Solid-phase epitaxial regrowth of amorphous layers in Si(100) created by low-energy, high-fluence phosphorus implantation
S. Ruffell, I. V. Mitchell, and P. J. Simpson

Citation: Journal of Applied Physics 98, 083522 (2005); doi: 10.1063/1.2113409
View online: http://dx.doi.org/10.1063/1.2113409
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/98/8?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Defect mitigation by ion induced amorphousization and solid-phase epitaxy
AIP Conf. Proc. 1525, 204 (2013); 10.1063/1.4802320

Solid-phase epitaxy of silicon amorphized by implantation of the alkali elements rubidium and cesium

Solid-phase epitaxial regrowth of amorphous silicon containing helium bubbles

P implantation into preamorphized germanium and subsequent annealing: Solid phase epitaxial regrowth, P diffusion, and activation
J. Vac. Sci. Technol. B 26, 430 (2008); 10.1116/1.2805249

Solid phase epitaxy of amorphous silicon carbide: Ion fluence dependence
J. Appl. Phys. 96, 1451 (2004); 10.1063/1.1766093
Solid-phase epitaxial regrowth of amorphous layers in Si(100) created by low-energy, high-fluence phosphorus implantation

S. Ruffell,a I. V. Mitchell, and P. J. Simpson
Department of Physics and Astronomy, University of Western Ontario, London, Ontario, N6A 3K7, Canada

(Received 22 February 2005; accepted 15 September 2005; published online 27 October 2005)

Medium energy ion scattering has been used to study the kinetics of solid-phase epitaxial growth (SPEG) of ultrathin amorphous layers formed by room-temperature implantation of 5 keV energy phosphorus ions into Si (100). The implants create P distributions with peak concentrations up to \( \sim 7 \times 10^{21} \text{ cm}^{-3} \). SPEG has been driven by rapid thermal annealing, \( 475 \text{ °C} \leq T_a \leq 600 \text{ °C} \), for times up to 2000 s. At each temperature, the regrowth velocity is enhanced in the early stages due to the presence of phosphorus but then slows sharply to a value more than an order of magnitude below the intrinsic rate. The critical phosphorus concentration at the transition point for \( T_a = 475 \text{ °C} \) regrowth is \( \sim 6 \times 10^{20} \text{ cm}^{-3} \) and increases steadily with anneal temperature. Time-of-flight secondary ion mass spectroscopy profiles confirm the onset of phosphorus push out, where the advancing recrystallization front enters the transition region. Supplementary cross-sectional transmission electron microscopy evidence confirms the existence of a local strain field. © 2005 American Institute of Physics. [DOI: 10.1063/1.2113409]

INTRODUCTION

A promising route to the formation of shallow (\( \sim 20 \text{ nm} \)) junctions for ultra-large-scale integration (ULSI) devices is low-energy ion implantation. Both high dopant activation and profile stability are required for implementation. Implantation of dopant atoms into single-crystal silicon results in radiation damage to the lattice and if the density of the damage cascades caused by primary and knock-on collisions with the lattice atoms is high enough, amorphization is achieved. Low-temperature (<600 °C) annealing then results in recrystallization via solid-phase epitaxial growth (SPEG) leaving a single-crystal layer containing a high fraction of activated dopant, often at concentrations well in excess of the solid solubility.1–9 Both acceleration and retardation of \( a\)-Si regrowth due to the presence of impurities have been reported. In contrast to the situation for conventional implant energies, however, little work has been reported on the kinetics of regrowth of very shallow amorphous layers, and on the issue of associated impurity movement during annealing.1–9

Early investigations into SPEG of amorphous silicon (\( a\)-Si) layers (0.1–4 \( \mu \text{m} \)) used Rutherford backscattering spectrometry (RBS) or time-resolved reflectivity (TRR) to monitor the changing thickness of the amorphous layer during annealing.3–9 Neither has the required depth resolution for very shallow layers. In this paper we report a study of the regrowth kinetics of \( a\)-Si surface layers of 20 nm or less, created by implantation of the \( n\)-type dopant P and exploiting the high depth resolution of medium energy ion scattering (MEIS) (<1 nm). We find that regrowth proceeds initially at a faster rate than the impurity-free rate but then crosses over to a value much lower than the intrinsic velocity. We identify P push out in a region that exhibits the presence of a strain field. The study complements a previous report on lower fluence P implantation, where no retardation in regrowth velocity was found.10

EXPERIMENT

\( a\)-Si (100) wafers of 100 mm diameter and \( p\) doped with boron for a resistivity of 4–7 \( \Omega \text{ cm} \) were implanted at room temperature with 5 keV energy \( ^{31}\text{P} \) ions on the University of Surrey’s 200 kV Danfysik high-current implanter. Implant fluences were \( 5 \times 10^{15} \) and \( 1 \times 10^{16} \text{ cm}^{-2} \) (two lower fluences, \( 5 \times 10^{14} \) and \( 1 \times 10^{15} \text{ cm}^{-2} \), were studied in Ref. 10). Wafer normals were tilted 7° off the beam.

12 \( \times \) 12 mm\(^2\) samples were cleaved from the implanted wafers for each annealing temperature/time study. Annealing was performed in an AET thermal RX rapid thermal annealer (RTA) in a flowing nitrogen ambient. Each annealing cycle consisted of a 2 min purge followed by a 20 s ramp up to 400 °C which was then held for 2 min allowing the RTA to stabilize, eliminating overshoot when ramping up to the anneal temperature as well as establishing a sharp amorphous/crystalline (\( a\)/\( c\)) interface. The final temperature was reached with a 5 s ramp up and held for the specified time.

The amorphous layer thickness was measured using the UWO MEIS system with a beam of 100 keV energy protons; a full description of the system can be found elsewhere.11 Samples were oriented such that the beam of 100 keV \( ^{1}\text{H}^+ \) ions was incident in the \( \langle 101\rangle \) direction with the energy spectrum of the scattered protons being collected in \( \langle 101\rangle \) blocking direction (i.e., at 90° to the incident beam). Simulated spectra (using the QUARK-MEIS program12) were compared with the experimental spectra for \( a\)-Si layer thickness extraction. The dominant parameter in determining the thickness of
the $a$-Si from the silicon peak in the MEIS spectra is the stopping power of H in Si at $\sim$100 keV. This is known to an accuracy of $\sim$2\%,$^{13}$ therefore, the uncertainty in the measured thickness is of this order.

The surface oxide thickness was measured before and after annealing by nuclear reaction measurements using the resonance at 850 keV in the $^{16}$O($d,p)^{17}$O reaction. No change in thickness was detected. The result is consistent with the spectral evidence from the MEIS analysis for oxygen.

High-resolution cross-sectional transmission electron microscopy (XTEM) analysis was performed on selected samples at McMaster University using their JEOL 2010F field-emission TEM/STEM microscope to reveal the nature of the residual and regrown layers and thicknesses. TEM images also provided information on end-of-range (EOR) range defect formation, defect density, and type. Phosphorus depth profiles were obtained with high depth resolution using an IONTOF IV time-of-flight secondary ion mass spectroscopy (ToF-SIMS) instrument, which is described elsewhere.$^{14}$

RESULTS

Figure 1 shows the high-energy portion of the MEIS spectra from 5 keV, $5 \times 10^{15}$ cm$^{-2}$ implanted samples annealed for different times at 575 °C. The primary feature is the scattering from the Si atoms in the $a$-Si layer, which is enhanced relative to the scattering from the Si atoms in the underlying crystal by a factor of $\sim$20. The width of the Si peak decreases with annealing time as the $a$-Si layer recrystallizes.

The thickness of the $a$-Si layer in the as-implanted $5 \times 10^{15}$ cm$^{-2}$ sample was measured by MEIS to be 17.5 nm. Figure 2 shows the regrown thickness as a function of annealing time, for six anneal temperatures between 500 and 600 °C. For each anneal temperature, the data may be approximated by two regimes of constant but different velocity.

The initial regrowth velocity is high even at a temperature of 500 °C, where it is at least 0.04 nm s$^{-1}$; the limited detail during early regrowth allows only a lower limit to be set. In the second regime the regrowth velocity has decreased to a new value which is more than an order of magnitude below the intrinsic (impurity-free) rate. The “breakpoint” between the two regimes moves closer to $t=0$ with increasing anneal temperature, and correspondingly the thickness of regrown silicon increases. The behavior is significantly different from that of lower-fluence implants, where the regrowth rate is enhanced over the intrinsic rate and remains constant, within the resolution of the measurements, over the complete regrowth [$5 \times 10^{14}$ and $1 \times 10^{15}$ cm$^{-2}$ (Ref. 10)].

Figure 3 is an Arrhenius plot of regrowth velocity in the retarded regime versus anneal temperature, for the $5 \times 10^{15}$ cm$^{-2}$ fluence sample. We derive an activation energy of $2.11 \pm 0.16$ eV, compared with $2.06 \pm 0.14$ and

FIG. 1. MEIS spectra taken from a 5 keV, $5 \times 10^{15}$ cm$^{-2}$ P implant in Si before and after annealing at 575 °C for times up to 500 s. Also shown is a spectrum from an unimplanted (virgin) Si sample. 100 keV protons are channeled in the (101) direction and spectra are collected in the (101) blocking direction. The Si peak decreases in thickness with annealing.

FIG. 2. Thickness of regrown $a$-Si vs annealing time in the temperature interval of 500 °C $\leqslant T_A \leqslant 600$ °C for a 5 keV, $5 \times 10^{15}$ cm$^{-2}$ P-implanted sample. The breakpoint for retarded regrowth moves monotonically towards $t=0$ with increasing anneal temperature. The lines indicate approximate behavior only.

FIG. 3. Arrhenius plot of regrowth velocity with annealing temperature for the 5 keV, $5 \times 10^{15}$ cm$^{-2}$ P-implanted sample in the retarded regrowth regime. The extracted activation energy is comparable to that found for lower-fluence implants. Regrowth in the retarded regime is over an order of magnitude slower than the intrinsic rate.
2.26±0.11 eV for 5×10^{14} \text{ cm}^{-2} and 1×10^{15} \text{ cm}^{-2} fluence implants, respectively. The mean value for the intrinsic regrowth rate in silicon is in fair agreement with those previously published.\(^1\)\(^-\)\(^4\) The peak of the P profile lies at a depth of \(~6\) nm, i.e., as regrowth proceeds the \(a/c\) interface advances through an increasing P concentration. For 5×10^{14} and 1×10^{15} \text{ cm}^{-2} fluences, regrowth produced no measurable change in the as-implanted P profile.\(^10\) (See Fig. 7, which shows the SIMS profiles for 5×10^{14} \text{ cm}^{-2} recorded under as-implanted and partial regrowth conditions). Under the assumption that there are negligible profile distortion artifacts associated with the SIMS measurement and there is no phosphorus redistribution until retardation sets in, we use the \textit{as-implanted} SIMS profile to find the local P concentration at the depth where retardation first appears. Figure 4 shows the \textit{critical} concentrations extracted in this way for both the 5×10^{15} and 1×10^{16} \text{ cm}^{-2} implant samples as a function of the annealing temperature. The critical concentrations increase monotonically with temperature and the relationship for both implants may be reasonably approximated by a single curve.

Figure 5 shows a XTEM image taken from the 1×10^{16} \text{ cm}^{-2} fluence implant, following a 600 °C, 60 s annealing. Recrystallization is incomplete. The thickness of the remaining \(a\)-Si layer as measured by MEIS is 7.3 nm, in excellent accord with the XTEM value. The dark region just below the \(a/c\) interface indicates the presence of strain in the regrown silicon lattice. (A band of dislocations can also be seen at a depth of \(~25\) nm, to be compared with the MEIS measure of 20 nm for the original \(a\)-Si layer thickness).

Figures 6 and 7 are SIMS profiles taken from partially regrown samples. For the 5×10^{15} \text{ cm}^{-2} implant (Fig. 6), segregation of phosphorus into the \(a\)-Si ahead of the regrowth front is clearly visible. There is no evidence for segregation during regrowth of the 5×10^{14} \text{ cm}^{-2} implant (Fig. 7).

FIG. 4. Critical concentration of P (for which regrowth slows severely) vs annealing temperature. Data are shown for the 5×10^{15} \text{ cm}^{-2} fluence implant; two data points are also shown for the 1×10^{16} \text{ cm}^{-2} fluence implant.

FIG. 5. XTEM image taken from a partially recrystallized \(a\)-Si layer created by the 5 keV, 1×10^{16} \text{ cm}^{-2} phosphorus implant in silicon. The sample has been annealed at 600 °C for 60 s. A 7.3 nm \(a\)-Si layer remains below the native oxide. A band of dislocations is visible at \(~25\) nm depth. The original \(a\)-Si layer thickness was measured by MEIS methods to be 20 nm.
accommodation of the dopant into the silicon lattice. It was
no evidence for phosphorus push out ahead of the
before and after partial regrowth by annealing at 500 °C for 10 s. There is
decrease in regrowth rate was found to occur whenever the
interface approached a critical concentration of the im-
that Pb precipitates provided nucleation sites for polycrystal-
served for Sb nor As and we found no evidence for it here
precipitates of the impurity. Williams and Elliman6,7 found
sates form during annealing of high concentrations of P in
solid solubilities than In, their critical concentrations should be
higher. This was indeed found: the maximum incorporated concentrations measured by Williams and Elliman1 were
565 °C anneal profile back to the interface at 8 nm, and the
maximum activated concentrations of P measured for the an-
5 keV implants, −8 × 10^{20} cm^{-3} (see Ref. 16).
In the very high-impurity-concentration regimes, crystal-
lization can proceed via polycrystalline growth, rather than
SPEG, provided that there are available nucleation sites, e.g.,
precipitates of the impurity. Williams and Elliman5,7 found that Pb precipitates provided nucleation sites for polycrystal-
line growth of silicon in the high-concentration (implanted)
Pb regime. In the case of Ar implants in silicon, it was sug-
gested that Ar bubbles provided nucleation sites for poly-
crystalline formation. Such regrowth behavior was not ob-
served for Sb nor As and we found no evidence for it here
(see Fig. 5). Since there is some evidence that SiP precipi-
tates form during annealing of high concentrations of P in
polycrystalline regrowth behavior may be anticipated at
higher annealing temperatures, an issue that warrants further
investigation.

The activation energy we have measured for regrowth in
the retarded regime is lower than that for intrinsic silicon by
0.53 eV (Ref. 10) but is similar to the values extracted for the
5 keV, 5 × 10^{14} and 1 × 10^{15} cm^{-2} implanted samples,
where regrowth was accelerated, suggesting that the recrystal-
tallization dynamics are similar in both growth regimes.

FIG. 7. SIMS profiles extracted from the 5 keV, 5 × 10^{15} cm^{-2} P implant
before and after partial regrowth by annealing at 500 °C for 10 s. There is
no evidence for phosphorus push out ahead of the a/c interface.

FIG. 6. SIMS profiles extracted from the 5 keV, 5 × 10^{15} cm^{-2} P implant
before and after partial regrowth by annealing at 565 °C for 200 s. Push out
of phosphorus in front of the a/c interface is observed.

DISCUSSION

Williams and Elliman6-8 investigated SPEG kinetics for
high-fluence, 50–80 keV energy implants and observed retard-
tation in regrowth velocity at high concentrations for Sb,
In, Pb, and As implants. As for the case of P reported here, a
decrease in regrowth rate was found to occur whenever the
a/c interface approached a critical concentration of the im-
planted impurity (>1 at. %), the critical value depending on
the impurity species. Growth retardation was attributed to
local strain developing at the a/c interface associated with
accommodation of the dopant into the silicon lattice. It was
suggested that strain slows the regrowth process and pro-
motes push out of the impurity into the amorphous phase
ahead of the recrystallization front.

For In implants of 80 keV,7,8 SPEG at 555 °C was se-
verely retarded when the local In concentration exceeded 5
× 10^{19} cm^{-3} [equilibrium solubility is 5 × 10^{17} cm^{-3} (Ref.
15)]. There was little incorporation of In into the lattice in
the regrown region. Segregation of In into the amorphous
silicon resulted in push out towards the surface. Below these
concentrations (typified by an In implant fluence of 5
× 10^{14} cm^{-2}) no push out was observed and the a-Si recryst-
tallized completely to the surface, accompanied by a high
percentage incorporation of In in the regrown layer. Similar
trends were observed for As and Sb.7,8 It is expected that the
impurity concentration at the a/c interface at the onset of
retarded regrowth will increase with equilibrium solid solu-
ability of the impurity. Since As and Sb have higher solid
solubilities than In, their critical concentrations should be
higher. This was indeed found: the maximum incorporated concentrations measured by Williams and Elliman1 were
~9 × 10^{21} and ~5 × 10^{19} cm^{-3} for As and In, respectively,
for annealing at temperatures below 650 °C. The solid solu-
bility of P in Si is slightly lower than that of As but higher
than that of In,15 hence a value intermediate between As and
In might be expected. The critical P concentration we find for
onset of retarded regrowth and P push out for annealing at
600 °C is ~3.2 × 10^{21} cm^{-3} (see Fig. 4). This is to be com-
pared with a value ~1 × 10^{21} cm^{-3} projected from the
565 °C anneal profile back to the interface at 8 nm, and the
maximum activated concentrations of P measured for the an-
nealed 5 keV implants, −8 × 10^{20} cm^{-3} (see Ref. 16).

The kinetics of SPEG of thin amorphous layers created
in silicon by high-fluence (Φ > 1 × 10^{15} cm^{-2}) 5 keV P im-
plants have been studied via MEIS. The work complements
the previously reported study on lower-fluence implants.10 Upon annealing at low temperatures (T_{a}
=600 °C) regrowth is initially enhanced relative to that of
intrinsic a-Si, as observed previously in lower-fluence
implants. However, as the regrowth front intercepts critical
concentrations of P (>6 × 10^{20} cm^{-3}), regrowth is severely re-
tarded and proceeds at a rate that is more than an order of
magnitude slower than in impurity-free silicon. Lattice strain
is observed in XTEM images taken from partially regrown
samples. It is suggested that the reduced regrowth rate is due

CONCLUSIONS

The kinetics of SPEG of thin amorphous layers created
in silicon by high-fluence (Φ > 1 × 10^{15} cm^{-2}) 5 keV P im-
plants have been studied via MEIS. The work complements
the previously reported study on lower-fluence implants.10 Upon annealing at low temperatures (T_{a}
=600 °C) regrowth is initially enhanced relative to that of
intrinsic a-Si, as observed previously in lower-fluence
implants. However, as the regrowth front intercepts critical
concentrations of P (>6 × 10^{20} cm^{-3}), regrowth is severely re-
tarded and proceeds at a rate that is more than an order of
magnitude slower than in impurity-free silicon. Lattice strain
is observed in XTEM images taken from partially regrown
samples. It is suggested that the reduced regrowth rate is due
to strain buildup at the *a/c* interface as large concentrations of P are incorporated into the silicon lattice. In this regrowth regime, segregation of phosphorus from the *c*-Si layer into the *a*-Si ahead of the regrowth front is also observed. These characteristics have been found by Williams and Elliman\(^6\)–\(^8\) for a variety of common dopants, and we believe share common origin. We conclude that an improved understanding of the kinetics in the high-concentration regime will be needed for process engineering of ultrashallow junctions via implantation and low-temperature annealing.

**ACKNOWLEDGMENTS**

The authors would like to thank R. Gwilliam (University of Surrey) for providing the implants and G. Botton and F. Pearson (McMaster University) for the XTEM work. This work has been supported by the Natural Sciences and Engineering Research Council of Canada.

\(^12\)F. A. Trumbore, Bell Syst. Tech. J. 39, 205 (1960).