Pulse measurements of small area thin film $\mu$c-Si:H/ZnO:B photodiodes

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Abstract. We introduce a triggered optoelectronic system operating in a pulse mode in the near infrared and visible spectral range 0.75–3 eV. The system measures current-voltage ($I-V$) characteristics in dark and under visible light illumination as well as electroluminescence (EL) spectra of small area thin film photodiodes and light emitting diodes with size below 1 mm$^2$. The usefulness of the setup is demonstrated by measurement of optoelectronic properties of a hydrogenated microcrystalline silicon ($\mu$c-Si:H) $p$-$i$-$n$ diode deposited on a semi-transparent nanostructured ZnO:B electrode. No s-shaped $I-V$ characteristics were observed under white illumination near an open circuit voltage $U_{oc}$ indicating a negligible charge accumulation near $\mu$c-Si:H/ZnO:B interface. The weak infrared EL correlates with the current density.

1. Introduction

Thin film $p$-$i$-$n$ diodes based on hydrogenated amorphous (a-Si:H) and microcrystalline silicon ($\mu$c-Si:H) layers deposited by plasma enhanced chemical vapour deposition (PECVD) are the most common types of thin film diode [1]. The intrinsic layer $i$ can be tailored to optimize the depletion region whereas the doped $p$-type and $n$-type layers can be made thin to be optically transparent. The thin film diodes have been used for decades in applications such as solar cells, TV screens and scanners [2]. Thin conductive oxides (TCO) are used as optically transparent and electrically conductive electrodes. The nanostructured, boron-doped ZnO layers consisting of pyramidal grains with size about 200 nm combine high optical scattering of visible light, high transparency in the infrared region and moderate sheet resistances of 30 $\Omega$/sq [3, 4].

We have studied extensively nanostructured materials [5]. However, finding technologically compatible materials is challenging [6]. For example, the photoluminescence intensity strongly correlates with the presence of isolated silicon nanoparticles in the mixed amorphous and crystalline phase reaching maximum in samples with crystalline volume fraction at about 50 % and diminishes abruptly in samples with crystalline volume fraction above 80 % prepared by PECVD with SiH$_4$/H$_2$ concentration below 5% [7].

The photocurrent spectroscopy reveals that quality of intrinsic layer strongly depends on material type and nanoscale morphology of the substrate [8]. The s-shaped photocurrent is a characteristic signature of a restricted charge transport related to a charge accumulation near one of the electrodes [9]. To study the energy and charge transfer through nanostructured interfaces we need a highly sensitive optoelectronic system for measuring the current-voltage ($I-V$) characteristics as well as photoluminescence (PL) and electroluminescence (EL) spectra in the visible and near infrared region.
In this paper we describe in detail an upgraded setup for a basic optoelectronic characterization of small area photodiodes and demonstrate its usefulness by measuring the $I-V$ characteristics and EL spectra of thin film $p-i-n$ diodes based on $\mu$c-Si:H deposited on semi-transparent nanostructured ZnO:B electrode.

2. Experimental

2.1. Preparation of diode

The diode structure is shown in Figure 1A. A nanostructured ZnO:B thin film, about 2 $\mu$m thick was deposited on fused silica glass by a low-pressure metalorganic chemical vapor deposition technique in a single process step by doping with boron only the nucleation stage of the growth [4]. The ZnO:B surface was cleaned 2 min in pure $\text{H}_2$ using 13.56 MHz radio frequency plasma discharge with power 9 W in a stainless steel vacuum deposition chamber with two electrode (capacitive) configuration with a residual pressure of $10^{-5}$ Pa after 12 hours heating, pumping and degassing [10]. The $\mu$c-Si:H layers were deposited from silane $\text{SiH}_4$ (purity 5.0) diborane $\text{B}_2\text{H}_6$ and phosphine $\text{PH}_3$ diluted in $\text{H}_2$ (purity 6.0) using 13.56 MHz radio frequency chemical vapour deposition (PECVD), the substrate temperature 220°C, pressure 30 Pa and power 18 W. The $\text{H}_2$ and $\text{SiH}_4$ flow rates were 50 and 2.25 sccm. The 60 nm thick intrinsic $\mu$c-Si:H layer was deposited 12 min. The 25 nm thick $p$-type boron (3 min) and the 25 nm thick $n$-type phosphorus (5 min) doped layers were prepared using 1% diborane and phosphine addition into the $\text{SiH}_4$. Finally, an array of 12 metallic electrodes (0.8×0.8 mm) was deposited by vacuum evaporation. The selected silane concentration 4.5% corresponds to the hydrogenated silicon layer with high crystallinity and low photoluminescence [7].

2.2. A setup for current-voltage characteristics

The $I-V$ characteristics of diodes were measured in dark and under white light illumination in a pulsed mode using a Keithley #3390 arbitrary waveform generator, a 5½-digit Keithley #6485 picoammeter and a 100 mW/cm$^2$ white LED synchronized by TTL pulses. Samples were illuminated through glass substrates masked by an aperture to illuminate only a selected diode. The Keithley #3390 arbitrary waveform generator provided arbitrary waveform voltage pulses up to ±10V with the step 20 mV as well as synchronizing TTL pulses. A protective resistor 100 $\Omega$ was applied to limit current to 10 mA at

![Figure 1](image_url)
1 V. Unlike digital multimeters, picoammeters offer low input voltage drop (low voltage burden) and selectable input current ranges from 2 nA up to 20 mA. However, due to a relatively high inductance, the picoammeter had to be disconnected from the circuit before changing the current range. This had been done with a PC controlled Signal Recovery Model 3830 multiplexer. After changing the current range, the zero check needed to be performed with the picoammeter input amplifier reconfigured to low input signal. The zero correct feature was enabled to algebraically subtract the voltage offset specific to the selected current range during current measurements.

2.3. A setup for optoelectrical characterization of light emitting diodes

The new setup for optoelectrical characterization of light emitting diodes, shown in Figure 2, evolved from our previous setup designed for steady-state PL spectroscopy in near infrared and visible spectral range $0.75 – 3$ eV [11]. In a new setup, the T-Cube™ LED Driver Thorlabs LEDD1B (max current 1.2 A) drives the Thorlabs MWWHLP1 2W white LED (color temperature 3000 K, full angle 125°). The output power can be varied using the manual control knob and modulated using an external trigger signal. The condenser lens L1 (focal length $f=15$ mm, diameter Ø 20 mm) concentrates light into parallel beam with adjustable visible light power density up to 100 mW/cm$^2$. The sample S is illuminated by a parallel beam through an aperture A. The translation XYZ stage (three Thorlabs MT1 Single-Axis Translation Stages) allows to move the sample in all 3 directions with 10 µm precision. The stage, white LED and objective are essential to focus small area diodes onto the input slit of the monochromator. The new setup shares with the previous one the optical detection part including the objective L2 (f = 25 mm, Ø 25 mm, uncoated UV fused silica aspheric Lens, EdmundOptics #48536), monochromator Horiba H20IR with 600 g/mm holographic grating, dichroic mirror DM and photodetectors D1 and D2. The photodetectors have fW sensitivity: Thorlabs PDF10A/M fixed gain amplified Si photodiode D1 with the transimpedance gain 1pA/V, noise equivalent power NEP 1.4 fW/Hz$^{1/2}$, spectral range 320 – 1100 nm and 0-20 Hz bandwidth and the Thorlabs PDF10C/M fixed gain amplified InGaAs photodiode D2 with the transimpedance gain 10pA/V, NEP 7.5 fW/Hz$^{1/2}$ spectral range 800 – 1700 nm and band width 0–25 Hz. The monochromatic light with the photon energy above 1.3 eV is reflected toward the photodetector D1 via Thorlabs DMLP950R Longpass Dichroic Mirror whereas the monochromatic light with the photon energy below 1.3 eV is transmitted toward the photodetector D2, see Figure 3A. Figure 3A also compares the spectral responsivity of both photodetectors. Both detectors are connected to the Signal Recovery Model 5105 dual phase lock-in amplifier via the Signal Recovery Model 3830 multiplexer that switches between them at the energy 1.3 eV. Since the spectral response was calibrated by the calibrated halogen lamp in wavelength scale, the presentation of spectra in energy scale requires an additional correction [12].

Figure 2. The setup for optoelectrical measurements: Light source LED, condenser lens L1, aperture A, sample S on XYZ translation stage, objective lens L2, optical filter F, focusing lens L3, input slit S1, monochromator MCH, output slit S2, condenser lens L4, dichroic mirror DM, focusing lenses L5 and L6, photodetectors D1 (Si) and D2 (InGaAs). Available slits 0.1, 0.25, 0.5, 1 and 2 mm correspond to the spectral resolution 1, 2, 4, 8, and 16 nm.
Figure 3. A. Transmittance (T) and reflectance (R) of the dichroic mirror and the spectral responsivity of Si and InGaAs photodiodes. B. The normalised intensity of spectral irradiance of 2W white LED compared to the ASTM E-490 AM0 Standard Solar Spectrum. Data were provided by Thorlabs, Inc. https://www.thorlabs.com/ and https://www.pveducation.org/pvcdrom/appendices/standard-solar-spectra.

Figure 3B compares the normalized intensity of spectral irradiance of the white LED and standard solar spectra. It is obvious that the white LED spectrum differs significantly from the solar spectrum. The white LED produces negligible ultraviolet and infrared light. However, the white LED is useful by providing visible light pulses with adjustable intensity to minimize sample heating.

3. Results and discussion
An idealized diode equivalent circuit is shown in Figure 1B. Its dark I-V characteristic is implicitly given by the Equation 1

$$I(U) = I_0 \left( e^{\frac{q}{k_B T} \left( \frac{U-(R_0+R_S)I}{R_p} \right)} - 1 \right) + \frac{U-(R_0+R_S)I}{R_p} - I_{ph} \quad (1)$$

Here $q = 1.602 \times 10^{-19} \text{ C}$ is the elementary charge, $k_B = 1.381 \times 10^{-23} \text{ J/K}$ is the Bolzmann constant, $T = 300 \text{ K}$ the room temperature, $n$ an ideality factor, $R_P$ a parallel resistance, $R_S$ a serial resistance, $R_0$ a resistance of a protective resistor, $U$ an applied voltage, $I$ a current and $I_0$ a saturation current. Since the serial resistance of the picoammeter is negligible, the total serial resistance of the circuit is the sum of the resistance $R_0$ of a protective resistor and a serial resistance of the diode $R_S$. The ideality factor $n = 1$ is characteristic for diffusion currents whereas the ideality factor $n = 2$ is characteristic for generation-recombination currents [13].

Prior fitting the I-V characteristic using Equation 1, a parallel $R_P = \lim_{U \to \infty} \left( \frac{dI}{dU} \right)^{-1} = 2 \text{ M}\Omega$ and a total serial resistance $R_S + R_0 = \lim_{U \to \infty} \left( \frac{dI}{dU} \right)^{-1} = 101 \text{ } \Omega$ were evaluated from the differential resistance $\left( \frac{dI}{dU} \right)^{-1}$ shown in Figure 5B.
The trapezoid waveform pulses eliminate commutation voltage spikes induced by an inductive load of picoammeter at the rectangular pulse edges, see Figure 4. The optimal frequency for I-V measurements was 2 Hz, the picoammeter reading time 100 ms delayed from the trigger pulse by 100 ms.

The non-linear fitting of the dark I-V characteristic described by the implicit function $I = I(U, I)$ was carried out for $U \in (-0.2, 0.4)V$ via Wolfram Mathematica software using only two constrained fitting parameters $I_0 > 0$ and $n \in (1.2)$. The voltage range has been selected for fitting because for small voltages the dark I-V characteristics are dominated by leakage and diffusion or generation and recombination currents as described by Equation 1. The fitted results reveal the ideality factor $n \approx 1$, the serial resistance $R_S = 1 \Omega$ and the saturation current $I_0 = 50$ pA.

The absolute value of the dark current as a function of the applied voltage $U$ is shown in Figure 5A together with fitted curve using Equation 1. The reverse dark currents at $U < -0.2$ $V$ are probably dominated by the edge effects due to the small diode area [13]. The $I(U)$ appears to be a linear function for $-0.2$ $V < U < 0.2$ $V$ indicating that the exponential term is negligible and the diode behaves as an ohmic resistor with resistance $R_0$ and a leakage current $I \approx \frac{U}{R_0}$. Since the saturation current $I_0$ is much lower then the leakage current, it cannot be directly observed in Figure 5A. The diffusion model fits the measured current well for voltages $0.2$ $V < U < 0.4$ $V$ whereas the forward current at $U > 0.4$ $V$ is dominated by effects not included in Equation 1, such as increase of resistance of doped layers due to high current injection. The forward current is limited at high voltage by the protective resistor $R_0$.

Figure 6A compares the I-V characteristics measured in dark and under visible light illumination in a linear scale. In contrast to our previous paper [14], no S-shape is observed near the open circuit voltage $U_{oc}$ indicating the negligible charge accumulation near $\mu$-Si:H/ZnO interface. Under illumination we detected at zero voltage a photocurrent $I_{ph} = -0.12$ mA corresponding to the current density $I_{ph} = -19$ mA/cm$^2$, an open circuit voltage $U_{oc} = 0.4$ $V$, fill factor 61% and an energy conversion efficiency 6%. Thus, our results confirm that nanostructured ZnO thin film has proven to be a good candidate as transparent electrode. It should be noted that the I-V characteristics are partly influenced by the presence of the protective resistor $R_0$. However, due to a relatively low current, the voltage drop at the protective resistor is negligible for the evaluation of $I_{ph}$ and $U_{oc}$.

The EL spectra and the plot of the total EL integrated in the spectra range 0.75–2 eV as a function of the current density are shown in Figure 6.
The weak electroluminescence observed in the infrared region diminishes above 1.2 eV. No visible light EL was detected. The inset figure shows that the total intensity of EL increases linearly with forward current density. Thus, the fact that Figure 6 shows the relatively weak EL that is shifted to lower energy is related to high crystallinity of the investigated sample [7].

![Figure 5](image1.png)

**Figure 5.** A. The absolute value of a dark current $I$ as a function of applied voltage $U$ (black squares) with the fitted curve (blue solid line). B. The differential resistance $R = \left(\frac{dI}{dU}\right)^{-1}$ (black points) as a function of applied voltage $U$ with the smoothed interpolation curve (blue solid line).

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![Figure 6](image2.png)

**Figure 6.** A The $I$-$V$ characteristics measured in dark (black) and under visible light illumination 100 mW/cm$^2$ (red). B. The electroluminescence spectra at selected current densities (corresponding to black markers in the inset figure) and the plot of the total electroluminescence in the measured spectra range 0.75–2 eV as a function of the current density together with linear regression model (blue line).
4. Conclusions

Our optoelectronic setup previously developed for photoluminescence spectroscopy in the visible and near infrared region has been extended for measurements of optoelectronic properties of small area thin film photodiodes using an arbitrary waveform generator as a pulse voltage source, a white light source and a picoammeter operating in triggered pulse mode. Three preventive measures were successfully implemented to avoid diode damage: a protective resistor to limit the maximum current; trapezoidal voltage pulses to avoid commutation spikes and a switch disconnecting the picoammeter during the current range change to isolate its high inductance load. Using the setup, we have observed that the dark \(I-V\) characteristics of thin film \(p-i-n\) diodes based on \(\mu\)c-Si:H with high crystallinity content deposited on semi-transparent nanostructured ZnO:B electrode are dominated by leakage and diffusion currents for small voltages. No s-shaped photocurrent has been observed near the open circuit voltage \(U_{\text{oc}}\) indicating the negligible charge accumulation near \(\mu\)c-Si:H/ZnO:B interface. The weak EL appears only in the infrared region and diminishes above 1.2 eV. The low EL background makes the diode suitable for future studies of a radiative recombination related to a charge transfer at an interface between nanostructured surface and a surface of embedded nanoparticles.

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