Time-Resolved In-Situ Temperature Measurements Using Band-Edge Absorption Spectroscopy During MBE Growth

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It is a well-known problem in molecular beam epitaxy (MBE) that the real sample temperature is in most cases unknown during the growth process. We have used a commercial band-edge absorption spectroscopy system to determine the sample temperature during bake-out and growth of different types of samples. Time-resolved in-situ measurements show how the sample temperature is influenced by different external effects and also demonstrate some limitations of precise temperature determination. This helps to understand the temperature behavior of GaAs-based samples during a growth run.

1. Introduction

One of the most crucial parameters in semiconductor epitaxy processes is the substrate temperature. In strongly chemistry-based techniques, e.g., metal-organic vapor-phase epitaxy, it has a major influence on the chemical reactions between incoming atoms or molecules and thus the efficiency of these processes. In molecular beam epitaxy, the more important effect is the change of surface mobility of the adsorbed adatoms[2] with temperature. It influences the crystal quality and defect density. Also the ratio of adsorption and desorption of particles of different species (which determines the material composition) can be temperature-dependent. Nearly all properties of the grown material like luminescence spectrum and efficiency, surface roughness or carrier mobilities are strongly influenced by the substrate temperature during the epitaxial process ([1], pp. 183 ff.).

In MBE growth chambers, the sample temperature can be determined in different ways, namely thermocouple (TC), pyrometry or RHEED[3]-assisted methods, as well as band-edge absorption spectroscopy (BAS). Each method offers different degrees of precision, reproducibility, and range of use:

- **Thermocouple**
  The thermocouple is usually located behind the sample holder near the sample heater and has no physical contact with the rotating sample. The entire temperature range of interest is covered and the measurement is reproducible. Therefore it is predestined for temperature control.

[2]In crystal growth, atoms which are adsorbed at a substrate surface are called *adatoms*. Their behavior is influenced by chemical bonding to the surface material.

[3]Reflection high-energy electron diffraction (RHEED) is a technique to investigate the surface condition of a crystalline sample by the diffraction pattern caused by a focused electron beam.

- **Pyrometer**
  Pyrometers detect black-body radiation emitted from the sample itself. To obtain a suitable black-body spectrum, the sample must have a temperature of 400 °C or more. The emission factor (0.7 for GaAs [2]) may have to be corrected for changes in the emission characteristics of the sample holder or of the transmissivity of the chamber viewport over time. Heat radiation reflections from the effusion cells can have strong influences on the registered spectrum and the calculated temperature.

- **RHEED**
  During bake-out of GaAs wafers, desorption of the oxide layer on top of the sample takes place. This transition from amorphous to ordered surface condition can be recognized in an abrupt change of the RHEED pattern from diffuse scattering to a diffraction pattern according to a structured surface. This transition happens at a substrate temperature of 582 ±1 °C [3]. A second but very inaccurate use of RHEED is to distinguish between different patterns caused by different surface conditions, which depend on the temperature but also on the arsenic flux. This method has very limited use since the patterns change only slowly over a temperature range of several tens of Kelvin.

- **Band-edge absorption spectroscopy**
  BAS is based on intrinsic absorption of light passing through semiconductor material. Detected with a spectrometer, the wavelength of the absorption edge in the measured spectrum can be related to a certain temperature. Observing the shift to longer wavelengths with increasing temperature allows to determine the substrate temperature over a wide range.

2. Principles of Band-Edge Absorption Spectroscopy

Semiconductors experience a reduction of their bandgap energy E_g with increasing temperature. This shift can be described by the empirical Varshni formula [4]

$$E_\mathrm{g}(T) = E_\mathrm{g}(0\,\mathrm{K}) - \frac{\alpha T^2}{\beta + T} \quad .$$

The material-dependent parameters α and β for intrinsic GaAs are noted in Table 1. More sophisticated models of the temperature dependence of semiconductor bandgaps have been established by Viña et al. [6] and Pässler et al. [7].

Table 1: Varshni parameters of intrinsic GaAs according to Thurmond [5].

Parameter	Value
$E_\mathrm{G}(0\,\mathrm{K})$	1.519 eV
α	$5.405 \cdot 10^{-4}$ eV/K
β	204 K

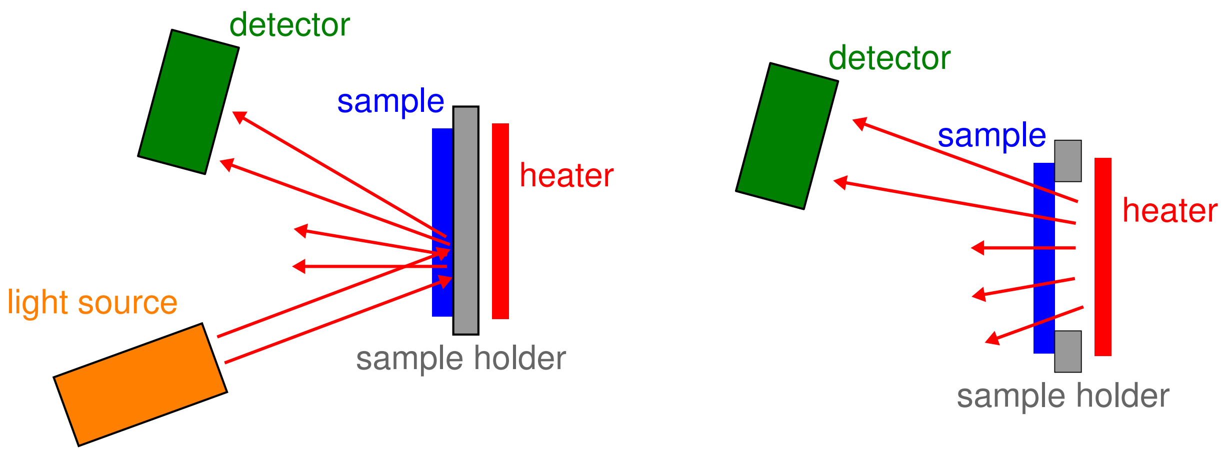

Fig. 1: Schematic drawing of the reflection mode (left) and the transmission mode (right) of band-edge absorption spectroscopy. The reflection mode requires an external light source and one additional viewport in the growth chamber.

In BAS, light has to pass at least once through a semiconductor substrate. For high-bandgap material (e.g., sapphire) the visible range is favored, for lower-bandgap semiconductors like GaAs, the near-infrared spectral range from 800 to 1400 nm is appropriate for detection of the absorption edge. The measurement can be done in reflection mode as shown in the left part of Fig. 1, which means that the sample is illuminated by an external light source with a continuous spectrum. The light enters the substrate and is scattered at the unpolished back side of the wafer. This mode can be used for both, indium-mounted and indium-free-mounted wafers. For this configuration an additional viewport of the vacuum system is needed. With indium-free-mounted wafers on substrate holders with an opening, one can use the black-body-like radiation from the substrate heater. In this transmission mode (right part of Fig. 1), the light is scattered at the unpolished back side of the wafer before passing through the material. In both modes, scattering is important to make the setup more insensitive to the location of the detector. Light with higher energy than the bandgap energy is strongly absorbed when passing the semiconductor, while lower-energy photons are transmitted nearly without losses. This leads to an optical spectrum as shown in Fig. 2. Spectral shifts indicate changes in the temperature of the semiconductor due to the temperature-dependent bandgap.

2.1 Experimental setup

The MBE system used for these investigations is a solid-source Riber 32 growth chamber, equipped with two gallium cells, three aluminum cells, one indium cell and a valved arsenic cracker. Doping can be introduced by a solid-source silicon cell for n-type material and a CBr_4 gas line for p-doping. The system reaches a base pressure of $2 \cdot 10^{-11}$ Torr by means of the attached cryo pump and an ion getter pump.

For temperature determination by BAS, we have used the commercially available BandiT system (NIR Model). The system consists of the controller with integrated spectrometer and computer interface, the detector head for fiber coupling, and a halogen lamp for

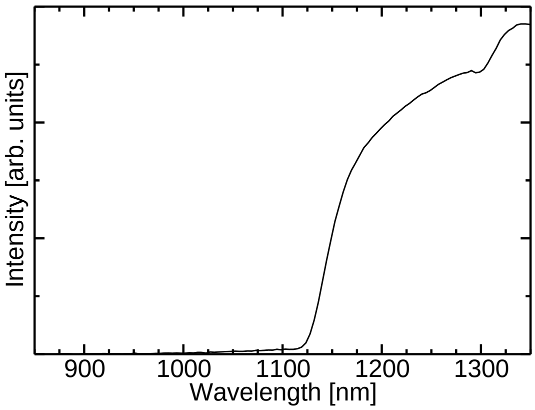

Fig. 2: Transmission spectrum of light passing through an undoped GaAs substrate at a temperature of 582 °C (verified by RHEED transition).

reflection mode measurements[4] (see Fig. 3). The detector head with the fiber coupler was connected to the pyrometer viewport of the chamber which is directed onto the sample if the manipulator with the substrate holder is in growth position. The halogen lamp, which is necessary for reflection mode measurements, could not be installed because of the lack of an adequate second viewport. So only transmission mode measurements were performed. This limits the lowest measurable temperature to approximately 400 °C. Below this temperature, the black-body-like substrate heater emission spectrum is too weak for a reliable detection of the absorption edge.

The BandiT system does not refer to a theoretical band-edge but relies on comparison with reference data supplied by the manufacturer. These references are specified by the material, thickness, doping type, doping level and manufacturer of the substrate. Our substrate material was not included in the supplied substrate database. As a best suited reference we chose a substrate with same doping and doping level and similar thickness than our actual wafer type. This might be the reason why the determined temperature varies from the real one by approximately 5 K. This deviation was determined by observing the deoxidation behavior with the RHEED system. Nevertheless the data are much more precise than those obtained with thermocouple measurements or pyrometry at lower temperatures.

The software subtracts from the measured spectrum a black-body part which is not correlated to absorption features. The remaining, corrected and normalized spectrum is used to create a linear fit to the lower part of the absorption edge. The intersection of this straight line and the abscissa results in a wavelength which is compared with the above-mentioned reference data to determine the substrate temperature.

Problems occur when the black-body part dominates the received spectrum. This can be the case when, due to misalignment, the detector head collects light not from the sample but from other hot parts in the chamber like for example the substrate holder. In some geometrical circumstances, strong black-body radiation from the glowing cells can directly be reflected into the detector by the polished wafer surface. Under such conditions, the fit algorithm cannot properly determine the actual temperature.

[4]More information about the BandiT system and its specifications can be found at the manufacturer's website: *http://www.k-space.com/Products/BandiT.html*

Fig. 3: Hardware of the BandiT band-edge absorption spectroscopy system, consisting of a controller with spectrometer, a fiber-coupled detector head and a halogen lamp.

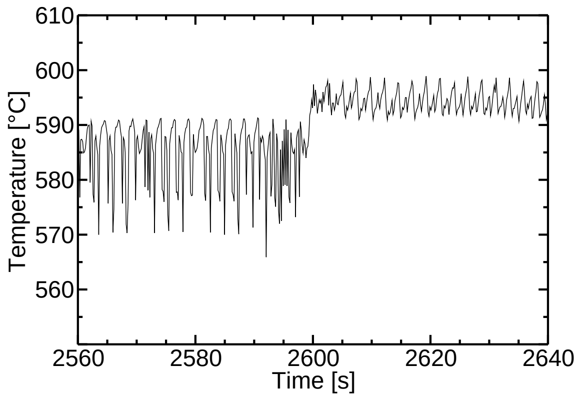

Fig. 4: Spurious temperature oscillations caused by the rotation of the substrate. At 2600 s, the Ga shutter was opened, which results in a rise of the sample temperature.

2.2 Time-resolved measurements

The BandiT system enables real-time measurements and data recording. The algorithm calculates the temperature from each spectrum every 1 to 2 seconds and saves it in a data file. The measured spectra are only shown on the computer screen but are not saved, since the amount of data would be far too large. Thus after measurement it is not possible to check the fit results and the original spectra.

The sample holder is rotating during preparation and growth to ensure good homogeneity or at least radially symmetric growth conditions. During rotation, the wafer can tilt by approximately some tenths of a degree, which influences the obtained spectrum. This results in a spurious variation of the calculated substrate temperature. As can be seen in Fig. 4, these oscillations can exceed 10 K. The time period of the oscillations in the recorded temperature can clearly be correlated to the rotation period of the sample holder.

From time to time the system produces some measurement errors. These can be identified by drastic one-point outliers in the saved temperature function. Especially during cool-down or at lower substrate temperatures the errors occur because of the low intensity of the heater's black-body radiation. These artefacts have been deleted in the diagrams shown here.

Time-resolved measurements of the temperature were performed during the entire growth of the samples presented in what follows.

3. Time-Resolved Investigations During MBE Growth

Two samples, namely an edge-emitting laser structure containing a quantum dot active region and a vertical-cavity surface-emitting laser (VCSEL), have been investigated during their complete growth process. The long growth times and thick layers are the sources of several effects which should be taken into account in future applications of band-edge absorption spectroscopy.

3.1 Sample A: quantum dot edge-emitting laser

The sample is an edge-emitting laser structure with five $In_{0.7}Ga_{0.3}As/GaAs$ quantum dot (QD) layers in the active region for an emission wavelength of about 1250 nm. The active region is surrounded by two 1.3 µm thick AlGaAs layers containing up to 50 % aluminum. The lower one is n-doped (Si), the upper one is p-doped (C), both up to a level of $2 \cdot 10^{18}\,\mathrm{cm}^{-3}$.

Growth conditions

The layer stack was grown on a 500 µm thick n-doped GaAs wafer with (001)-oriented surface. The wafer was thermally deoxidized under arsenic flux at a thermocouple temperature of 540 °C. The BAS temperature for deoxidation was 589 °C. This temperature was also used for the growth of the AlGaAs layers. In MBE growth, lower substrate temperatures are chosen for the growth of indium-containing layers to decrease indium desorption. For the quantum dot layers, the growth temperature was decreased to 420 °C (TC) or 470 °C (BAS). Previous experiments had shown that this growth temperature leads to optimized optical properties and good crystal quality of the quantum dots.

Experimental results

The complete temperature profile determined by the BandiT system is shown in Fig. 5. At the beginning, the temperature is quite stable during the growth of the first AlGaAs cladding layer. Because the absorption edge is caused by the lowest bandgap, the higher bandgap of the cladding layers should not be problematic. For the second cladding layer one can see a slightly oscillating temperature. Because the thermocouple showed stable behavior, these oscillations seem not to be caused by the heater but originate from the BandiT device. As a possible reason, Fabry–Pérot resonances of light passing the growing AlGaAs layer may influence the obtained spectra in such a way that the fitting algorithm determines a slightly changing temperature.

Figure 6 depicts a more detailed graph of the temperature profile during growth of the quantum dot layers. The recurring temperature drops indicate ten-second-long growth interruptions between quantum dot layer and barrier material. The Ga cell (Ga1) used for the barrier was kept at 886 °C. The cell growth of the QDs involved a second Ga cell (Ga2) at 718 °C and an In cell at 658 °C. During all this time, the thermocouple temperature and the temperature controller output were quite constant, which means that heat generation by the substrate heater was also constant. Rising substrate temperatures can clearly be correlated to the openings of different shutters. If the hot Ga1 cell is opened, the substrate temperature is 2 K higher than with the combination of the Ga2 and In cells. This shows that the hot cells act as additional head sources from the front side, which increase the sample temperature but do not influence the thermocouple measurement behind the sample. This effect is expected to be larger for higher growth rates that require higher cell temperatures.

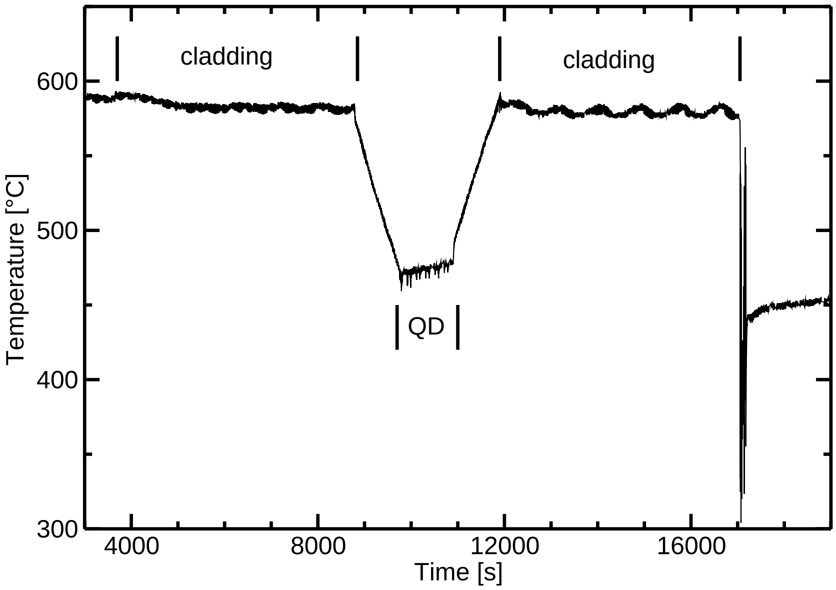

Fig. 5: Temperature profile determined with band-edge absorption spectroscopy of sample A. The oscillations during growth of the second cladding layer are no real fluctuations of the sample temperature but are caused by the measurement method.

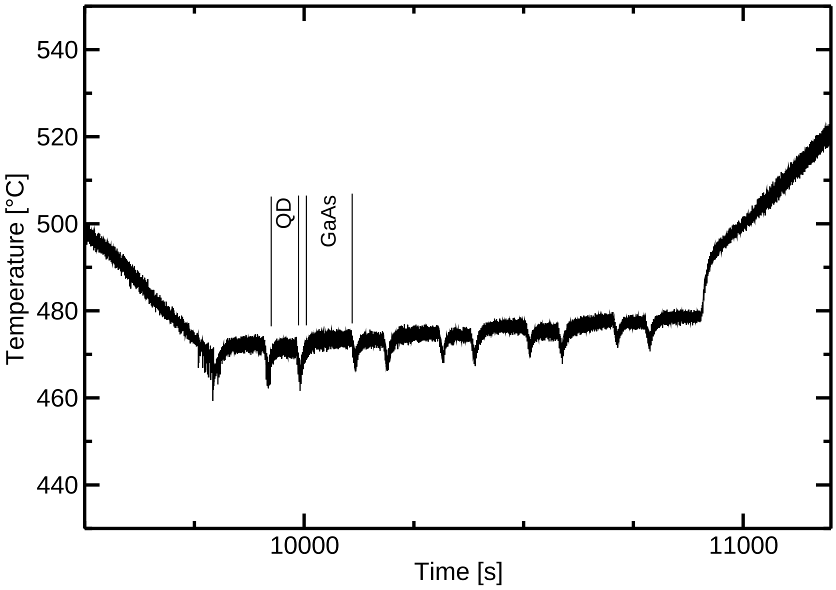

Fig. 6: Detailed time-dependent temperature during growth of the quantum dot active region of sample A. The temperature dips indicate closure of all shutters for 10 seconds, separating quantum dot and barrier material growth.

3.2 Sample B: vertical-cavity surface-emitting laser

The second investigated sample is a VCSEL structure. The main difference to sample A are the Bragg mirrors which are necessary for constituting the vertical cavity. The Bragg mirrors consist of periodically repeated AlGaAs layers with varying aluminum content from 20 % to 90 %, which results in a periodic variation of the refractive index. The period length of these layers is designed to be one half of the wavelength in the material. In this special VCSEL, the first grown mirror contains ten repetitions, the second one 38 mirror periods. The active region is composed of three $In_{0.06}Ga_{0.94}As/Al_{0.27}Ga_{0.73}As$ quantum wells with 8 nm thickness.

Growth conditions

The sample was grown on a (001)-oriented n-doped GaAs substrate with a thickness of 350 μm. The removal of the oxide layer could be observed by RHEED at a thermocouple temperature of 530 °C, while BAS determined the sample temperature to be 580 °C. For the growth of the quantum well region, the temperature was reduced to prevent huge indium desorption and to obtain good optical properties.

Experimental results

The calculated BAS temperature is varying in a range of up to 70 K around the initial temperature, which can be seen in Fig. 7. These strong oscillations are caused by the growing Bragg mirror. However, in contrast to simple expectations, the oscillation period cannot be correlated to the growth of the periodic Bragg mirror layers. A closer look at the recorded data in Fig. 8 shows a temperature drop of a few Kelvin when shutters get closed. During the growth of each mirror period, three sheets of delta doping are incorporated by closing all cells except the doping sources. As described earlier, this can be identified by a small temperature drop. Figure 8 reveals that one mirror period is grown within 760 s. The huge temperature oscillations have a time period of 1050 s. Periodic structures lead to a massive distortion of the detected spectrum and thus to a deviation of the calculated temperature. These results clearly show the limits of BAS. For complicated layer structures it can be applied only to monitor the preprocessing and start of the growth.

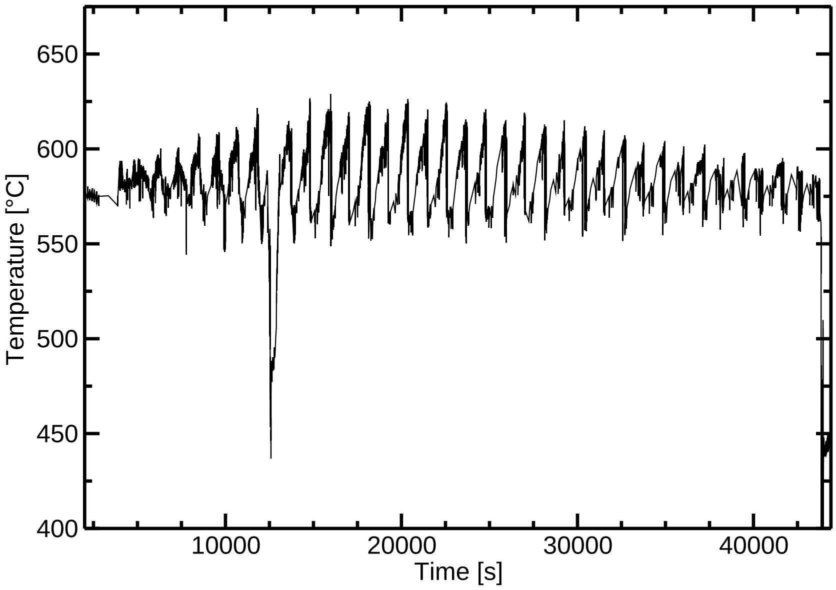

Fig. 7: Temperature profile determined with band-edge absorption spectroscopy of sample B. The spectral influence of the Bragg mirror layers on the detected signal lead to strong spurious temperature fluctuations.

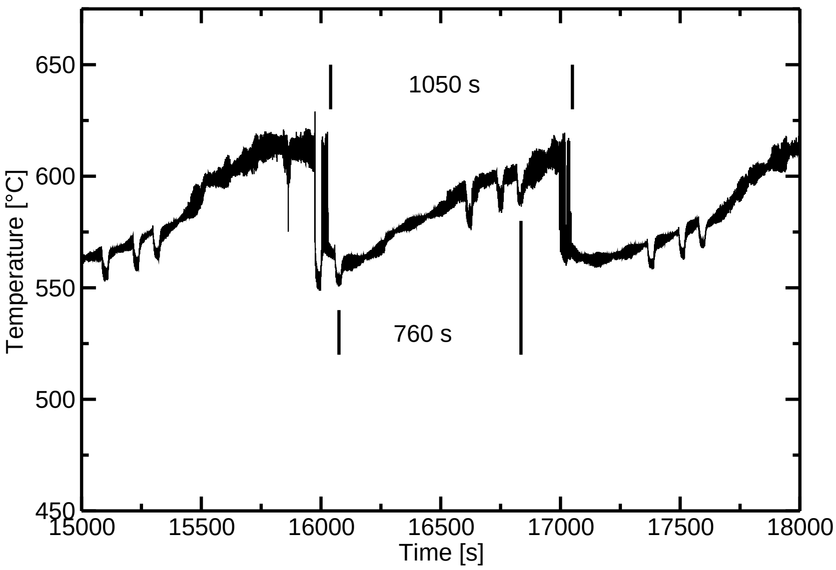

Fig. 8: Detailed temperature plot during growth of sample B. The oscillation period of $\approx 1050\,\mathrm{s}$ is not equal to the growth time of one Bragg mirror period ($760\,\mathrm{s}$).

4. Conclusion

Band-edge absorption spectroscopy, which is based on the physical properties of the sample material, is an additional method for substrate temperature measurement in MBE systems. The resulting temperature is much more realistic than values obtained from thermocouple or pyrometer which are strongly influenced by the geometry of the growth chamber. As long as non-periodic layer structures are grown, BAS can be used for ongoing monitoring and recording of the sample temperature. Periodic layer stacks lead to strong oscillations of the calculated temperature, caused by major changes of the detected spectrum.

References

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