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Ion Beam Synthesis of $IrSi_3$ by Implantation of 2 MeV Ir Ions

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ION BEAM SYNTHESIS OF $IrSi_3$ BY IMPLANTATION OF 2 MeV Ir IONS+

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ABSTRACT

The formation of a buried $IrSi_3$ layer in (111) oriented Si by ion implantation and annealing has been studied at an implantation energy of 2 MeV for substrate temperatures of 450–550°C. Rutherford backscattering (RBS), ion channeling and cross-sectional transmission electron microscopy showed that a buried epitaxial $IrSi_3$ layer is produced at 550°C by implanting $\geq 3.4 \times 10^{17}$ Ir/cm^2 and subsequently annealing for 1 h at 1000°C plus 5 h at 1100°C. At a dose of 3.4×10^{17} Ir/cm^2, the thickness of the layer varied between 120 and 190 nm and many large $IrSi_3$ precipitates were present above and below the film. Increasing the dose to 4.4×10^{17} Ir/cm^2 improved the layer uniformity at the expense of increased lattice damage in the overlying Si. RBS analysis of layer formation as a function of substrate temperature revealed the competition between the mechanisms for optimizing surface crystallinity vs. $IrSi_3$ layer formation. Little apparent substrate temperature dependence was evident in the as-implanted state but after annealing the crystallinity of the top Si layer was observed to deteriorate with increasing substrate temperature while the precipitate coarsening and coalescence improved.

INTRODUCTION

The iridium silicides are an interesting system because of their high Schottky barrier heights to n-type Si (e.g., 0.93 eV for Si(100)/IrSi) [1] and their correspondingly low barrier to p-type Si, which make them especially attractive for long wavelength (up to 10 µm) infrared detection [2]. Studies [3] of the iridium silicides using surface reaction techniques have shown that polycrystalline layers of IrSi, $IrSi_{1.7}$ and $IrSi_3$ form at temperatures of 300°, 600° and 960°C, respectively. Of these $IrSi_3$ is particularly interesting for production by mesotaxy [4] because it has the highest Si content of the known silicides (75 at %), high temperature stability, and a hexagonal structure known to epitaxially align with Si(111) [5].

Mesotaxy is the technique by which a buried epitaxial layer is produced by ion implantation followed by annealing. It was first successfully used in 1987 by White et al. [4] to produce $CoSi_2$ and has been recently reviewed by Mantl [6]. The first attempt to produce $IrSi_3$ by mesotaxy was reported by Yu et al. [7] using 130 keV Ir ions, but their room temperature implants, which amorphized the implanted region, resulted in polycrystalline $IrSi_3$ films. More recently Short et al. [8] used 0.5–1.0 MeV Ir ions and a 525°C substrate temperature to produce an epitaxial film. In this paper we report on the formation of epitaxial $IrSi_3$ using 2 MeV Ir ions and its dependence on substrate temperature in the region of 450–550°C.

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EXPERIMENTAL PROCEDURE

Ion implantation was performed by irradiating 2.5 cm square samples of (111) oriented Si with 2 MeV Ir ions. The samples, mounted on a heated nickel holder and heat sunk with a graphite solution, were irradiated with 3.4-4.4 x 10^{17} Ir/cm^2 at substrate temperatures (T_S) of 450°, 500° and 550°C as monitored by a thermocouple located in the holder. Average beam current densities ranged between 0.36 and 0.63 μA/cm^2 over the 1.27 cm^2 implantation area. After irradiation, a 200-nm-thick layer of SiO_2 was deposited to protect the samples from oxidation during annealing, which was carried out in a tube furnace for 1 h at 1000°C plus 5 h at 1100°C using a reducing atmosphere of 96% Ar/4% H_2. Both as-implanted and annealed samples were analyzed by Rutherford backscattering/ion channeling (RBS) along the <111> axis using 2 MeV He ions and a 160° scattering geometry. A sample was selected for analysis by cross-sectional transmission electron microscopy (XTEM).

RESULTS

RBS analysis showed that the best buried $IrSi_3$ layers were produced at T_S = 550°C. Fig. 1 shows the <111> aligned and random spectra obtained from as-implanted and annealed samples irradiated with 3.5 x 10^{17} Ir/cm^2 at 550°C. The Ir portion of the as-implanted spectra is similar to that observed in high-dose Co implantation, being roughly Gaussian in shape with some channeling evident. However, the Si portion of the spectra shows a much greater level of damage in the top Si layer than is normally seen when implanting with lighter mass ions such as Co [4,6]. Indeed there is a region of enhanced damage which extends from the surface to a depth of about 200 nm (channels 525–575). This feature persists at the lower substrate temperatures as well and suggests that a different damage/in-situ annealing mechanism is operative near the surface. The surface damage peak has also been observed in 1.0 MeV irradiatied samples [8,9] and is attributed to stacking faults [8].

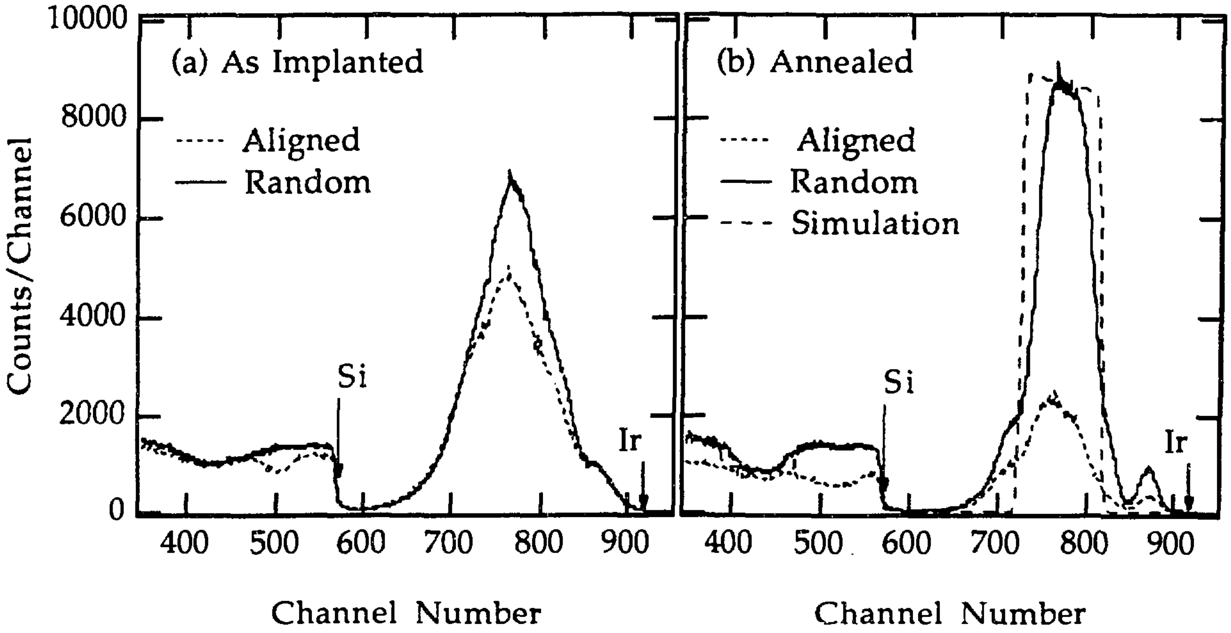

Fig. 1. RBS aligned and random spectra for (a) as-implanted and (b) annealed samples implanted with 3.4 x 10^{17} Ir/cm^2 at 2 MeV and T_S = 550°C.

Upon annealing this sample, a buried layer forms with the stoichiometry of $\mathrm{IrSi_3}$, as indicated in Fig 1b, but it is also evident in the Ir portion of the spectra that not all the Ir has been incorporated into the film. For comparison, the simulated yield for a 190 nm thick $\mathrm{IrSi_3}$ layer below 420 nm of Si is included to show what the ideal spectrum would like if all the implanted Ir had coalesced into the film. XTEM analysis of the sample confirmed the presence of a continuous buried $\mathrm{IrSi_3}$ layer with atomically sharp interfaces. Diffraction analysis indicated that the layer is epitaxial but composed of three domains with orientations to the Si substrate described by Chu et al. [5] as mode A:

$$(2\bar{1}\bar{1}0)\,\mathrm{IrSi_3} \,||\, (111)\,\mathrm{Si} \text{ and } [01\bar{1}0]\,\mathrm{IrSi_3} \,||\, [1\bar{1}0]\mathrm{Si}$$

$$(2\bar{1}\bar{1}0)\,\mathrm{IrSi_3} \,||\, (111)\,\mathrm{Si} \text{ and } [01\bar{1}0]\,\mathrm{IrSi_3} \,||\, [01\bar{1}]\mathrm{Si}$$

$$(2\bar{1}\bar{1}0)\,\mathrm{IrSi_3} \,||\, (111)\,\mathrm{Si} \text{ and } [01\bar{1}0]\,\mathrm{IrSi_3} \,||\, [\bar{1}01]\mathrm{Si}.$$

The other epitaxial modes observed by Chu [5] were not observed but may be present in small quantities. The layer thickness was also observed to vary in thickness between 120 and 190 nm. This variation corresponds with the shoulders seen in the Ir distribution of Fig 1b.

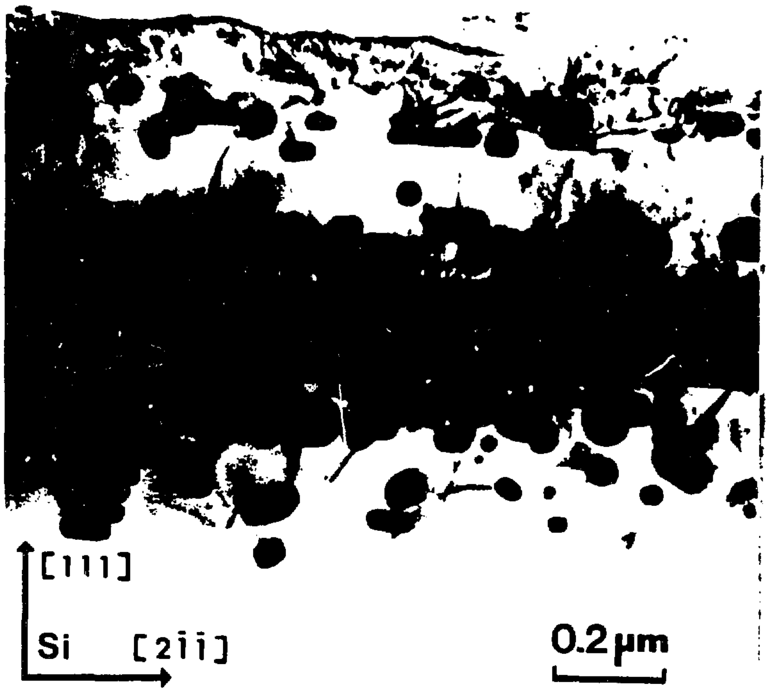

Fig. 2. Cross-sectional electron micrograph of the sample described in Fig. 1.

As shown in Fig. 2, XTEM also revealed the presence of three bands of large precipitates above and below the film. The largest, most dense band is located below the $\mathrm{IrSi_3}$ layer and is about 300 nm in depth. The two bands above the layer are less dense and narrower, about 100 nm deep. One lies just above the film while the other is centered at a depth of about 190 nm. The depth of this band corresponds with the small Ir peak seen just below the surface in Fig 1b and with the edge of the Si surface peak in the aligned spectrum of Fig 1a. The average size of the precipitates in the upper bands is smaller than that of the lower band. A band of precipitates below the layer is also seen at 1 MeV, but the density is higher and the average size smaller [8].

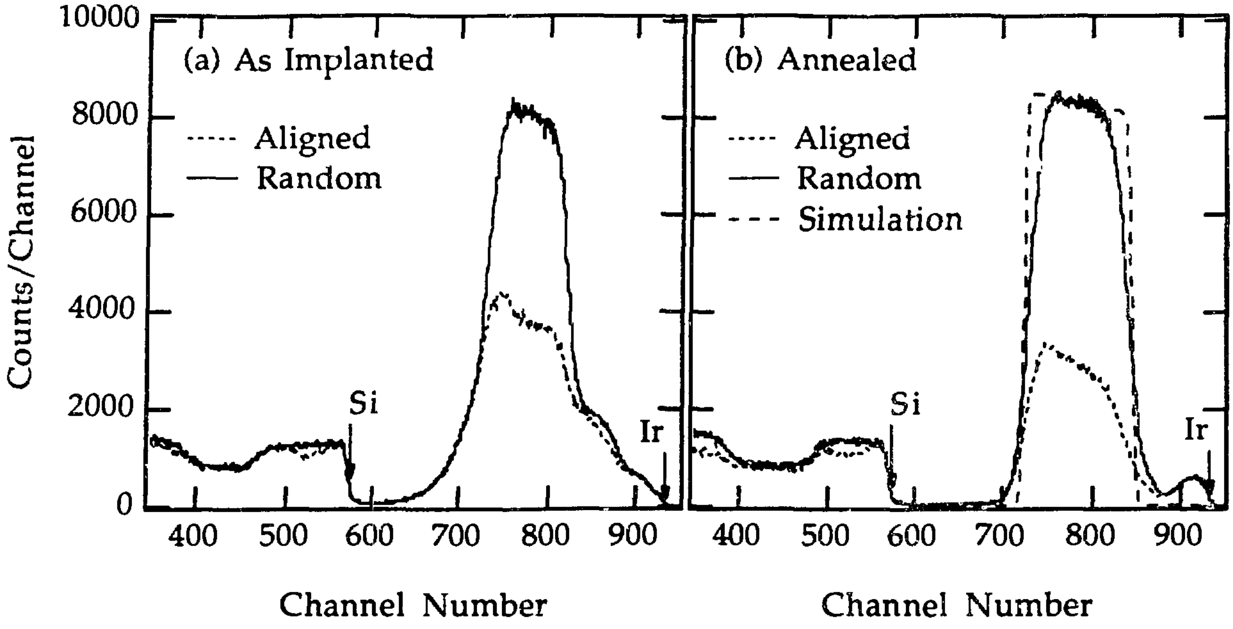

Fig. 3 RBS aligned and random spectra for (a) as-implanted and (b) annealed samples implanted with 4.4×10^{17} Ir/cm^2 at 2 MeV and $T_S = 550°C$.

A more uniform layer is produced at 2 MeV by increasing the dose, but at the expense of surface crystallinity. Fig. 3 shows the RBS results obtained from a sample implanted at $T_S = 550°C$ with 4.4×10^{17} Ir/cm^2. At this dose the $IrSi_3$ stoichiometry is reached in the as-implanted state. Furthermore, the rectangular shape and the significantly improved channeling indicate that an $IrSi_3$ layer has already formed. After annealing further coalescence occurs, but most of the Ir appears to have been incorporated into the buried layer during irradiation. Comparison with the lower dose case (Fig. 1) indicates that the layer has sharper interface and that the coalescence is more complete. However, the damage in the top Si layer is higher; the near-surface region is completely disordered while at the low dose it remains crystalline. On the other hand, the crystallinity of the $IrSi_3$ is probably about the same as that of the lower dose case. Although the X_{min} of the Ir peak is a little larger in the high dose spectrum, some of this increase can be attributed to the increased dechanneling of the He beam in the completely disordered surface region.

Studying layer formation as a function of T_S at a constant dose of 3.4×10^{17} Ir/cm^2 revealed the competition between the mechanisms for optimizing surface crystallinity vs. $IrSi_3$ layer formation. For $T_S \leq 500°C$ a buried layer appears to form but its stoichiometry is $IrSi_x$, $x \approx 4$, which is most likely a dense network of $IrSi_3$ precipitates in a Si matrix. Only at $T_S = 550°C$ does a stoichiometric $IrSi_3$ layer form. Thus, the minimum dose for layer formation decreases as T_S increases because a more favorable precipitate morphology for mesotaxy develops. Interestingly, this occurs in spite of the decrease in Ir concentration after irradiation at $T_S = 550°C$. At $T_S \leq 500°C$, the Ir concentration at the peak of the Ir distribution is 21%, but it decreases to 18% at $T_S = 550°C$. Unfortunately, as layer formation improves damage to the overlying Si increases. This is shown in Fig. 4 in which X_{min} is plotted vs. T_S for selected regions of the RBS spectra. As T_S increases, X_{min} near the Si surface increases by a factor of

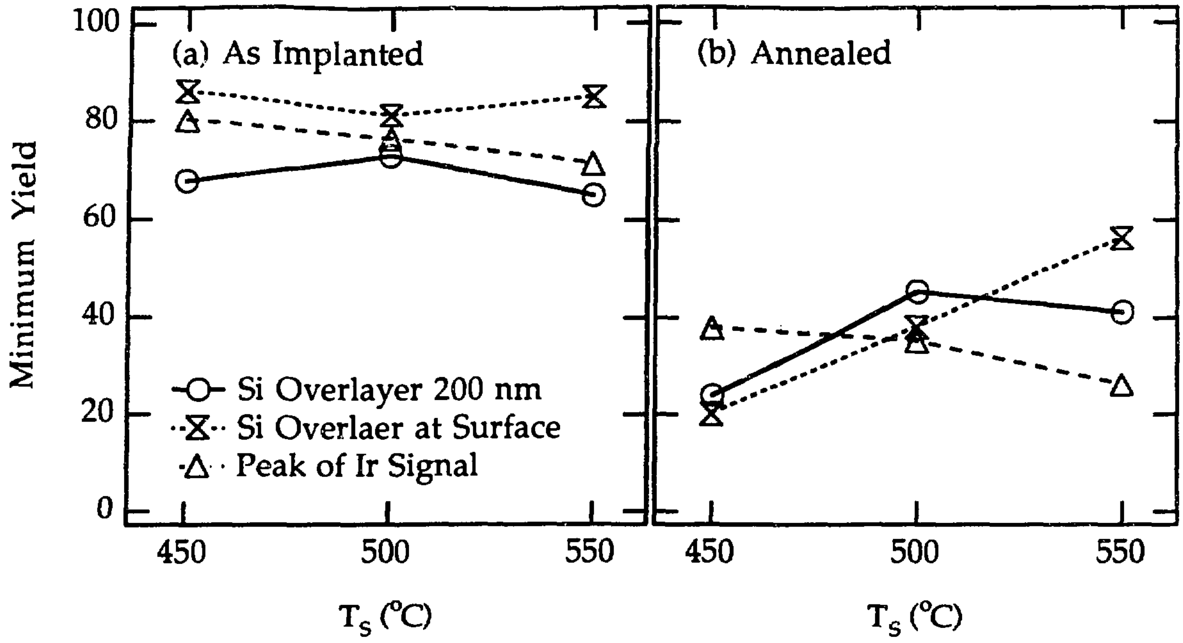

Fig. 4. Ratio of aligned to random yields (X_{min}) for three selected regions of the RBS spectra plotted as a function of T_S.

three, while in the Ir region it is slowly decreasing. The effect is even more pronounced at 1 MeV [9].

DISCUSSION

The results have shown that a buried $IrSi_3$ layer can be produced by mesotaxy with 2 MeV Ir ions at T_S = 550°C. The $IrSi_3$ layer is epitaxial, but made up of the three domains discussed previously. Near the critical dose for layer formation, coalescence is incomplete resulting in a nonuniform film sandwiched between bands of large precipitates. Increasing the dose appears to improve the layer uniformity and possibly eliminate the precipitate bands on either side, but at the expense of the crystallinity of the surface region which becomes completely disordered. Annealing for longer times or higher temperatures may lead to an improved structure, but similar attempts with 1 MeV Ir implanted samples broke up the layer into large precipitates. Implanting at substrate temperatures ≤ 500°C reduces damage accumulation in the Si overlayer but layer coalescence is hindered by what appears to be an unfavorable precipitate morphology in the as implanted state. It appears that better $Si/IrSi_3/Si$ heterostructures can be produced by lowering the implantation energy. At 0.5–1 Me, it is possible to make a buried $IrSi_3$ layer which is free of the precipitate bands seen to sandwich the layer at 2 MeV and, at the same time, maintain crystallinity in the Si overlayer [8,9].

Short [8] has argued that successful buried $IrSi_3$ formation falls only within a narrow window of implantation parameters. The energy must be high enough to make a buried layer, but low enough to minimize the critical dose and implant distribution width. Our results support this hypothesis, but it is not clear whether the ripening mechanism is hindered by the broader distribution of Ir at 2 MeV or simply by the increased damage due to the higher dose needed to make a continuous film.

CONCLUSIONS

The formation of buried $IrSi_3$ films in Si(111) by ion implantation and annealing has been studied at an implantation energy of 2 MeV for substrate temperatures of 450–550°C. The results showed that a buried layer of $IrSi_3$ could be successfully produced by implanting $\geq 3.4 \times 10^{17}$ Ir/cm^2 at 550°C and subsequently annealing for 1 h at 1000°C and 5 h at 1100°C. Although RBS analysis indicated a stoichiometric layer of $IrSi_3$ layer at a dose of 3.4×10^{17} Ir/cm^2, XTEM analysis revealed a nonuniform layer and bands of precipitates above and below the film. RBS analysis of layer formation as a function of substrate temperature revealed the competition between the mechanisms for optimizing surface crystallinity vs. $IrSi_3$ layer formation. Little apparent substrate temperature dependence was evident in the as-implanted state, but after annealing the crystallinity of the top Si layer was observed to deteriorate with increasing substrate temperature while the precipitate coarsening and coalescence improved. It is unlikely that better Si/$IrSi_3$/Si heterostructures can be produced at this energy; lower energies and doses appear to offer a better alternative [8,9].

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