

# Non-cryogenic Infrared Absorption Spectroscopy for Direct Boron-Hydrogen Pair Quantification

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**Abstract.** Infrared absorption spectroscopy (FT-IR) done at room temperature can be successfully used for the quantification of boron-hydrogen pairs in crystalline silicon in the  $10^{14}$  to  $10^{15}$   $\text{cm}^{-3}$  range, where the detection limit is found to be in the low  $10^{14}$  range. If the fraction of hydrogen that pairs with boron is known, it can be used to draw conclusions about the total hydrogen content in c-Si. Several measurements over the course of formation and dissociation of boron-hydrogen pairs can be obtained comparatively easily due to the lower effort at room temperature. Unlike other methods aiming for the unspecific change in net doping apparently caused by the formation of BH-pairs, the analysis of local vibrational mode (LVM) excitation is highly specific and allows to distinguish between BH-pair formation and other effects impacting hole concentration. Besides the analysis of LVM excitation, the interaction of infrared light with the free electron plasma (Drude's model) allows for a quantification of hole concentration as well, and thus allows for a direct cross-check with the LVM analysis.

## INTRODUCTION

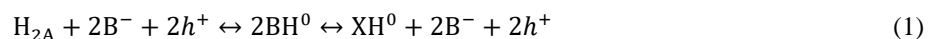
In the context of Light- and elevated Temperature-induced Degradation (LeTID) hydrogen is suspected to contribute to the formation of recombination-active defects [1,2]. Unfortunately, the quantitative link between hydrogen bulk concentration and defect passivation/formation is not easy to establish due to its comparatively low concentration in the  $10^{14}$  to  $10^{15}$   $\text{cm}^{-3}$  range. Indirect hydrogen quantification studies take advantage of the tendency of hydrogen to form dopant-hydrogen pairs and thus change the resistivity [3,4], however, this change is unspecific and changes in resistivity may arise from other sources as well.

Fourier-transformed infrared (FT-IR) absorption spectroscopy, on the other hand, allows for a detection of local vibrational modes (LVM) of impurities such as dopant-hydrogen pairs. In the past, this has been done preferentially with time-consuming measurements at cryogenic temperatures [5,6,7]. Within this contribution, the applicability of room temperature FT-IR spectroscopy is evaluated and extended by investigations on the net doping.

## EXPERIMENTAL

### Boron Hydrogen Pair Dynamics

Boron-hydrogen pair (BH) formation between FT-IR measurements in this study was triggered by annealing in darkness at 220°C. The assumption of first order reaction kinetics of the probably occurring reaction [8,9]



where  $XH^0$  denotes for an electronically neutral state of hydrogen which could be binding to other impurities, effusion or the  $H_{2C}$  dimer predicted by Voronkov and Falster [8]. Since the formation of BH pairs consumes a hole  $h^+$  which is released again after subsequent dissociation, a dark anneal has a substantial impact on hole concentration  $p$ . Neglecting a possible  $p$ -dependence due to  $p \gg [BH]$  suggests a double exponential curve

$$[BH](t) = A_1 \cdot \exp(-t/t_1) + A_2 \cdot \exp(-t/t_2) + A_\infty \quad (2)$$

with time constants  $t_{1,2}$  and amplitudes  $A_{1,2}$  for formation and dissociation of boron-hydrogen pairs. The constant  $A_\infty$  would equal to zero for complete dissociation of BH pairs, however, there might be a reaction equilibrium between  $BH^0$  and  $XH^0$  such that  $[BH] \neq 0$  in the long term.

## Absorption in Silicon

In FT-IR spectroscopy, the loss in transmittance of infrared light by absorption (and reflection) is measured. According to Beer-Lambert's law, signal strength essentially depends on optical path length. Hence, weak absorption of impurities present only in low concentration can be countered by a large sample width. Loss in transmittance occurs due to two interactions of infrared light with the sample: (i) Excitation of local vibrational modes (LVMs) of polar impurities like boron-hydrogen pairs (BH) with the integrated absorption coefficient  $\alpha_{BH}$  being proportional to the concentration of absorbing centers  $[BH]$  [10]. (ii) Excitation of the quasi-free electron plasma with Drude's model predicting a  $1/\tilde{\nu}^2$  ( $\tilde{\nu}$  – wavenumber) dependency

$$\alpha_{\text{Drude}} \propto \frac{\omega_p^2}{\tilde{\nu}^2} \propto \frac{p}{\tilde{\nu}^2} \quad \text{with} \quad \omega_p^2 \propto p \quad (3)$$

with plasma frequency  $\omega_p$  depending on hole concentration  $p$ . Thus, the change in hole concentration relative to a reference condition ( $\alpha_{\text{Ref}}, p_{\text{Ref}}$ ) can be calculated from Drude absorption  $\alpha_i$  by

$$\Delta p = p_{\text{Ref}} \cdot (1 - \alpha_i/\alpha_{\text{Ref}}) \quad (4)$$

Due to the formation of BH pairs,  $p$  deviates from the doping concentration  $N_{\text{dop}}$ , thus  $p = N_{\text{dop}} - [BH]$ . The absorption coefficient spectra were obtained from transmittance  $T$  data according to Beer-Lambert's law with an optical path width  $d = 9.8$  mm:

$$T = \frac{I_{\text{sample}}}{I_0} = \exp(-\alpha d) \quad (5)$$

where  $I_{\text{sample}}$  ( $I_0$ ) denotes for transmitted beam intensity of the sample (with empty sample holder). By neglecting surface reflection effects, the determined concentration of absorption centers is prone to error of about 10%. Absorption spectra  $\alpha_{BH}$  were obtained by fitting the Drude background (Eq. (3)) together with a Gaussian (fit range between 1600 and 2400  $\text{cm}^{-1}$ ) to describe the BH stretching mode excitation.

## Sample Preparation

For the study on boron-hydrogen pair dynamics presented here, hydrogen-rich amorphous silicon nitride ( $\text{SiN}_x\text{:H}$ ) of thickness 200 nm was deposited on 1  $\Omega\text{cm}$  B-doped, chemically polished float-zone (FZ) silicon wafers of 250  $\mu\text{m}$  thickness in a PECVD process (reactive gases:  $\text{SiH}_4\text{:NH}_3=27\text{:}13$ ; temperature 400°C; carrier gas:  $\text{N}_2$ ). The samples were exposed to high temperatures (around 870°C peak sample temperature) in a fast-firing furnace with a fast cool-down rate to introduce hydrogen into the silicon bulk. Afterwards, the samples were cut in 10 mm wide stripes and the edges were mechanically polished to improve light coupling by providing an optically smooth surface. The final optical path length after polishing was found to be  $d = 9.8$  mm. Furthermore, a multitude of stripes were stacked to increase the volume sampled during FT-IR measurements.

Samples for the resistivity measurements were produced by thermal vapor deposition of aluminum contacts and subsequent laser pulses to ensure good contact [11] on bare, chemically polished FZ-Si:B wafers (1  $\Omega\text{cm}$ ). Resistivity measurements were made with a setup that is described elsewhere [4].

Between each measurement, all samples were dark annealed on a hotplate at  $T = 220^\circ\text{C}$  to trigger BH formation and subsequent dissociation.

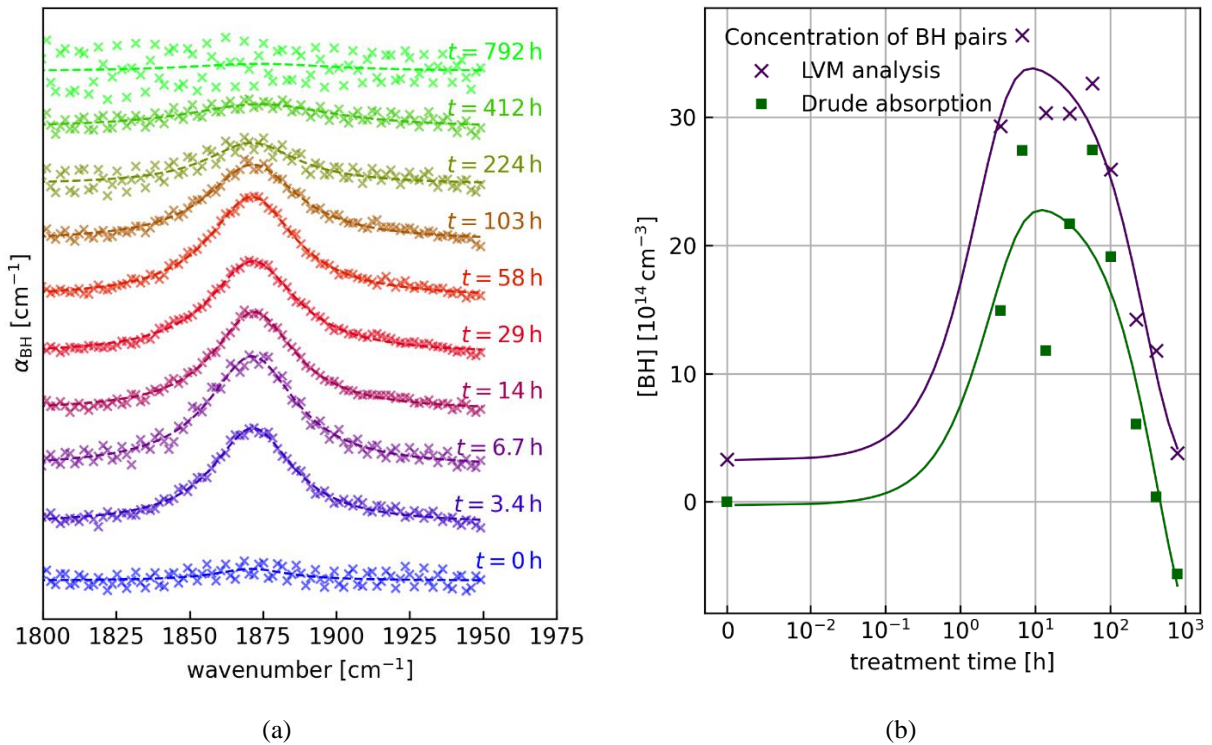
The absorption coefficients  $\alpha_{\text{BH}}$  and  $\alpha_{\text{Drude}}$  were determined from transmittance data taken with a Vertex series tool (Bruker), resolution  $\nu = 2 \text{ cm}^{-1}$ , where each measurement was averaged for 15 min to sufficiently reduce noise level. The visible scattering, especially for spectra with low BH pair excitation, is not related to noise, but to unavoidable interference caused by internal reflection.

## RESULTS AND DISCUSSION

In Fig. 1 a) one can clearly see the expected rise and fall of the absorption caused by the BH stretching mode at  $\tilde{\nu} = 1868 \text{ cm}^{-1}$  for different times during the dark anneal.

The integrated peak area was converted to an absolute binding concentration present in the sample with a calibration factor obtained from previous work [12]. The concentration calculated in this way is shown in Fig. 1 b) for different times. As can be seen, the formation and dissociation of the pairs matches the model (see Eq. 1) shown before, i. e. the fit with two exponential functions is sufficient to describe the data.

The great advantage of BH-pair quantification by FT-IR is not only the direct detection of specific LVMs, but also the determination of the absolute concentration. Other methods relying on the change in net doping (e. g. [3,4]) always only yield the difference to a reference state that is not necessarily free of BH-pairs, and, therefore, probably underestimate the true BH-pair concentration. For example, taking only the change in [BH] in Fig. 1 b) into account and thus neglecting the initially present concentration of  $2.5 \times 10^{14} \text{ cm}^{-3}$  results in a maybe still acceptable underestimation of 10% in this case. However, neglecting initially present BH pairs can become increasingly critical when it comes to statements on apparently hydrogen-free samples.



**FIGURE 1.** (a) Baseline-corrected absorbance signal of the BH stretching mode at different times  $t$  during the formation and subsequent dissociation of boron-hydrogen pairs. Dashed lines show fitted Gaussian curves to the raw data (scatter is caused by interference fringes). (b) Change in BH concentration during annealing at  $220^\circ\text{C}$  in darkness derived by either the absorption of the BH stretching mode (LVM) or relative change of free carrier absorption (Drude's model) with respect to  $p_{t=0}$ . Lines represent double exponential fits expected for first order reactions (Eq. 2).

Another main advantage of performing FT-IR measurements at room temperature is the additional information on hole concentration  $p$  contained in the Drude term  $\alpha_{\text{Drude}}$  that would not be given at cryogenic temperatures where doping freezes-out partially and plasma excitation is strongly suppressed. However, it should be noted that quantification of hole concentration by FT-IR is subject to the above-mentioned restrictions and allows only to quantify a change in hole concentration  $-\Delta p = p - p_{\text{Ref}}$  unless the dopant concentration  $N_{\text{dop}}$  in the absence of BH pairs is sufficiently well known, i. e. to a fraction of [BH].

The data thus generated are in good agreement with the previous observations considering the LVM of BH, regarding amplitude and time constants of BH dynamics, as shown in Fig. 1 b). The differences between the data sets, especially the different initial value and part of the offset, are due to the different nature of the evaluation: concentrations from the vibrational mode are absolute, while the concentration from the change in hole concentration corresponds only to a difference to a reference state. This would only give an accurate result for a reference state with no BH pairs present which does not occur in our experiment.

## CONCLUSION

The detection of boron-hydrogen pairs by means of absorption spectroscopy is possible at room temperature. This direct quantification is able to determine absolute concentrations of the binding concentration and is not restricted to changes. During measurements at room temperature, the doping does not freeze out and additional conclusions can be made about the change in hole concentration. This method could be used to check whether resistivity changes in silicon are related to boron-hydrogen pair formation/dissociation or caused by something else.

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