A set-up to study the formation of proton-induced primary defects in wide band-gap semiconductors at cryogenic temperatures by space charge spectroscopy

Matthias Schmidt[1], Johan Janse van Rensburg[1], Hannes de Meyer[1], Walter E. Meyer[1], Danie F. Auret[1], Florian Schmidt[2], Holger von Wenckstern[2]

1 Department of Physics, University of Pretoria, Private bag X20, 0028 Hatfield, South Africa
2 Universität Leipzig, Institut für Experimentelle Physik II, Halbleiterphysik, Linnéstraße 5, 04103 Leipzig, Germany

E-mail: schmidt.matthias@matschmi.de

Abstract. We report on a new set-up to investigate electronic states of primary proton-bombardment-induced defects in wide band-gap semiconductors at cryogenic temperatures. The set-up consists of an ion accelerator with a vacuum chamber and a cryostat aligned in the beam-line. The defect studies are carried out in the same chamber by space charge spectroscopy such that no room temperature annealing of the sample is required between introduction and investigation of the defects. In contrast to existing facilities of this type, the sample can be optically excited in addition. This allows for photo-ionisation experiments like photo-capacitance spectroscopy or optical deep-level transient spectroscopy. These methods are essential for the investigation of electronic states of primary defects which anneal below room temperature since they allow for scanning for defect states in the entire band-gap at any temperature. First results measured on a zinc oxide thin film sample are presented.

1. Introduction

Lattice defects or impurities often introduce electronic states into the band-gap of semiconductors. Thereby, even in concentrations of less than 1 ppm, they strongly influence the concentration of free charge carriers in the material. This in turn affects macroscopic properties like conductivity and optical absorption. Thus, understanding the electronic properties of defects and their formation is a precondition for every semiconductor application.

Studying defects experimentally is usually divided into two tasks: Firstly, the controlled incorporation of impurities into the material; secondly their detection. Bombarding semiconductors with high energy protons has been proven to induce lattice defects in the crystal, in particular vacancies and interstitial atoms. These can then be investigated by space charge spectroscopy (SCS) which is known to be a powerful tool to detect and characterise electronic states of defects in low concentrations.

In this paper we describe our recently built set-up for in-situ studies of electronic defect states induced by proton bombardment into wide-band-gap semiconductors. In particular it is possible to induce as well as to characterise primary defects at cryogenic temperatures ($T \approx 20\,\mathrm{K}$) without heating the sample to room temperature between these experiments. This is crucial

since primary defects can be highly mobile, like for instance the mono-vacancy or the self-interstitial in silicon [1]. They may anneal-out or form defect-complexes even below room temperature. The detection and characterisation of the electronic defect states of these levels can in principle be carried out by established space charge spectroscopic methods like deep-level transient spectroscopy (DLTS). However, in a DLTS experiment the temperature-dependence of the thermal emission rate $e^{\mathrm{th}}_{\mathrm{n,p}}$ of charge carriers (electrons or holes, respectively) from localised states into the bands is measured. For a point defect in a non-degenerate semiconductor it is given by [2]

$$e^{\mathrm{th}}_{\mathrm{n,p}} \propto \sigma_{\mathrm{n,p}} T^2 \exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}} T}\right), \tag{1}$$

where T is the sample temperature and k_{B} is Boltzmann's constant. From Eq. 1 it can be seen that levels deep in the band-gap cannot be investigated at low temperatures because $e^{\mathrm{th}}_{\mathrm{n,p}}$ is too low to be conveniently measured since such levels usually exhibit high thermal activation energies E_{a} and small charge carrier capture cross-sections $\sigma_{\mathrm{n,p}}$. The problem is that in the case of primary defects, the increase in temperature necessary to detect their electronic states by SCS can lead to an anneal-out of the defect itself.

Our approach to overcoming this problem is to conduct SCS experiments in which the photo-ionisation of the electronic defect states is measured instead of their thermal ionisation. These experiments have in common that the sample is illuminated with monochromatic light. The rate at which a trapped charge carrier is optically emitted into either the conduction or the valence band is measured as a capacitance transient. The optical emission rates are almost independent of the sample temperature but depend on the photon flux $\Phi(h\nu)$ as well as the photo-ionisation cross-section spectrum $\sigma^{\mathrm{o}}_{\mathrm{n,p}}(h\nu)$ of the defect state [3]

$$e^{\mathrm{o}}_{\mathrm{n,p}} = \sigma^{\mathrm{o}}_{\mathrm{n,p}}(h\nu)\Phi(h\nu). \tag{2}$$

$\Phi(h\nu)$ is given by the spectrum of the light source. Our new set-up therefore enables us to induce lattice defects into a semiconductor and to investigate the entire band-gap for their electronic states at low temperatures.

Wide band-gap semiconductors are promising materials for opto-electronic devices operating in the near ultra-violet spectral range. The semiconductor zinc oxide (ZnO) exhibits a band-gap of 3.4 eV at 2 K [4]. It is considered to be radiation-hard [5, 6] which makes it an interesting material for UV sensors in harsh environments, e.g., in satellites. In this paper we present first results of SCS measurements on proton-induced primary defects in a ZnO thin film. These results suggest that the observed radiation-hardness of ZnO at room temperature is mainly due to an anneal-out of primary defects even at a temperature of 120 K.

2. Description of the set-up

Our set-up (Fig. 1a) consists of a Van-de-Graaff accelerator suitable for the acceleration of protons and alpha-particles up to energies of 2 MeV. Aligned in the beam-line of the accelerator is a high vacuum chamber with a closed-cycle helium cryostat suitable for the temperature range from 20 K to 380 K. The temperature is measured by a Lakeshore 340 temperature controller using a calibrated silicon diode. The sample is mounted on the cold-finger of the cryostat. Attached to the vacuum chamber is an electrical feed-through which allows the conduction of electrical measurements, in particular space charge spectroscopy. Capacitance transients and the admittance of the sample are measured by an Agilent 4284A LCR meter or a Boonton 7200 capacitance bridge and are recorded by a PC.

The feature that makes our set-up unique is the possibility of simultaneous optical excitation. Light stemming from a 1000 W Hg/Xe arc lamp is passed through a Cornerstone 284 (0.25 m) grating monochromator (line density 600 lines/mm). After the monochromatisation an optical

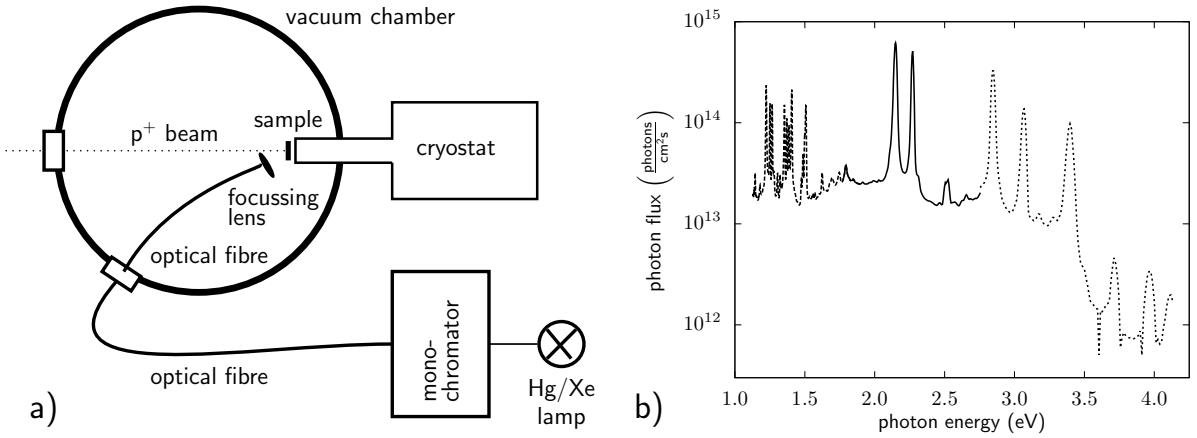

Figure 1. a) Sketch of the set-up. b) Spectral dependence of the photon flux on the sample measured by a calibrated silicon photo-detector. The different line-styles indicate the ranges, in which different filters were used. The monochromator slits were opened by 1mm resulting in a spectral resolution of approximately $\Delta\lambda = 5\,\mathrm{nm}$.

fibre guides the light into the vacuum chamber where it is focussed onto the sample. The optical set-up is suitable for the wavelength range from 1100nm to 300nm. The photon-flux on the sample was measured as a function of the wavelength using a calibrated silicon photo-detector (Gamma Scientific FlexOptometer), see Fig. 1b.

3. Samples

The proton-bombardment measurements were conducted on ZnO thin film Schottky diodes. Details of the sample preparation are discussed in [7] and [8]. On an *a*-plane sapphire substrate an approximately 200 nm thick layer of highly aluminium doped, metallically conducting ZnO was grown by pulsed laser deposition (PLD). This layer serves as the ohmic back contact of the samples. Subsequently a nominally undoped layer of ZnO (thickness 1500 nm) was pulsed laser deposited. This is the material in which the defect studies were carried out. The Schottky contacts were then fabricated from resistively evaporated palladium (thickness 9 nm).

4. First results

The results presented in this section have already been published in one of the PhD thesis of one of the authors (M.S.) [9]. In order to get a feeling for which defects are induced by high-energy proton bombardment of ZnO and which amongst them are stable up to room temperature or anneal out even at cryogenic temperatures respectively, we bombarded a ZnO Schottky contact at 20 K with 1.6 MeV protons. The proton fluence amounted to $6 \times 10^{13}\,\mathrm{cm}^{-2}$. Due to the lattice damage caused by the collisions of protons with the host atoms, the sample became highly resistive after the bombardment and the capacitance dropped to zero. The temperature was slowly increased and at approximately 120 K primary defects began to anneal out resulting in an increase of the sample capacitance. A further increase in temperature resulted in a strong increase of the capacitance[1]. At room temperature the capacitance of the proton-bombarded sample was only slightly smaller than in the as-grown state. From a subsequent capacitance-temperature measurement in which the capacitance of the sample did not drop to zero for $T < 120\,\mathrm{K}$ it can be concluded that the observed strong increase of the capacitance after the

[1] Unfortunately one of the pins used to contact the sample lost contact at 220 K.

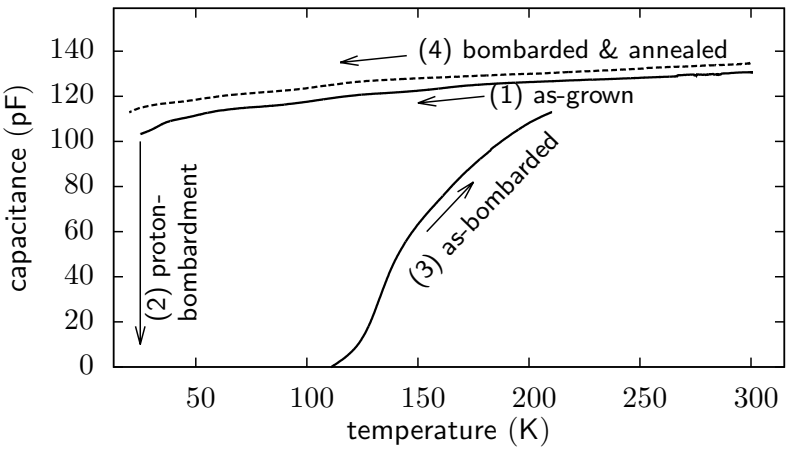

Figure 2. Capacitance vs. temperature measured on a ZnO Schottky contact during a temperature cycle: (1) As-grown sample was cooled from room temperature to 20 K. (2) Sample was bombarded with 1.6 MeV protons, fluence: $6 \times 10^{13}\,\mathrm{cm}^{-2}$. (3) Temperature was increased to 300 K. (4) Sample cooled to 20 K. During the cycle the sample was reverse biased at 2.5 V.

bombardment indeed stemmed from an annealing out of primary defects. The cooling cycle is depicted in Fig. 2.

Electronic defect states induced by proton-bombardment, which are stable up to room temperature were investigated by capacitance-voltage spectroscopy (CV) and DLTS. Therefore different Schottky contacts on the ZnO thin film sample were proton-bombarded (1.6 MeV) at different fluences ranging from $2 \times 10^{13}\,\mathrm{cm}^{-2}$ to $3 \times 10^{14}\,\mathrm{cm}^{-2}$. Using van Opdorp's method [10], the depth profiles of the net doping density were determined from the CV data:

fluence (cm^{-2})	N_{net} (cm^{-3})
0	4×10^{16}
2×10^{13}	5×10^{16}
6×10^{13}	5×10^{16}
1×10^{14}	3×10^{16}
3×10^{14}	4×10^{16}

Obviously, within the error bars of the experiment, the net doping density was not significantly changed by the proton bombardment. This in turn means that most of the lattice damage anneals out immediately after the bombardment and that furthermore the number of induced stable donors equals that of the induced stable acceptors.

In order to study the impact of the proton bombardment on deep-levels in the upper third of the ZnO band-gap, DLTS measurements were performed on those samples subsequent to the CV measurements. The DLTS measurements were conducted using 1 ms filling pulses that almost flattened the bands. During the recording of the capacitance transients, the samples were reverse biased at 2.5 V. The resulting spectra are depicted in Fig. 3(a) and reveal the presence of the well-known deep-levels E1 and E3 [11], T2 [12] and E4 [11, 13]. Evidently the concentrations of T2 and E3 are not affected by the proton bombardment of the samples. The concentration of E1 is slightly increased after the bombardment. But the DLTS peak height is almost equal in all bombarded samples, independent of the fluence. However, the E4 concentration[2] –which

[2] Here E4 is assumed to be almost uniformly distributed in the space charge region. First optical capacitance-voltage measurements [9] however hint at E4 concentrations gradients towards the bulk in the samples.

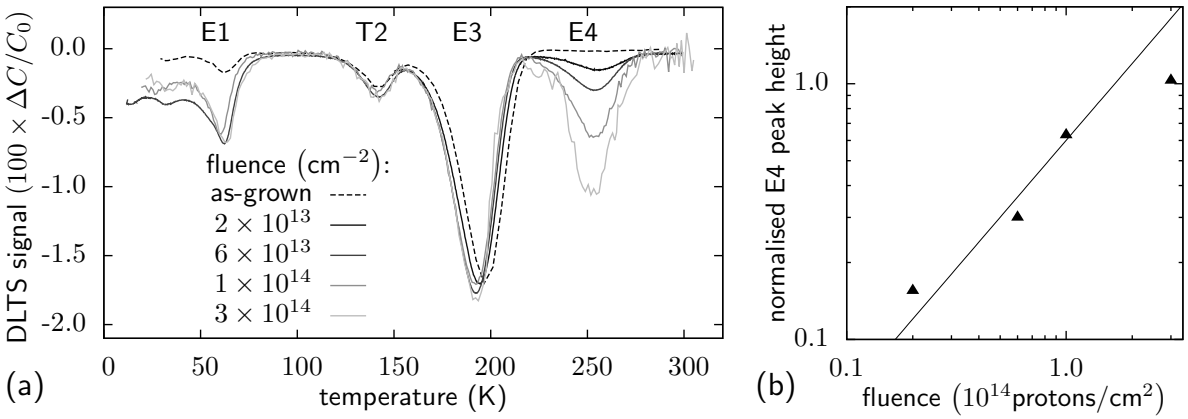

Figure 3. (a) Deep-level transient spectroscopy measurements on 1.6 MeV proton-bombarded Schottky contacts on a ZnO thin film sample (rate window: 200 Hz). Obviously the E4 deep-level is induced by the bombardment. (b) Determination of the E4 introduction rate from the E4 DLTS peak height (normalised on the maximum peak height). The straight line is a linear fit to the data which suggests an E4 introduction rate of $3\,\mathrm{cm}^{-1}$. (For the linear regression only the E4 concentrations measured for fluences up to $10^{14}\,\mathrm{cm}^{-2}$ were considered. The introduction rate for E4 decreases for larger fluences.)

was not traceable in the as-grown sample– increases almost linearly with increasing fluence up to $5 \times 10^{14}\,\mathrm{cm}^{-3}$. In the following we want to elaborate on this deep-level.
A straight line fitted to the DLTS peak height vs. fluence data and intersecting the origin yields an E4 introduction rate of approximately $3\,\mathrm{cm}^{-1}$, see Fig. 3(b). This is very close to the value of $2.4\,\mathrm{cm}^{-1}$ reported by Auret *et al.* [5, 6] for the proton-bombardment-induced deep-level EP1. Employing standard Arrhenius evaluation of the temperature-dependent thermal emission rate for electrons, the E4 activation energy and the high-temperature limit of the electron capture cross-section were determined to 540 meV and $2 \times 10^{-13}\,\mathrm{cm}^2$, respectively. Again these values agree well with activation energy and high-temperature limit of the electron capture cross-section for the EP1 defect. Since the formation of vacancies can be expected during the proton bombardment, our finding that E4 is proton-induced also supports the suggestion by Frank *et al.* [13] that E4 is a state of the oxygen vacancy.

5. Conclusions

In this paper we have presented our new set-up suitable for the in-situ investigation of primary, proton bombardment induced electronic defect states by means of space charge spectroscopy. Owing to the possibility of conducting the proton irradiations and the defect studies in the same vacuum chamber as well as being capable of optically exciting the sample during space charge spectroscopic experiments, the set-up enables us to scan the *entire* band-gap of a wide-band-gap semiconductor for defect states. This means that no unintentional annealing step between the introduction of defects by high-energy protons at cryogenic temperatures and their investigation is necessary and thus an annealing out of primary defects can be avoided. First measurements on Pd/ZnO thin film Schottky diodes were performed and show that the previously observed radiation-hardness of ZnO mainly results from an anneal-out of radiation damage even at temperatures as low as $\approx$ 120 K. Room-temperature capacitance-voltage measurements on 1.6 MeV proton-bombarded Pd/ZnO Schottky diodes confirmed that the net doping density

was not significantly changed by the protons for fluences up to $3 \times 10^{14}\,\mathrm{cm}^{-2}$. However, DLTS experiments on the same samples revealed that the E4 deep-level is induced by the protons and is stable at room temperature. This is in line with previous observations on proton-bombarded ZnO single crystals[3] [5, 6, 14].

Acknowledgments
The authors wish to thank the mechanical workshop of the Department of Physics at the University of Pretoria for the fabrication of numerous parts of the set-up. To H. Hochmuth, M. Lorenz and M. Grundmann we are much obliged for the growth of the ZnO thin film sample. The authors are indebted to Deutsches Zentrum für Luft- und Raumfahrt e.V. for the financial support. Matthias Schmidt was funded by the Postdoctoral Fellowship Program of the University of Pretoria. We thank two referees for their thorough review of the manuscript and highly appreciate their comments and suggestions. This work is based upon research supported by the National Research Foundation (NRF). Any opinion, findings and conclusions or recommendations expressed in this material are those of the author(s) and therefore the NRF does not accept any liability in regard thereto.

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[3] In [5, 6] the deep-level was labelled EP1. However, it exhibits a similar Arrhenius plot of its temperature-dependent electron emission rate as the E4 level. Furthermore we found (not shown here) that the proton-induced deep-level we detected in this study can be photo-ionised and exhibits the same optical threshold as reported by Ellguth *et al.* [15] for the E4 level. Therefore it is highly probable that EP1 and E4 are identical.