HYDROGEN AND DEFECTS IN LASER ANNEALED AMORPHOUS SILICON¹

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Hydrogenated amorphous silicon was crystallized by pulsed laser annealing to yield hydrogenated crystalline silicon. Nuclear reaction analysis was used to measure hydrogen concentrations and depth distributions. Infrared absorption measurements were used to study the chemically bonded hydrogen. The ir measurements also reveal that divacancies may remain in the lightly-damaged underlying crystalline region after annealing with laser energies sufficient to produce recrystallization. Divacancies anneal out by 350°C and defect structures in the vicinity of the bonded hydrogen change between 200 to 500°C. No evidence for point defects or chemically bonded hydrogen was found after anneals above 500°C.

It is well-documented (1) that pulsed laser annealing of ion-implanted silicon can yield material without macroscopic defects as measured by techniques such as ion backscattering/channeling and transmission electron microscopy. However, the performance of many types of devices fabricated from laser annealed Si which appears to be perfect from a microstructural viewpoint suggest that point defects may remain after pulsed laser annealing. More direct evidence for the existence of point defects in laser annealed material has also been found from electrical measurements (2) and energy levels ascribed to these defects have been measured by deep-level transient spectroscopy. (3) Since point defects limit the application of laser annealing in device fabrication, it is important to understand the origin of these defects and the annealing conditions under which they occur.

In an attempt to study the point defects in laser annealed Si, we have investigated laser annealing in hydrogenated amorphous silicon (a-Si:H). Defects in crystalline silicon (c-Si) result in chemical trapping (4) of hydrogen which is detect-

¹This article sponsored by the U.S. Department of Energy, Division of Basic Energy Sciences, under Contract DE-AC04-76-DP00789.

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able by infrared absorption. Nuclear reaction analysis detects both chemically bonded and physically trapped hydrogen.

Amorphous silicon was produced by Si self-ion implantation and hydrogenation was achieved by H^+ implantation. This technique permits control over the hydrogen concentration. For the studies reported herein, the implanted samples were annealed with single 20 nsec pulses from a Q-switched ruby laser. As noted previously, (5) recrystallization is inhibited at large hydrogen concentrations (≥ 2 at.%) and the material blisters under laser annealing. We have even observed some blistering on crystallization for peak H concentrations of 1.5 at.%. Presumably this blistering results from the formation of H_2 in the melt which is physically trapped in the sample when the crystallization front sweeps through from the substrate. Changes in the H depth distribution and Si-H spectra produced by laser annealing are shown in Fig. 1. The H distribution changes markedly on recrystallization. While

FIGURE 1. Infrared absorption spectra and hydrogen profiles measured by nuclear reaction analysis for 1×10^{16} 20 keV H/cm^2 before and after laser annealing.

the ar-implanted H depth distribution is nearly Gaussian centered at $0.22 \mu\text{m}$, after annealing the H distribution is essentially uniform from the initial implant depth to the surface.

Evidence for physical trapping is obtained by comparing the chemically bonded H determined from the intensity of the Si-H vibrational modes with the retained H measured by nuclear reaction analysis as shown in Fig. 1. While the nuclear reaction analysis measurements show that samples with 1×10^{16} H/cm^2 contain $\sim 50\%$ of the initial hydrogen after annealing,

the intensity of the Si-H bands in the c-Si are only 2.2% of their value in the a-Si. The Si-H absorption cross section for c-Si is somewhat reduced relative to its value in a-Si (0.75 its value in a-Si), (6) but this difference cannot account for the intensity reduction measured for the data shown in Fig. 1. Indeed, most of the hydrogen retained in laser recrystallized a-Si:H is physically trapped--i.e., not chemically bonded to Si.

For H concentrations lower than those discussed above, a-Si:H can be annealed with pulsed Nd or Ruby lasers to yield single crystal silicon without macroscopic defects as measured by TEM. Ion channeling measurements also indicate that the laser crystallized layers are single crystal material. The annealing energy dependence of the channeling yield and the hydrogen retained after pulsed annealing is shown in Fig. 2 for a-Si implanted with 4×10^{15} H/cm². The Si had been made amorphous by implantation of 1×10^{16} 200 keV Si⁺/cm², which yields an amorphous layer of ~ 0.4 μ m. The laser energy required to recrystallize a-Si:H is slightly greater than that for nonhydrogenated a-Si, and for $E > 2.5$ J/cm² single crystal Si is obtained. However, even for the highest laser energies used, the ratio of the aligned channeling yield to the random backscattering yield, χ_m , is slightly higher ($\sim 1\%$) in the hydrogenated case than in virgin Si. As previously noted, (5) appreciable hydrogen is lost during laser annealing, and for an implant of 4×10^{15} H/cm², only $\sim 8 \times 10^{14}$ H/cm² is chemically bonded to Si.

FIGURE 2. Annealing energy dependence of the channeling yield χ_m and the hydrogen concentration in a-Si implanted with 4×10^{15} H/cm².

Infrared spectra for the Si-H vibrational modes illustrating the changes induced by laser annealing are shown in Fig. 3. In implantation-produced a-Si, the H is bonded predominantly in monohydride (SiH₃) centers (7) which gives a broad line centered at 1985 cm⁻¹. After laser annealing relatively strong crystalline Si-H bands are observed at 1960, 2100, and 2180 cm⁻¹ and weaker bands near 1925, 2030, and 2060 cm⁻¹. For incomplete laser anneals, an even more complex crystalline Si-H spectrum is observed than that shown in Fig. 3. In well-

annealed a-Si:H we always observe the Si-H bands at 1960, 2010, 2060, and 2180 cm^{-1} . Although the spectrum after 300K implantation of H into c-Si exhibits more Si-H bands than does laser recrystallized Si:H, the modes at 1960 and 2010 cm^{-1} seem to be unique to laser recrystallized Si.

A comparison of the Si-H spectra of c-Si:H produced by laser annealing and by H-implantation is given in Fig. 4. Although essentially all of the wide variety of Si-H bonding configurations as measured by ir absorption can be obtained in laser annealed Si for incomplete anneals (5) which leave highly defected c-Si, well annealed laser produced c-Si:H has a

FIGURE 3. Comparison of Si-H spectra before and after laser annealing of a-Si:H. The as-implanted spectrum was multiplied by 0.4 to account for the H loss on annealing.

FIGURE 4. Comparison of the ir spectra for Si-H in laser annealed a-Si:H and H-implanted a-Si before and after a 300K anneal.

relatively simple spectrum with fewer types of defects than implantation produced c-Si:H. The ir spectrum of laser annealed c-Si:H also differs from that obtained after 300°C thermal annealing of implantation-produced c-Si:H as shown in Fig. 4. Such annealing removes many of the implantation-produced defects. We infer from these results that the defect configurations in the vicinity of Si-H bonds formed during the melt in laser produced c-Si:H are different from those in implantation produced c-Si:H.

In addition to the defects associated with Si-H bonding, divacancies were always observed in laser recrystallized a-Si that was produced with 200 keV Si^+ implantation. The change in the divacancy intensity on laser annealing is shown in Fig. 5 for a 2.8 J/cm^2 anneal. While we were unable to remove all of the divacancies in material implanted with 200 keV Si^+ for

laser energies below the surface damage threshold, divacancies produced by low energy implants (40 keV Si^+) could be removed by laser annealing. These observations lead us to conclude that the divacancies are in the crystalline material in the tail of the damage distribution under the implantation-produced amorphous layer and are not in the recrystallized region. If the melt depth does not penetrate through this underlying defected region, these point defects remain after annealing. Therefore, laser annealing at energies insufficient to melt through this lightly defected region can produce material with microstructure which appears perfect from ion channeling or TEM measurements but contains point defects in the unmelted crystalline region beneath the annealed region. Although we do not find evidence for point defects in the region melted during laser annealing when hydrogen was not present, melt depths of several times the ion range are needed to remove point defects produced in the underlying crystal. Therefore pulsed laser annealing with a Q-switched ruby laser is limited to shallow implant applications.

FIGURE 5. Divacancy spectra in as-implanted and laser annealed a-Si:H. The inset illustrates the divacancy-containing region.

FIGURE 6. Annealing behavior of the divacancies and major Si-H modes in laser annealed a-Si:H.

An important consideration for device fabrication using laser annealing is the subsequent processing temperature which must be used to remove these residual point defects. The annealing behavior for the divacancies and Si-H bands are shown in Fig. 6. While the divacancies simply anneal out by 350°C, the Si-H annealing behavior is more complex. The intensities of the dominant Si-H bands increase at temperatures $\leq 350^\circ\text{C}$ and are then removed by annealing at 500°C. Since the frequencies of the Si-H modes are determined by the local defect structure, these intensity increases are attributed to changes in point defects in the vicinity of the chemically bonded

hydrogen. The ultimate intensity decrease and disappearance of the Si-H modes is due to the loss of chemically-bonded hydrogen from c-Si, and after subsequent heating of laser annealed Si at $\geq 500^\circ\text{C}$ we observe no evidence for point defects in the material.

In summary, laser annealing of a-Si:H with low (≤ 2 at.%) H concentrations yields c-Si:H in which H is both chemically and physically trapped, and the physical trapping increases with the H concentration. The H is bonded chemically to Si in association with point defects and these defect structures change with thermal annealing below 500°C . After thermal annealing at $T > 500^\circ\text{C}$, no evidence is found for point defects or chemically bound H. The concentration of divacancies produced by 200 keV Si^+ is independent of the H concentration and they are not completely removed with laser annealing at energies below the surface damage threshold. Laser annealing following low energy (40 keV Si^+) implants removes the implantation-produced divacancies. These results indicate that, for the higher energy implants, divacancies exist in the crystalline region below the melt penetration depth.

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