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Growth of β-$FeSi_2$ layers on Si (111) by solid phase and reactive deposition epitaxies

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Abstract

Iron silicides were grown on Si (111) substrates by Solid Phase Epitaxy (SPE) and Reactive Deposition Epitaxy (RDE) to identify the optimum conditions to obtain the semiconduting β-$FeSi_2$ phase. The films were produced under different growth and annealing conditions and analyzed in situ and ex situ by X-ray Photoelectron Spectroscopy, and ex situ by Conversion Electron Mössbauer Spectroscopy. The use of these techniques allowed the investigation of different depth regions of the grown layer. Films of the ε-FeSi and β-$FeSi_2$ phases were obtained as well as the mixtures Fe_3Si+ε-FeSi and ε-FeSi+β-$FeSi_2$. The sequence Fe_3Si→ε-FeSi→β-$FeSi_2$ was found upon annealing, where the phase transformation occurred due to the migration of silicon atoms from the substrate to the surface region of the grown layer. The best conditions for the phase transformation in SPE samples were met after annealing in the range 700 – 800 °C. For the RDE samples, the transition to the beta phase occurred between 600 and 700 °C, but pure β-$FeSi_2$ was obtained only after two hours of annealing at 700 °C.
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1. 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 [1]. Some silicides of transition metals present basic properties that qualify them for optoelectronics [2–8]. The beta phase of $FeSi_2$ is especially important due to its direct gap (0.85 – 0.89 eV), close to the absorption minimum of the optical fibers [5,9–12]. The demonstration of light emission at 1.5 μm in a device based on β-$FeSi_2$ confirmed this expectative [13].

The Fe-Si phase diagram presents four stable compounds: the Fe-rich metallic and magnetic silicide (DO_3 type) Fe_3Si, the metallic ε-FeSi phase, the semiconducting β-$FeSi_2$ phase and the high-temperature metallic α-$FeSi_2$. The α-$FeSi_2$ phase is stable at high temperatures, and forms after annealing the β-$FeSi_2$ above 940 °C [5]. Non-intentionally doped β-$FeSi_2$ layers are usually p-type, with hole mobility of the order of 1–3 cm^2/V.s at 290 K, and carrier concentration of around 10^{19} cm^{-3} [14,15]. The production of β-$FeSi_2$ layers of good quality and controlled doping is a challenge to overcome in order to allow the spreading of technologies based in this material. Nevertheless, the variety of the existing compounds and the complex kinetics of the processes, make the properties of the iron silicide films strongly dependent on the deposition methods, such as Solid Phase Epitaxy (SPE) [16], Reactive Deposition Epitaxy (RDE) [17], Molecular Beam Epitaxy [18], ion beam synthesis [19,20], Metal-organic Chemical Vapor Deposition [21], spark plasma sintering [22], sputtering deposition [23], sintering [24], ball milling [25] and pulsed laser deposition [26].

In this work we investigate the formation of iron silicides grown by SPE and RDE fabricated under different conditions (substrate temperature and annealing temperature and time). In situ and ex situ X-ray Photoelectron Spectroscopy (XPS)

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and ex situ Conversion Electron Mössbauer Spectroscopy (CEMS) were used to determine the chemical composition, morphology, and phase distribution. The best conditions for the formation of pure β-$FeSi_2$ phase were identified.

2. Experimental details

Fe-silicides of different stoichiometries were prepared in an ultra-high vacuum evaporation system at a base pressure of about 10^{-7} Pa. For the SPE samples a thin layer of iron was deposited on an atomically clean silicon substrate held at room temperature, followed by a high temperature anneal to form the silicides. The RDE samples were fabricated by iron deposition on a hot Si surface, and the silicide formation occurred concomitantly to the iron deposition.

The Si (111) substrates were degreased with organic solvents and then dipped in a solution of NH_4OH: H_2O_2 : H_2O (1 : 1 : 4) kept at 80 °C, for oxidation of its surface before introduction into the system. Subsequently, this oxide was removed by a HF buffer solution (pH = 5.0), with NH_4F as the buffering specie. A new stage of oxidation was then carried out, this time using a solution of H_2O : H_2O_2 : HCl (4 : 1 : 1) kept at 80 °C. The removal of this new oxide layer was done using a solution of H_2O : HF : NH_4F (250 : 1 : 100) with pH = 7.8. After a rinse in high purity water the substrates were dried under N_2 gas flow.

High purity Fe (99.999%) was deposited from an electron beam evaporation source. For all samples an iron film with a nominal thickness of 20 nm was deposited as monitored by an Inficon quartz crystal oscillator. The samples were prepared under several combinations of substrate temperatures and annealing temperatures and times, as shown in Table 1.

In-situ XPS spectra were obtained with a VG-CLAM (Combined Lens and Analyzer Module) hemispherical sector analyzer and a X-ray gun model XR3E2 - Fisons-VG operating at 300 W. Ex situ XPS spectra were obtained in a VG ESCALAB 220i-XL system operating at 150 W. In both situations non-monochromatized Al Kα radiation (hν = 1486.6 eV) was employed. Before the ex situ measurements the samples were cleaned by sputtering for 1 h with Ar^+ ions of 1.5 KeV energy and a sample current of 1 μA, which removes of ca. 12 monolayers of material. The energy scale of the spectrometers was calibrated with the binding energy of Au $4f_{7/2}$. Surface charging effects were taken into account by calibrating spectra with binding energy of the Si 2p peak (99.7 eV from Ref. [27]). Photoelectron peaks were fitted by a Gauss–Lorentz combination. Relative atomic concentrations were calculated from the intensities of the Si 2p and Fe 3p spectral lines after subtracting a background by the Shirley's method [28]. The sensitivity factors were taken from Scofield [29].

CEMS was employed with a ^{57}Co/Rh source and constant acceleration drive mode. Electrons emitted from the surface near region (~100 nm) were counted in a He/ CH_4 gas flow detector.

Table 1
Growth conditions for the RDE and SPE films

Sample	Substrate temperature (°C)	Annealing (Temperature/time)
RDE 1	400	400 °C/2 h
RDE 2	500	none
RDE 3	500	500 °C/2 h
RDE 4	600	600 °C/2 h
RDE 5	700	none
RDE 6	700	700 °C/1 h
RDE 7	700	700 °C/2 h
RDE 8	800	800 °C/2 h
SPE 1	RT	700 °C/2 h
SPE 2	RT	800 °C/2 h

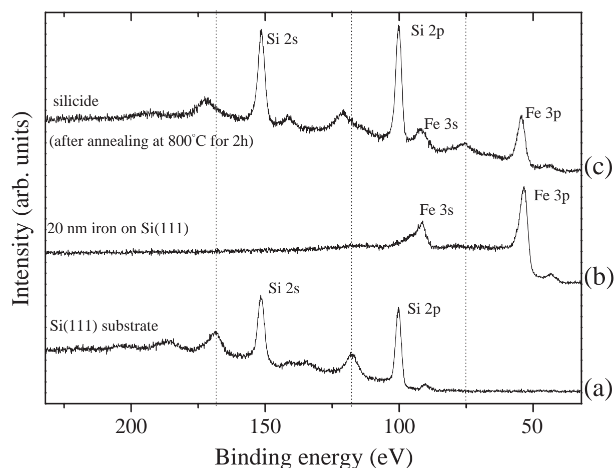

Fig. 1. XPS spectra of (a) the silicon substrate, (b) of the 20 nm iron film on Si (111) and (c) of the silicide, for a SPE sample.

3. Results and discussion

3.1. XPS measurements

Before the deposition of iron, the cleanness of the substrate was verified by taking XPS spectra in the region of

Table 2
C_{Si}/C_{Fe} ratio, $Fe2p_{3/2}$ line asymmetry and silicide type for the same samples described in Table 1

Sample	C_{Si}/C_{Fe}		Asymmetry	Silicide
	In situ	Ex situ		
RDE 1	–	0.3	Yes	Fe_3Si
RDE 2	–	0.7	Yes	ε-FeSi
RDE 3	–	1.4	Yes	ε-FeSi
RDE 4	–	1.3	Yes	ε-FeSi
RDE 5	2.1	1.8	Yes	ε-FeSi
RDE 6	–	2.5	No	β-$FeSi_2$
RDE 7	2.4	2.0	No	β-$FeSi_2$
RDE 8	3.2	2.3	No	β-$FeSi_2$
RDE 9	–	2.1	No	β-$FeSi_2$
SPE 1	3.2	1.9	No	β-$FeSi_2$
SPE 2	3.5	–	No	β-$FeSi_2$

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