# Ion beam synthesis of buried $\alpha$-$FeSi_2$ and $\beta$-$FeSi_2$ layers

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Using high dose implantation of $Fe^+$ into (111)Si, followed by rapid thermal annealing (RTA) at 1150 °C for 10 s, we fabricated continuous buried layers of the metallic $\alpha$-$FeSi_2$ phase. Rutherford backscattering experiments indicate that these layers contain a large number of Fe vacancies, up to 18%. By implanting through a $SiO_2$ mask, we produced Schottky diodes with idealty factors of $1.4 \pm 0.1$ and a Schottky barrier height of $\Phi_B = 0.84 \pm 0.03$ eV on (111) *n*-Si. In this letter we report for the first time the formation of the semiconducting stoichiometric $FeSi_2$ ($\beta$-$FeSi_2$) phase by annealing the buried $\alpha$-$FeSi_2$ layers below the phase transition temperature of 937 °C; specifically at 750 °C for 20 h.

The transition metal silicide $FeSi_2$ is a very interesting material for basic research and also for possible device application in silicon technology. $FeSi_2$ crystallizes in two phases, the tetragonal, metallic $\alpha$-$FeSi_2$ which is stable above $\approx$937 °C, and the orthorhombic semiconducting $\beta$-$FeSi_2$, which is stable at lower temperatures.[1,2] Since metallic $\alpha$-$FeSi_2$ grows epitaxially on (111)Si,[3] it should be possible to use it for the fabrication of Schottky diodes or permeable base transistors on Si, as demonstrated for $CoSi_2$.[4] $\beta$-$FeSi_2$ is of particular technological interest, because optical measurements on polycrystalline[5] and single crystalline[6] thin films have shown $\beta$-$FeSi_2$ to be a semiconducting silicide. Electron spectroscopic studies have revealed a direct gap at about 0.8 eV.[7] Thus it should be possible to produce optoelectronic devices in the infrared region. Since band-gap narrowing in the base improves the current gain of a Si bipolar transistor,[8] small base regions with abrupt interfaces are very important for higher switching speeds in transistors. Therefore, $\beta$-$FeSi_2$ could be a candidate for base material of a hetero-bipolar-transistor (HBT) in silicon. Recent bandstructure calculations of $\beta$-$FeSi_2$ indicate an indirect band gap.[9,10] Thus it may be very important to fabricate continuous, single-crystalline layers to investigate this difference between the experimental data and the theoretical calculation.

In recent years ion beam synthesis (IBS) has developed into a promising technique for the production of buried epitaxial silicides, e.g., the formation of epitaxial $CoSi_2$[11,12] or $CrSi_2$.[13] In this work we report the first results of the fabrication of buried $\alpha$- and $\beta$-$FeSi_2$ in (111)Si using IBS.

Implantations with energies of 200 keV and doses of $1\times10^{17}$, $2\times10^{17}$, and $3\times10^{17}$ $Fe^+$ $cm^{-2}$ were used to generate a Gaussian shaped depth profile of $^{56}Fe^+$ ions beneath the surface of (111)-oriented Si wafers (*p*-type, $\approx$100 Ω cm). In addition, we fabricated structured silicides by implantation through a $SiO_2$ mask in *n*-type (111)Si ($\approx$1 Ω cm). During implantation the wafers were fastened with clips to a heated Cu block that was maintained at 350 °C to keep the surface crystalline by dynamic annealing. The as-implanted and annealed samples were analyzed using a variety of techniques. The Fe distribution and the stoichiometry were measured by Rutherford backscattering (RBS) and evaluated by using the RUMP program.[14] Silicide phases were determined by x-ray diffraction (XRD). The crystal quality was checked by $He^+$-ion channeling experiments. The layer structure was investigated in cross-sectional specimens using a JEOL 2000 EX transmission electron microscope (TEM), operated at 200 keV. Four point sheet resistivity measurements and *I-V* characteristics measurements (with a HP 4145B Semiconductor Parameter Analyzer) were performed to check the electrical properties of the silicide films and the silicide-silicon interfaces.

Transmission electron microscopy (not shown) indicates that Fe already precipitates in the form of iron disilicide during the implantation with a tendency to epitaxy. XRD measurements also denote that $\beta$-$FeSi_2$ is the predominant silicide phase in the as-implanted state. Figure 1(a) shows the RBS and channeling spectra of a sample implanted with $2.8\times10^{17}$ $Fe^+$ $cm^{-2}$. The channeling spectrum shows partial alignment of the $\beta$-$FeSi_2$ precipitates embedded in the Si matrix. In order to fabricate buried $\beta$-$FeSi_2$ layers by coarsening and coalescence of the precipitates, various annealing studies have been performed in a tube furnace at temperatures above the phase transition temperature. As shown by RBS (not shown) annealing below 937 °C does lead to a redistribution of precipitates towards the center of the as-implanted Fe distribution. The backscattering data of this sample indicate the formation of stoichiometric $\beta$-$FeSi_2$ at the center, but no redistribution of Fe in the tails of the distribution; thus suggesting the presence of a continuous $\beta$-$FeSi_2$ layer in the center and a large number of $\beta$-$FeSi_2$ precipitates on both sides of the layer. Surprisingly, additional annealing of such samples did not produce continuous layers with planar interfaces; on the contrary, samples implanted with $2\times10^{17}$ $Fe^+$ $cm^2$ appear disrupted after an annealing at 750 °C for 5 h. At higher doses the layers tended to be more stable, but they also disintegrated after long anneals ($\approx$20 h).

We have developed an alternative method for producing $\beta$-$FeSi_2$ by first fabricating $\alpha$-$FeSi_2$ and then transforming it to $\beta$-$FeSi_2$ by furnace annealing below the phase transition temperature of 937 °C. The $\alpha$-$FeSi_2$ phase was produced by ion implantation followed by RTA. Figure

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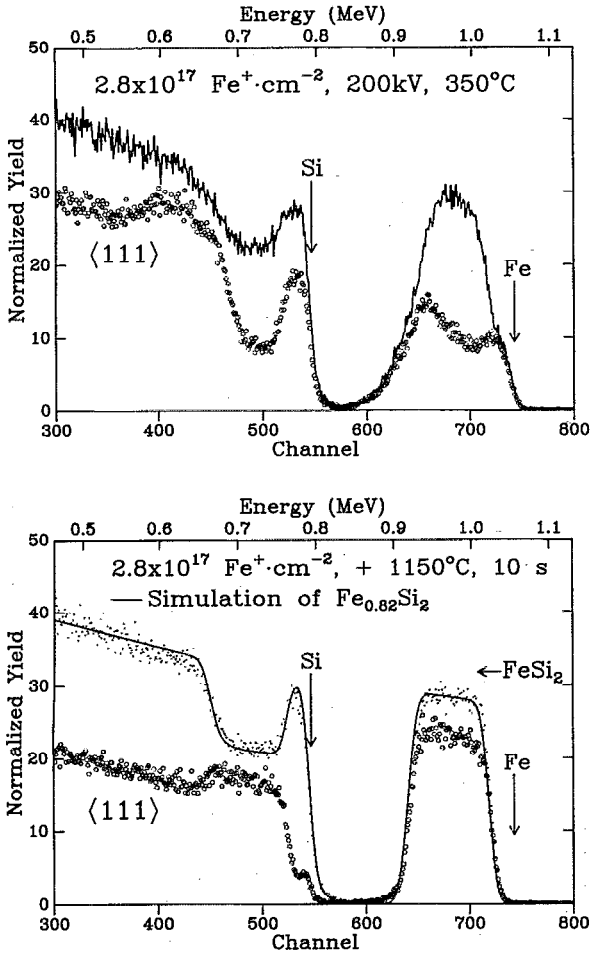


FIG. 1. (a) RBS (solid line) and channeling (circles) spectra of an as-implanted sample in (111)Si. (b) RBS (dots) and channeling (circles) spectra of the sample of (a) after annealing at 1150 °C for 10 s. The simulation of the RBS spectrum (solid line) indicates a Fe vacancy concentration of about 18% for $\alpha$-$FeSi_2$.

1(b) shows the RBS (dots) and channeling spectra (circles) of a sample implanted with $2.8\times10^{17}$ $Fe^+$ $cm^{-2}$ and annealed at 1150 °C for 10 s. These spectra exhibit the presence of a continuous buried layer of $\alpha$-$FeSi_2$ with sharp interfaces but with a relatively poor crystal quality with a minimum yield value of $\chi_{min}\approx75\%$. However, the Si top layer shows a reasonable crystal quality of $\chi_{min}\approx12\%$. Optical microscopy (not shown) showed grains with sizes ranging from 20 to 50 $\mu$m in diameter. The channeling results suggest that these $\alpha$-$FeSi_2$ grains show some degree of alignment. Details of the microstructure of this layer as revealed by TEM are presented in Fig. 2 (implantation dose: $3\times10^{17}$ $Fe^+$ $cm^{-2}$). This image shows a continuous buried layer of about 140 nm thickness with very sharp interfaces below a Si top layer. The very rough surface of this Si layer is from overetching the $SiO_2$ cap, which was evaporated prior to annealing to prevent oxidation. XRD measurements indicate only the presence of the metallic $\alpha$-$FeSi_2$ phase. From the phase diagram of Fe-Si we can deduce that the $\alpha$-$FeSi_2$ layer contains a large number of Fe vacancies (8.5%–20.5%).[1] As indicated by the arrow, marked "$FeSi_2$", in Fig. 1(b) the Fe backscattering yield of

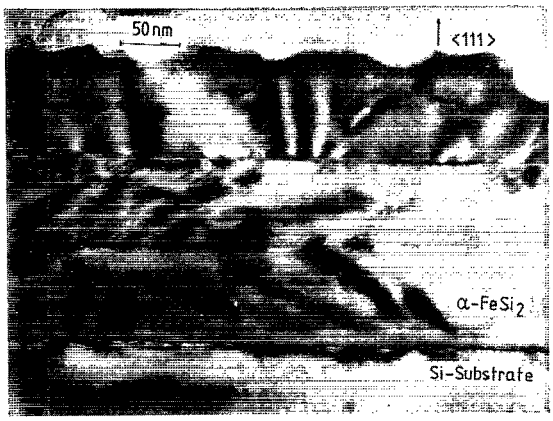


FIG. 2. Cross-sectional micrograph of an $\alpha$-$FeSi_2$ layer after implantation of $3\times10^{17}$ $Fe^+$ $cm^{-2}$ at 200 keV and RTA annealing. Bright-field image with electron beam parallel to [011].

$\alpha$-$FeSi_2$ does not reach the value of stoichiometric $FeSi_2$. A simulation of the RBS spectrum (solid line) is consistent with the experimental data for a 125 nm thick, off-stoichiometric $Fe_{0.82}Si_2$ layer buried by a 60-nm-thick Si top layer. The deviation from the stoichiometric value indicates the presence of 18% structural Fe vacancies in the $\alpha$-$FeSi_2$ phase.

After RTA anneal at 1150 °C, $\alpha$-$FeSi_2$ was transformed by a second anneal in a tube furnace at 750 °C for 20 h into a continuous buried crystalline layer of $\beta$-$FeSi_2$. Figure 3 shows the RBS spectra of the $\alpha$-$FeSi_2$ layer before (solid line) and after the annealing (dotted line). These RBS spectra clearly show a decrease of the thickness of the $\alpha$-$FeSi_2$ layer and an increase of the backscattering yield to a value equal to that for stoichiometric $\beta$-$FeSi_2$. The corresponding channeling spectrum of this layer shows an aligned Si top layer with a minimum yield $\chi_{min}\approx17\%$, but no alignment of the buried $FeSi_2$ layer is found. We believe that the layer consists of grains with various crystal orientations. From solid phase epitaxy it is known that two different crystallographic orientation relationships of

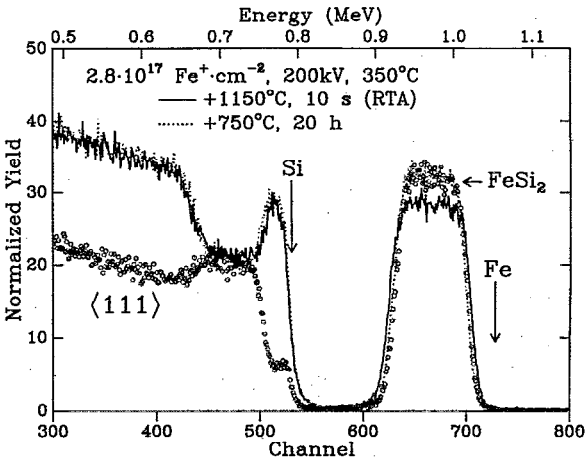


FIG. 3. RBS spectrum of a buried $\alpha$-$FeSi_2$ layer before (solid line) and after (dotted line) annealing at 750 °C for 20 h in a tube furnace. The channeling spectrum (circles) refers to the 750 °C annealed sample.

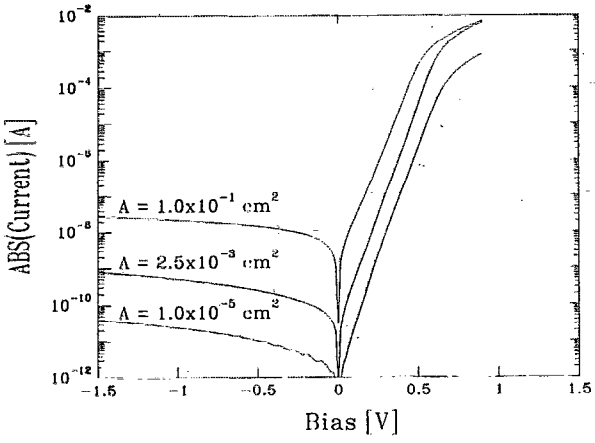


FIG. 4. *I-V* characteristics of $\alpha$-$FeSi_2$ *n*-type silicon Schottky diodes for different diode areas *A*. The analysis of these *I-V* measurements indicate a Schottky barrier height of $\Phi_B = 0.84 \pm 0.03$ eV.

$\beta$-$FeSi_2$ exist on (111)Si: the (101) and (110) planes.[15,16] These twofold-symmetry $\beta$-$FeSi_2$ planes are joined to the threefold (111)Si symmetry plane. This means that epitaxy is composed of three equivalent and equiprobable azimuthal orientations.[15] From the orthorhombic structure of this material we can conclude that the $\beta$-$FeSi_2$ (110) and (101) planes will show no deep channel minima and thus we cannot expect ideal channeling conditions in normal direction. So far the epitaxial relationship of these $\beta$-$FeSi_2$ grains and the (111)Si matrix is unclear, but preliminary electron diffraction investigations (not shown) clearly indicate the presence of the orthorhombic $\beta$-$FeSi_2$ phase.

The electrical resistivity measurements on metallic $FeSi_2$ yielded values of about 250 $\mu\Omega$ cm at room temperature. These are in reasonable agreement with published data of 267 $\mu\Omega$ cm for [001]- and 250 $\mu\Omega$ cm for [100]-oriented single-crystalline samples, fabricated by a floating zone method.[17] By implanting through an $SiO_2$ mask, Schottky diodes with different areas have been fabricated in *n*-type (111)Si, as shown in Fig. 4. The logarithm of the absolute current versus voltage plot for different diode-areas displays diode characteristics. The obtained ideality factors *n* for these *I-V* characteristics depend slightly on the area of the diodes, for small diode-areas ($<3\times10^{-3}$ $cm^2$) $n = 1.3 \pm 0.05$ and for large areas (0.1–0.12 $cm^2$) $n = 1.5 \pm 0.1$. For all diode areas the analysis of these *I-V* measurements using thermionic emission theory indicates a relatively high Schottky barrier height of $\Phi_B = 0.84 \pm 0.03$ eV for the $\alpha$-$FeSi_2$ *n*-type silicon interface. First results of measuring the *I-V* characteristics over a range of temperatures (*I-T* measurements) for diodes with small areas ($<3\times10^{-3}$ $cm^2$) also yield Schottky barrier heights of about 0.83 eV, as obtained from the slope of the Arrhenius plot of $\ln(I/T^2)$ against $T^{-1}$. Capacitance voltage (*C-V*) measurements indicate even higher barrier heights (0.94–1.05 eV); however, a slight curvature of the $1/C^2$ vs *V* plots suggests a redistribution of the donor distribution in the vicinity of the $\alpha$-$FeSi_2$ layer. This curvature made it difficult to extract reliable barrier height values with this technique. A dopant redistribution is not unexpected due to the ion implantation and the annealing at 1150 °C. This redistribution of the dopants will be the topic of further investigations.

In summary we have shown that it is possible to fabricate buried polycrystalline metallic $\alpha$-$FeSi_2$ with very sharp interfaces in (111)Si by high dose implantation and subsequent annealing at 1150 °C for 10 s in an RTA. This metallic layer can then be transformed into the semiconducting $\beta$-$FeSi_2$ layer by an additional prolonged annealing step below the phase transformation temperature. These first results demonstrate the feasibility of ion beam synthesis as a method for fabricating both phases of $FeSi_2$. The buried $\alpha$-$FeSi_2$ layers have specific resistivities of about 250 $\mu\Omega$ cm and show a relatively high Schottky barrier height of $\Phi_B \approx 0.84$ eV to *n*-type (111)Si substrates.

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