Extended Abstracts of the 1997 International Conference on Solid State Devices and Materials, Hamamatsu, 1997, pp. 438-439

Invited

Oxygen-Hydrogen Interactions in Silicon

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1. Introduction

Heating either Czochralski (CZ) or Float Zone (FZ) Si in $D_2(H_2)$ gas at atmospheric pressure to temperatures in the range 900-1300°C leads to the rapid in-diffusion of deuterium (hydrogen). SIMS measurements (D_2) yield a solubility $H_s = 9.1 \times 10^{21} \exp(-1.80\ eV/kT)\ cm^{-3}$. In hydrogenated boron doped CZ or FZ Si ([B] ≈ $10^{17}\ cm^{-3}$), there is formation of H-B (or D-B) pairs that are detected by infrared (IR) absorption spectroscopy. Heating such material at ≈ 175°C leads to an increase in [H-B] by a factor of 3, implying the presence of additional "hidden" hydrogen in as-quenched samples. It was argued that this hidden hydrogen was in the form of H_2 molecules since 2 MeV electron irradiation leads to the formation of the H_2^* defect, also detected by IR absorption, without a change in the concentration of [H-B] pairs [1].

2. Results

These investigations have now been extended to lightly boron or phosphorus doped ($5 \times 10^{14}\ cm^{-3}$) CZ (or FZ) samples up to 1.7 cm in length. We observe the formation of an oxygen-hydrogen complex, with a frequency of 1075.1 cm^{-1} that shifts to a higher frequency of 1076.6 cm^{-1} for oxygen-deuterium complexes. Deconvolutions of the absorption profiles and those for samples pre-heated in 25:75, 50:50 and 75:25 mixtures of H_2 and D_2 show that the perturbation of the bond-centered interstitial oxygen atom (O_i) is caused by adjacent H_2, H-D or D_2 centers and that there are 2 distinct configurations, i.e. $(O_i\text{-}H_2)_1$ and $(O_i\text{-}H_2)_2$. Estimates of the concentrations of the complexes, based on the strength of the O_i absorption, imply that there is again hidden hydrogen present. A search in the high frequency spectral range reveals the presence of new absorption lines corresponding to three distinct types of H_2 complexes, labelled ν_1, ν_2 and ν_3. Each complex shows isotopic shifts to give modes ν_{1HH}, ν_{1HD} and ν_{1DD}, etc (see Table).

The dispositions of the three modes in each set, with ν_{HD} essentially midway between ν_{HH} and ν_{DD}, indicate that they are due to the vibrations of H_2, HD and D_2 molecules and not some other species such as H_2O (see Table). It is proposed that the molecules acquire small dipole moments because of internal electric fields caused by the trapping atom or defect. For example, theory has demonstrated that the isolated O_i atom acquires a negative charge of -1.2 e so that the two Si neighbors become positively charged (+0.6e).

The strengths of the ν_1 and ν_2 modes correlate with that of the 1075 cm^{-1} line, for a range of as-quenched samples and following anneals of samples up to a temperature of 300°C, confirming the assignment to $O_i\text{-}H_2$, based on the deconvolution analysis. ν_3 shows an anti-correlation with the 1075 cm^{-1} line and must be due to an $X\text{-}H_2$ centre, where X is an unknown impurity of defect. In FZ silicon, ν_1 and ν_2 are not detected, but ν_3 is present. The ν_3 mode is also found in boron doped ($10^{17} cm^{-3}$) material and the molecules responsible might correspond to the hidden hydrogen in this material. The relatively low frequencies of the H_2 vibrational modes are ascribed to a transfer of electron density from the H-H bond to form a weak bond to the adjacent O_i atom [2].

3. Conclusions

We deduce that hydrogen diffused into Si at a high temperature or introduced during growth is present primarily as H_2 molecules once the crystal has cooled to room temperature unless very rapid quenching occurs and the crystals contain acceptor impurities in a concentration of ~$10^{17}\ cm^{-3}$.

Acknowledgments

We thank R. E. Pritchard, M. J. Ashwin, J. H. Tucker and E. C. Lightowlers for their contribution to this work. We thank EPSRC (Grant GR/K96977) for financial support.

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Table 1. Vibrational frequencies

Defect	ν_{HH} (cm^{-1})	ν_{HD} (cm^{-1})	ν_{DD} (cm^{-1})	ν_{HH}/ν_{DD}
ν_1(Si)	3788.9	3304.3	2775.4	1.365
ν_2(Si)	3730.8	3285.3	2716.0 2714.9	1.374
ν_3(Si)	3618.3	3264.8	2642.5	1.369
H_2(Si)[3]	4158	-	2990	1.391
H_2(Si)[4]	4157	3629	2991	1.390
H_2(GaAs)[5]	3934.1	3446.5	2842.6	1.384
H_2 (gas)[5]	4161.1	3632.1	2993.6	1.390
H_2O (gas)[6]	3756 3657	3707 2727	2788 2671	1.347 1.369

The Raman frequency for the HD molecule was not reported in reference 3.