Thermal shock cleavage of silicon (111) thin crystals

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Clean thin samples of silicon (111) have been irradiated by 350–400 ns dye-laser pulses of 590 nm radiation under ultrahigh vacuum (UHV) conditions. Results obtained using a UHV transmission electron microscope on the thermal shock cleavage of these samples are reported. Classic cleavage along {111} planes was observed at relatively low fluences (less than 0.04 J/cm^2). The observations on the sample morphology before and after laser irradiation demonstrate that under the conditions that yield to cleavage, there is no long range diffusion of point defects and there is no tendency for the cleavage to occur at pre-existing defects. Although in some cases, cleavages occur at locations that are logically weak, in general, there appears to be no correlation between the cleavage sites and the three-dimensional crystal structure.

I. INTRODUCTION

Laser processing of semiconductors is emerging as an important technological application in the microelectronics industry.[1,2] Laser irradiation can be used as an annealing source, to assist thin film growth and device fabrication, and to produce atomically clean surfaces, metastable surface structures, and surfaces with unique electronic properties.[1–5] However, laser irradiation can cause damage. Thermal stress cracking, surface ripples, crater, or micropit formation were often observed in bulk silicon wafers subjected to an intense laser beam which is usually of high enough power to cause local melting and resolidification.[6–10] Damage studies at low power were rarely performed and the importance of these may have been overlooked, particularly for thin samples.

There are many questions concerning the interaction mechanism of lasers with materials. Microstructure characterization of the laser processed material has always been important since this determines many of the electrical properties. Transmission electron microscopy of both plan view and cross section specimens prepared retroactively has been the most often used technique.[11–13] For example, the defect states of implanted silicon annealed by laser were found to be different from thermally annealed specimens,[12] which resulted in a distinctive character in the recovery of the carrier concentration. Since pulsed laser heating and quenching can occur in a fraction of a second, it is unlikely for long range diffusion to occur. In principle, one can always obtain circumstantial evidence using electron microscopy retroactively on a bulk sample, but there will always be ambiguities. An alternative is to study the laser interaction with a thin specimen *in situ*.

In this article, we present results of pulsed laser damage of clean, thin samples of silicon (111) studied in an ultrahigh vacuum (UHV) transmission electron microscope. Damage in the form of microscopic (in some cases macroscopic) cleavage started to occur at a laser fluence of 0.04 J/cm^2. This fluence level was more than two orders of magnitude smaller than that used to cause catastrophic damage in bulk silicon examined by previous authors.[7–10] Cleavage in the thin regions (<100 nm in thickness) did not seem to have any correlation with pre-existing defects such as stacking faults. By comparing the size of stacking fault tetrahedra which pre-existed in the specimen before and after the laser treatment, we were able to demonstrate that there is negligible long range bulk diffusion during the laser pulses. Higher laser fluences (about 0.22 J/cm^2) cleaved thicker regions and there were dislocations associated with the cleavage surfaces. We were not able to go to any higher energy levels since these shattered the samples. During all of this work there was no evidence of any melting of the sample surface or bulk.

II. EXPERIMENTAL METHOD

Experiments were carried out on three different (111) oriented samples. Sample #1 was boron doped with a concentration of about $1\times10^{18}/cm^3$; samples #2 and #3 were also boron doped with a concentration of about $1\times10^{19}/cm^3$. All samples were prepared by first ultrasonically cutting out 3 mm disks, polishing to a thickness of about 100 μm, and then dimpling in the center to a thickness of about 20 μm. The dimpled sides were then chemically etched in a solution of 10% HF and 90% HNO_3. This produced wedge shaped samples with a small hole in the central region and a fairly large electron-transparent region.

The samples were then loaded in the side chamber of a Hitachi UHV H-9000 transmission electron microscope[14] and baked for a period of 1–2 days at about 200 °C to bring the pressure down to the low 10^{-10} Torr range. The samples were cleaned by cycling between argon ion beam (3–4 kV) sputtering and electron beam annealing to 500–800 °C.[15] A clean and smooth surface was obtained for sample #1 giving the boron induced $\sqrt{3}\times\sqrt{3}R30°$ reconstructions after electron beam annealing. No surface reconstructions were obtained from samples #2 and #3 since they became contaminated (at the monolayer level) due to a few micron sized grains of phosphor from a piece of equipment in the microscope. It is rather necessary to use

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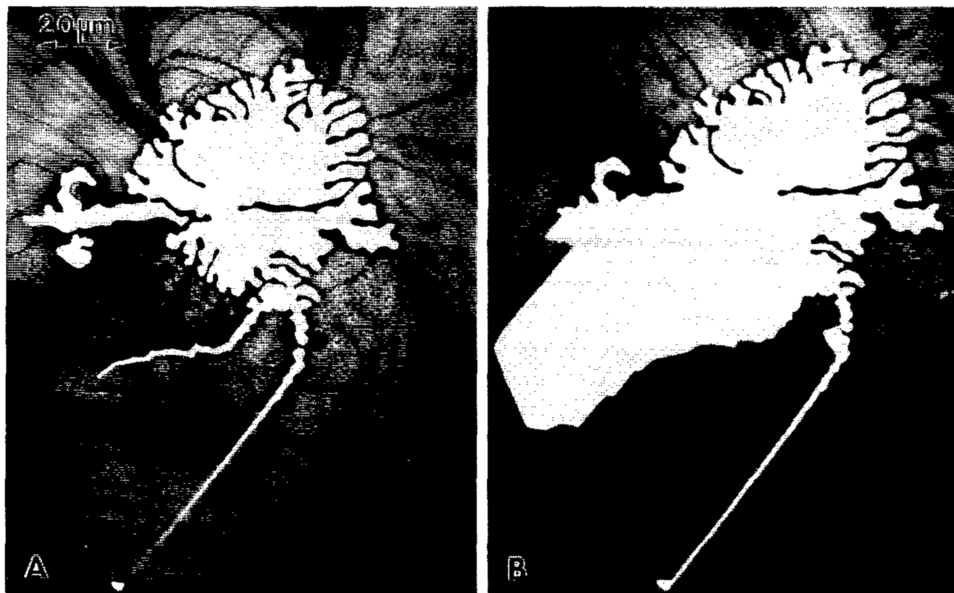

FIG. 1. Low magnification TEM images of sample #3 after (a) two laser pulses at 0.034 J/cm^2 and five pulses at 0.048 J/cm^2, (b) five more pulses at 0.041 J/cm^2. The long narrow fingers around the hole (white area) are due to the sample coarsening during thermal annealing. Crack lines are seen in (a) and some areas were cleaved in (b).

a clean sample with a well characterized surface in the laser experiment, because the properties of sample surfaces are known to have effects on the laser damage results.[7] The elimination of a surface contamination or oxide layer rules out the possibilities of these acting as heat barriers or inducing chemical reactions during laser irradiation.

The laser beam was introduced into the side chamber of the microscope through a quartz window, and the irradiated specimen was transferred to the microscope immediately afterward for observations, all under UHV condition. The laser irradiation was provided by a Candela SLL-250 pulsed dye laser with a Rhodamine 6G dye dissolved in a mixture of methanol:water (50:50) giving a broad wavelength spectrum, from 570 to 660 nm with a peak at about 590 nm. The laser pulses are 350–400 ns in length with a maximum output power of 1 J. Initial experiments included a lens for beam focusing; in later work this was avoided since it produced a very high power and tended to completely shatter the samples. In all cases, the 3-mm-diam specimen was evenly illuminated. The microstructure of the sample during the cleaning and laser irradiation processes was analyzed in the electron microscope primarily using electron diffraction and conventional bright field/dark field imaging techniques.

III. RESULTS

A. Low fluence, ~0.04 J/cm^2

Results on sample #3 performed with low power laser pulses after sputtering and thermal annealing are presented first. The only significant change in the material was cleavage along {111} planes after repetitive laser pulses. Figure 1(a) is a low magnification transmission electron microscope (TEM) image showing an overview of the specimen with some crack lines after two pulses at 0.034 J/cm^2 and five pulses at 0.048 J/cm^2. (Long narrow fingers around the hole were caused by the coarsening of the specimen during thermal annealing.) Figure 1(b) is after five more pulses at 0.041 J/cm^2 showing cleavage in various areas; only one large piece cleaved during the process and other cleavages were more or less on the microscopic scale. [The bend contours in the images appear different due to a slight difference in the sample tilt between Figs. 1(a) and 1(b), as is the case for the later images as well.] Three enlarged areas are shown in Fig. 2. It is quite obvious from Figs. 2(a) (before) and 2(b) (after) that cleavage occurred in narrow parts of the specimen (arrowed) and the two fingers protruding out were broken off. However, it is somewhat harder to explain the sites of the cleavage in the two areas shown in Figs. 2(c), 2(d), and 2(e), 2(f). The cleavages in Fig. 2(d) are not from the narrowest part of the region and a small finger was left behind. In Fig. 2(f), the cleavage did not occur at the stacking fault [indicated by the arrow in Fig. 2(e)] as might be expected, but at a point where no defect could be seen. During the experiment, dislocations in the sample were not disturbed by the laser pulses.

A significant result concerns the effect of the laser on pre-existing stacking fault tetrahedra (SFT), and stacking faults in the specimen. The SFT and stacking faults were formed as a result of thermal annealing of point defects induced by ion beam sputtering. The evolution of these stacking fault tetrahedra and the stacking faults was followed during laser pulse treatments and a subsequent thermal annealing, and some of the representative images are shown in Fig. 3. Figures 3(a) and 3(b) are a pair of bright field and (220) dark field images taken after two laser

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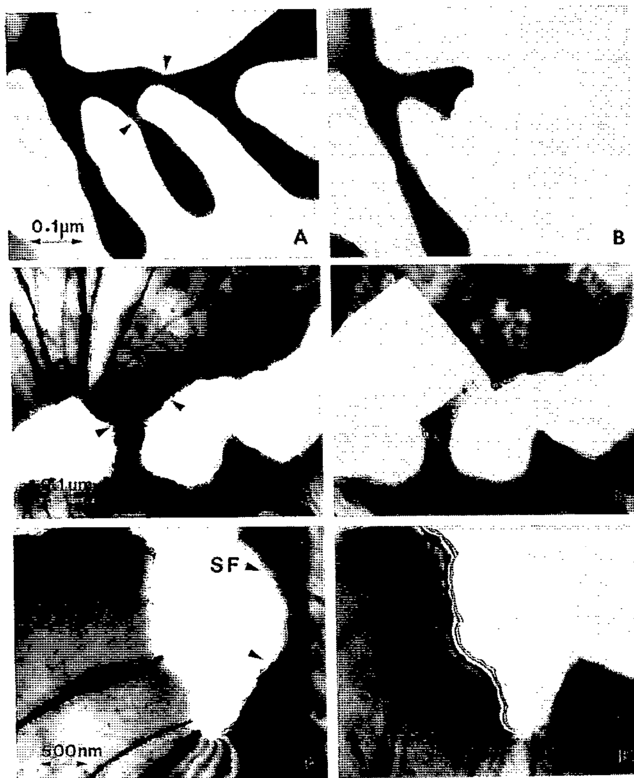

FIG. 2. TEM images showing three enlarged areas of Fig. 1(a), [(a), (c), (e)], and Fig. 1(b) [(b), (d), (f)] of sample #3. The arrows in (a), (c), and (e) indicate the locations of the cleavages. Also in (e) an arrow points to a stacking fault above the cleavage line.

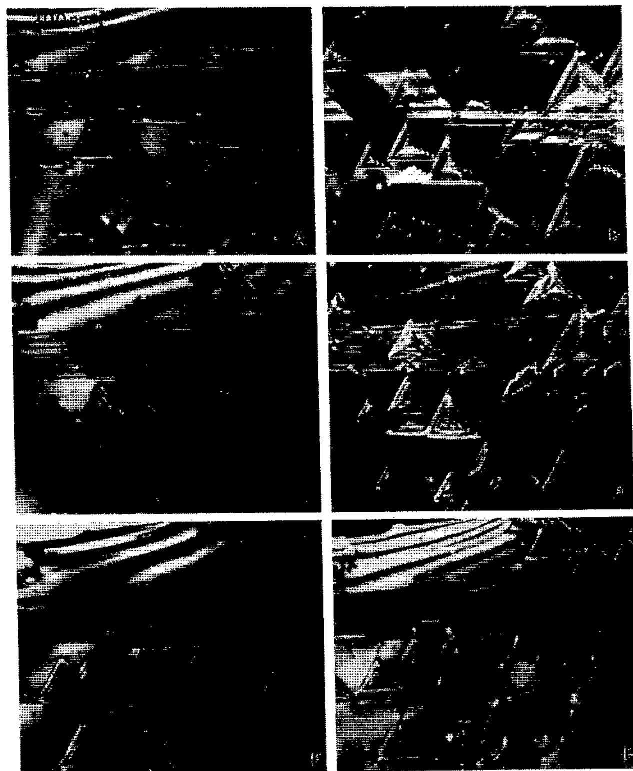

FIG. 3. Bright field and (220) dark field images showing the evolution of stacking fault tetrahedra during laser irradiation and thermal annealing: (a) and (b) after two laser pulses at 0.034 J/cm^2; (c) and (d) after another 5 laser pulses at 0.048 J/cm^2 and (e) and (f) after thermal annealing at 600 °C. Note that the tetrahedra have grown in (e) and (f) due to long range diffusion of point defects during thermal annealing, but no size change was observed after laser irradiation [(a)–(d)]. The difference in the thickness fringes inside the SFT is due to the sample tilt.

pulses of 0.034 J/cm^2 at a 20 s interval. No apparent change in the sample could be found when these two micrographs were compared to the ones taken before the laser irradiation. A subsequent laser treatment involved five more pulses of 0.048 J/cm^2 separated by 2 s. There was still no change in this area [Figs. 3(c) and 3(d)]. Careful measurements of the micrographs showed no evidence of the growth of the SFT in size. However, thermal annealing resulted in the growth of the SFT in size as is clearly evident in Figs. 3(e) and 3(f). The difference in the thickness fringes inside the SFT in these three sets of images is again due to the sample tilt. We can conclude from this set of data that long range diffusion of point defects is negligibly small during laser irradiation.

B. Higher fluence, ~0.22 J/cm^2

With higher laser power, the results tended to be more catastrophic in character. Indeed, at a fluence of about 4.0 J/cm^2, the whole 3 mm disk of sample #1 completely shattered. The results obtained after a single laser pulse of 0.22 J/cm^2 on sample #2 are shown in Fig. 4. Cleavage of a somewhat thicker region (100–200 nm) of the sample with the formation of dislocation lines below the cleavage surface is seen. Cleavage planes are {111}, and dislocations with Burger's vectors of $\mathbf{b}=(\mathbf{a}/2)[110]$ ($\mathbf{a}$ is the lattice constant) were determined to be of a mixed nature using conventional electron microscopy techniques.

IV. DISCUSSION

The above results indicate that thermal shock upon laser irradiation may have been enough to crack, cleave and break thin silicon samples at a low laser fluence of about 0.04 J/cm^2. Using pre-existing models[2] for laser heating, we have calculated that the temperature immediately following the laser pulse is on the order of 500 °C at the top surface, and about 60 °C lower at the bottom of a 100-nm-thick sample. The difference in thermal expansion at the top and bottom surfaces would cause a sample to bend and generate a shock wave that will drive the cleavage. Unlike the case with bulk silicon, we cannot be certain that cleavage does not occur during heating rather than during cooling. In our experiment, single low energy pulses had no effect on the specimen, while repeated laser pulses caused the sample to cleave. During a single pulse, there might not have been enough instantaneous bending to cause damage to the sample, but repetitive heating and cooling may have weakened certain areas and these fatigued areas would have been more susceptible to thermal shock under the following pulses. In some cases, for instance Figs. 2(a) and 2(b), cleavage occurred at narrow regions which would serve as stress concentrators. However, not every narrow region cleaved, so generalizations

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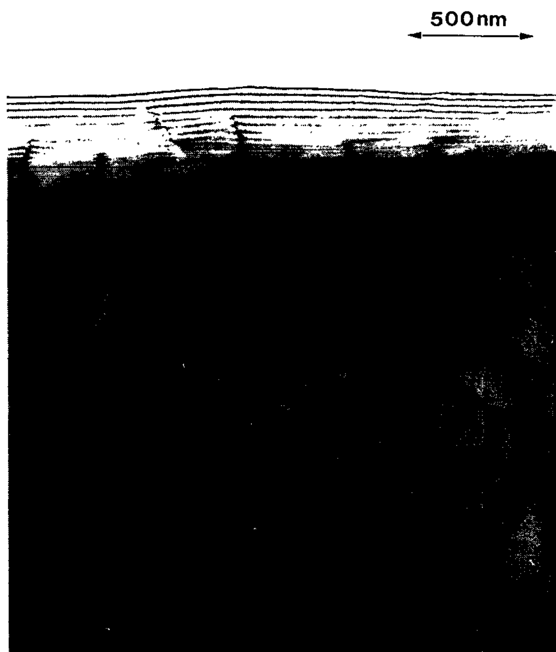

FIG. 4. Bright field image showing a cleavage surface in a slightly thicker region of sample #2 after a single laser pulse at 0.22 J/cm^2. Dislocation lines are the byproduct of the laser damage process.

appear to be dangerous. Furthermore, cleavage did not seem to originate from weak areas in the sample such as stacking faults. A possible answer is that the cleavage process is chaotic rather than simply behaved; alternatively, hot-spots within the laser beam may be significant.

As the cleavage proceeds, it can change direction and nucleate dislocations; this is much more apparent at the higher power levels which are presumably associated with high stresses. All of these processes are nondiffusive in character. However, there is no evidence that dislocations are intimately involved in the cleavage in any way and appear to be secondary products only.

In summary, it is demonstrated that mechanical damage in a thin silicon specimen can occur at a very low pulsed laser fluence as thermal shock induces sample cleavage. This observation suggests that not all laser-beam damage processes are associated with high fluxes.

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