# Reflection Difference Spectroscopy on II- VI Semiconductors; a Tool to Investigate Surface Processes In Situ During Growth

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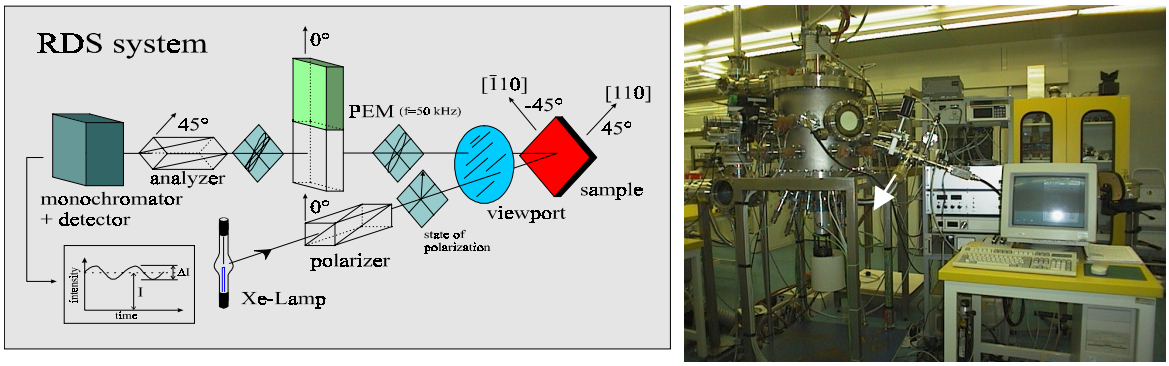
In this contribution the last year's work on Reflection Difference Spectroscopy is described in order to understand the physical and chemical processes occurring at the surface of the growing II-VI materials in situ in an molecular beam epitaxy chamber during epitaxial growth. The main focus in the last year was laid onto the investigation of dichroism in the epilayer due to surface stress or a surface electric field.

## 1. Introduction

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 noninvasive and nondestructive. 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.




(a) (b)

Fig. 1: (a): The alignment of the optical components of the RDS system; (b): A photo of the experimental setup of the UHV MBE chamber with the attached RDS in the cleanroom at Linz University (arrow).

The measured signal is the difference between the near normal incidence reflectances of light linearly polarized along the two principal axes 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.

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:

a) *In situ* Determination of In Plane Stress and Strain Anisotropy in ZnSe/ZnTe/CdTe (001) Layers on GaAs.

b) *In situ* Observation of Doping Efficiency and Doping Processes during crystal growth.

c) *In situ* investigation of the growth mode of Mn and MnTe layers in CdTe.

d) Reflectance difference spectroscopy of Mn intra-ion transitions in p-doped diluted magnetic semiconductors.

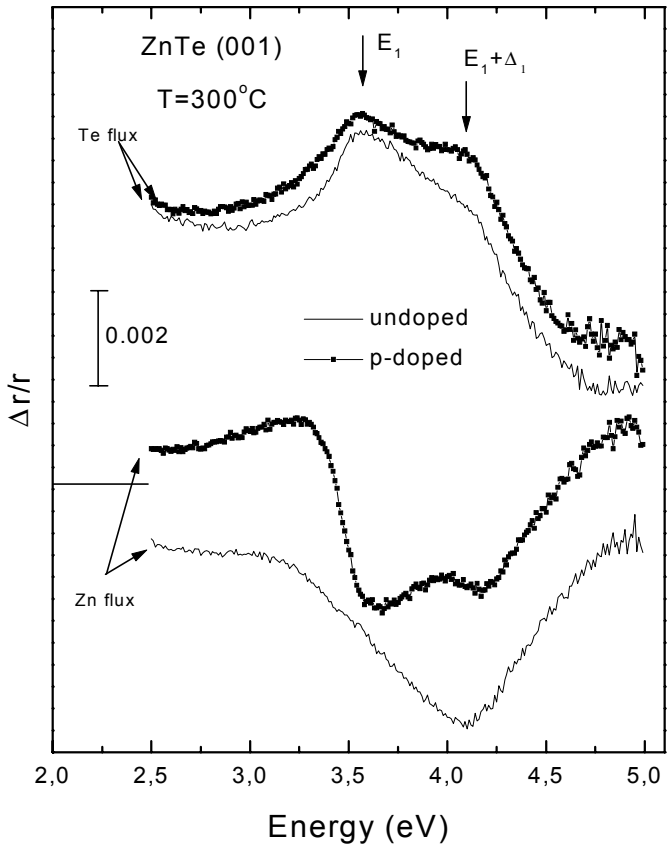



Fig. 2: Changes of the RDS spectra with and without doping. It can be seen that the broad surface related structures centered around 3.5 eV for Te surface termination and around 4.2 eV for Zn Termination are superimposed by sharper bulk related peaks when the samples are doped.

# 2. Results

## 2.1 Anisotropic in-plane strain

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].

## 2.2 Linear electro-optic effect

The linear electro-optic effect (LEO), i.e., the change of the dielectric function, respectively, of the refractive index with applied electric fields, can be used for monitoring the doping concentration. Because the Fermi level in the bulk material changes with the activated dopant concentration, and at the surface a pinning of the Fermi level occurs, there is a built-in field and a depletion zone.[2], [4].

We have used reflectance difference (RD) spectroscopy (uv – visible energy range) during the growth and doping process of CdTe (001) and ZnTe (001) layers by molecular beam epitaxy (MBE). The MBE chamber is equipped with an electron cyclotron resonance cell to generate N plasma and a $ZnCl_2$ effusion cell for the p and n-type doping, respectively. After the first stages of the growth and prior doping, different spectral features were found as we changed from Cd(Zn) to Te stabilized conditions due to surface anisotropy. However, as the doping of the growing layer further increased, the RD spectra of both surfaces showed resonances around $E_1$ and $E_1 + \Delta_1$ interband transitions due to the linear electro-optic (LEO) effect. Although RD spectra exhibit similar line shapes dominated by surface transitions, differences due to the LEO can be isolated. Figure 2 above shows the changes of the RDS spectra with and without doping. It can be seen that the broad surface related structures centered around 3.5 eV for Te surface termination and around 4.2 eV for Zn Termination are superimposed by sharper bulk related peaks when the samples are doped.

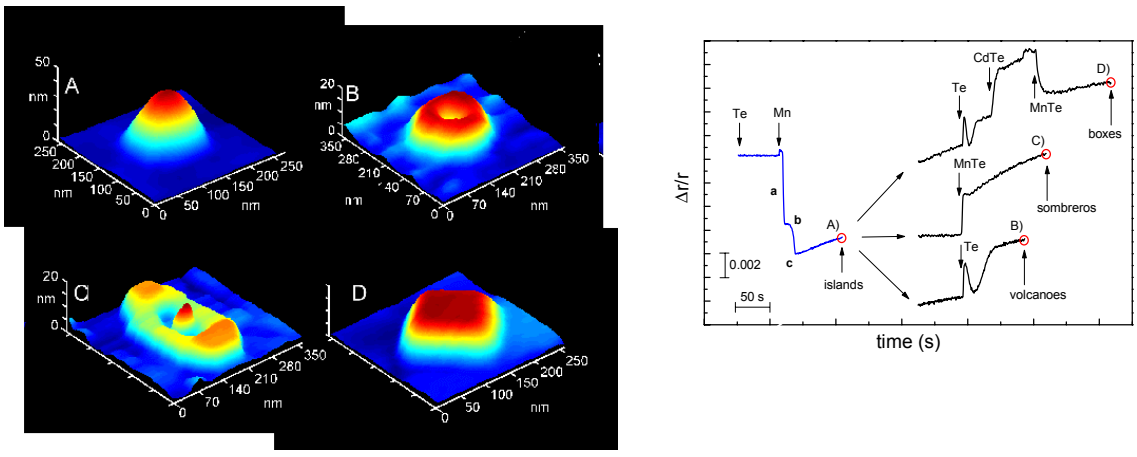



Fig. 3: On the left side the topography of the different dots, measured with AFM ex situ is shown; on the right side the RDS transients, leading to the different sizes are shown. The shutter sequence is displayed in the inset.

## 2.3 Self-assembling Mn-based nanostructures on CdTe

Another major topic were self-assembling Mn-based nanostructures on CdTe, where the reproducibility of size and shape for epitaxially grown self-assembling Mn-based nanostructures was achieved by tracing the formation process via reflectance difference spectroscopy. Pure Mn crystallites were at first fabricated on a semiconductor surface and in a second stage a variety of queer, strain-induced island morphologies was obtained with the deposition of semiconducting materials on the magnetic precursors. The exact control pursued, the possibility of shape tuning and the size range, let foresee forthcoming studies and applications in the field of confinement in low dimensions [1], [8].

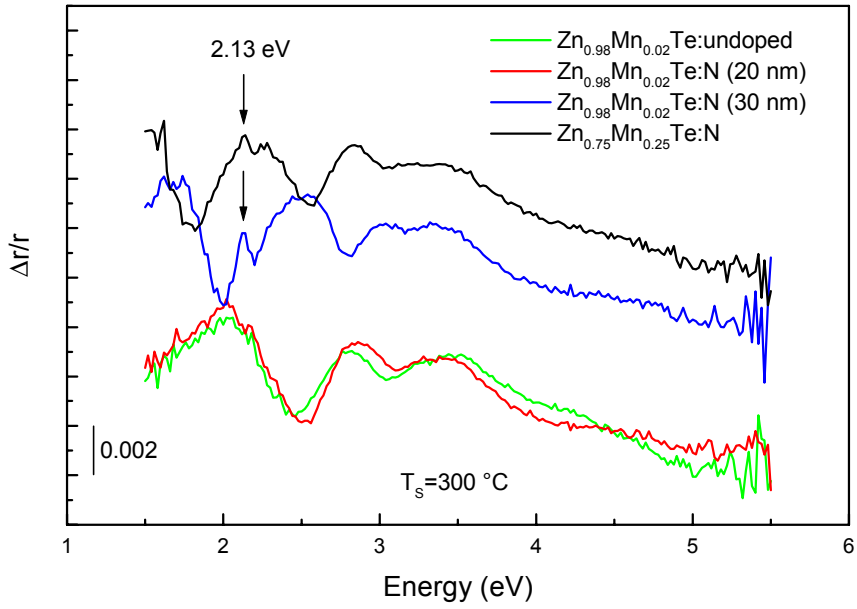



Fig. 4: Four RDS spectra of doped and undoped $Zn_{1-x}Mn_xTe$. It can be seen that at 2.13 eV an extra peak is occurring, which is ascribed to intra Mn transitions due to the symmetry breaking of the electric field.

## 2.4 Reflectance difference spectroscopy of Mn intra-ion transitions in p-doped diluted magnetic semiconductors

By performing in-situ reflectance difference spectroscopy (RDS) during and upon the epitaxial growth of the diluted magnetic semiconductor ZnMnTe heavily p-doped with N, it was possible to observe below and in the band gap region features occurring from intra-Mn d-level transitions. Since Mn on substitutional Zn sites is in a cubic environment and RDS measures the difference between the reflectances of light polarized along the two in-plane eigenstates, these transitions are detectable because of the breaking of the C4 rotational symmetry. In undoped materials the spectroscopic window for observation may open only for high values of magnetic ions concentration, whereas in doped crystals it was possible to detect the transitions at growth temperature and at Mn concentrations as low as 2% [5].

## Acknowledgements

Funding: ÖAW (APART), FWF, ÖAD, EC- Competitive and Sustainable Growth

## Collaborations

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- Defense Research Agency, UK,

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