Selective and epitaxial deposition of $\beta$-FeSi$_2$ onto silicon by RTP-CVD

J. Regolini, F. Trincat, Isabelle Berbezier, J. Palleau, J. Mercier, D. Bensahel

To cite this version:

J. Regolini, F. Trincat, Isabelle Berbezier, J. Palleau, J. Mercier, et al.. Selective and epitaxial deposition of $\beta$-FeSi$_2$ onto silicon by RTP-CVD. Journal de Physique III, EDP Sciences, 1992, 2 (8), pp.1445-1452. <10.1051/jp3:1992189>. <jpa-00248816>
SELECTIVE AND EPITAXIAL DEPOSITION OF $\beta$-FeSi$_2$ ONTO SILICON BY RTP-CVD

J.L. Regolini, F. Trincat, I. Berbezier, J. Palleau, J. Mercier and D. Bensahel

France Telecom, Centre National d'Etudes des Télécommunications, BP 98, 38243 Meylan Cedex, France

(Received 1st February, accepted 13 March 1992)

ABSTRACT

We present the preparation for the first time of selective and epitaxial $\beta$-FeSi$_2$ on oxidized and patterned 4"-silicon wafers. These layers are obtained by Low Pressure Chemical Vapor Deposition using a Rapid Thermal Processing (RTP) system and in a temperature/time range of 750-850°C / 2 minutes. The iron source is a chlorination chamber where high purity iron is heated under HCl/Ar or Cl$_2$/Ar gas in order to form volatile chlorinated iron species which are then transported into the reaction chamber. The layers obtained are single crystal islands most of them oriented with the substrate. They are P-type as deduced from electrical results performed on layers grown on N- and P-type substrates (diode and ohmic contact respectively). Structural results and selectivity of this RTP-CVD $\beta$-FeSi$_2$ will be presented and discussed.

INTRODUCTION

The primary interest of transition metal silicides is in contacts and interconnects for silicon technology. However, the semiconducting nature of several silicides which could be potential materials for new optoelectronic devices integrated into a silicon chip has also been established(1).

$\beta$-FeSi$_2$ is the semiconducting phase of iron disilicide with a measured band gap of about 0.87 eV (1) which makes it an ideal coupler for optical fibers with optimal transmittance at 1.4 $\mu$m.

Several studies have been devoted to this material to characterize it from the fundamental point of view (1-4) and in all these cases the material was grown by solid phase reactions on single or polycrystalline silicon. On single crystal silicon, thin epitaxially grown layers have been obtained showing two different epitaxial relations with the substrate (2) and many remaining compositional as well as structural (twins, dislocations or strain) defects are responsible for the sub-band gap optical absorption (5).

In this paper we report for the first time the use of CVD to grow stoichiometric $\beta$-FeSi$_2$ using a Rapid Thermal Processing (temperature switching) termed Limited Reaction Processing (LRP) (6). Structural properties and selectivity will be presented for samples prepared under different conditions.
EXPERIMENTAL

Essentially, the reactor is a horizontal air cooled quartz tube where the 4" wafer is self-supported and heated by a set of power lamps. The reactor is permanently held under hydrogen flux and the working pressure, about 2 Torr.

One of the most important problems for large applications of silicide CVD is to find an easy-to-handle and safe metal precursor. This is the case for iron, of which one of the precursors, iron tetra-carbonyl, is a gas but very poisonous. Another iron precursor is ferrocene, a solid with high vapor pressure at room temperature, but the sublimation rate is not easy to control and there is carbon incorporation into the films. It is well known that "in situ" metal chlorination is used to obtain precursors for metals such as Ta or W (7).

Thus we fabricated an iron source, outside the reactor, which consists of a reaction chamber containing high purity iron wire and through which flows HCl or Cl₂ gas diluted in Ar while the wire is heated above 300°C. The resulting reaction products, solid or gaseous at equilibrium can be calculated by the minimization of the total Gibbs energy of the chemical system: Fe, Cl, H.

According to the Janaf Tables (8) there are five chlorinated iron compounds: FeCl, FeCl₂, FeCl₃, Fe₂Cl₄ and Fe₂Cl₆, which are solids but with a high vapor pressure when the temperature is above 300°C. We carried out calculations for the Fe/ClH and Fe/Cl₂ systems in order to find out which one is the more suited to obtaining FeCl₃, as the latter has the highest partial pressure at that temperature (9).

Using the equilibrium and reaction constants from Ref. 8, both systems are solved using the iterative Newton's method (10) with a total HCl or Cl₂ source pressure of 1 Torr and within a temperature range of 300 to 1300°K.

![Graph](image-url)

**Figure 1.** The partial pressure of FeCl₂ and its dimer as a function of temperature
Fig. 1 shows the results obtained with the Fe/HCl system. At high temperature the FeCl$_2$ partial pressure is about 10% of the total HCl pressure. The FeCl$_2$ dimer and other species partial pressure are completely negligible and this is also the case for FeCl$_3$.

On the other hand, the Fe/Cl$_2$ system shows a total chlorine consumption to form mainly FeCl$_2$ again, and Fe$_2$Cl$_4$. The FeCl$_3$ partial pressure and that of its dimer are very low. However, as this is an open system, there is an excess of chlorine which flows permanently carried by Ar gas. Thus, FeCl$_2$ may be transformed into FeCl$_3$ by the reaction at high temperature (11):

$$2 \text{FeCl}_2 + \text{Cl}_2 \rightarrow 2 \text{FeCl}_3.$$ 

In this way we produce nearly 1 Torr of FeCl$_3$ which is the most volatile species to be transported into the reaction chamber.

The feeding gases are SiH$_4$, H$_2$, He and (on a separate line) the FeCl$_3$ diluted in Ar. All samples were given an external chemical cleaning and an "in situ" thermal cleaning under H$_2$. The deposition cycles were very fast for this type of material, around 2 to 10 min at temperatures between 750 and 850°C and with a cooling time of 2 min to room temperature. No post annealing followed for any of the samples.

RESULTS AND DISCUSSIONS
LAYER CHARACTERIZATION

Verification of the film composition and layer thickness was made by Rutherford Backscattering Spectroscopy (RBS). All the films grown between 750 and 850°C show a stoichiometric composition to within an experimental error which is well below 10%.

![X-Ray diffraction spectrum](image)

**Figure 2.** X-Ray diffraction spectrum obtained from 1000 Å thick silicide layer grown at 850°C.
A representative x-ray diffraction pattern is shown in Fig. 2 for a 150 nm film. These data were obtained using copper Kα radiation and from them we identify β-FeSi₂ as the only phase present. The peaks are labeled with the Miller indices of this phase and there are no reasonable matches between the peaks and the α-FeSi₂, the high temperature metallic phase.

In Fig. 3 we show a scanning electron micrograph (SEM) of a FeSi₂ layer deposited from a SiH₄/He/FeCl₃/Ar mixture on a P-type <111> silicon substrate for 2 min at 750°C. The measured layer thickness is 750 Å. From this figure the surface shows a granular aspect with some protrusions or hillocks. There is a strong tendency toward island formation. Nevertheless, the films look metallic and have a mirror like surface mainly for smaller thicknesses. We do not observe the ring shaped structure reported in Ref. 3. Thus a nucleation barrier does not seem to be involved. By high-resolution cross-section transmission electron microscopy and diffraction we observe that most of the islands are epitaxially grown as observed in Figure 4. The interface region is abrupt giving a well defined silicide-silicon heterojunction. In this case the (111) silicon planes, spaced at 3.13 Å (horizontal in the figure) are parallel to the (202) silicide planes spaced at 3.07 Å.

Roughness measurements performed with a mechanical profilometer show a peak to peak amplitude of 40 nm for a 140 nm layer thickness grown at 750°C and about 60 nm for a 100 nm at 850°C. The surface roughness increases with growth temperature (and layer thickness at constant temperature). These results and the abruptness of the interface suggest a Stransky-Krastanov

Figure 3.- Scanning electron micrograph of a 750 Å thick β-FeSi₂ grown on <111> Si substrate.
growth mode (12), which is not too surprising considering the rather large lattice mismatch (1.9%) and thicknesses of the structures.

![Figure 4](image)

**Figure 4.** High resolution transmission electron micrograph of the FeSi$_2$(top)/Si(bottom) interface. Horizontal (111) Si planes are parallel to (202) silicide planes.

**SELECTIVE DEPOSITION**

Selectivity against the silicon dioxide mask has also been obtained but in this case the reactive gas mixture has to be carefully controlled. An excess of silane concentration induces selectivity loss as does the use of hydrogen when used as a diluent agent or carrier gas. Thus using the SiH$_4$/He/Cl$_2$/Ar gas system, we obtain full selectivity and stoichiometric composition within the mentioned temperature range. In Fig. 5 we present an optical micrograph where the light regions correspond to SiO$_2$ and the dark ones to the silicide, the minimum features being 0.5 μm. The layer thickness is 190 nm and the silicon substrate consumption is about 130 nm.

To minimise this substrate consumption the silane concentration should be increased until some nuclei start to appear over the oxide. However even when the selectivity is completely lost there is still substrate consumption, showing that this system presents a quite different behaviour.
from the previously studied titanium disilicide under equivalent conditions (13). Indeed, using the TiCl$_4$/SiH$_4$/H$_2$ gas mixture selective TiSi$_2$ deposition with no substrate consumption was obtained. Furthermore, in this new FeCl$_3$/SiH$_4$/H$_2$ (or He) system, if the dilution gas is hydrogen the deposit is not selective even without silane. The iron trichloride is reduced by H$_2$ giving metallic clusters or nuclei over the oxide. Using He as dilution gas selectivity is obtained until there is about 5% silane in the mixture.

**Figure 5.** Optical micrograph showing the selective deposit of FeSi$_2$. Light regions are SiO$_2$ and the minimum features are 0.5 μm.

The global system behavior can be represented by a set of chemical surface reactions where they are all thermodynamically possible:

I) System FeCl$_3$/H$_2$/<Si> (no silane)
   Over silicon seeds
   \[ 2 \text{FeCl}_3 + 3 \text{H}_2 + 4 <\text{Si}> \rightarrow 2 \text{FeSi}_2 + 6 \text{HCl} \] [1]
   Over the oxide
   \[ 2 \text{FeCl}_3 + 3 \text{H}_2 \rightarrow 2 \text{Fe} + 6 \text{HCl} \] [2]

II) System FeCl$_3$/He/<Si> (no silane)
   Over silicon seeds
   \[ 4 \text{FeCl}_3 + 11 <\text{Si}> \rightarrow 4 \text{FeSi}_2 + 3 \text{SiCl}_4 \] [3]
   Over the oxide: no deposit

III) System FeCl$_3$/SiH$_4$/He/<Si>
   Over silicon seeds
   \[ 4 \text{FeCl}_3 + 2 \text{SiH}_4 + 7 <\text{Si}> \rightarrow 4 \text{FeSi}_2 + 8 \text{HCl} + \text{SiCl}_4 \] [4]
   Selectivity and minimum substrate consumption
   Over the oxide selectivity is possible via:
4 FeCl₃ + SiH₄ --> 4 FeCl₂ + SiCl₄ + 2 H₂  [5]

From [3] and [4] it can be seen that from the same amount of FeCl₃ the same quantity of β-FeSi₂ is obtained but in the second case (with silane) the SiCl₄ volatile formation is reduced by a factor of three. However, if we want to reduce it further, we lose the selectivity, as the by-product HCl is not sufficient to etch the starting Si nuclei over the oxide (14).

If we propose a possible reaction with no silicon substrate consumption, for example:

FeCl₃ + 2 SiH₄ --> FeSi₂ + 3 HCl + (5/2) H₂  [6]

we observe that the Gibb's free energy of the total reaction is more negative in reaction [4] than in reaction [6], which means that the system will always take some silicon from the substrate, as experimentally measured. Of course, no account has been taken of the kinetic aspects which can give significant quantitative differences in comparing [3] and [4]. For the same temperature/time cycle and following equation [3], we measured about 500 nm substrate consumption for 500 nm of FeSi₂ deposition. Following reaction [4], these figures are 130 and 190 nm respectively. The 130 nm can be explained by the formation of FeCl₂ as a volatile specie at the expense of the silicide. The involved reaction is also thermodynamically favorable.

The electrical, optical and electro-optical properties will be published elsewhere. Briefly, the semiconducting behavior is very clear, the layers are P type and the mobility at 50 °K about 55 cm²/V/s.

CONCLUSION

In conclusion, the selective and epitaxial deposition of semiconducting iron disilicide has been obtained by CVD in an RTP system using solid iron as primary source for the volatile chloride. The crystalline quality has been shown but a more systematic study concerning the quality of the material for thin thicknesses is necessary. However, the usefulness of solid sources with RTP systems has once again been demonstrated.

ACKNOWLEDGEMENTS

The authors thank J. C. Oberlin, I. Sagnes, and G. Bremond for measurements and fruitful discussions. R. Carré and D. Laviale are also acknowledged for their technical assistance and Mrs. M. Timmins for reading of the manuscript.
REFERENCES

1).- M. C. Bost and J. E. Mahan, J. Appl. Phys. 58 (1985) 2696
2).- N. Cherief, C. D'Anterroches, R. C. Cinti, T. A. Nguyen Tan and J. Derrien
7).- E. Blanquet, C. Vahlas, C. Bernard, R. Madar, J. Palleau and J. Torres,
   J. de Physique C5 (1989) 557
9).- P. Pascal,"Nouveau Traité de Chimie Minerale", Masson et Cie Editeurs,
   XVIII, 14 (1959)
10).- J. Legras, "Méthodes et Techniques de l'analyse numérique", Dunod
    Paris, 1971
13).- J. L. Regolini, D. Bensahel, J. Mercier and G. Bomchil
14).- J. L. Regolini, D. Bensahel, L. Mercier and E. Scheid
    J. Crystal Growth 96 (1989) 505