Application Note AN M55

Research on Shallow Impurities in Silicon

Quantification of shallow impurities in Silicon

Nowadays most electronic devices are controlled by Silicon based processors. Furthermore the photovoltaic market has rapidly grown since the turn of the millennium and the vast majority of solar cells relies on Silicon as well. Therefore the worldwide demand for pure Silicon and as a consequence also its price has strongly increased and has influenced the financial world.

For industrial Si quality control the Bruker CryoSAS is for sure the ideal FTIR analysis system, fulfilling all requirements for an industrial environment. On the other hand for research and development applications, solutions based on INVENIO R and VERTEX research FTIR spectrometers provide more flexibility and are discussed within this application note. Besides the concentration of Carbon and Oxygen (see application note 54) also the content of so-called shallow impurities is of prime importance since they significantly affect the electrical properties (e.g. the resistivity) of the material. Shallow impurities can be subdivided into the group V elements P, As and Sb, acting as electron donors and the group III elements B, Al, Ga and In, affecting the Silicon as electron acceptors (see figure 1).

Of all the above named shallow impurities, Boron and Phosphorous take on a special position since their concentrations are typically the highest of all shallow impurities and are therefore of particular interest.

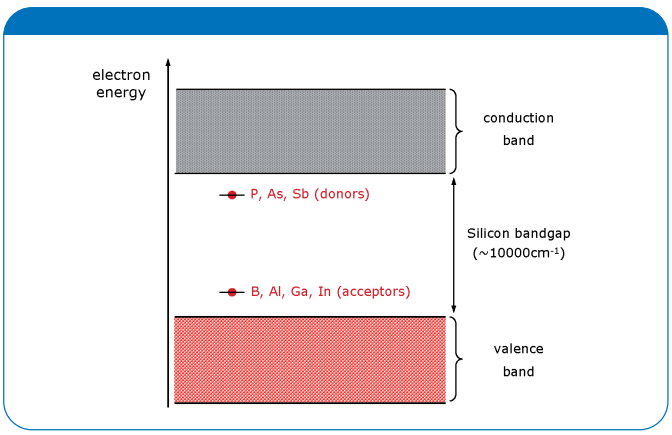

Fig. 1: Simplified electron energy level scheme of shallow impurities in Silicon: donor levels are situated closely below the conduction band while acceptor levels are closely above the valence band.

Far infrared FTIR analysis of shallow impurities

The far infrared (FIR) quantification of shallow impurities is based on the method described in ASTM F1630 respectively SEMI MF1630 and, according to these standards, it requires single crystal Silicon. However this method is also of interest for polysilicon because polysilicon can be converted into single crystal Silicon, e.g. by the process described in ASTM F1723 respectively SEMI MF1723 or related techniques.

Unlike most FTIR based quantification methods the analysis of shallow impurities does not rely on vibrational but on electronic transitions. Shallow impurities exhibit a series of sharp absorption lines in the FIR due to transitions of donor bound electrons respectively acceptor bound holes. In fact the detection of these transitions requires that the sample is cooled down below 15K in order to make sure that the impurities are not ionized. In other words: the heat energy kB*T (Boltzmann constant times temperature in Kelvin) must be considerably smaller than the binding energy between the electron (respectively hole) and the impurity of interest. Although a small standard cryostat with only one sample position is in principle sufficient, such a configuration is time consuming and rather uncomfortable. In order to improve the sample throughput, Bruker offers an alternative, more sophisticated cryostat with an automated sample holder for up to 6 samples, which still fits inside the sample compartment of the VERTEX 80v vacuum FTIR spectrometer (see fig. 2). All sample positions can be addressed via software control within one cooling cycle, providing a more comfortable solution. The same cryostat is also suitable for Carbon quantification in Silicon where the lowest detection limits are achieved by low temperature measurements at 77K (see application note 54). This means that Bruker can provide a high accuracy all-in-one solution for low temperature analysis of all relevant Silicon impurities.

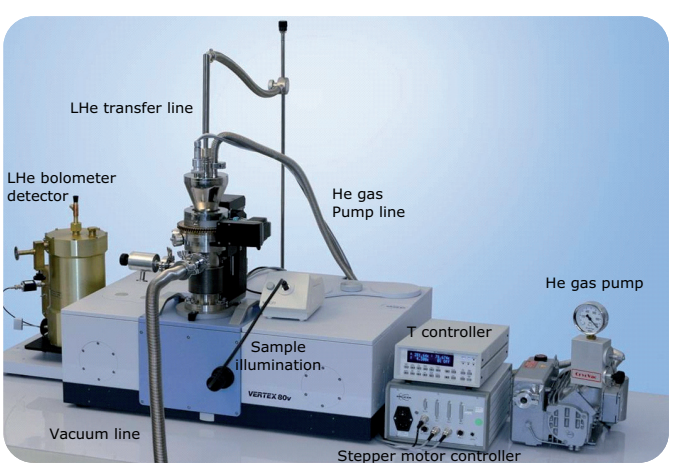

Fig. 2: VERTEX 80v with automated cryostat for shallow impurity quantification in FIR transmission mode. For lowest detection limits down to the single digit ppt range (10^{-12}), a liquid He cooled bolometer detector is required (see left hand side). For moderate concentrations a room temperature DTGS detector inside of the detector compartment is sufficient. The additional illumination with visible light is realized via fiber optics adapted to the front side of the sample compartment.

It is essential that the sample is illuminated with an additional visible light source during the measurement: if the sample contains both donors and acceptors (e.g. Phosphorous and Boron) they partly compensate each other and the measurement would only result in the net majority carrier concentration. The visible illumination avoids this error: it contains photons with an energy larger than the Si bandgap, and continuously excites electrons and holes neutralizing the compensated impurities. Because the method requires a spectral resolution in the order of 0.5 cm^{-1} the sample must have a minimum thickness of approx. 3 mm so as to avoid that interference fringes cover the signal. In order to achieve best results the sample has to be double sided polished.

For far infrared quantification of shallow impurities, a vacuum FTIR spectrometer such as the VERTEX 80v is highly recommended because particularly in the FIR residual water vapour exhibits strong absorption lines due to rotational transitions which may mask the weak signals of interest. The highest sensitivity with an achievable detection limit in the order of 1 ppt ($5*10^{10}$ atoms/cm^3) for Boron and Phosphorous can be reached using a liquid Helium cooled bolometer detector. Figure 3 shows a bolometer measurement on a 4mm thick sample, cooled down to 5 K: the whole series of absorption lines is due to Boron and Phosphorous related impurity transitions.

According to ASTM F1630 or SEMI MF1630, the Boron and Phosphorous content are determined by integration

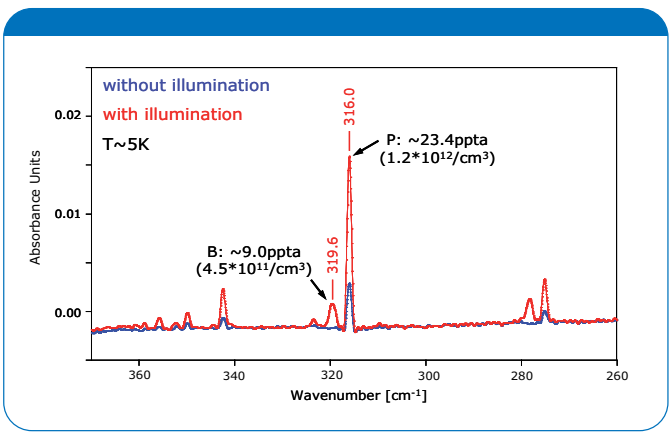

Fig. 3: FIR absorbance of a 4 mm sample at T = 5 K measured with a liquid He cooled bolometer detector. Although the measurement duration was only 40 s, a detection limit for Boron and Phosphorous clearly below 10 ppt was achieved. Comparison of the blue and the red curve proves the necessity of the additional visible illumination.

of the bands at 319.6 cm^{-1} respectively 316.0 cm^{-1}. Based on Lambert-Beer's law, the impurity concentration can be determined by multiplication of the integrated band area by the corresponding calibration factor and taking into account the sample thickness. The whole data evaluation can comfortably be realized by the OPUS/SEMI package using evaluation algorithms based on the above mentioned standards (see figure 4).

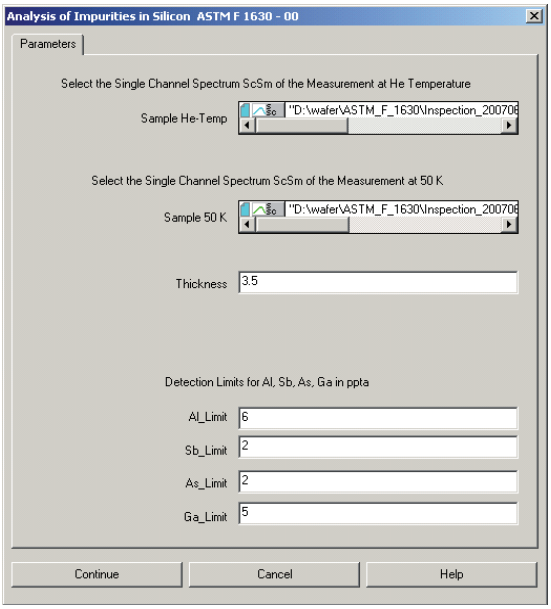

Fig. 4: Screenshot of the OPUS/SEMI software for evaluation of shallow impurities from FIR transmission measurements. The quantification of Boron and Phosphorous is standard while for the remaining, less common shallow impurities the user can define detection limits.

The shallow impurity absorptions related to Al, As, Sb and Ga are situated in the range between 290 cm^{-1} and 550 cm^{-1} and can be measured with the same FIR setup as Boron and Phosphorous. Only Indium is an exception since it causes transitions at approximately 1176 cm^{-1} and thus requires additional mid infrared components.

The purity requirements for solar grade Silicon are typically less demanding than those for electronic grade Silicon. Therefore a standard room temperature DTGS detector is often adequate to investigate this material type: as shown in figure 5, already with this setup detection limits well below 100 ppt ($5*10^{12}/cm^3$) for Boron and Phosphorous can be reached.

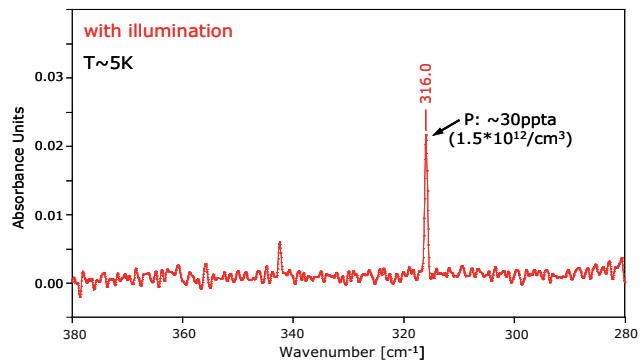

Fig. 5: FIR absorbance of a 3.5 mm sample at ca. T = 5 K, measured with a room temperature DTGS detector. The measurement duration was approximately 8 minutes. While a Phosphorous concentration of 30 ppt was clearly detected, the Boron concentration of this sample was below the detection limit.

Photoluminescence FTIR analysis of shallow impurities

Besides the FIR approach, shallow impurities can alternatively be quantified by near infrared (NIR) photoluminescence (PL). This method is described in detail in ASTM F1389 respectively SEMI MF1389 and also requires single crystal Silicon. The different spectral range of the PL method compared to the FIR approach is pointed out in figure 6.

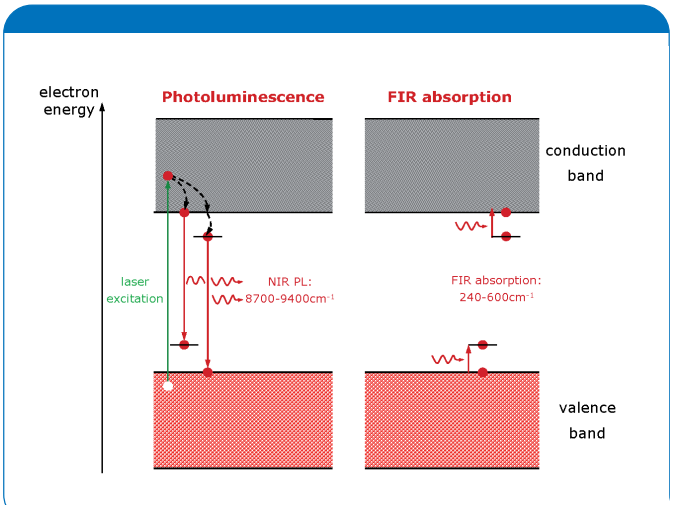

Fig. 6: Simplified electron energy level scheme for shallow impurities in Silicon in order to clarify the different spectral range of photoluminescence and FIR transmission method.

For cooling down the sample has to be immersed into liquid Helium (temperature ~4.2 K) and is excited with a visible (typically green) excitation laser. The signal of interest is the photoluminescence emitted due to the recombination of so-called excitons (bound electron hole pairs). While the free

excitons give rise to an emission at approximately 8850 cm^{-1}, a fraction of excitons is captured by shallow impurities. The resulting PL signal of shallow impurity bound excitons is a series of emission lines the spectral position of which is sensitive to the type of impurity (see figure 7). Compared to the FIR method the quantification via photoluminescence has pros and cons. The overall PL intensity and thus the sensitivity depend strongly on the surface treatment (typically a combination of polishing and etching).

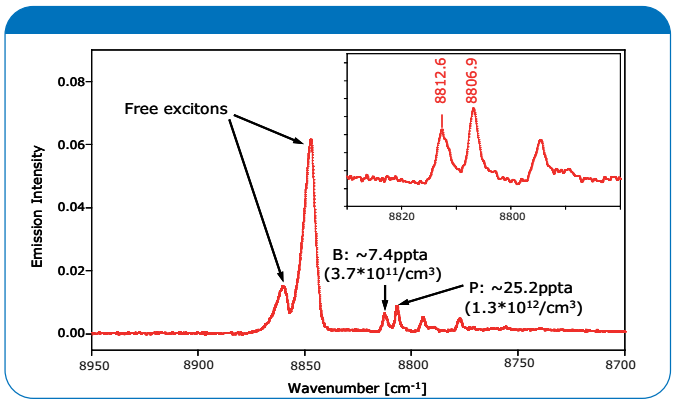

Fig. 7: NIR photoluminescence measurement on Silicon, containing Boron and Phosphorous in the low ppt range. The data was acquired at liquid Helium temperature (4.2 K), using a customized PL module with bath cryostat and 532 nm excitation laser, adapted to a VERTEX 80 FTIR spectrometer equipped with NIR beam splitter and high gain InGaAs detector. The measurement duration was 8 minutes using a spectral resolution of 0.5 cm^{-1}

Provided the surface properties are ideal, the achievable detection limit of the PL method can be lower than in the FIR spectral range with bolometer detection. Using optimized detectors and excitation conditions, even detection limits less than 1ppta are achievable via the photoluminescence method. Furthermore low temperature photoluminescence may also be used for the analysis of epitactical Si layers e.g. deposited via CVD from trichlorosilane. Furthermore the penetration depth of the laser is in the order of a few microns, meaning that there is practically no lower limit for the sample thickness. On the other hand the PL configuration is more complex than the FIR setup, although NIR PL detection does not necessarily require a vacuum spectrometer. Because the excitation laser creates significant additional heat a rather large liquid Helium bath cryostat is required to keep the sample at sufficiently low temperatures. An alternative cryostat solution basing on pulse-tube cooling without the need of cryogenic liquids is also available. The measurement is implemented in an external customized module adapted to the FTIR spectrometer. Besides the cryostat the module contains the excitation laser with automated intensity control, excitation optics and PL collection optics which couple the emitted light into the FTIR spectrometer where it is finally analyzed (see figure 8). In contrast to the FIR cryostat, the PL cryostat cannot be used for quantification of Carbon and Oxygen (see application note 54), which might be a disadvantage if these impurities are of interest as well.

Fig. 8: Customized module for Silicon impurity photoluminescence, adapted to a VERTEX 80v FTIR spectrometer. The samples are mounted in a liquid Helium bath cryostat in order to compensate the heat, created by the visible excitation laser

The underlying quantification principle is the evaluation of the PL intensity ratio of impurity bound to free excitons which is proportional to the concentration of the corresponding impurity type. In order to account for intensity dependent effects, the accuracy of the PL approach benefits from calibrated samples with known impurity concentrations (e.g. determined by FIR transmission). Also in case of photoluminescence the data evaluation can be carried out with the OPUS/SEMI software package whereas the quantification algorithm is closely related to the approach of the above mentioned ASTM respectively SEMI standards.

Bruker has more than 30 years of experience regarding the infrared analytics of the whole range of materials, including semiconductors. The world's leading researchers and Si manufacturers trust in our products and in our know-how for reliable and sensitive quantification of impurities. Do not hesitate to contact your local Bruker representative in order to find out the ideal configuration for your application.

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