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STRUCTURAL DEFECTS IN LASER-AND ELECTRON-BEAM ANNEALED SILICON*

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Laser and electron beam pulses provide almost an ideal source of heat by which thin layers of semiconductors can be rapidly melted and solidified with heating and cooling rates exceeding 10^8 °C/sec. Microstructural modifications obtained as a function of laser parameters are examined and it is shown that both laser and electron beam pulses can be used to remove displacement damage, dislocations, dislocation loops and precipitates. Annealing of defects underneath the oxide layers in silicon is possible within a narrow energy window. The formation of cellular structure provides a rather clear evidence of melting which leads to segregation and supercooling, and subsequent cell formation.

I. INTRODUCTION

Laser (photon) and electron beams on interaction with semiconductors such as silicon provide large concentrations of excited (or hot) carriers. This energy can be transferred rapidly $<10^{-10}$ s to the lattice, thus it is possible to heat and melt thin ($<1\mu\text{m}$) layers of semiconductors in less than a nanosecond (1). The rapid heating and cooling (exceeding 10^8 °C/s) rates obtained by pulsed laser and electron beams offer a new technique for semiconductor processing (2-3). The purpose of this paper is to summarize the microstructures obtained by laser and electron beam processing and discuss their correlation with physical properties. The areas to be covered include annealing of displacement damage, growth of epitaxial layers, removal of dislocations, loops and precipitates, microstructural modifications underneath the oxide layers, segregation and cell formation.

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II. CHOICE OF LASERS, ELECTRON BEAMS AND SAMPLE PREPARATION

The work described here will emphasize Q-switched ruby lasers (wavelength $\lambda = 0.694\mu\text{m}$, pulse duration $\tau = 15 - 50 \times 10^{-9}$ seconds, energy density $E = 0.6 - 3.0 \text{ J cm}^{-2}$). Pulse electron-beam annealing was accomplished with an electron-beam generator (SPI-PULSE 5000, SPIRE Corporation) in a vacuum of 5×10^{-5} torr. Mean electron energy was 12 keV, pulse duration was 50×10^{-9} seconds, and pulse energy density was about 1.1 J cm^{-2} . The laser- and electron-beam diameters were 2 and 5 cm respectively.

Experiments covered in this review were done on (100) and (111) silicon single crystals. Ion implantations were carried out at room temperature under high vacuum conditions, at energies 35 to 150 keV with doses in the range of 1×10^{14} to 5×10^{16} ions cm^{-2} . To study the crystallization of deposited layers, thin layers of pure or doped silicon were deposited on (100) and (111) silicon substrates by an electron-beam evaporation method and then laser annealed in vacuum. High temperature diffusion of boron and phosphorous using B_2O_3 and PH_3 gas, respectively, leads frequently to the formation of precipitates and/or dislocation loops in the diffused region. Laser pulses have been used to remove these imperfections. Some of the ion implanted specimens were thermally annealed to produce dislocations and the growth of these dislocations was studied in the laser-melted layers. Segregation of impurities and formation of a cell structure was investigated in silicon specimens implanted with impurities with low solubility and distribution coefficient such as Fe, In, Ga, and Sb.

III. ANNEALING OF DISPLACEMENT DAMAGE

Fig. 1 shows microstructures as a function of increasing pulse energy density in an (100) arsenic implanted ($E = 100$ keV, dose = $1.4 \times 10^{16} \text{ cm}^{-2}$) silicon specimen (4). The above dose of arsenic ions produced an amorphous layer about 1600 Å thick. Annealing with one pulse ($E = 0.63 \text{ J cm}^{-2}$, $\tau = 25 \text{ n s}$) caused a region about 1000 Å thick to become polycrystalline and the remaining ~600 Å mostly amorphous. Annealing with pulses of energy densities above $\sim 1.1 \text{ J cm}^{-2}$ produced completely defect-free regions. Arsenic - distribution profiles were measured on companion samples and it was found that the 0.63 J cm^{-2} pulse caused considerable redistribution of arsenic from the surface to a depth of about 950 Å. This was interpreted to mean that at this energy the melt-front penetrated to $\sim 950 \text{ Å}$, giving rise to large arsenic redistribution in this region only. The calculated diffusion distances in

FIGURE 1. Annealing of displacement damage ($^{75}\text{As}^+$, 100 keV, $1.4 \times 10^{16} \text{ cm}^{-2}$) in silicon; microstructures after annealing with laser pulses of different (but uniform) energy densities are shown: a) $E = 0.63 \text{ J cm}^{-2}$, b) $E = 1.41 \text{ J cm}^{-2}$; pulse duration was 25 n sec.

solid state close to melting point are $\sim 1 \text{ \AA}$. From $E \geq 1.07 \text{ J cm}^{-2}$, the arsenic redistribution was observed over the entire range and a complete annealing of damage was observed. These results clearly showed that for a complete annealing of displacement damage it was necessary that the melt-front penetrated beyond the damage-boundary so that the underlying defect-free substrate could act as a seed for the crystal growth.

In another experiment on an arsenic implanted specimen (similar to that of Fig. 1) the energy density of the laser pulse was spatially nonuniform such that the various stages of annealing could be observed on the same specimen (3). The region labeled P in Fig. 2 contains residual damage in the form of polycrystals, in the region D dislocations and their tangles are near the surface and the region C is completely defect-free. From a comparison of these results with those obtained using uniform laser pulses it is deduced that the pulse energy density increased from region P to D to C indicating that there is threshold in the energy density of a laser pulse above which a complete annealing of displacement damage is realized.

Similarly arsenic-implanted specimens were annealed by electron-beam irradiation (3). The electron beam was spatially non-uniform such that some areas received above the threshold energy for complete annealing (the threshold for these specimens was $\sim 1.1 \text{ J cm}^{-2}$) and some below this threshold. It was found that near a transition region microstructures were similar to those in Fig. 2. The similarity in microstructures between laser- and electron-beam annealed specimens indicates that both involve melting as the mechanism of annealing.

The lattice location of implanted arsenic ions in silicon specimens after pulsed laser and electron-beam annealing was studied by measuring aligned channeling spectra and detailed angular scans (5). Substitutional fractions of arsenic in silicon both in laser and electron-beam annealed specimens were close to 100%. χ_{min} values were very close to those expected from perfect crystals indicating a complete removal of displacement damage. The electrical measurements on companion specimens showed a total electrical activation of

FIGURE 2. Laser annealing in an arsenic implanted specimen (similar to that in Fig. 1) using spatially non-uniform pulses: pulse energy density $E \approx 1.1 \text{ J cm}^{-2}$.

dopants. The minority carrier diffusion length (MCL) in these specimens was preserved equal to the value for the virgin crystals. This is a significant advantage over the conventional furnace annealing where the whole sample is heated leading to a degradation in MCL presumably through the introduction of recombination centers.

IV. THERMAL ANNEALING OF LASER ANNEALED SPECIMENS

Although no residual damage was observed by electron microscopy down to microscope resolution of about $10 \text{ \AA}$ in ion implanted, laser annealed silicon, questions still remained concerning the point defects and/or small agglomerates thereof below the resolution limit. An attempt to answer some of these questions has been made by subsequently heating the laser-annealed specimens up to 900°C . As discussed by Frank (6), all point defects in silicon should be mobile by 900°C . In the laser annealed specimens in which implanted doses were below the solubility limits, only a very low density ($<10^{14} \text{ cm}^{-3}$) of small defect clusters ($<25 \text{ \AA}$ average diameter) was observed (7). Kimmerling and coworkers (8) using DLTS (Deep Level Transient Spectroscopy) measurements on laser annealed specimens, have also reported the presence of interstitial and vacancy-impurity (oxygen) complexes. In specimens where implanted doses exceeded the solid solubility limits, precipitation of dopants was observed after thermally annealing the laser annealed specimen (4). An example is shown in Fig. 3 for an antimony implanted, laser annealed specimen ($E = 100 \text{ keV}$, $^{121}\text{Sb} = 7.0 \times 10^{15} \text{ cm}^{-2}$), in which precipitates in the form of black spots are shown after heat treatment at 1000°C for 30 min. Thermal treatments decreased the concentration of electrically active carriers and the decrease was approximately equal to the number of antimony atoms contained in the precipitates (9).

V. GROWTH OF EPITAXIAL LAYERS

Laser pulses have been used to grow epitaxial layers on silicon substrates by a liquid-phase growth. Amorphous silicon deposited (using electron-beam evaporation) on conventionally cleaned (100) and (111) silicon faces, has been shown to grow defect-free after irradiation with ruby-laser pulses. For a defect-free growth it was found necessary that melt-front penetrate the substrate interface and also melt the impurity precipitates (SiO_2 , etc.) at the interface. Recently diodes and solar cells have been fabricated from laser-annealed

FIGURE 3. *Precipitation of antimony on heating the antimony implanted, laser annealed specimen (100 keV, $^{121}\text{Sb} = 7 \times 10^{15} \text{ cm}^{-2}$: a) after laser annealing, $E = 1.5 \text{ J cm}^{-2}$, $\tau = 20 \text{ ns}$, b) after subsequent thermal annealing the same specimen at 1000°C for 30 min.*

silicon crystals which were deposited with doped-amorphous layers (10). The electrical measurements revealed a complete electrical activation of dopants. Amorphous deposits exposed to the air for a long time sometimes show the presence of voids after the laser annealing (9, 11). This problem can be minimized by either carrying out the deposition at a slightly higher temperature or reducing the exposure of deposited specimens to air (9).

LEED (low energy electron diffraction) work (12) has shown that the concentration of impurities (oxygen, carbon, etc.) at the surface can be considerably minimized by laser-annealing in vacuum. The surface structures were found to be those of bulk silicon without any reconstruction after the laser annealing. Therefore the deposition and laser annealing in vacuum should avoid problems associated with the impurities at the interface or the absorption of air before the laser annealing, which presumably results in the formation of voids or bubbles.

VI. REMOVAL OF PRECIPITATES AND DISLOCATION LOOPS

The conventional technique of making p-n junction is by solid state diffusion at high temperatures. This high-temperature treatment frequently leads to formation of dislocation loops and/or precipitates; these defects produce undesirable effects like recombination and trapping of carriers. The laser pulses have been used to remove these defects, and consequently improve the electrical characteristics of junctions. The results on annealing loops and precipitates also provide some basic information on the melting phenomenon (13, 14).

Fig. 4a shows precipitates in a boron-diffused specimen before the laser treatment. The average size (third moment of the diameter) and number density of the precipitates were determined to be $97 \text{ \AA}$ and $3.0 \times 10^{11} \text{ cm}^{-2}$, respectively. The precipitates were contained in the first $200 \text{ \AA}$ thick layer from the surface. After one laser pulse, no defects were observed by electron microscopy as shown in Fig. 4b. The boron precipitates were dissolved to a depth of $0.4 \mu\text{m}$ by the laser pulse and exceeded the solubility limit of boron at 950°C . By subsequent heating at boron in the 950°C excess of solubility limit in the region 3000 to $4000 \text{ \AA}$ from the surface precipitated out as shown in Fig. 4c. The above results were in agreement with boron concentration profiles (SIMS) before and after the laser treatment (3). Electrical measurements before and after the laser treatment showed that free carrier concentration has increased considerably following the laser treatment and the increase was found to be equal to the number of boron atoms in the precipitates. The dissolution of boron precipitates and distribution of boron atoms over several thousand angstroms is consistent with the melting model (2).

If the phosphorous diffusion is done at about 1100°C for about an hour and the samples are cooled slowly in the furnace, phosphorous precipitates as well as dislocation loops are formed (13). The irradiations with laser pulses produced annealed, defect-free regions. From the thickness of defect-free regions, the depth of melt-front penetration, as a function of laser parameters has been derived.

VII. GROWTH OF DISLOCATIONS DURING LASER-MELTING AND SOLIDIFICATION (9, 15)

Laser pulses have been used to study the growth of dislocations in the laser-melted layers. A boron implanted, thermally annealed (dose = $3.0 \times 10^{15} \text{ cm}^{-2}$, annealed at 1100°C for 30 min) silicon specimen contained faulted, edge type $a/3\langle 111 \rangle$ dislocations and perfect, edge $a/2\langle 110 \rangle$ dislocations

FIGURE 4. a) bright-field of a boron-diffused (950°C, 30 min.) specimen; b) bright-field after the laser treatment showing no defects or precipitates; c) bright-field after annealing the laser-treated specimen at 950°C for 30 min.

emerging in the surface. When part of this specimen was irradiated with one laser pulse of 1.5 J cm^{-2} , $\tau = 20 \text{ ns}$ and examined by electron microscopy, it was found that $a/2\langle 110 \rangle$ dislocations from a depth of about $0.4 \mu\text{m}$ to the surface were oriented at $25 \pm 2^\circ$ toward the surface normal but keeping an edge orientation as shown in Fig. 5a. Similar results for perfect $a/2\langle 110 \rangle$ dislocations were obtained in (111) silicon specimens. Some of the ion implanted, thermally annealed specimens were deposited with amorphous silicon layers and laser-melted below the interface. The growth directions of these dislocations were also similar to those observed in Fig. 5a. It was observed frequently that only one end of the $a/2\langle 110 \rangle$ dislocations in the above edge orientation while the other end split into two dislocations (for example at 1 in Fig. 5a) according to the following dislocation reaction:

These $a/2[101]$ and $a/2[01\bar{1}]$ dislocations were of mixed type (29° from pure screw orientation). The dislocation of a given Burgers vector always grew in the same direction regardless of its origin. The depth at which splitting started was always found to be $0.4\text{ }\mu\text{m}$ in this specimen. The partial $a/3\langle 111 \rangle$ dislocations (at 2 Fig. 5a) associated with faults split as

$$a/3\langle 111 \rangle \rightarrow a/2\langle 01\bar{1} \rangle + a/6\langle 2\bar{1}1 \rangle . \quad (2)$$

The $a/6\langle 2\bar{1}1 \rangle$ partial dislocations grew in $\langle 110 \rangle$ directions in the fault plane and the growth of $a/2\langle 01\bar{1} \rangle$ dislocations was similar to the split dislocations as described in Eq. (1).

We argue that reorientation of dislocations occurs during melting, because for the reorientation in solid state, climb distances, for the $a/2[110]$ edge dislocations, of the order of $0.3\text{ }\mu\text{m}$ would be required. The calculated climb distances even close to the melting point of silicon are less than one angstrom. This melting phenomenon can also be used to completely remove dislocation type defects when the melt-front

FIGURE 5. Growth of edge and mixed dislocations during melting and solidification: a) an $a/2[110]$ edge dislocation at 1 and the splitting of this dislocation into two mixed dislocations at the other end, the splitting of an $a/3[111]$ partial dislocation is shown at 2; b) A complete removal of these defects as a result of laser irradiation ($E = 2.0\text{ J cm}^{-2}$, $\tau = 20\text{ ns}$).

exceeds the dislocation depth boundaries, as shown for boron implanted, thermally annealed silicon (Fig 5b) in which the pulse-energy density was increased to about 2 J cm^{-2} .

The observed direction of dislocation growth ($25 \pm 2^\circ$) away from the surface normal may be related to minimization of dislocation energy and/or rearrangement of atoms near the core of a dislocation in this anisotropic medium (16). It should be pointed out that these directions probably represent true crystal-growth directions. Under normal crystal growth from melt, there is sufficient time to change the dislocation direction via glide and climb processes.

VIII. ANNEALING THROUGH OXIDE LAYERS (9)

Laser annealing of silicon through SiO_2 layers is of great interest to device manufacturers. The feasibility of this process and electrical characteristics of the resulting sample have been reported by several authors (17). The purpose of this section is to provide a clear evidence of melting and removal of dislocations as a result of melting underneath the oxide layers in a narrow range of energy density of a laser pulse. If the pulse energy density exceeds this value, melting of the oxide layer is effected (melting point of Si = 1400°C , of SiO_2 = 1700°C), and then the dissolved oxygen leads to formation of stacking faults and other defects. Fig. 6a shows optical micrograph after one laser pulse ($E = 1.3 \text{ J cm}^{-2}$) of an arsenic implanted, thermally annealed specimen which had an oxide layer $\sim 250 \text{ \AA}$ thick showing a ripple pattern on the surface.

It has been proposed that this ripple pattern is obtained due to thermal expansion and subsequent stress relief resulting in a buckling of thin oxide layer during laser irradiation (17). An electron micrograph of this specimen (Fig. 7a) shows a clear evidence of melting beneath this layer. From the length of projected segments, the thickness of melted region was estimated to be about $0.25 \mu\text{m}$. When the energy density of a laser pulse was increased to $\sim 2.0 \text{ J cm}^{-2}$ a complete removal of dislocations occurred (Fig. 7b) indicating that the depth of melting had exceeded the depth boundaries of dislocations (at $\sim 0.6 \mu\text{m}$). Some samples were irradiated with spatially non-uniform laser pulses such that some areas of specimens received more energy than 2.0 J cm^{-2} and caused the melting of the oxide layer. As shown in Fig. 6b, the ripples are normal to the melt boundary, which is in agreement with previous observations. From electron diffraction experiments (Fig. 7c) it was shown that the left side of Fig. 7b (indicated as A) contained no oxide at the surface whereas the right side (indicated as B) had an oxide layer as

FIGURE 6. Optical micrographs after laser annealing from a (001) Si specimen with ~ 250 Å thick SiO_2 layer a) ripple pattern on the surface with a laser pulse $E = 1.3 \text{ J cm}^{-2}$, $\tau = 15\text{-}20 \text{ ns}$; b) after $E = 2.0 \text{ J cm}^{-2}$ pulse. Oxide melted in some areas (A) and the ripple pattern in the unmelted area (B) is normal to the melted boundary.

indicated by diffraction pattern shown in Fig. 7d. A dektak trace of specimen in Fig. 6b showed that the average elevation in the areas A and B is the same within experimental error (~ 30 Å) indicating that most of the oxide layer has melted and mixed with the silicon substrate. The most interesting observation was the presence of $a/3\langle 111 \rangle$ stacking faults and tetrahedra in the region which did not contain a oxide layer on the surface. It is speculated that dissolved oxygen disturbs the stacking during the growth leading to the formation of faults. Since oxygen is always present as contaminant in silicon and faults are not usually observed, it seems reasonable to assume that more than a critical concentration of oxygen is needed and that clusters of oxygen rather than single oxygen atoms are involved in the nucleation process of the faults.

IX. CELL FORMATION IN ION IMPLANTED, LASER ANNEALED SILICON

When In, Ga, Fe, and Sb implanted silicon specimens are laser annealed, a considerable segregation of impurities near the surface is observed. Sometimes these impurities are found

FIGURE 7. Electron micrographs from the specimens shown in Fig. 6: a) micrograph corresponding to the specimen of Fig. 6a where depth of melting was determined to be $0.25\mu\text{m}$, b) micrograph from the specimen of Fig. 6b showing oxide melted area A and oxide containing area B, c) SAD corresponding to area A and d) SAD corresponding to area B.

in the form of a cellular structure. Fig. 8a shows cells in an indium implanted (001) silicon specimen after one laser pulse. The average cell size was $450\text{ \AA}$. The thickness of the cell walls was about $50\text{ \AA}$ and they extended to a depth of about $500\text{ \AA}$. Fig. 8b is (001) selected area diffraction pattern in which indium 110 spots appear near 200 missing silicon reflections. The high resolution dark-field using one of the indium 110 spots is shown in Fig. 8c in which cell wall structure is clearly delineated. The cellular structure presumably results from the formation of a zone of "constitutionally supercooled" liquid ahead of the solidifying interface and a sinusoidal perturbation of composition near the interface (18, 19). The cells were found to form above a critical concentration for different impurities, in qualitative agreement with the theory (19).

FIGURE 8. Cell formation in In-implanted silicon after laser annealing ($E = 1.5 \text{ J cm}^{-2}$, $\tau = 15\text{-}20 \text{ ns}$): a) In segregated at the cell walls after one pulse, b) SAD pattern showing In spots and c) high resolution dark-field using In spots.

X. CONCLUSION

Laser and electron-beam annealing removes lattice damage much more effectively compared to thermal annealing, and dopants can be incorporated into electrically active substitutional sites at concentrations that exceed equilibrium solubility limits. Removal of precipitates, dislocations and loops provide a clear evidence of melting. The laser pulses can be used to improve thermally diffused junctions which frequently contain the above defects. Dislocations of a given Burgers vector always grow in a specific direction. Melting underneath the oxide layers to remove dislocations and other defects can be achieved without distributing the oxide layer on the top, below a pulse energy density at which the surface temperature reaches the melting point of oxide. In addition to these results cellular structures in Ga, In and Fe implanted and laser treated silicon, due to constitutional supercooling, provide a clear evidence of melting during pulse laser irradiation and may provide new insights into the physics of non-equilibrium systems.

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