases on the samples.

Results

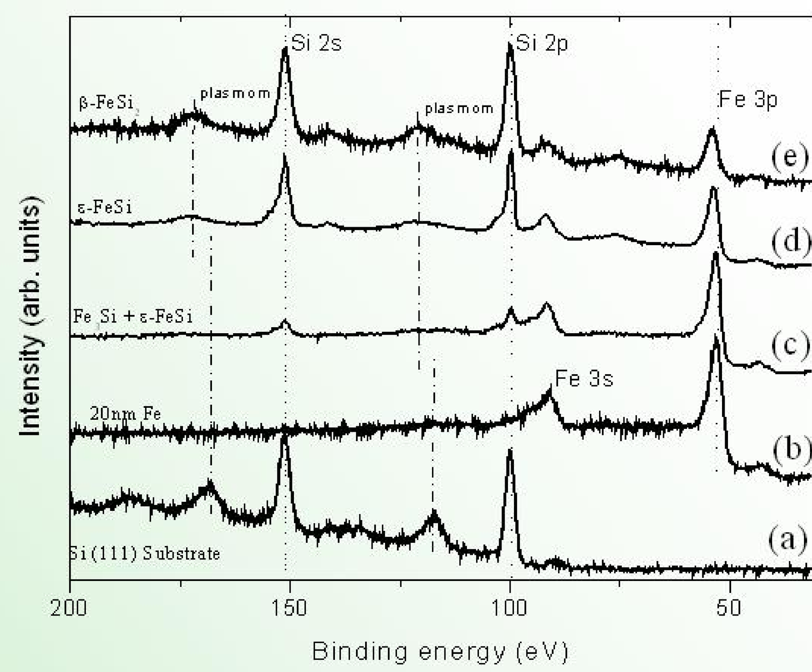


Fig 1: XPS spectra showing the formation of the iron silicides. In (a) XPS spectra of a silicon substrate, (b) 20 nm iron film deposited on the Si substrate, (c) after 2 hours of annealing at 400 °C, (d) after 2 hours of annealing at 500 °C, (e) after 2 hours of annealing at 800 °C.

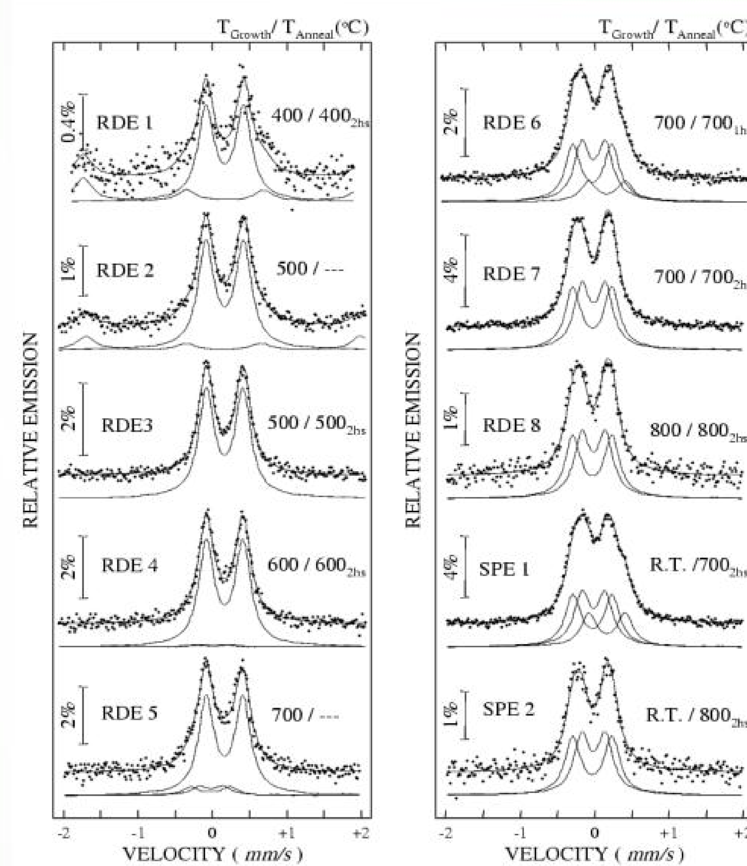


Fig. 2: Mössbauer spectra for all samples referred in this work. The different phases are well resolved and for some samples the co-existence of different phases is clearly shown.

Table I: Growth conditions for the RDE and SPE samples. CSi/CFe ratio calculated by XPS and CEMS, Fe2p3/2 line asymmetry, main silicide phase inferred from XPS data, and quantitative phase distribution as measured by CEMS.

Sample	T Growth	T annealing	C_{Si}/C_{Fe} XPS	Assimetry	Main phase	Fe_3Si (%)	ε-FeSi (%)	β-$FeSi_2$ (%)	C_{Si}/C_{Fe} CEMs
RDE 1	400 °C	400 °C/ 2h	0.30±0.01	Yes	Fe_3Si	46	54	0	0.5±0.1
RDE 2	500 °C	none	0.70±0.01	Yes	ε-FeSi	31	69	0	0.6±0.1
RDE 3	500 °C	500 °C/2h	1.40±0.03	Yes	ε-FeSi	0	100	0	1.0±0.2
RDE 4	600 °C	600 °C /2h	1.30±0.03	Yes	ε-FeSi	0	97	3	1.0±0.2
RDE 5	700 °C	none	1.80±0.04	Yes	ε-FeSi	0	85	15	1.1±0.2
RDE 6	700 °C	700 °C /1h	2.50±0.05	No	β-$FeSi_2$	0	15	85	1.8±0.3
RDE 7	700 °C	700 °C /2h	2.00±0.04	No	β-$FeSi_2$	0	0	100	2.0±0.4
RDE 8	800 °C	800 °C /2h	2.30±0.05	No	β-$FeSi_2$	0	0	100	2.0±0.4
SPE 1	RT	700 °C /2h	3.20±0.06	No	β-$FeSi_2$	0	25	75	1.7± 0.3
SPE 2	RT	800 °C /2h	3.50±0.07	No	β-$FeSi_2$	0	0	100	2.0±0.4

CEMS data suggest that by increasing the annealing temperature Fe_3Si is initially formed and is completely transformed into ε-FeSi at 500 °C. Further temperature increase turns ε-FeSi into β-$FeSi_2$, and complete phase transformation is achieved at 700 °C. The annealing time dependence has also shown that ε-FeSi is a pre stage for β-$FeSi_2$ formation. For SPE the β-$FeSi_2$ formation occurs between 700 and 800 °C and between 600 and 700 °C for RDE. This difference can be attributed to the fact that for SPE the migration of Si is through a Fe film while for RDE it occurs through a thin FeSi film being already formed during Fe-deposition.

Thin Solid Films 493 (2005) 30 – 34

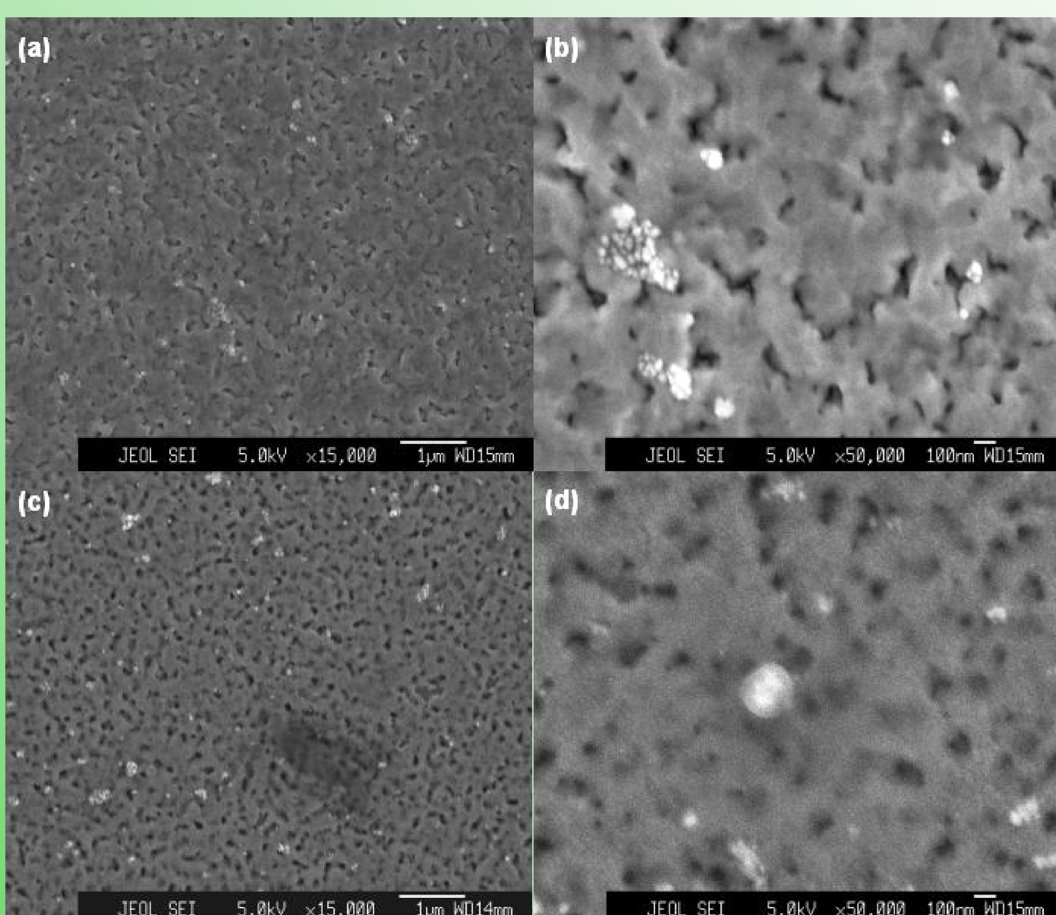


Fig. 3: SEM micrographs of samples RDE 5 (a) and (b), RDE 7 (c) and (d). Note the rough surface of these samples and the uncovered Si areas (dark areas).

Figure 3 present two SEM images of the surface of samples RDE5 and RDE7. Both, RDE5 and RDE7 samples exhibit:

- rough surfaces with deep holes (dark areas ~5 % of the surface area with a mean size of 177 nm^2).
- spatial distribution of the holes homogeneous over several micrometers

This means that the morphology of the films was not significantly changed by long annealing times.

Figure 4 shows AFM and MFM images, of the surface of sample RDE 7. These images show a very rough iron silicide film with dendrite-like formations and deep craters in agreement with the SEM observations.

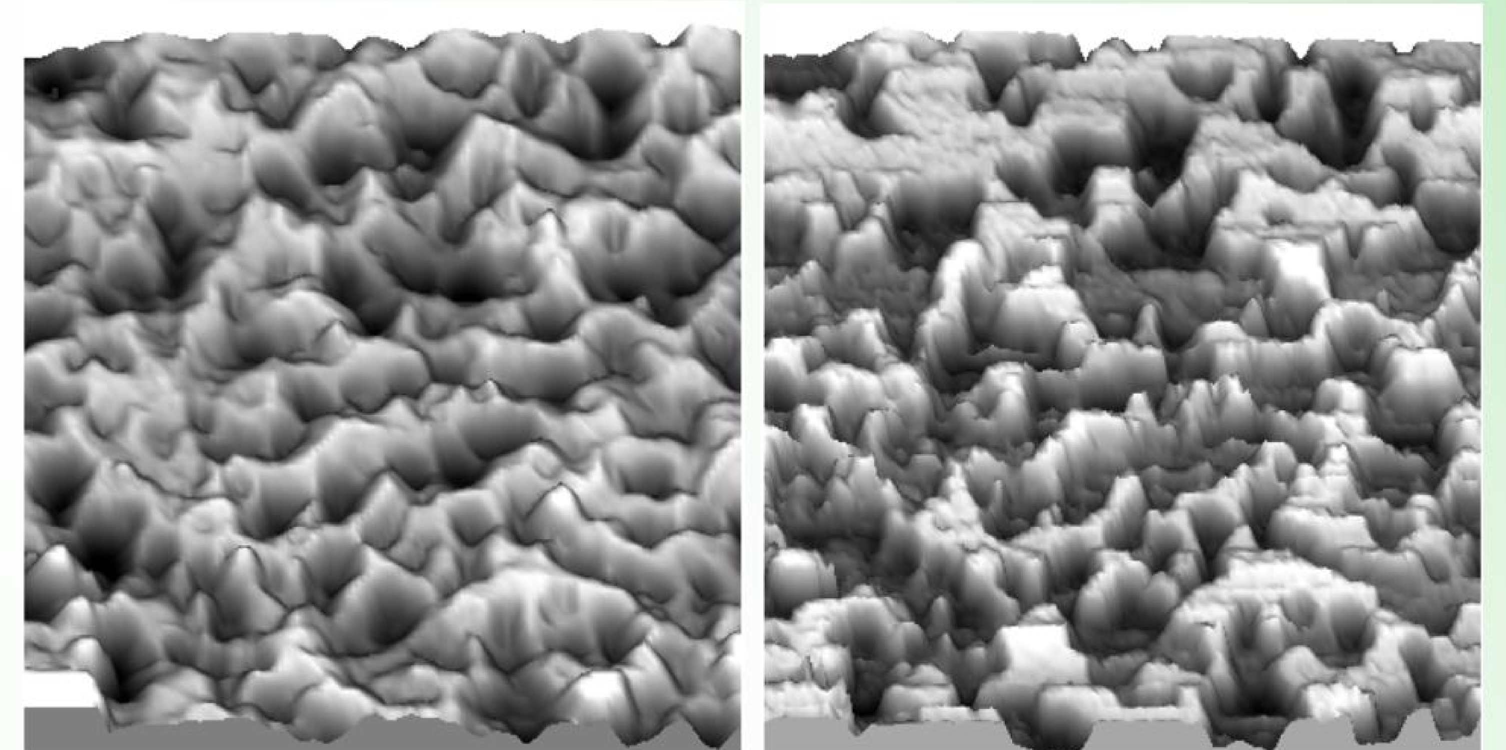


Fig. 4: AFM (left) and MFM (right) images of sample RDE7. The field of view corresponds to 3x3 μm2 and the vertical scales are 400 nm and 10 Hz, respectively.

MFM is a very good technique to visualize and measure the lateral distribution of magnetic phases in thin films. Particularly, a semi-quantitative analysis of Magnetic Force Microscopy was applied for the first time to identify the spatial distribution of β-FeSi2 on the Si substrate of sample RDE7. We found a susceptibility of 2.5x10-7 emu/gOe in the bright region of the sample. This value is in good agreement with the reported susceptibility in literature for p-doped β-$FeSi_2$ [*E. Arushanov, M. Respaud, J. M. Broto, Ch. Kloc, J. Leotin, and E. Bucher, Phys. Rev. B 53, 5108 (1996)*].

We conclude that from our MFM images the bright regions actually correspond to β-FeSi2 regions, in reasonable agreement with the expectations. Therefore, the holes observed in the AFM image should correspond to uncovered areas of the silicon substrate, and the iron silicide is completely located in the mountain-like formations.

Conclusions

Iron silicide films were grown by reactive deposition epitaxy and solid phase epitaxy on Si (111) substrates. Appropriated growth conditions for single-phase ε-FeSi and β-$FeSi_2$ were found in this study. The growth conditions for the phase transitions from Fe_3Si to ε-FeSi and from ε-FeSi to β-$FeSi_2$ were well defined for RDE samples. CEMS showed that all deposited iron reacted with silicon to form silicides in both methods of preparation.

It was also confirmed that some features of the XPS spectra can be used as a qualitative indication of the formation of different iron silicide phases.

AFM and MFM observations shown that the iron silicide films presented a rough morphology leaving uncovered Si patches on the samples.

This work was supported by: CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico; LNLS; CAPES; FAPEMIG Fundação de Amparo à Pesquisa do Estado de Minas Gerais

*miquita@fisica.ufmg.br