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Concentration of atomic hydrogen diffused into silicon in the temperature range 900–1300 °C

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Boron-doped Czochralski silicon samples with $[\mathrm{B}] \sim 10^{17}\ \mathrm{cm}^{-3}$ have been heated at various temperatures in the range 800–1300 °C in an atmosphere of hydrogen and then quenched. The concentration of [H-B] pairs was measured by infrared localized vibrational mode spectroscopy. It was concluded that the solubility of atomic hydrogen is greater than $[\mathrm{H_s}] = 5.6 \times 10^{18} \exp(-0.95\ \mathrm{eV}/kT)\mathrm{cm}^{-3}$ at the temperatures investigated.

Hydrogen atoms produced in a radio frequency hydrogen plasma diffuse into the surface of monocrystalline silicon heated to a temperature in the range 150–250 °C and form electrically neutral complexes with shallow donors and acceptors,[1,2] which are revealed by infrared localized vibrational mode (LVM) absorption spectroscopy. The hydrogen stretch mode of H-B pairs occurs at 1904 cm^{-1} (4.2 K),[3] and their concentration may be higher than 10^{19} cm^{-3}. Analyses of the hydrogen (deuterium) profiles by secondary-ion mass spectrometry (SIMS) have shown that the hydrogen concentration [H] is comparable with the shallow impurity concentration to a depth of 2–3 μm but then drops to a value less than $10^{15}\ \mathrm{cm}^{-3}$ which is below the detection limit of the SIMS technique. Very high hydrogen concentrations up to $10^{20}\ \mathrm{cm}^{-3}$ occur within 100 nm of the surface and are associated with extended structural defects.[4] Such near-surface effects also occur in undoped silicon,[5] but [H] again falls below the SIMS detection limit at depths greater than 100 nm. Thus there is no direct information about the solubility of hydrogen $[\mathrm{H_s}]$ in undoped bulk material in this low temperature range.

H-B pair defects dissociate on heating samples above 200 °C and the hydrogen can then no longer be detected spectroscopically.[1,2] It is inferred that stable H_2 or larger clusters form, as SIMS measurements show that hydrogen is not lost from the crystal by out-diffusion. According to this discussion, the formation of both H-B and H_2 defects would be expected if B-doped silicon, containing atomic hydrogen, were quenched rapidly from a "high temperature" ($\sim$1000 °C), at which neither of the pair defects are stable. It was deduced from early permeation measurements in which undoped monocrystalline silicon was heated in hydrogen gas at a pressure of 1 atm that its solubility increased from $3.4\times10^{14}\ \mathrm{cm}^{-3}$ at 1092 °C to $1.1\times10^{15}\ \mathrm{cm}^{-3}$ at 1200 °C (Fig. 1).[6] The slope of an Arrhenius plot yielded an energy of 1.9 eV. An extrapolation of these data to 400 °C would imply $[\mathrm{H}]\sim10^{7}\ \mathrm{cm}^{-3}$, consistent with the lack of detection of hydrogen by SIMS in bulk samples that had been heated in an H plasma.

We have carried out measurements on silicon samples heated at high temperatures in hydrogen gas but used a new procedure to detect the hydrogen. Samples of boron-doped Czochralski silicon ($[\mathrm{B}]\sim10^{17}\ \mathrm{cm}^{-3}$) about 1 mm in thickness were subjected to an RCA cleaning procedure and then heated in a similarly cleaned all-quartz-lined furnace in hydrogen at a pressure of 1 atm at various temperatures in the range 800–1300 °C for times up to 2 h. The heating was terminated by quenching the sample into silicone oil by allowing it to drop 45 cm from the heated zone. The surfaces of the sample were then cleaned and polished and infrared absorption spectra were obtained using a Bruker IFS 113v interferometer. The integrated absorption (IA) in the LVM hydrogen stretch line already mentioned was measured for the samples held at 4.2 K in an Oxford Instruments flow cryostat. The line was detectable for the samples which had been heated and quenched from

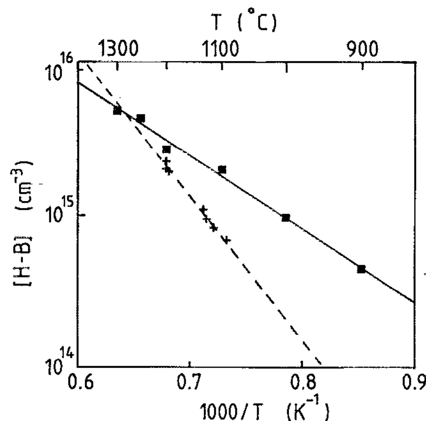

FIG. 1. Concentration of H-B pairs (solid squares) determined from the integrated absorption due to the H-B stretch mode. Values of the solubility of hydrogen in silicon (crosses) determined by van Wieringen and Warmoltz[6] are also shown.

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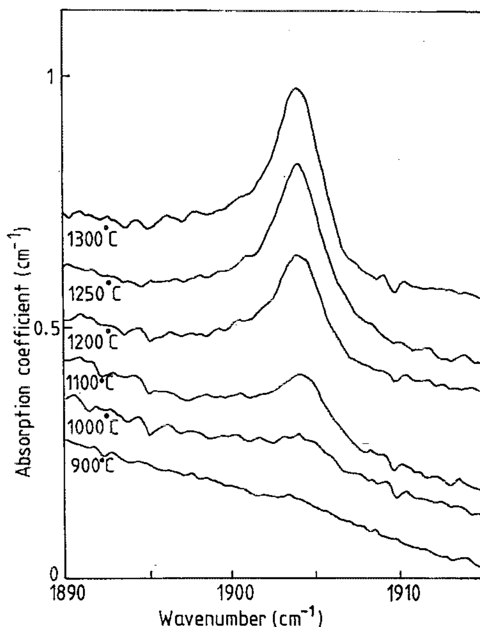

FIG. 2. Absorption (at 4.2 K) due to the H-B stretch mode in Czochralski silicon with $[B]\sim10^{17}$ cm^{-3} after annealing at the indicated temperatures in an atmosphere of hydrogen gas followed by a rapid quench to room temperature.

$T\geqslant900$ °C (Fig. 2), and the full width at half height Δ was found to be only 3.5 cm^{-1}. This value is significantly smaller than that of $\Delta\sim9$ cm^{-1} found for the H-B line in highly doped ion-implanted material passivated in an H plasma, but similar to that found for bulk silicon with $[B]=10^{17}$ cm^{-3} also passivated in an H plasma. The line is expected to broaden as [B] increases due to the increase in the lattice strain.

It was necessary next to convert values of IA into concentrations of [H-B] pairs. A calibration was established using two types of reference sample, (a) a layer with $[B]=3\times10^{18}$ cm^{-3} and a thickness of 5.2 μm grown by molecular beam epitaxy, and (b) an undoped epitaxial layer which had been implanted with ^{11}B to a total dose of 1.0×10^{16} cm^{-2} (see Ref. 7 for further details). These samples were passivated in an inductively coupled H plasma at a temperature of 185 °C using a gas pressure of 4 mBar and a power of 40 W. Treatments for periods in excess of 70 h led to the removal of all detectable free-carrier or photoionization electronic absorption from the boron indicating at least 90–95% compensation (passivation). Assuming that all the boron originally present paired with hydrogen, the two types of sample led to indistinguishable calibrations in which a value of IA = 1 cm^{-2} corresponded to a concentration of [H-B] of 3.0×10^{15} cm^{-3}. This calibration implies a dipole moment per unit displacement or apparent charge of the H-stretch mode of $\eta=1.5\pm0.1e$, in substantial agreement with estimates of η for the stretch modes of complexes of hydrogen[3] with Al and Ga impurities in Si. Use of the calibration enabled the concentrations of [H-B] to be determined for the samples heated and quenched in hydrogen (Fig. 1). The values so derived were somewhat higher than the early data[6] for $[H_s]$ even when the latter numbers were multiplied by a factor of 2 to convert from concentrations in molecules cm^{-3} to atoms cm^{-3}.

Before proceeding it was necessary to establish that the hydrogen present in the H-B pairs had originated from the hydrogen gas in the furnace and not hydrogen atoms in the silicone oil. A sample was heated in deuterium gas at 1300 °C for 20 min and quenched. An LVM line was then observed at 1390 cm^{-1} due to D-B pairs[3] rather than the line from H-B pairs. This observation proves that at high temperatures, hydrogen diffuses into silicon from the gas. If the hydrogen solubility is equal to the value of [H] immediately prior to quenching, the results shown in Fig. 1 imply $[H_s]\geqslant5.6\times10^{18}\exp[-0.95\ \text{eV}/kT]$cm^{-3}.

During the quench there could have been formation of relatively stable H_2 pairs or larger H clusters as well as H-B pairs. In addition, there could have been out-diffusion of hydrogen to the surface. The possibility that the latter process had occurred was investigated by measuring the IA of the LVM of H-B pairs in a sample that had been quenched from 1300 °C after which it was thinned progressively by grinding and polishing each of its two sides. The value of IA did not change, indicating that [H-B] was uniform throughout the thickness of the sample. It was thereby concluded that there was no significant out-diffusion of hydrogen during the quench.

It was demonstrated next that the heat treatment and quenching must have led to the introduction of hydrogen into undoped silicon, even though this hydrogen could not be detected spectroscopically. We have shown previously[5,8–11] that the introduction of atomic hydrogen into silicon containing interstitial oxygen at a concentration of $\sim10^{18}$ cm^{-3} from an H plasma leads to large enhancements in the oxygen diffusion coefficient D at low temperatures ($T<500$ °C). The measurement technique used was that of relaxation of stress-induced dichroism. Undoped Czochralski silicon samples were annealed for 2 h at 900 °C in hydrogen and quenched as already outlined for boron-doped material. On annealing these samples in a furnace there was also a rapid loss of dichroism which was uniform throughout their thickness. The value of D deduced from the relationship $D=a_0^2/64\tau$, where $a_0=5.42$ Å is the lattice spacing of silicon and τ is the measured relaxation time constant, yielded $D=7.1\times10^{-4}\exp(-2.0\ \text{eV}/kT)$ cm^{-2} s^{-1} (Fig. 3), characteristic of enhancements caused by the presence of hydrogen (cf, the normal values of D in the same figure).[12–15] The implication for the present work is that H_2 or larger hydrogen clusters must have been present in the quenched silicon to provide a source of fast diffusing interstitial atoms which collide with the oxygen atoms causing them to execute diffusion jumps at enhanced rates. The new data are in agreement with earlier measurements[15] made on silicon which had been preheated at 900 °C for 2 h: it was learned only recently that the samples had been heated in an atmosphere that contained 10% hydrogen gas.[16]

It is inferred that our quenched boron-doped silicon contained both H-B pairs and (say) H_2 pairs. During the quench, the rate of loss of atomic hydrogen would have

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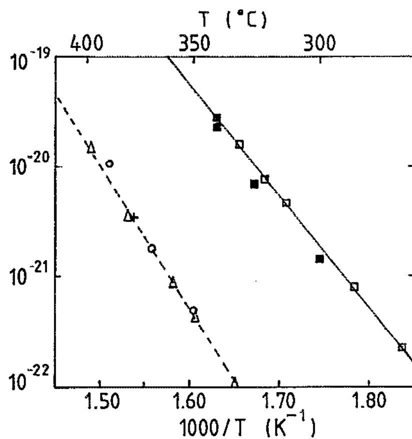

FIG. 3. Diffusion coefficient of oxygen in undoped Czochralski silicon annealed for 2 h at 900 °C in an atmosphere of hydrogen followed by a rapid quench to room temperature (solid squares) and previous results for similar material preheated in a 10% hydrogen atmosphere (open squares[15]). The normal diffusion coefficient of oxygen in silicon is also shown (dashed line).[12-15]

been expected to have the form:

$$\frac{d[\mathrm{H}]}{dt} = -4\pi D_{\mathrm{H}} r_c[\mathrm{H}][\mathrm{B}] - 8\pi D_{\mathrm{H}} r_c'[\mathrm{H}]^2,$$

where D_{H} is the diffusion coefficient of the hydrogen and r_c and r_c' are the capture radii for the formation of H-B and H-H pairs, respectively. The concentration of dissolved hydrogen would have been greater for the anneals at the higher temperatures and consequently the second term in the equation should then have become more important. It follows that (a) the values of the hydrogen solubility $[\mathrm{H}_s]$ should be greater than the concentrations of [H-B] shown in Fig. 1, and (b) the discrepancy should be greater, the higher the anneal temperature. As a result, the heat of solution of $[\mathrm{H}_s]$ would be higher than that indicated by the slope of the Arrhenius plot. However, the magnitude of any discrepancy with the data of Van Wieringen and Warmolz[6] cannot be determined at this time.

In conclusion, we have demonstrated that heating silicon to high temperatures in hydrogen gas leads to the introduction of atomic hydrogen. On quenching, there is formation of H-B pairs and other species such as H-H pairs. The former observation supports recent work in which the partial passivation of sulfur double donors to give H-S pairs in similarly treated Si was found to be due to hydrogen passivation although measurements of [H] were not reported.[17] We have found that the solubility is greater than the concentration given by $[\mathrm{H}_s] \geqslant 5.6\times 10^{18} \exp(-0.95\ \mathrm{eV}/kT)$.

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