Solid-phase epitaxial regrowth of amorphous layers in Si(100) created by low-energy, high-fluence phosphorus implantation

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Medium energy ion scattering has been used to study the kinetics of solid-phase epitaxial regrowth (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, \( 475 \degree C \leq T_A \leq 600 \degree C \), 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 \( T_A = 475 \degree C \) 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. The study complements a previous report on lower fluence P implantation, where no retardation in regrowth velocity was found.

EXPERIMENT

Si (100) wafers of 100 mm diameter and \( p \) doped with boron for a resistivity of \( 4 \sim 7 \Omega \text{ cm} \) 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 \( 5 \times 10^{15} \text{ and } 1 \times 10^{16} \text{ cm}^{-2} \) (two lower fluences, \( 5 \times 10^{14} \text{ and } 1 \times 10^{15} \text{ cm}^{-2} \), were studied in Ref. 10). Wafer normals were tilted 7° off the beam.

12 \times 12 \text{ 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. Samples were oriented such that the beam of 100 keV \( ^{1}\text{H} \) ions was incident in the (010) direction with the energy spectrum of the scattered protons being collected in (010) blocking direction (i.e., at 90° to the incident beam). Simulated spectra (using the QUARK-MEIS program\textsuperscript{12}) 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 100 keV. This is known to an accuracy of 2%,\textsuperscript{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 spectrometry (ToF-SIMS) instrument, which is described elsewhere.\textsuperscript{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 ~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±0.16 eV, compared with 2.06±0.14 and
2.26±0.11 eV for 5×10^{14} and 1×10^{15} cm^{-2} fluence implants, respectively. The mean value for the intrinsic regrowth rate in silicon is in fair agreement with those previously published.\(^1\) The peak of the P profile lies at a depth of \(\sim 6\) nm, i.e., as regrowth proceeds the \(a/c\) interface advances through an increasing P concentration. For 5×10^{14} and 1×10^{15} 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} 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 as-implanted SIMS profile to find the local P concentration at the depth where retardation first appears. Figure 4 shows the critical concentrations extracted in this way for both the 5×10^{15} and 1×10^{16} 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} 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 \(\sim 25\) 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} 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} cm^{-2} implant (Fig. 7).
DISCUSSION

Williams and Elliman\textsuperscript{6–8} investigated SPEG kinetics for high-fluence, 50–80 keV energy implants and observed retardation 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 implanted 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 promotes push out of the impurity into the amorphous phase ahead of the recrystallization front.

For In implants of 80 keV,\textsuperscript{7,8} SPEG at 555 °C was severely retarded when the local In concentration exceeded 5 \times 10^{19} \text{ cm}^{-3} [equilibrium solubility is 5 \times 10^{17} \text{ 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 \times 10^{14} \text{ cm}^{-2}) no push out was observed and the a-Si recrystallized completely to the surface, accompanied by a high percentage incorporation of In in the regrown layer. Similar trends were observed for As and Sb.\textsuperscript{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 solubility 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 Elliman\textsuperscript{7} were \sim 9 \times 10^{21} and \sim 5 \times 10^{20} \text{ cm}^{-3} for As and In, respectively, for annealing at temperatures below 650 °C. The solid solubility of P in Si is slightly lower than that of As but higher than that of In,\textsuperscript{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 \sim 3.2 \times 10^{21} \text{ cm}^{-3} (see Fig. 4). This is to be compared with a value \sim 1 \times 10^{21} \text{ 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 annealed 5 keV implants, \sim 8 \times 10^{20} \text{ cm}^{-3} (see Ref. 16).

In the very high-impurity-concentration regimes, crystallization can proceed via polycrystalline growth, rather than SPEG, provided that there are available nucleation sites, e.g., precipitates of the impurity. Williams and Elliman\textsuperscript{6,7} found that Pb precipitates provided nucleation sites for polycrystalline growth of silicon in the high-concentration (implanted) Pb regime. In the case of Ar implants in silicon, it was suggested that Ar bubbles provided nucleation sites for polycrystalline formation. Such regrowth behavior was not observed for Sb nor As and we found no evidence for it here (see Fig. 5). Since there is some evidence that SiP precipitates form during annealing of high concentrations of P in Si,\textsuperscript{17} 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 \times 10^{14} and 1 \times 10^{15} \text{ cm}^{-2} implanted samples, where regrowth was accelerated, suggesting that the recrystallization dynamics are similar in both growth regimes.

CONCLUSIONS

The kinetics of SPEG of thin amorphous layers created in silicon by high-fluence (\Phi > 1 \times 10^{15} \text{ cm}^{-2}) 5 keV P implants have been studied via MEIS. The work complements with the previously reported study on lower-fluence implants.\textsuperscript{10} Upon annealing at low temperatures (\TA \approx 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 \times 10^{20} \text{ cm}^{-2}), regrowth is severely retarded 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 $\alpha/c$ 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 $\alpha$-Si ahead of the regrowth front is also observed. These characteristics have been found by Williams and Elliman\textsuperscript{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.

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