

# Reflection Difference Spectroscopy on II- VI Semiconductors; A Tool to Investigate Surface Processes *in situ* During Growth

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As the materials and structures of semiconductor technology become more complex, interest in developing real time process monitoring techniques during crystal growth is rapidly increasing. Optical Probes are best suited to be applied simultaneously with crystal growth, because they are non-invasive and non-destructive. A technique currently strongly used is *Reflectance Difference Spectroscopy* (RDS), which can monitor *in situ* surface processes in real time under UHV (MBE, ALE) as well as under atmospheric pressure (CBE, OMCVD) conditions. The measured signal is the difference between the near normal incidence reflectances of light linearly polarized along the two principal axes is investigated as a function of time, photon energy, and/or surface condition. For cubic materials the uninteresting bulk reflection cancels in subtraction, leaving the signal from the lower symmetry surface. However, there are also identified sources for bulk anisotropy for zincblende (001) surfaces which break the 4-fold rotational symmetry. We mention spontaneous ordering, the linear electro-optic effect, dislocations, and quantum confinement.

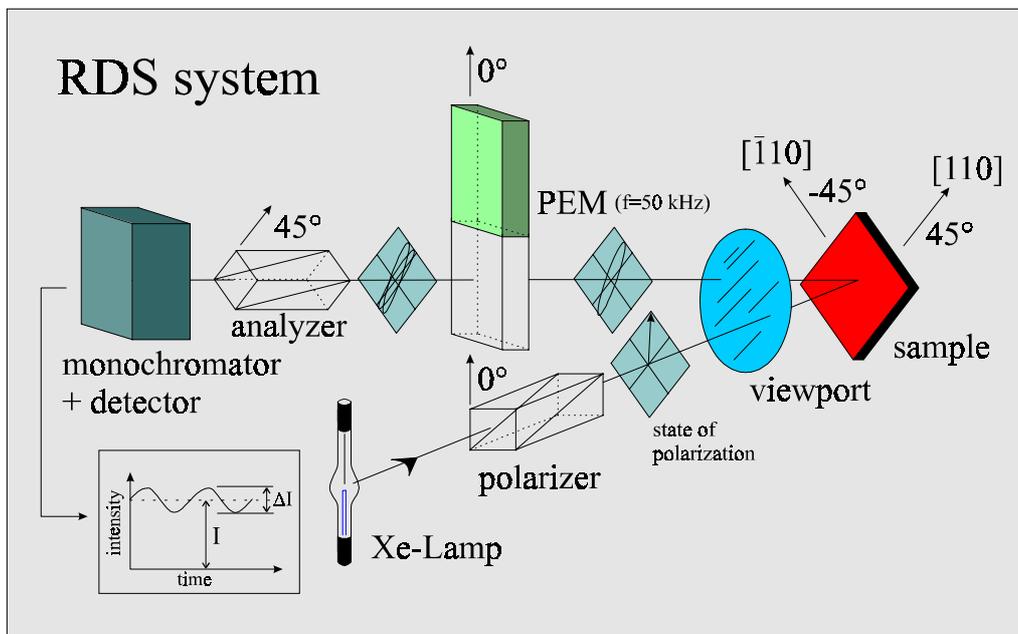


Fig. 1: The alignment of the optical components of the RDS system

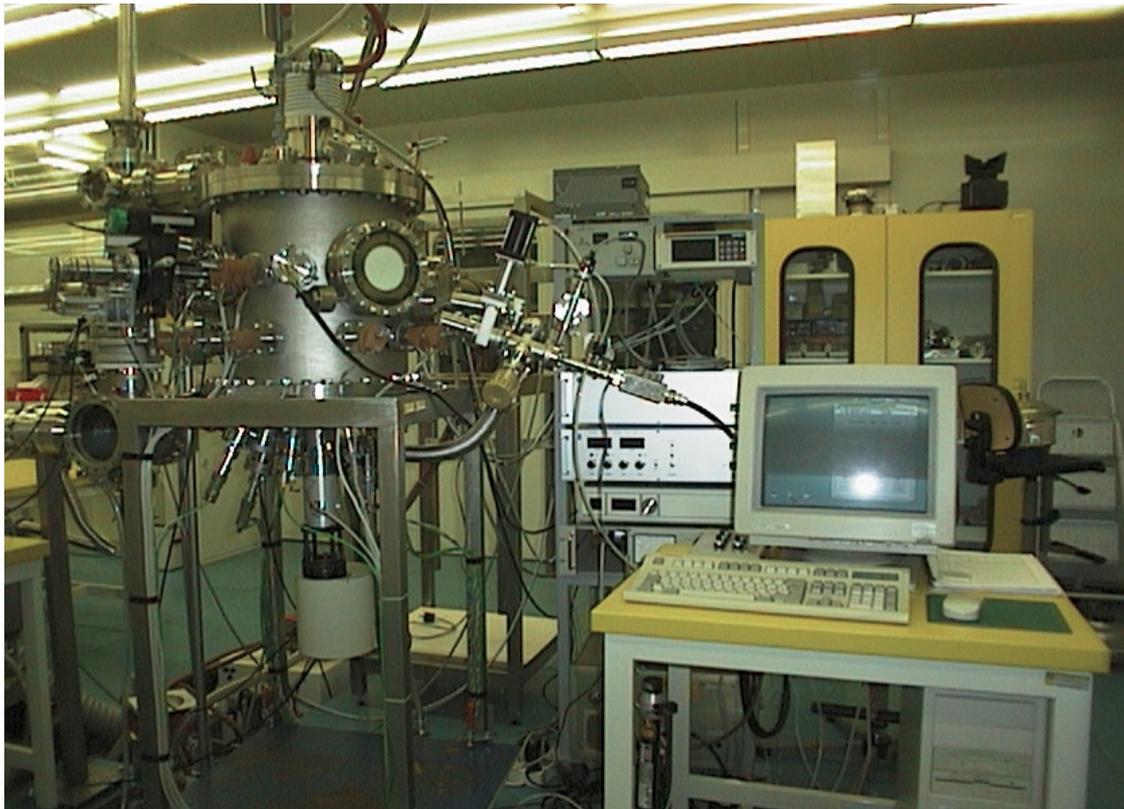


Fig. 2: A photo of the experimental setup of the UHV MBE chamber with the attached RDS in the cleanroom at Linz University (arrow).

Within the last years the understanding of information delivered by RDS and of kinetic RD data has grown considerably, however full exploitation of the power of these optical techniques needs further investigations, particularly when heteroepitaxial systems are concerned. Therefore, since the beginning of the work in February 1997, the major effort was directed onto these topics in II-VI semiconductors:

1. *In situ* determination of in plane stress and strain anisotropy in ZnSe/ZnTe/CdTe (001) Layers on GaAs.
2. On the origin of resonance features in RDS data of silicon.
3. *In situ* observation of stress relaxation in CdTe/ZnTe heterostructures by reflectance-difference spectroscopy at the critical thickness

ad 1) Is there an anisotropic in plane strain occurring due to dimerization for II-VI compounds? Furthermore we tried to find a theoretical description connecting the symmetry of the wave-functions and the polarization dependence of the optical transition matrix elements with the measured spectra (Bikus and Pir Hamiltonian) [6], [10]. Using reflectance difference spectroscopy we showed that Te surface termination on ZnTe induces, due to stress occurring from dimerization and the piezo-optic effect, a dichroism at the  $E_1$  and  $E_1 + \Delta_1$  critical points of the dielectric function of the ZnTe. The influence of Te dimers on the stress field in the epilayer was proven by comparing with *ex situ* measurements of anisotropically stressed ZnTe layers and *in situ* by enhancing the stress effect by inserting one atomic plane of Cd. Under Zn termination no stress was induced.

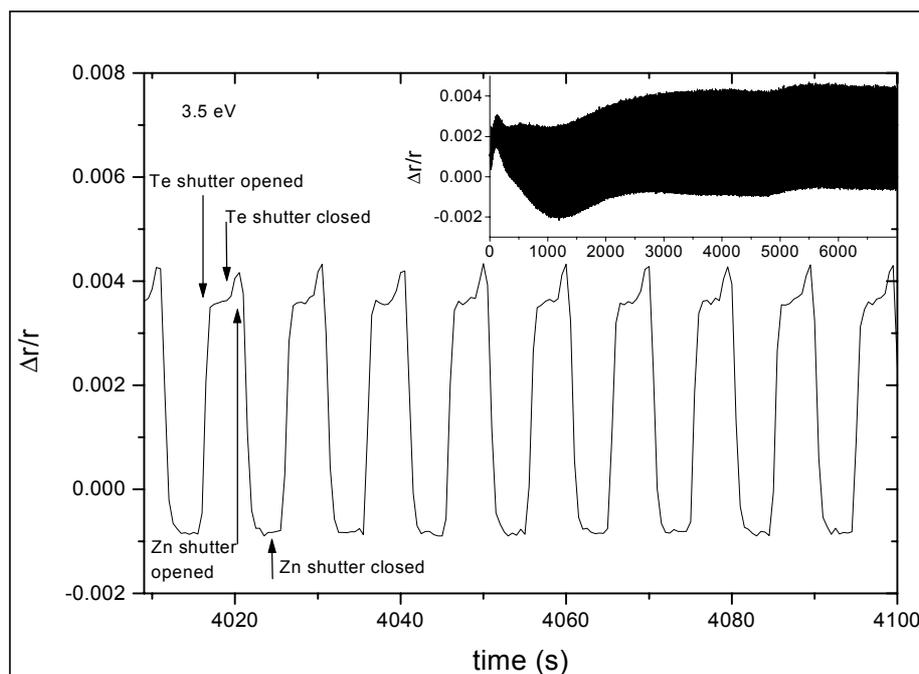


Fig. 3: Kinetic RD data taken during ALE growth of ZnTe (001) grown on GaAs at a photon energy of 3.5 eV. The inset displays RD data on a longer time scale.

ad 2) This also enabled us to shed light on the origin of sharp resonances in reflectance difference spectroscopy (RDS) data at the critical points of the dielectric function of bulk Si: The physical origin of sharp resonances in reflectance difference spectroscopy (RDS) data at the critical points of the dielectric function of bulk Si, previously assigned to surface-bulk transitions, to photon localization or to optical transitions from bound dimer states to excited dimer states was investigated. We show that uniaxial in-plane stress of bulk Si induces sharp resonances at exactly these critical points of Si via the piezo-optic effect. In the recent literature it was shown that surface reconstruction as well as dimerization exerts anisotropic stress, e.g. along the dimer direction, and the resulting strain is extending into the bulk. In our contribution we simulate this surface strain by externally stressing different Si faces and comparing *ex situ* measured RDS data of Si(001), Si(111), and Si(110) surfaces with RDS data measured *in situ* and density functional theory calculations.

ad 3) Understanding where the RDS features come from enabled us also for the first time to observe *in situ* the stress relaxation in CdTe/ZnTe heterostructures by reflectance-difference spectroscopy at the critical thickness. The first stages of epitaxial growth of CdTe on ZnTe and ZnTe on CdTe are monitored with reflectance difference spectroscopy. Spectroscopic reflectance difference data show strong optical anisotropy responses at the critical points of the bulk dielectric function at  $E_0$ ,  $E_1$  and  $E_1 + \Delta_1$  inter-band transitions of ZnTe, respectively CdTe, which indicate that anisotropic in-plane strain occurs during epitaxial growth. Applying a model it is possible to determine the in-plane strain due to the misbalance of  $60^\circ$  dislocations along the  $[1\bar{1}0]$  and  $[110]$  directions. Kinetic reflectance difference data taken at the  $E_1$  transition of the respective material exhibit with an accuracy of one monolayer the onset of the formation of misfit dislocations for these material systems. An example of this kinetic behavior is shown in Fig. 5.

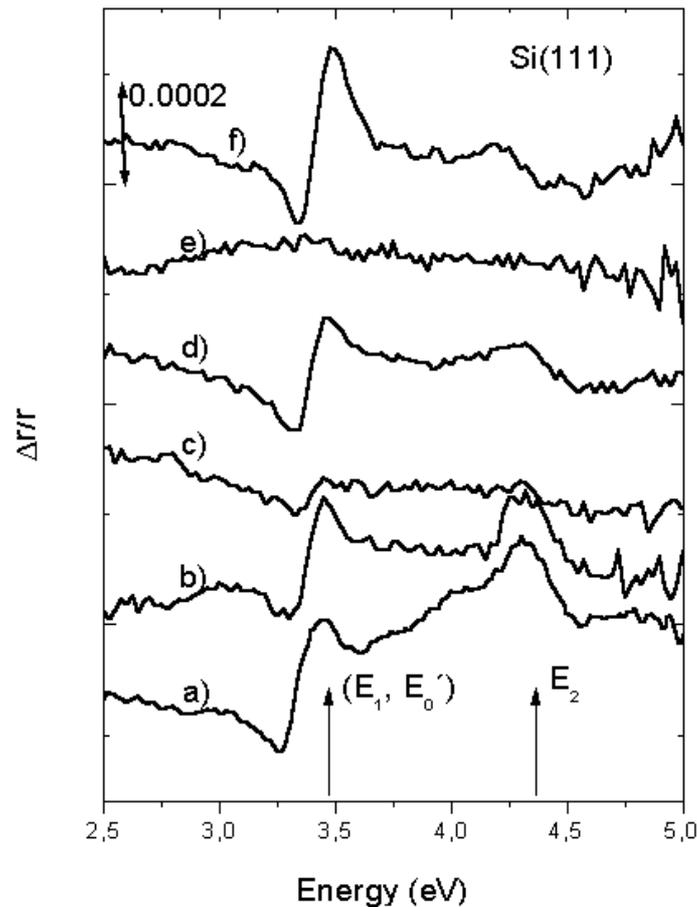


Fig. 4: Comparison between in situ RDS data obtained by other groups and our stress related features for example for the Si(111) surface: (a) displays the RD data of a Si(111): H surface  $5^\circ$  miscut towards the  $[11\bar{2}]$  direction; (b) shows *ex situ* measured data on Si(111) surfaces covered with natural oxides and  $2^\circ$  miscut; (c) same as Fig. 4(b) with the RDS head rotated by  $45^\circ$  from the  $[1\bar{1}0]$  direction towards the  $[2\bar{1}\bar{1}]$  direction; (d) same as Fig. 4(c) with the application of 25 MPa compressive stress along the  $[1\bar{1}0]$  direction; (e) the RD spectrum of a non miscut Si(111) sample; (f) same as Fig. 4(e) with the application of 25 MPa uniaxial stress along the  $1\bar{1}0$  direction.

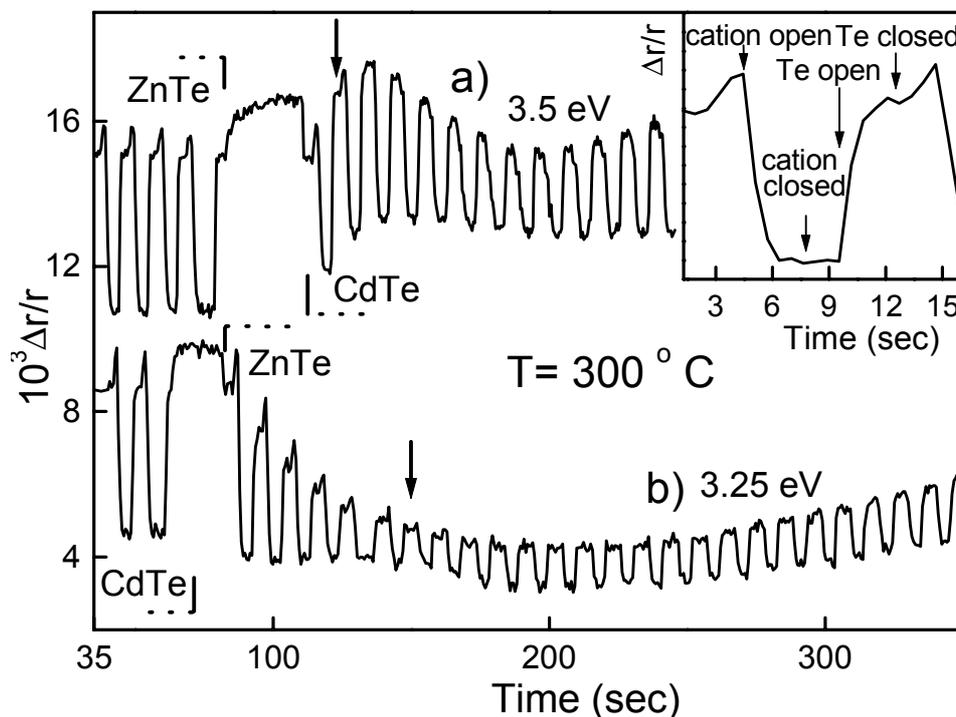


Fig. 5: In situ RD responses at the  $E_1$  critical points during interfaces formation by atomic layer epitaxy growth: a) CdTe on ZnTe(001) and b) ZnTe on CdTe(001). Both curves have been displaced vertically for the sake of clarity. The inset shows the shutter sequences for anion (Te) and cation (Cd or Zn) fluxes prior to interface growth on a shorter time scale.

## References:

- [1] A. Bonanni, H. Seyringer, H. Sitter, D. Stifter and K. Hingerl: "Control of morphology changes of self-assembled Mn-based nanostructures overgrown with mismatched material", *Appl. Phys. Lett.* 74, 3732, (1999)
- [2] D. Stifter, A. Bonanni, M. Garcia-Rocha, M. Schmid, K. Hingerl, H. Sitter: "In situ reflectance difference spectroscopy: Nitrogen-plasma doping of MBE grown ZnTe layers", *J. Cryst. Growth*, 201, 132 (1999)
- [3] A. Bonanni, D. Stifter, K. Hingerl, H. Seyringer, H. Sitter: "In-situ characterisation of the growth dynamics in MBE of Mn-based II-VI compounds: self-organised Mn structures on CdTe", *J. Cryst. Growth*, 201, 707 (1999)
- [4] D. Stifter, M. Schmid and K. Hingerl, A. Bonanni, m. Garcia Rocha and H. Sitter: "In situ reflectance difference spectroscopy of II-VI compounds: A real time study of N plasma doping during molecular beam epitaxy", *Jour. Vac. Sci. & Techn.* **B17**, 1697 (1999)

- [5] A. Bonanni, K. Hingerl, H. Sitter, D. Stifter: "Reflectance Difference Spectroscopy of Mn Intra Ion Transitions in p- doped diluted magnetic semiconductors", *phys. Stat.sol.* 215, 47 (1 999)
- [6] T. Hanada, T. Yasuda, A. Ohtake, K. Hingerl, S. Miwa, K. Arai, and T. Yao: "In Situ Observation of Strain Induced Optical Anisotropy of ZnS<sub>1-x</sub>Se<sub>x</sub>/GaAs(110) during Molecular Beam Epitaxy", *Phys Rev.* B60, (8909) (1999)
- [7] D. Stifter, K. Hingerl, H. Sitter: "Zerstörungsfreie Messung dünner Schichten mit polarisationsoptischen Methoden", *e&i, ÖVE*, **116**, 315, (1999)
- [8] A. Bonanni, G. Prechtl, W. Heiss, F. Schinagl, S. Holl, H. Krenn, H. Sitter, D. Stifter and K. Hingerl: "Reflectance Difference Spectroscopy and magneto-optical analysis of digital magnetic heterostructures", *Jour. Vac. Sci. & Techn.* **B17**, 1722(1999)
- [9] K. E Miller, K. Hingerl, C. Brabec, A. J. Heeger, and N. S. Sariciftci: "Reflectance Anisotropy Spectroscopy of Oriented Films of Semiconducting Polymers", submitted to *J. Chem. Phys.*, submitted
- [10] R. E. Balderas-Navarro, K. Hingerl, W. Hilber, D. Stifter, A. Bonanni, and H. Sitter: "In situ reflectance-difference spectroscopy of doped CdTe and ZnTe grown by molecular beam epitaxy", submitted to *J. Jour. Vac. Sci. & Techn.*, submitted

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