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AND LASER PROCESSING

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NEW MATERIALS PROPERTIES ACHIEVABLE BY ION IMPLANTATION DOPING AND LASER PROCESSING*

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ABSTRACT

It is well established that ion implantation techniques can be used to introduce selected impurities into solids in a controlled, accurate and often unique manner. Recent experiments have shown that pulsed laser processing of materials can lead to surface melting, dopant redistribution and crystal regrowth, all on extremely short time scales ($\sim 1 \mu$ sec.). These two processes can be combined to achieve properties not possible with normal materials preparation techniques, or to alter materials properties in a more efficient manner. Investigations will be presented utilizing the combined techniques of positive ion scattering-channeling, x-ray scattering and transmission electron microscopy which show that supersaturated alloys can be formed in the surface regions ($\sim 1 \mu$ m) of ion implanted, laser annealed silicon single crystals, and that these surfaces undergo a unique one dimensional lattice contraction or expansion depending on the dopant species. The resultant surface has a lattice parameter significantly different from the bulk, is free from any damage defects, has essentially all the dopant atoms in substitutional sites and the impurity concentrations can exceed solid solubility limits by more than an order of magnitude.

INTRODUCTION

Ion implantation is gaining acceptance in numerous materials areas as a precise, controllable and often unique method for introducing impurities into the near-surface regions of solids.¹⁻⁴ One of the most attractive features of ion implantation doping is its ability to circumvent many of the constraints associated with normal materials preparation techniques (such as solubility, high temperature diffusion, etc.). However, in many applications such as semiconductor device fabrication where it is necessary to anneal the device in order to remove radiation damage to the single crystal host and incorporate the implanted impurities into electrically active lattice sites, thermal processing can negate many of these advantages. Recent experiments indicate that pulsed laser annealing⁵⁻⁶

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and pulsed electron beam annealing⁷ offer attractive alternatives to thermal annealing for processing ion implanted materials. These techniques result in extremely rapid ($\leq 1 \mu$ sec.) heating (melting) and cooling (crystal regrowth) of only the near-surface ($\sim 1 \mu$ m) regions of the solid. In this paper we show that ion implantation doping and rapid surface melting followed by self-quenching can be combined to achieve new alterations in materials.

NEW MATERIALS PROPERTIES

1. Supersaturated Alloys

The mechanisms associated with surface melting, crystal regrowth, dopant redistribution, and lattice site occupation have been deduced from a series of recent experiments for Si single crystals implanted with B, P, As, Sb, Cu and Fe and annealed with a pulsed ruby laser^{6,3} or electron beam.⁷ One aspect of this work is illustrated by the results of Fig. 1 which show an ion scattering-channeling analysis of (100) orientation Si single crystals. These crystals were implanted in a random direction with 100 keV ^{121}Sb ions to a dose of $1.6 \times 10^{16} \text{ cm}^{-2}$ and annealed with a single laser pulse ($\sim 60 \times 10^{-9}$ sec pulse width, 1.6 J/cm^2 energy density). The as-implanted spectrum analysis indicates that the Sb implantation has rendered the Si single crystal amorphous to a depth $\sim 0.15 \mu\text{m}$. Analysis after laser annealing

Fig. 1. Ion scattering-channeling analysis of ^{121}Sb -implanted, laser-annealed Si.

(triangles) with the 2.5 MeV He beam incident parallel to the [110] axial direction shows a channeling spectrum nearly identical to the virgin Si crystal spectrum (squares) indicating that a high degree of lattice order has been restored. Transmission electron microscope investigations, confirmed that no resolvable damage remained in the regrown surface for implanted Sb doses $\leq 1.4 \times 10^{16} \text{ cm}^{-2}$. For some very high Sb doses, like those to be discussed shortly, stereomicroscopy showed some retained defects in the first 300-400 Å of the surface but none were observed at greater depths. It has been deduced that this nearly perfect recrystallization occurs because the crystal surface melts to a depth $\sim 1 \mu\text{m}$ and regrows onto the single crystal bulk by liquid phase epitaxial regrowth at a rate ~ 2.7 meters/sec, where the total regrowth process occurs in $\sim 1 \mu\text{sec}$. During the time the implanted surface region ($\sim 0.5 \mu\text{m}$) is molten (~ 200 nanoseconds), the Sb is distributed by diffusion in the molten silicon. The mechanism which incorporates such large dopant concentrations into substitutional lattice sites during recrystallization is not known, however.

The consequences of this dopant redistribution and crystal regrowth can be seen from the Sb concentration profiles in Fig. 2 which were extracted from ion scattering measurements on randomly oriented samples. The shape of the as-implanted profile in Fig. 2 for a dose of $2.74 \times 10^{16} \text{ Sb atoms/cm}^2$ is typical of that for all doses. After laser annealing this as-implanted Sb profile was transformed into that shown by the circles with a retained dose of $1.78 \times 10^{16} \text{ Sb atoms/cm}^2$. The other two profiles show retained Sb concentrations following pulsed laser annealing of lower dose Sb implants. The varying shape of the profiles with increasing dose is also associated with a loss of Sb from the surface. This effect is discussed in a separate paper.⁹ Detailed ion channeling analyses of the scattered ion yields from Si and Sb in the near-surface regions as a function of the angle of incidence to major axial directions of these same samples were also performed. The results of these detailed angular scans showed that the Sb was almost totally substitutional (99%) for the two lower dose implants, as well as for the high dose case (90%). Furthermore, all the substitutional Sb was found to be in electrically active sites.

Fig. 2. Comparison of measured ^{121}Sb profiles for several implant doses following laser annealing.

The significance of these results is highlighted by the dashed line in Fig. 2 which shows the equilibrium solid solubility limit for Sb in Si near the melting point. All the samples represented in Fig. 2 are supersaturated Si (Sb) alloys in which Sb has been incorporated into substitutional lattice sites at concentrations well in excess of the limits possible with normal diffusion or melt-grown doping. Similar supersaturated surface alloy systems have been fabricated by implanting B, P and As into Si and laser annealing. These new materials are possible because of the combined manipulations of ion implantation doping and rapid surface processing. Even though the resultant alloys are supersaturated they are stable up to temperatures $\sim 600^\circ\text{C}$; above these temperatures the dopants begin to precipitate.¹⁰

2. One Dimensional Lattice Alterations

Creation of these supersaturated surface alloys has been shown to result in large deviations from cubic symmetry of the near-surface lattice.¹¹ This effect was studied using silicon crystals with [100] surface normals which were ion implanted with 35 KeV ^{11}B ions to doses of $1.0 \times 10^{16} \text{ cm}^{-2}$ and $2.5 \times 10^{16} \text{ cm}^{-2}$ and annealed with a pulsed ruby laser (50 x 10^{-9} sec. pulse, 1.7 J/cm^2 energy density). Measurements of the laser annealed profiles showed relatively flat boron concentrations from the surface to $\sim 0.2 \mu\text{m}$ where the concentration decreased sharply. The measured boron concentrations in the plateau region were $\sim 5 \times 10^{20}$ and $1.25 \times 10^{21} \text{ cm}^{-3}$, and transmission electron microscope investigations showed no resolvable defects. X-ray Bragg reflection profile measurements made¹¹ on these samples to study the magnitude and direction of the lattice alterations in the boron doped layers showed large one-dimensional contractions along the surface normal. Profile measurements for the 400 and the asymmetric 440 and $\bar{4}\bar{4}0$ reflections on the $1 \times 10^{16} \text{ B/cm}^2$ implanted sample are shown in Fig. 3a. Using the large peak from the bulk silicon substrate as a reference ($\Delta\theta = 0$) the Bragg reflections from the boron doped, laser annealed layers were found at angular deviations $\Delta\theta_1$, $\Delta\theta_2$, and $\Delta\theta_3$ for the 400, 440 and $\bar{4}\bar{4}0$ reflections, respectively. From these measurements and from similar measurements on the higher doped sample as tabulated in Table I, it was possible to determine the angle β of the lattice contraction relative to the [440] lattice direction as well as the magnitude of the contraction. The results of this analysis are tabulated in Table I in which the angle β was found to be 45° from the [440] direction for both the low and high dose cases (i.e. only along the [100] surface normal). The contractions were found to be as large as -0.55% and -1.32%, respectively. Results of similar measurements on an antimony implanted sample are also shown in Table I where the lattice expansion was found to be one dimensional along the surface normal for this case as well. For the antimony case, the x-ray diffraction patterns from the doped layer did not have such well defined peaks as those shown in Fig. 3a. This can be traced to the lack of a well defined plateau region in the dopant depth distribution as

indicated in Fig. 2 for antimony doses above $7 \times 10^{15} \text{ cm}^{-2}$. The analysis for antimony is therefore somewhat less accurate as indicated by the greater uncertainty in Table I.

Table I. X-ray Parameters Measured on the Ion Implanted Layers.

Dose	$1.0 \times 10^{16} \text{ B/cm}^2$	$2.5 \times 10^{16} \text{ B/cm}^2$	$1.6 \times 10^{16*} \text{ Sb/cm}^2$
$\Delta\theta_1$ (sec)	780	1944	-510
$\Delta\theta_2$ (sec)	180	504	-120
$\Delta\theta_3$ (sec)	1260	3312	-900
$\beta(^{\circ})$	45.7 ± 1.5	45.2 ± 1.5	45.8 ± 3
$\frac{\Delta d}{d}(400)$	-0.55×10^{-2}	-1.32×10^{-2}	$+ 0.36 \times 10^{-2}$

*($1.32 \times 10^{16} \text{ Sb/cm}^2$ retained after laser annealing)

Ion channeling measurements were also made on the high dose Boron implanted ($2.5 \times 10^{16} \text{ cm}^{-2}$) Si sample and the results are depicted in Fig. 3b. These measurements utilized the channeling effect of 1.25 MeV He ions to accurately measure the angles of the [110] and [111] axes of the implanted-annealed surface layer relative to the [100] surface normal. Monitoring the yield of ions scattered from $< 2000 \text{ \AA}$ of the surface (as represented schematically by the dashed lines on the spectra in Fig. 3b), detailed angular scans such as those in the upper right hand corner of Fig. 3b were measured for each axis. This procedure located the angular differences of the major axes from the [100] with an accuracy $\sim 0.02^{\circ}$. The results of these measured angular differences are recorded in the first row of the table in Fig. 3b, along with the angles expected for normal cubic symmetry (second row). Assuming a one-dimensional contraction such as that deduced from the x-ray measurements, and utilizing the measured x-ray diffraction lattice parameter change for this sample, one obtains the calculated angles shown in the last row of the table. The angles calculated from the x-ray measurements are in excellent agreement with those from the channeling measurements, and the two results are consistent with a one-dimensional contraction of the lattice along the surface normal such as the schematic model at the bottom of Fig. 3b. This unidirectional lattice change for such large strains is unique to the implantation, laser annealing process in semiconductors. The contraction or expansion occurs, of course, because the volumes occupied by the dopant atoms in substitutional sites are smaller or larger than that occupied by silicon atoms in the lattice. The x-ray measurements showed that boron and phosphorous contracted the lattice and that antimony expanded the lattice while arsenic, which is nearly the same size as silicon, caused essentially no change. The magnitude of the lattice changes varies in proportion to the doping concentration, and the one dimensionality is a result of the inability of the strain to induce dislocations at the surface under the laser annealing conditions. The

thin, doped layers are therefore constrained to the surface of the underlying substrate and are allowed to contract (or expand) only in the direction normal to the substrate surface. Misfit dislocations at the interface, generated during high temperature annealing in thermal diffusion doped samples with high dopant concentrations, tend to destroy the one dimensionality for diffused silicon. Consequently, the formation of highly doped layers without interfacial dislocations is a direct result of the laser processing.

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ONE DIMENSIONAL LATTICE CONTRACTION

RESULTS

	[110], [110]	[111], [111]
MEASURED	90.76°	110.17°
CUBIC	90.00°	109.47°
CALCULATED		
WITH $\frac{\Delta d}{d} = 1.32\%$	90.75°	110.17°
ALONG [100]

Fig. 3a. X-Ray Bragg Reflection Profiles.
Fig. 3b. Schematic representation of ion channeling measurements.

CONCLUSIONS

Pulsed laser and electron-beam annealing are important new techniques in materials science. They are particularly complementary to ion implantation doping because the surface heating (melting) occurs over about the same depth as the implantation range and with such

rapidity that many of the unconventional advantages of ion implantation doping are retained. The most immediate impact of these combined techniques will obviously be in the semiconductor industry where ion implantation is already used extensively. Compared to thermal annealing, laser processing achieves better crystal regrowth, results in more complete electrical activation, and processes just the surface layer and thus does not degrade the minority carrier lifetime of the base regions of devices.⁵ As a process step it is more rapid than thermal annealing, can be accomplished in air or vacuum, can be focused to selectively anneal integrated circuit components, and could even be used to post-anneal highly doped diffused components as a means of achieving higher electrical activation and dissolution of precipitates.¹²

The new materials alterations possible with these combined techniques will be of use for both practical and fundamental reasons. There seems little doubt that the large deviation from cubic symmetry resulting from the one-dimensional contraction or expansion of the Si lattice will alter the bulk properties as well as the surface properties of the solid. Similarly, the excessive concentration of substitutional dopants will have an effect. These combined effects should provide new experimental tests of band structure calculations, surface reordering and relaxation models, the time dependence of defect annealing, crystal regrowth mechanisms, and impurity segregation effects¹³ just to mention a few. Preliminary estimates¹⁴ have shown that band structure changes in 1% expanded or contracted pure Si can cause energy shifts $\sim \pm .10$ eV. The combined effects of this and the supersaturated dopant concentrations present are not known. Anomalous electrical activity of solar cells fabricated from boron-implanted laser-annealed silicon¹⁵ may be related to these materials alterations.

Although the one-dimensional lattice contraction (expansion) is likely to be confined to materials with properties similar to Si and Ge, ion implantation doping and the rapid surface melting followed by self-quenching should be applicable to a wide range of materials. Areas where successful application are likely include surface metal alloys, metastable superconducting compounds, amorphous metals, quenched phase systems, metal-insulator bonding, and regrowth and alloying of thin film composites.

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