78-230

CONF-781167--5

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To be presented at the Laser-Solid Interactions and Laser Processing Symposium, Boston, Massachusetts, November 28-December 1, 1978

EFFECT OF THERMAL ANNEALING IN BORON IMPLANTED, LASER ANNEALED SILICON

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Operated by
UNION CARBIDE CORPORATION
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U. S. Department of Energy
Oak Ridge, Tennessee

December 1978

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ABSTRACT

Electron microscopy and x-ray techniques have been used to investigate dislocation generation, precipitation of dopants and intrinsic defects, and the relaxation of unidirectional strains after thermal annealing of boron implanted, laser annealed silicon. It is shown that the number density of dislocations created near the interface after thermal annealing is small and therefore the unidirectional nature of the contraction in the doped layer is essentially retained. A small number density of defect clusters (mostly vacancy dislocation loops, average size 20Å) was also observed after thermal annealing at 1000°C. Boron depth profile changes, as determined by secondary ion mass spectroscopy, indicated an increase in boron concentration near the surface in addition to the expected broadening of profiles after thermal annealing.

INTRODUCTION

Electron microscope studies have shown that a complete annealing of displacement damage (i.e., no residual damage in the form of dislocations, stacking faults, loops or precipitates down to microscope resolution of 10Å) in ion implanted silicon can be achieved by pulse laser annealing.[1] The dopant concentration profiles in the near surface region have been shown to be substantially redistributed in that the nearly Gaussian, as-implanted profiles become uniform in the near surface region and then decrease exponentially.[2] X-ray studies have shown that this laser treatment produces a unidirectional contraction in the boron doped layers.[3] With implanted boron doses ranging from 0.3×10^{16} to 2.5×10^{16} cm^{-2} in these studies, doped layers with concentrations extending from below to well above the solubility limit in silicon were produced with large contractions along the surface normals. Whereas these nonequilibrium conditions were observed to be stable at room temperature, the question of the stability of the supersaturated boron concentration and the unrelaxed interfacial strains at elevated temperature is of particular interest and has been studied as reported here.

*Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

EXPERIMENTAL

In this investigation (001) Czochralski- grown (2-6 Ω-cm, phosphorus doped) silicon crystals ~0.5mm in thickness obtained from Monsanto Corporation were implanted with 0.3, 1.0 and 2.5 x 10^{16} cm^{-2}, $^{11}B^+$ ions in a vacuum of 10^{-8} torr. The implanted specimens were subsequently irradiated with single pulses from a Q-switched ruby laser (Energy density, E = 1.5 J cm^{-2}, λ = 0.694μm, pulse duration 50 x 10^{-9} seconds). Following the laser irradiation, the specimens were annealed at selected temperatures in the range of 600 - 1100°C under a flowing argon atmosphere. Electron microscope specimens were prepared by thinning chemically from the back side while masking the front surface.

The lattice strains in the doped layers were measured using x-ray Bragg reflection profiles for the 400 reflection and the asymmetric $\bar{4}40$ and 440 reflections. The measurements were carried out on a two axis spectrometer using nondispersive (1,-1) geometry and CuKα radiation. In addition, transmission x-ray topography (MoKα radiation) was used to investigate dislocation structures at the interface.

The effects of the laser annealing and subsequent thermal annealing on the dopant distribution were studied by secondary ion mass spectroscopy (SIMS). The primary beam from an ion microprobe (O_2^+, 16.0 keV, 15 x 10^{-9} amp, 5μm dia) was raster scanned over an area (50 x 40μm) while sputtered $^{11}B^+$ ions were detected from ~15% of the rastered area.

RESULTS

Following thermal annealing up to 1000°C of the 0.3 x 10^{16}B/cm^2 implanted, laser annealed specimen, no dislocations were observed by x-ray topography or transmission electron microscopy. In addition, the carrier concentration as determined by Hall measurements was found to be unchanged. The x-ray Bragg profile measurements for this sample following thermal annealing showed that the strain in the doped layer decreased about 30% in magnitude but the direction remained along the surface normal. For specimens implanted with 2.5 x 10^{16}B/cm^2, the boron concentration exceeded the solubility limit and precipitation of boron was observed at 600°C; the precipitation increased substantially upon heating to 900°C. Hall measurements indicated a concomitant decrease in the carrier concentration which was approximately equal to the number density of boron atoms contained in the precipitates.[1] Electron microscope observations made after thermal annealing of these high dose specimens revealed the presence of a cross-grid of dislocations in the [110] and [1$\bar{1}$0] directions. The number density was, however, low (~10^4 cm^{-2}).

Turning now to the intermediate dose (1.0 x 10^{16}B/cm^2) crystal, Fig. 1 is an x-ray topograph of the laser treated specimen following a 5 minute thermal anneal at 1000°C. This topograph shows a rather low density cross-grid of dislocations in the central part, which was annealed by the laser treatment. The number density of

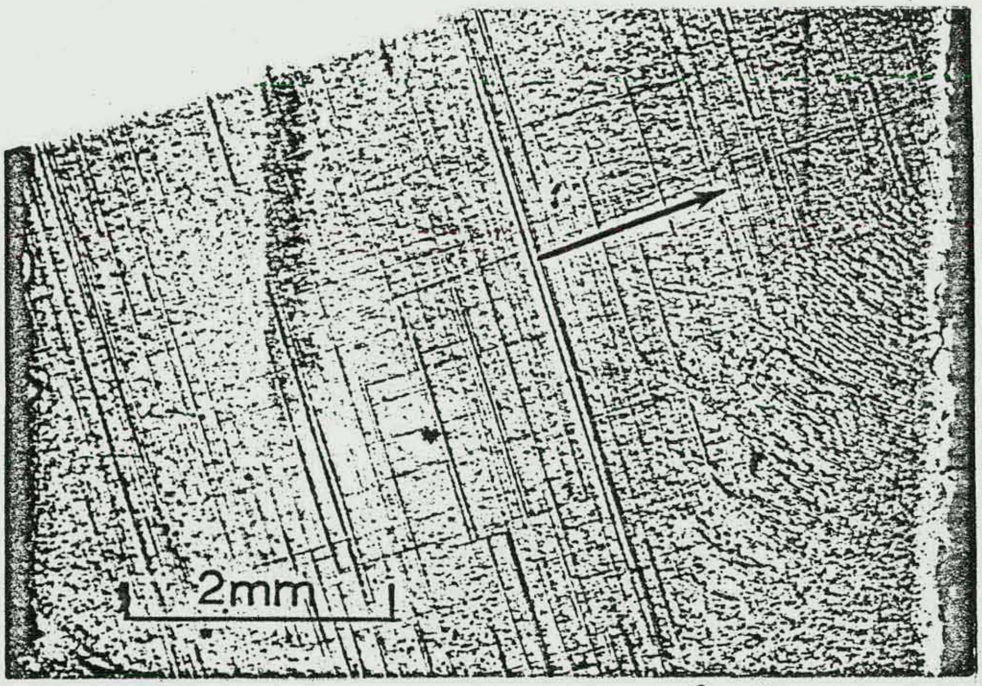

Fig. 1. X-ray transmission topograph of boron implanted ($1 \times 10^{16} cm^{-2}$) laser annealed silicon using the 220 reflection after heating to 1000°C.

these dislocations was determined to be $<10^3 cm^{-2}$. Fig. 2 shows a bright-field electron micrograph of a small region of this part of the crystal in which the cross-grid of dislocations is delineated as well. From contrast analyses, the Burgers vectors of these dislocations was determined to be $a/2[101]$ or $a/2[10\bar{1}]$ and from stereomicroscopy it was found that the cross-grid is located in a band ~200Å thick near the interface region 0.3μm below the surface. In some cases these dislocations crossed each other at the same level and reacted as shown at R in Fig. 2 while in other cases the crossing dislocations were separated by a small distance and were unable to react as shown at D in Fig. 2.

Upon close examination, a small number density of defect clusters (average size 20Å, density $5.0 \times 10^{14} cm^{-3}$) was observed in addition to the dislocations in the fully annealed portion of the crystal as shown in Fig. 3. Most of these clusters were identified to be vacancy type dislocation loops.

Before the thermal annealing treatment the strain in the plateau region near the surface was -0.55×10^{-2} for the $1.0 \times 10^{16} B/cm^2$ implant, whereas after the 1000°C heat treatment the strain was reduced to -0.24×10^{-2}. This reduction (~60%) is substantially larger than that found after annealing the low dose crystal; however, within the experimental errors, the contraction remained one-dimensional, along the surface normal. In addition to the long straight dislocations observed in Fig. 1, there is also a distribution of unidentified rows of defects (seen most clearly in the lower right) appearing in the outer region of the crystal that received less laser energy than the threshold for complete annealing of the implantation displacement damage. The extreme lower right region contains neither dislocations nor the rows of defects but the Bragg profiles from this region showed

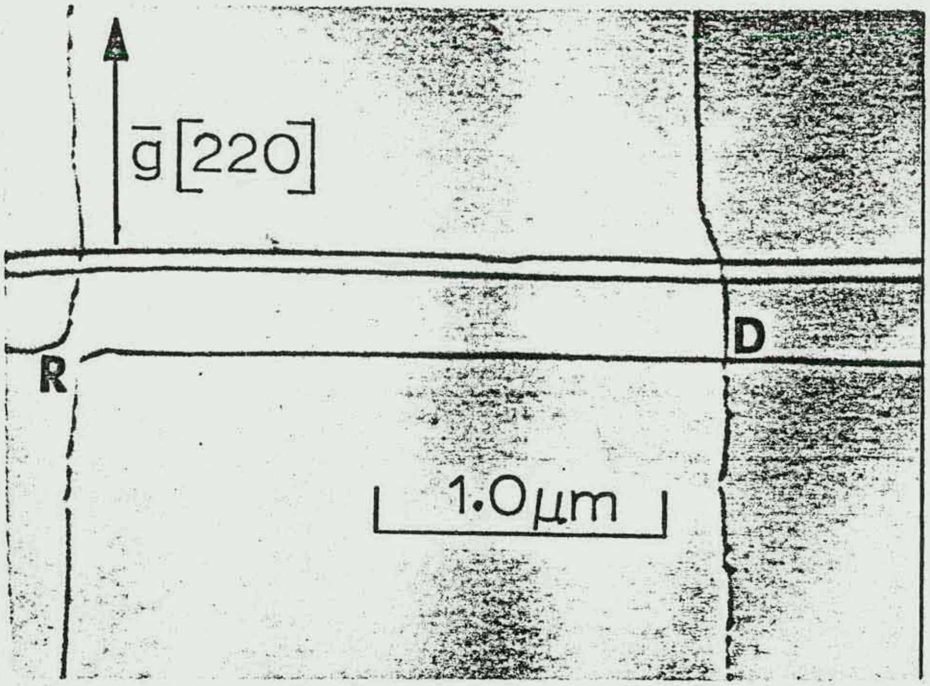

Fig. 2. Bright-field transmission electron micrograph from a small area in Fig. 1 showing a cross-grid of dislocations.

some of the ion implantation damage to have been retained, as evidenced by a lattice expansion rather than a contraction in this area. The background of small spots visible in the topograph were shown by stereo topography to be distributed throughout the entire crystal and not related to the ion implantation or laser treatment.

SIMS measurements of the boron concentration profiles as a function of depth for the 1.0×10^{16} B/cm^2 specimens are shown in Fig. 4. The as-implanted profile and the profile after the laser annealing was found to be the same as that reported earlier.[2] After thermal annealing, significant changes were observed in the boron profile in addition to the broadening expected as a result of the thermal diffusion. That is, there is an enhanced concentration

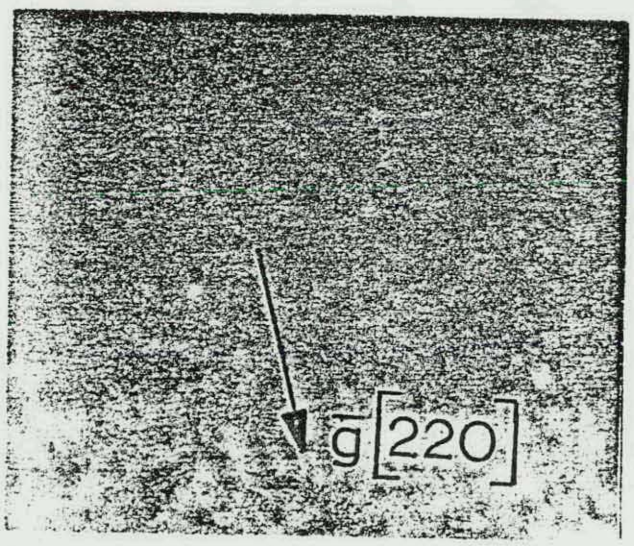

Fig. 3. Bright-field electron micrograph showing black-white images of dislocation loops under dynamical diffraction condition. The length of the arrow is 400Å.

of boron atoms near the surface. Although some variations were noted from sample to sample, the overall features of the boron depth distribution shown in Fig. 4 were consistently observed in the SIMS measurements following thermal annealing.

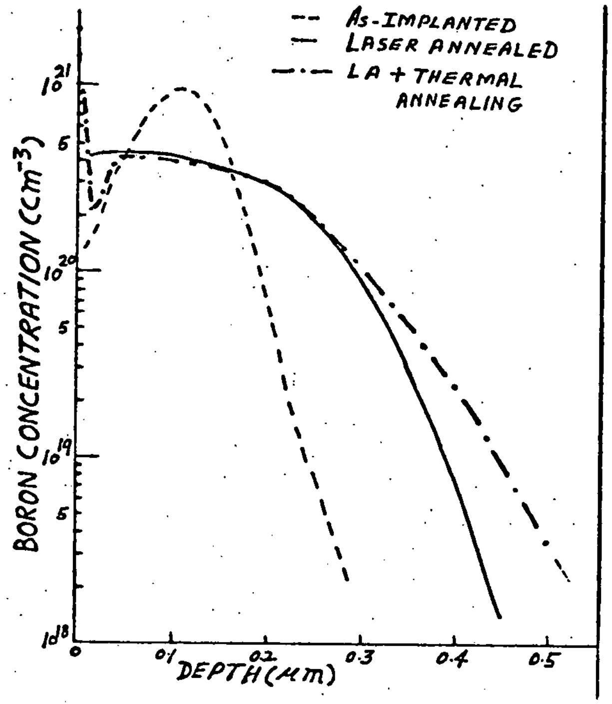

Fig. 4. Boron concentration profiles as determined by SIMS measurements.

DISCUSSION

The lattice contraction along the surface normal of the implanted, laser annealed silicon crystals produces stresses σ in the plane of the crystal given by

$$\sigma = 2\varepsilon\, G\left(\frac{1+\nu}{1-\nu}\right) \qquad (1)$$

where ε is the strain (lattice parameter change) normal to the surface, G is the shear modulus and ν is the Poisson's ratio for silicon. When the resolved shear stress on the slip planes (calculated using Eq. (1)) reaches the yield stress for silicon, the generation of interfacial misfit dislocations can be expected, provided sources to nucleate the dislocations exist. In this study ε (as determined by the x-ray measurements) was found to be -0.55×10^{-2} and -1.32×10^{-2} for the 1×10^{16} and 2.5×10^{16} B/cm^2 implants, respectively. These values give rise to resolved shear stresses of 5.0×10^9 dynes cm^{-2} and 1.2×10^{10} dynes cm^{-2}. In view of measured[4,5] yield stress measurements for pure silicon (at ~ 800°C) of $1 - 5 \times 10^9$ dynes/cm^2 the observation of dislocation generation in these specimens at 1000°C is not surprising.

Based on the present observations of dislocations along [110] and [1$\bar{1}$0] dislocations with 60° Burgers vectors resulting from the plastic deformation, a straight forward mechanism of formation is proposed. Taking an a/2[101] Burgers vector as an example, it is proposed that dislocations with this Burgers vector and lying along the [110] direction are generated at the free surface and subsequently slip down the $(\bar{1}11)$ planes. Similarly, $a/2[101]$ dislocations lying along the $[1\bar{1}0]$ directions would slip down the $(1\bar{1}1)$ planes. This mechanism is consistent with the observations of this study and the reaction of two dislocations with $a/2[101]$ Burgers vector is shown at R in Fig. 2. The $a/2[101]$ Burgers vectors makes a 60 degree angle with both the $[110]$ and $[\bar{1}10]$ directions, indicating that the dislocations in this network are of mixed character. It should be pointed out that the dislocation network generated here was produced by a plastic deformation process; this is apparently in contrast to that for the generation of dislocations during thermal annealing of room temperature implanted, but not laser annealed specimens. In the latter case, the dislocation networks were found to consist of pure edge type dislocations with Burgers vectors parallel to the specimen surface and were presumably formed by a dislocation climb mechanism.[6] Under high-temperature implant conditions a mixture of the above types of networks would be expected and the evidence for this has been obtained.[7]

The number of dislocations generated during thermal annealing would not be expected to significantly affect the one-dimensional nature of the lattice strains in these samples because dislocation densities $\gtrsim 10^5\ cm^{-2}$ would be required to relieve these stresses. This is in agreement with the x-ray observations; however, the reductions in the magnitude of the strains observed after thermal annealing seem to be larger than that expected and must be investigated further.

The origin of the small vacancy type dislocation loops and the cause of the enhancement of the boron concentrations near the crystal surfaces after the high temperature treatments have not been determined. Evidence does exist from Deep Level Trapping Spectroscopy (DLTS) measurements[8] for the presence of small concentrations of vacancies in the form of A-centers following laser annealing. A decreased chemical potential near the surface coupled with enhanced nucleation and precipitation would be possible mechanisms for the increased amount of boron at the surfaces after thermal annealing. However, these effects need to be studied in detail.

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