European Action towards Leading Centre for Innovative Materials

ZnO based heterostructures for optoelectronic applications

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Outline

1) Motivation

2) Evaluation of the band offset in heterojunctions by Capacitance vs. Voltage (C-V) measurements

3) Structural, electrical and optoelectronic characteristics of the n-ZnO/p-4H-SiC and n-$Zn_xMg_{(1-x)}O$/p-Si heterojunctions

4) Status of the laboratory up-grading

5) Current/future work

6) Conclusions

ZnO physical properties and technological advantages respect to GaN

- Wide direct band gap like GaN (~3.4 eV @ RT) but 2 times higher exciton binding energy (~60 meV).[1]

- Higher steady state saturation velocity expected (~2×10^7 cm/s @ E > 5×10^5 V/cm) than GaN (~1×10^7 cm/s @ E > 3×10^5 V/cm).[2]

- Radiation hard, free carrier removal rate ~100 times less than that in GaN (1.8 MeV protons @ RT).[3]

- Possibility of wet etching in conventional acid mixtures (with low acid content) at safe temperatures.[4]

- Wide range of deposition techniques (from spin coating up to MBE) and possible substrates (from polymer to single crystal ZnO).[4,5]

1) *Ü. Özgür et al. J. Appl. Phys.* ***98****, 041301 (2005)*

2) *S. K. O' Leary et al. Sol. Stat. Comm.* ***150****, 2182 (2010)*

3) *F. D. Auret et al Appl. Phys. Lett.* ***79****, 3074 (2001)*

4) *H. Morkoc and Ü. Özgür ZnO Wiley VCH (2009)*

5) *Chen et al. Nanoscale Research Letters* ***7****, 214 (2012)*

Current application and material related issues

- ZnO is already used as transparent electrodes for solar cells and flat panel displays and realization of varistors.

- p-type doping in ZnO has not been accomplished necessary for bipolar device realization (high temperature, high frequency devices, high efficiency lighting devices for general illumination, UV emitters and detectors, space electronics, bipolar spintronics).

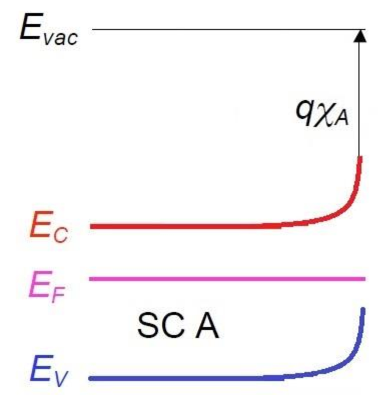
Possible alternative:

heterostructures i.e. combine n-ZnO with semiconductors with established p-type technology

band offsets in heterojunctions is of major importance to understand device operation and potential

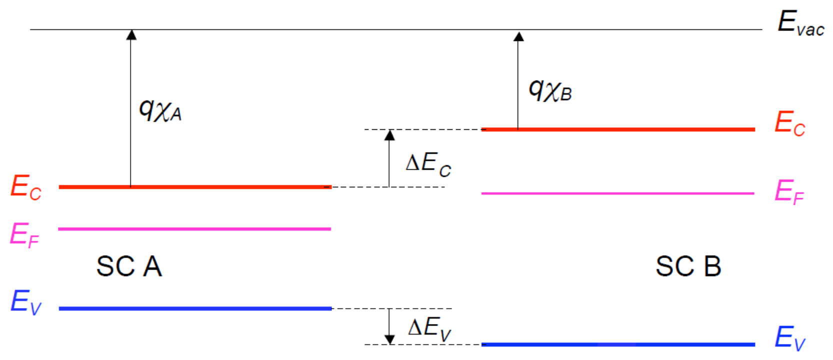
Band alignment in heterostructures

- Simple Anderson model[1] (based on the electron affinity χ).



- Assumes the heterostructure interface equal to the free semiconductor interface not taking into account that:
  1) χ is not a truly bulk property
  2) Microdiffusion, chemisorption, interface reconstruction etc

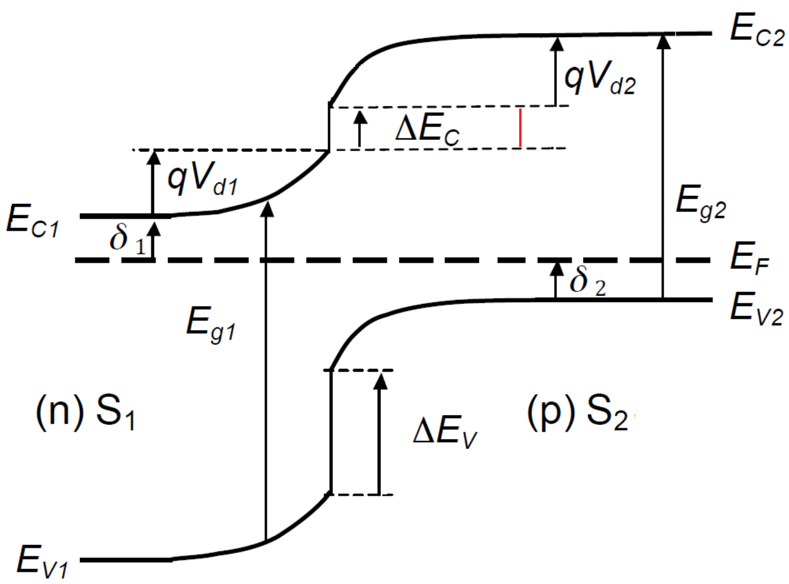
- Absolute electron affinity values in the case of ZnO have little meaning (~900 meV variation due to adsorbates).[2]



- Generally only ~10-30% of the conduction band offset is related to χ differences.[3]

1) *R. L. Anderson, Solid Stat. Electron.* ***5****, 341 (1962)*
2) *V. E. Henrich and P. A. Cox, The surface science of metal oxides, Cambridge University Press (1996)*
3) *J. P. Kleider, Band line-up theories and determination of band offsets from electrical measurements, Springer (2012)*

How to measure the conduction and valence band misalignment



- The conduction band offset ΔE_C is given by:

$$\Delta E_C = E_{g2} - (qV_d + \delta_1 + \delta_2)$$

with δ_1/δ_2 equal to:

$$p_{S2} = \frac{1}{4}\left(\frac{2k_B T m_{S2}}{\hbar^2 \pi}\right)^{\frac{3}{2}} e^{\frac{-\delta_{S2}}{k_B T}}$$

$$n_{S1} = \int_0^{+\infty} \sqrt{2E}\,\frac{{m_{S1}}^{3/2}}{\pi^2}\,\frac{1}{exp\big((E+\delta_{S1})/k_B T\big)+1}$$

and qV_d that can be measured by C-V considering that:

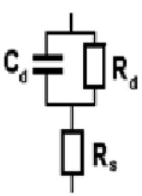
$$C_d = A\sqrt{\frac{e\varepsilon_{S1}\varepsilon_{S2}n_{S1}p_{S2}}{2(\varepsilon_{S1}n_{S1}+\varepsilon_{S2}p_{S2})}}\frac{1}{\sqrt{V-V_d}} \quad \Rightarrow \quad \frac{1}{{C_d}^2} \propto (V - V_d)$$

Details on the capacitance measurements for evaluating ΔE_c

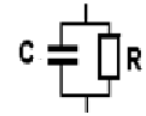
- Non uniform doping, interfacial states, series resistance, R_s, can cause deviations from the expected $1/C_d^2 \propto V\text{-}V_d$ dependence i.e. affect the measurements of ΔE_c.

- Measurements at different frequencies, $\omega/2\pi$, must be performed to distinguish between non-uniform doping and interfacial states contribution.

- In addition the influence of R_s on C_d must be considered:



$$= Z^{-1} = \frac{\varpi^2 C_d^{\,2} R_s + \frac{1}{R_d}\left(1+\frac{R_S}{R_d}\right)}{\left(1+\frac{R_S}{R_d}\right)^2 + \varpi^2 C_d^{\,2} R_S^2} + j\frac{\varpi C_d}{\left(1+\frac{R_S}{R_d}\right)^2 + \varpi^2 C_d^{\,2} R_S^2} \quad \overset{?}{\Leftrightarrow}$$



$$= Z^{-1} = \frac{1}{R} + j\varpi C$$

$$R_S \ll R_d \qquad \varpi C_d R_S \ll 1 \quad \Rightarrow \quad C \rightarrow C_d$$

The n-ZnO/p-4H-SiC heterostructure: advantages and possible applications

- Low lattice and thermal mismatch of wurtzite polytype of SiC respect to ZnO (5% and 1% for 6H-SiC).[1]

⇩

4H-SiC is expected to be an excellent candidate for ZnO epitaxy

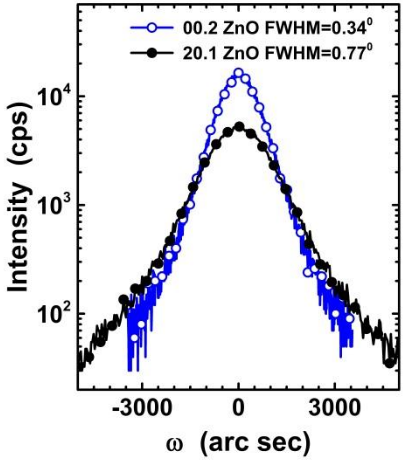
- Previous attempts revealed heterojunctions with up to 7 orders in rectification.[2]
- Both semiconductor have a wide band gap (3.2 eV @ RT for 4H-SiC).[3]

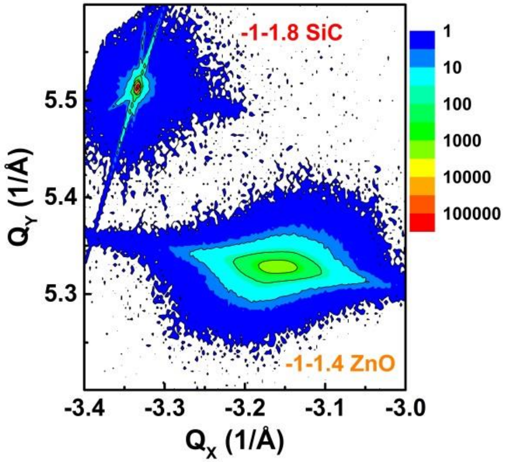
⇩

Possible choice for the realization of UV/visible blind detectors: optoelectronic properties of the devices should be checked

1) *A. B. M. A. Ashrafi et al. Appl. Phys. Lett.* ***84****, 2814 (2004)*
2) *M Guziewicz et al. Material Science Forum* ***717****, 1323 (2012)*
3) http://www.ioffe.rssi.ru/SVA/NSM/Semicond/SiC/bandstr.html#Basic

The structural characteristics of the ALD ZnO film grown on 4H-SiC



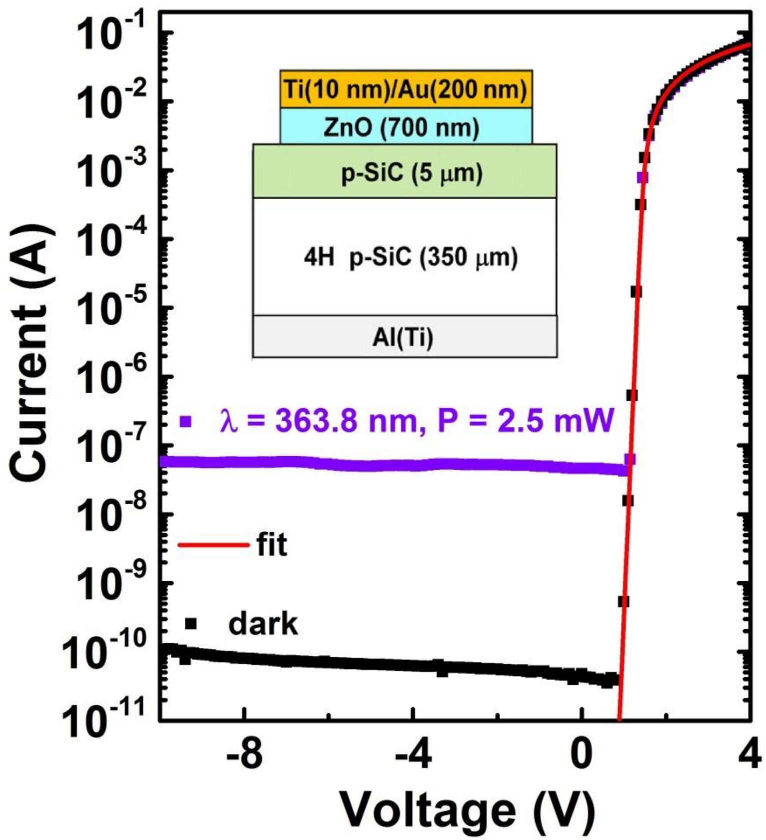


- ~700 nm thick ZnO film grown by ALD (Savannah 100 reactor).
- Deposition @ 300 ^oC, DEZn and DI water as precursors, N_2 as purging gas.
- Good crystal quality, rocking curve FWHM of the 00.2 peak ~0.34^o (to be compared with ~1.43^o for PLD films @ 200 ^oC and ~0.13^o for RS-MBE films @ 450 ^oC).[1,2]
- Percentage lattice deviation below ~0.3%.

M. Guziewicz, R. Schifano, E. Przezdziecka, J. Z. Domagala, W. Jung, T. A. Krajewski, and E. Guziewicz, Appl. Phys. Lett. ***107****, 101105 (2015)*

1) *J. H. Kim et al. J. Alloys Compd.* ***489****, 179 (2010)*
2) *A. El-Shaer et al. Superlattices Microstruct.* ***42****, 387 (2007)*

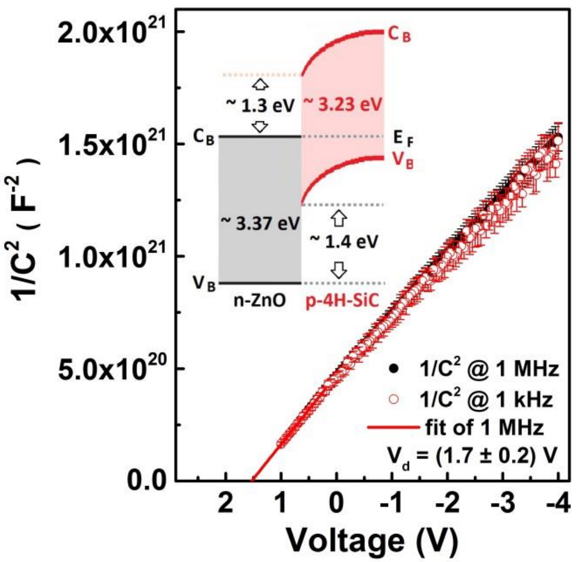
The electrical characteristics of the n-ZnO/p-4H-SiC heterostructure



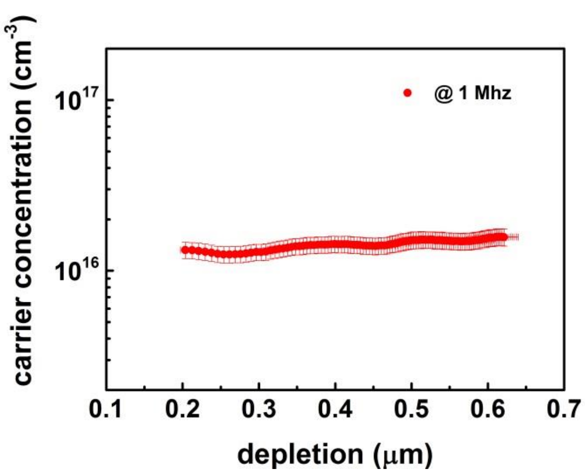
M. Guziewicz, R. Schifano, E. Przezdziecka, J. Z. Domagala, W. Jung, T. A. Krajewski, and E. Guziewicz, Appl. Phys. Lett. ***107****, 101105 (2015)*

- Semitransparent Al/Ti Ohmic back contact (~10% transmittance).
- Mesa structure realized by etching the excess ZnO below the top Ti/Au Ohmic contact.
- High rectification ratios (10^9), ideality factor close to 1 (1.17±0.04) very low leakage current density (~6 10^{-8} A/cm^2) and (~10^3) light to dark reverse current ratio.
- Superior electrical performances respect to previously reported devices.

Band alignment in the n-ZnO/p-4H-SiC heterostructure



M. Guziewicz, R. Schifano, E. Przezdziecka, J. Z. Domagala, W. Jung, T. A. Krajewski, and E. Guziewicz, Appl. Phys. Lett. ***107****, 101105 (2015)*



- No differences between C-V measurements performed at different frequencies (1 MHz-1 kHz range @ RT).

- Deviation from the expected linearity of $1/C^2$ vs V due to carrier concentration oscillations vs. depth.

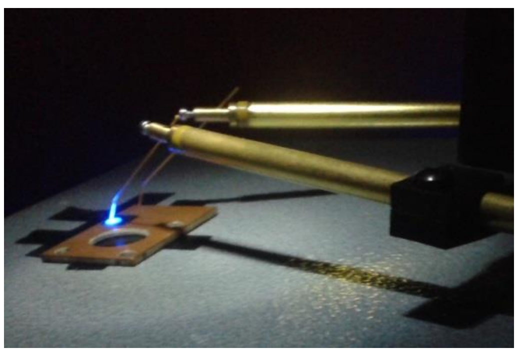
- Type II band alignment, ΔE_c=(1.3±0.2) eV in agreement with the values extracted from XPS measurements (1.5±0.2) eV.[1]

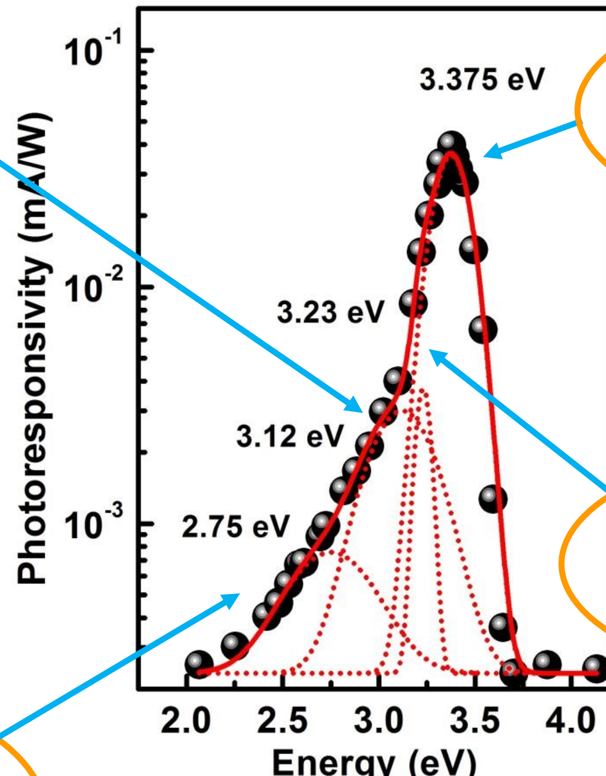
1) H. B. Fan et al. Appl. Phys. Lett. ***92****, 192107 (2008)*

Optoelectronic response of the n-ZnO/p-4H-SiC heterostructure

Photoresponsivity measurements reveals 4 Gaussian contributions (back side illumination i.e. through the 4H-SiC substrate).

Defect contribution possibly related to V_{Zn} in ZnO[2]





Band to band photogenerated carriers in ZnO

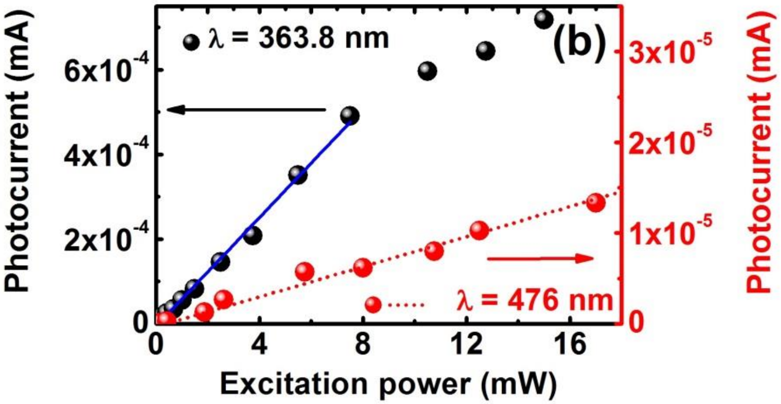
Band to band photogenerated carriers in 4H-SiC

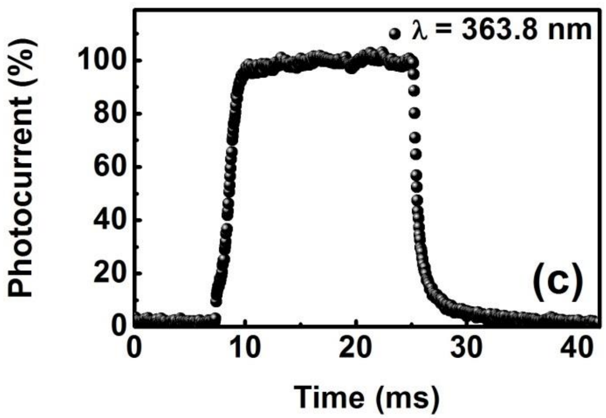
Defect contribution possibly related to polytypes inclusions in 4H-SiC[1]

M. Guziewicz, R. Schifano, E. Przezdziecka, J. Z. Domagala, W. Jung, T. A. Krajewski, and E. Guziewicz, Appl. Phys. Lett. ***107****, 101105 (2015)*

1) *W. J. Choyke et al Optical properties of SiC 1997-2002, Springer (2004)*
2) *F. X. Xiu et al. Appl. Phys. Lett.* ***87****, 252102 (2005)*

Power and time response of the n-ZnO/p-4H-SiC heterostructure under illumination





M. Guziewicz, R. Schifano, E. Przezdziecka, J. Z. Domagala, W. Jung, T. A. Krajewski, and E. Guziewicz, Appl. Phys. Lett. ***107****, 101105 (2015)*

- Linear response for the peaks occurring at ~2.75 eV and 3.375 eV (below 8 mW excitation power).
- Photoresponsivity equal to (0.07±0.01) mA / W @ 3.375 eV (~70 times lower than the best reported value for n-ZnO/p-6H-SiC).[1]
- Not optimized device for back side detection. Total reduction of the laser light down to ~1% due to back Ohmic contact and 4H-SiC absorption.
- Rise time and fall times are found equal to ~2 ms and limited by charging/decharging of defects in the active region of the device.

1) Ya. I. Alivov et al. Appl. Phys. Lett. 86, 241108 (2005)

The n-ZnO/p-Si heterostructure for photovoltaic applications

- Theoretical possibility to achieve high efficiency solar cells, while reducing the fabrication complexity respect to ordinary Si based solar cells.[1]

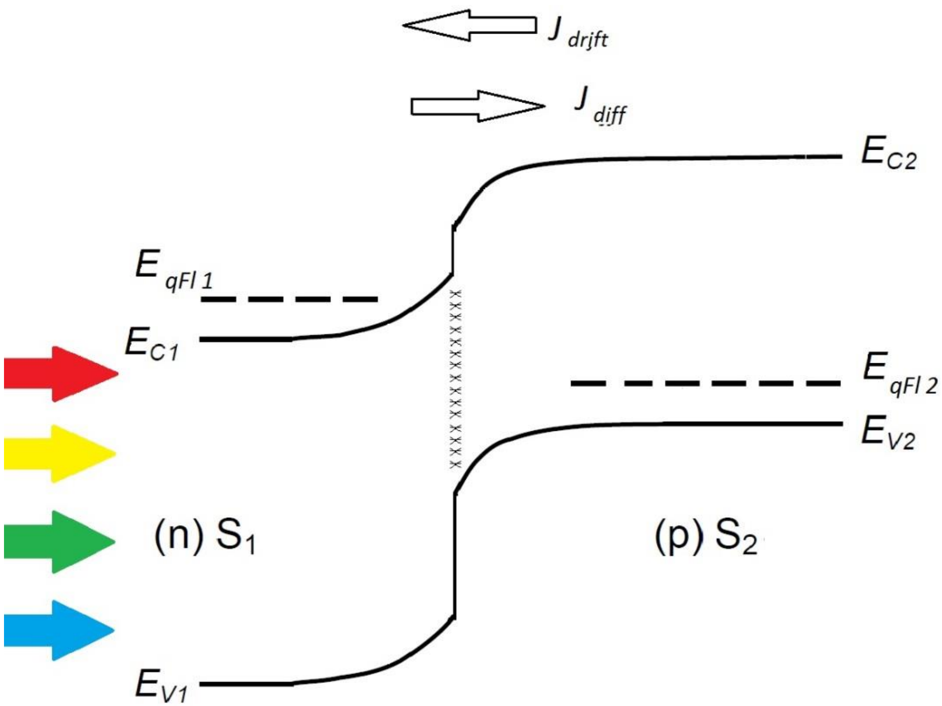
- Efficiencies in the 4.4-5.9% range have been obtained in previous attempts (even by using Ag nanoparticles to increase the photon harvesting/direct creation of electron hole pairs).[2,3,4]

- Low efficiencies so far achieved are related to the presence of interface recombination centers due to the large lattice mismatch between Si (~5.43 Å) and ZnO (~3.25 Å) and different crystal structure (diamond like vs. wurtzite).

Interface engineering is required to increase the efficiency

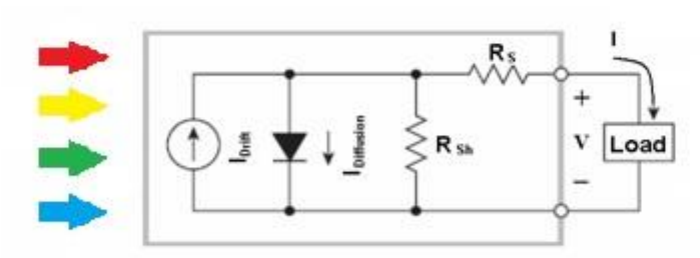
1) *B. Hussain et al. Sol. Energy Mater. Sol. Cells* ***139****, 95 (2015)*
2) *R. Pietruszka et al. Mater. Sci. Semicond. Process.* ***25****, 190 (2014)*
(3) *E. Kozarsky et al. 38Th IEEE Photovoltaic Specialist Conference 1217 (2012)*
(4) *J. Kim at al. Mater. Lett.* ***75****, 99 (2012)*

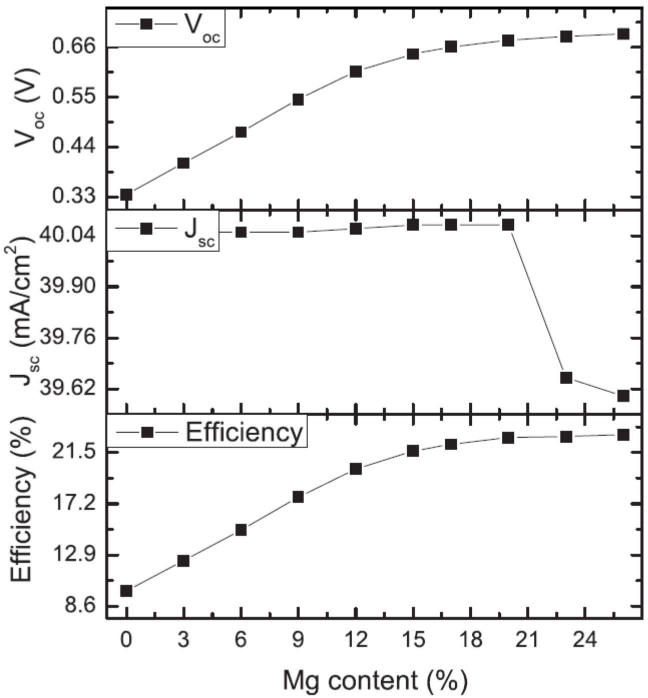
Recombination through interfacial defects



- Two currents contribution flowing under illumination: J_{drift} (photogenerated) J_{diff} (diffusion).
- Interfacial recombination centers provide a shunt for J_{diff} (type II band alignment).
- Recombination rate, *R*, is equal to: $v_{el}\sigma n$ with v_{el}, rms thermal velocity, σ capture cross section n density of electrons.
- Reduce the band misalignment reduces n at the interface i.e. reduces *R* .

Tuning the conduction band alignment in n-ZnO/p-Si heterostructures



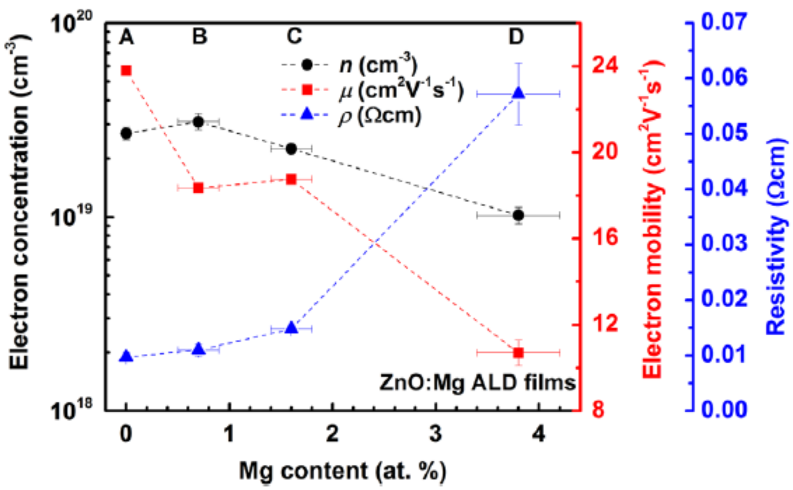


K. E. Knutsen, R. Schifano et al. Phys. Stat. Sol. A 210 ,585 (2013)

- The conduction band misalignment can be reduced by Mg incorporation.[1]
- Theoretically by increasing the Mg content up to ~20 at.% the expected solar cell efficiency can reach ~24% (ΔE_c varying from -0.3 eV to +0.024 eV).[2]
- Due to the reduction in the interfacial shunting effect V_{oc} is expected to increase.
- Experimentally tested Mg contents up to ~4 at.%.

1) *Ü. Özgür et al. J. Appl. Phys.* ***98****, 041301 (2005)*
2) *K. E. Knutsen, R. Schifano et al. Phys. Stat. Sol. A* ***210*** *,585 (2013)*

Effect of Mg incorporation on the $Zn_{(1-x)}Mg_xO$ films electrical properties



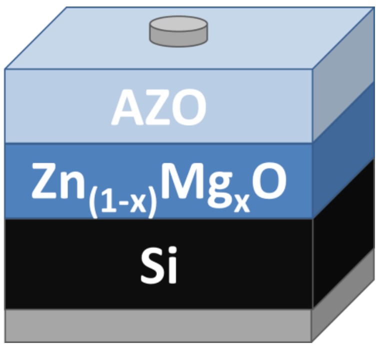
R. Pietruszka , R. Schifano, T. A. Krajewski, B. S. Witkowski, K. Kopalko, L. Wachnicki, E. Zielony, K. Gwozdz, P. Bieganski, E. Placzek-Popko, and M. Godlewski Solar Energy Materials & Solar Cells ***147****, 164-170 (2016)*

- ~350 nm thick $Zn_{(1-x)}Mg_xO$ film grown by ALD (Savannah 100 reactor).
- Deposition @ 160 ^oC, DEZn bis(methylcyclopentadienyl) and DI water as precursors, N_2 as purging gas.
- Mg content determined by EDX measurements A=0, B=0.7, B=1.6 C=3.8 at.%.

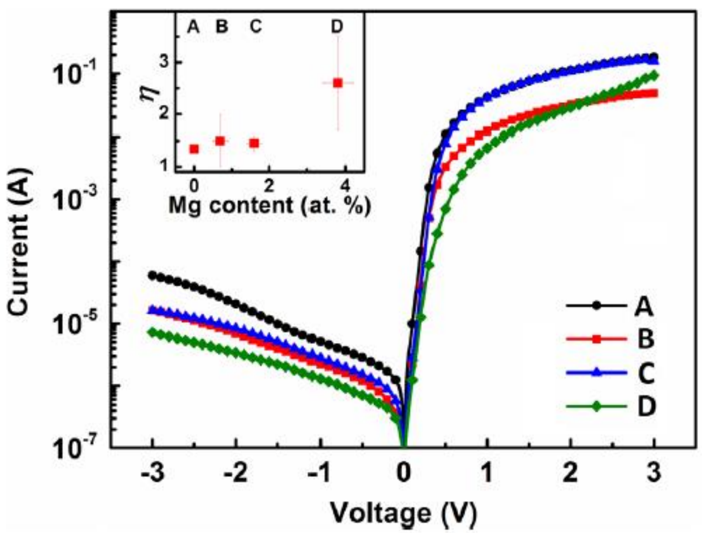
- Incorporation of Mg causes a 2-3 decrease in the carrier concentration and mobility, consistent with previously reported results attributed to less effective doping and larger effective mass due to Mg introduction.[1,2]

1) *D. J. Cohen et al. J. Appl. Phys.* ***96****, 459 (2004)*
2) *K. Matsubare et. al. Appl. Phys. Lett.* ***85****, 1374 (2004)*

Electrical properties of the resulting devices



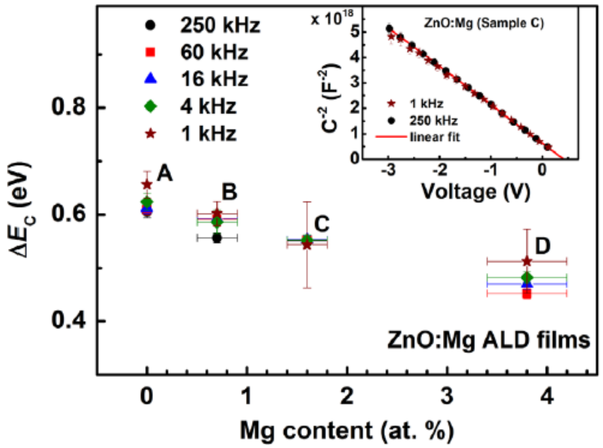
	Mg [%]
A	0
B	0.7 ± 0.2
C	1.6 ± 0.2
D	3.8 ± 0.4

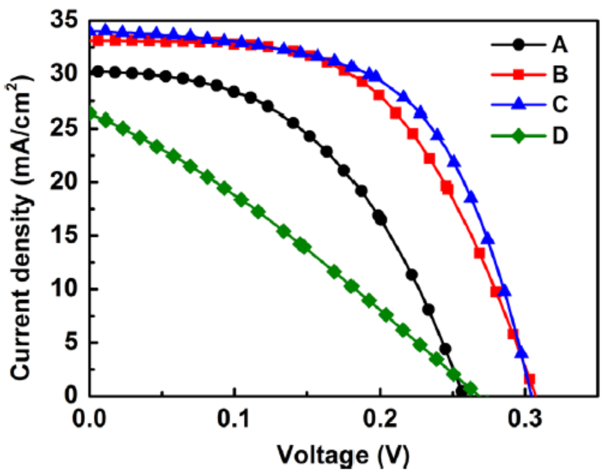


- Additional ~250 nm thick AZO film grown by ALD (Savannah 100 reactor).
- Deposition @ 160 ºC, DEZn, DI water and TMAl as precursors, N_2 as purging gas.
- Good rectification ratio of the resulting structures.
- Ideality factor, η, below 2 for Mg content < 2 at.%.

R. Pietruszka , R. Schifano, T. A. Krajewski, B. S. Witkowski, K. Kopalko, L. Wachnicki, E. Zielony, K. Gwozdz, P. Bieganski, E. Placzek-Popko, and M. Godlewski Solar Energy Materials & Solar Cells ***147****, 164-170 (2016)*

Conduction band alignment vs. optoelectrical properties



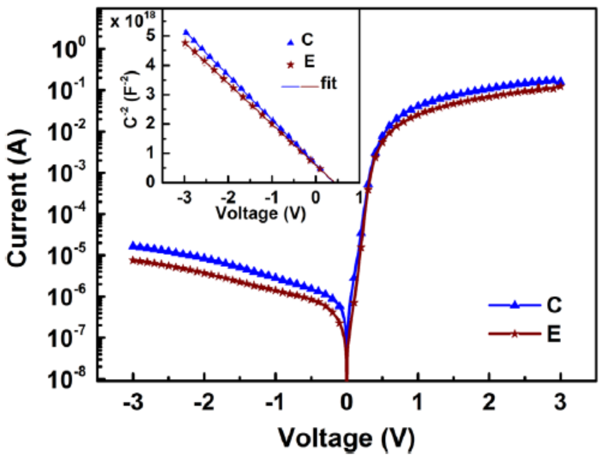


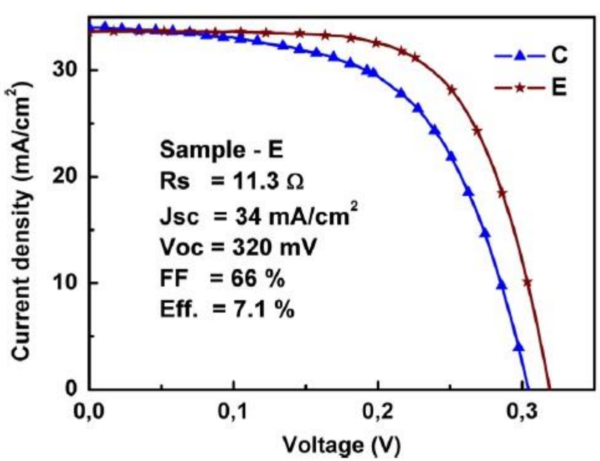
- Decrease in ΔE_c from (0.63±0.03) eV to (0.48±0.03) eV for Mg content up to ~4 at.%.
- ΔE_c ~0.3 eV larger than in the theoretical study.
- The efficiency increases up to ~6% for Mg content equal to ~1.6 at.%.

	Mg [%]	R_S [Ω]	R_p [Ω]	J_{SC} [mA/cm^2]	V_{OC} [mV]	FF [%]	Eff [%]
A	0	(17 ± 4)	$\geq 10^6$	30.3	257	48	3.7
B	0.7 ± 0.2	(21 ± 1)	$\geq 10^6$	33.1	307	55	5.6
C	1.6 ± 0.2	(12 ± 2)	$(8.0 \pm 0.3) \times 10^3$	34.0	304	58	6.0
D	3.8 ± 0.4	(120 ± 10)	$(1.3 \pm 0.7) \times 10^3$	26.4	268	29	2.1

*R. Pietruszka , R. Schifano, T. A. Krajewski, B. S. Witkowski, K. Kopalko, L. Wachnicki, E. Zielony, K. Gwozdz, P. Bieganski, E. Placzek-Popko, and M. Godlewski Solar Energy Materials & Solar Cells **147**, 164-170 (2016)*

Effect of the deposition temperature on the photovoltaic response

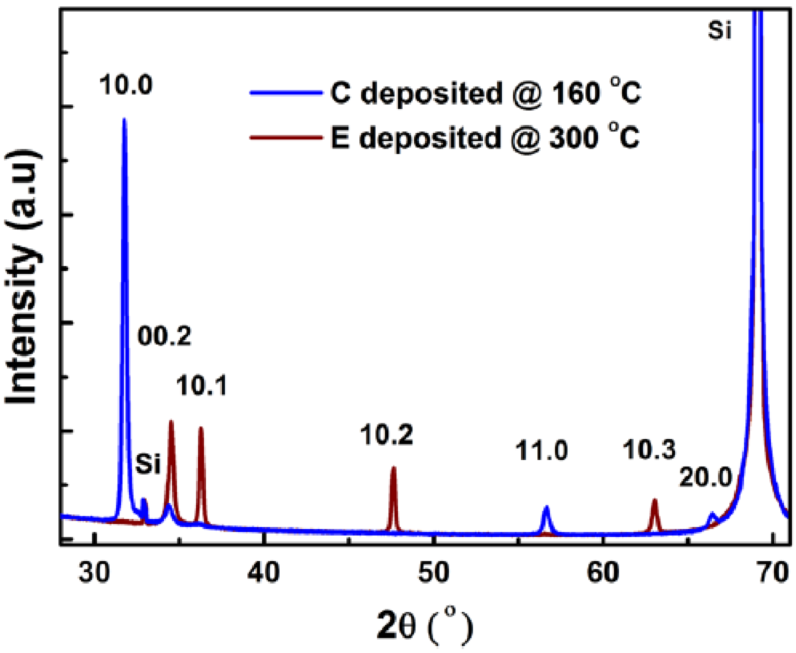




- Investigated additional devices with the $Zn_{(1-x)}Mg_xO$ deposited at 300 ^oC Mg content < 2 at.%.
- Similar electrical properties of the films.
- Similar electrical properties of the devices realized with no significant differences in the ΔE_c (~0.54 eV) extracted from C-V measurements.
- ~1.1% increase in efficiency due to the larger V_{oc} and higher R_p for the device with the $Zn_{(1-x)}Mg_xO$ film deposited at 300 ^oC.

*R. Pietruszka , R. Schifano, T. A. Krajewski, B. S. Witkowski, K. Kopalko, L. Wachnicki, E. Zielony, K. Gwozdz, P. Bieganski, E. Placzek-Popko, and M. Godlewski Solar Energy Materials & Solar Cells **147**, 164-170 (2016)*

Effect of the deposition temperature on the films crystallographic pattern



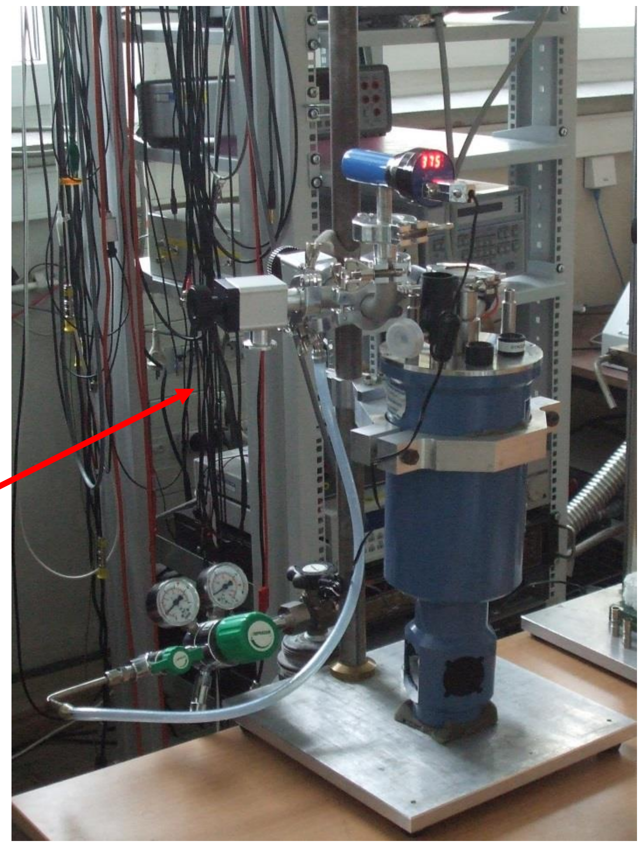
*R. Pietruszka , R. Schifano, T. A. Krajewski, B. S. Witkowski, K. Kopalko, L. Wachnicki, E. Zielony, K. Gwozdz, P. Bieganski, E. Placzek-Popko, and M. Godlewski Solar Energy Materials & Solar Cells **147**, 164-170 (2016)*

- Mg suppress the growth in the *c* direction.[1]
- Enhancement in the *c*-direction growth mode when the deposition is performed at 300 °C.
- ~1.1% increase in efficiency attributed to the significant differences in interfacial/bulk defects as suggested by the different crystallographic pattern.

*1) G. Luka et al. J. Mater. Sci. **49**, 1512 (2014)*

Status of the laboratory upgrading (1)

- ZnO surface conductivity depends is very sensitive to the presence adsorbates. This will provide a leakage current path during electrical measurements.

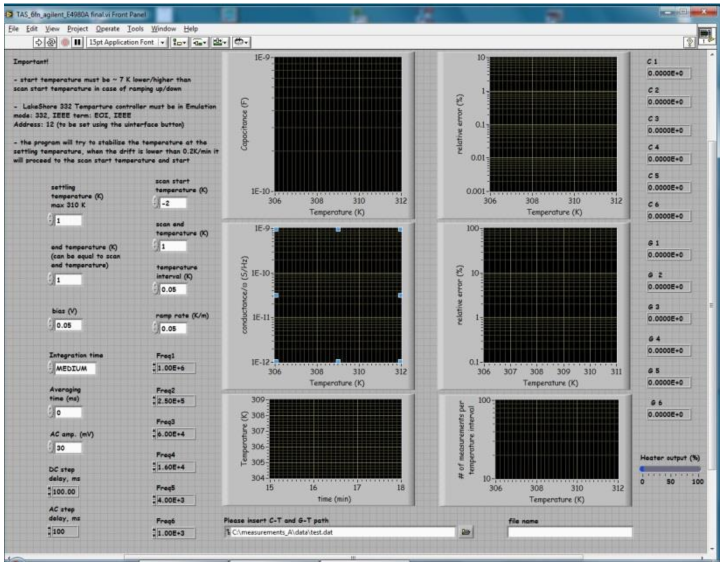


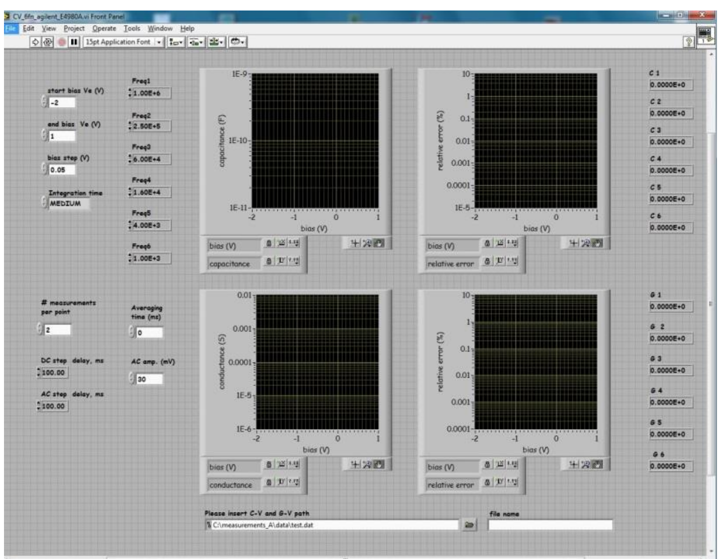
$$e_D = \beta T^2 \sigma_{app} \exp\left(\frac{-\Delta H}{k_B T}\right)$$

Possibility to perform the measurements in inert gas (N_2)

Extended temperature range up to 500K

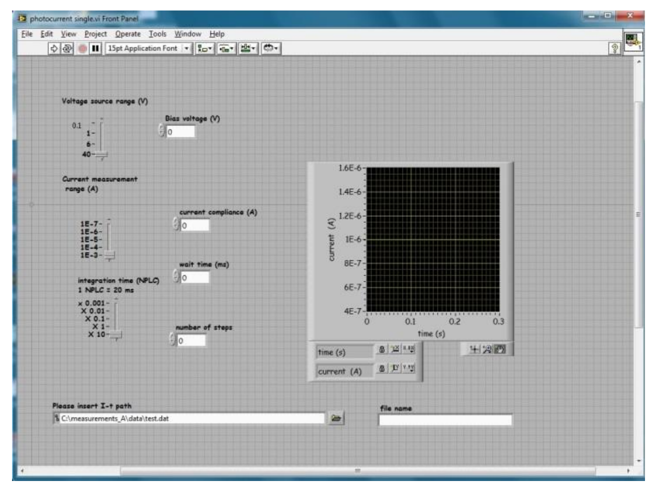
Status of the laboratory upgrading (2)



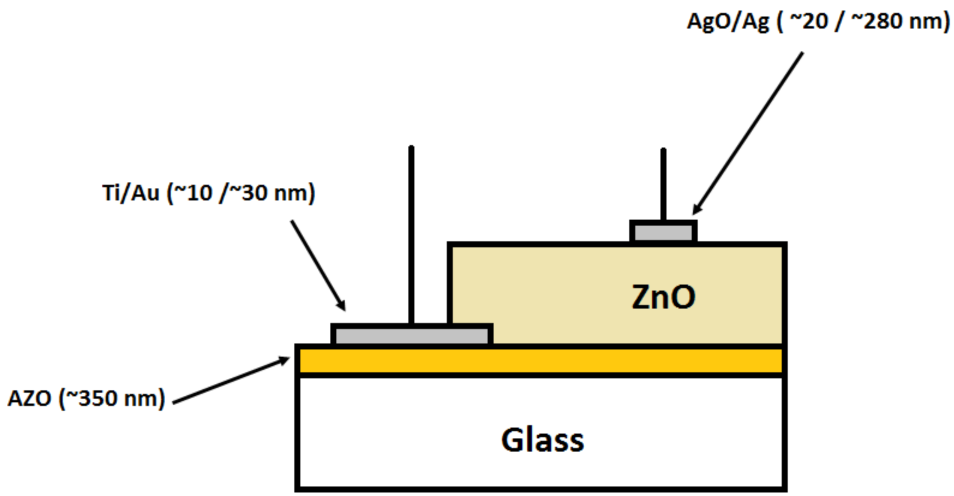


- A new rod suitable for the characterization of larger samples with several Schottky contacts deposited on the same film has been constructed (K.K. and K.G.).

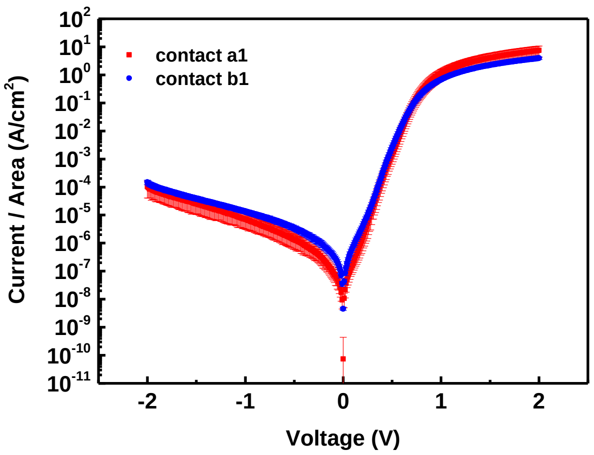
- Labview programs for measuring Thermal admittance spectroscopy, C-V and G-V at 6 frequencies simultaneously and photocurrent transients have been written and tested.



Current/future work: Schottky diodes to ALD grown ZnO

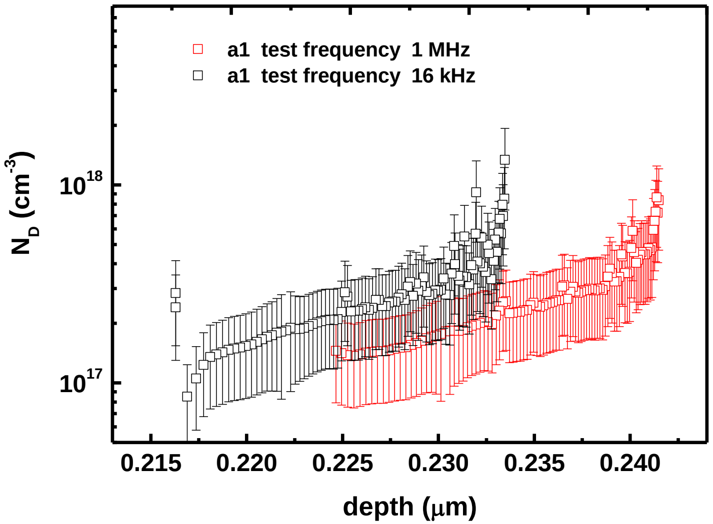


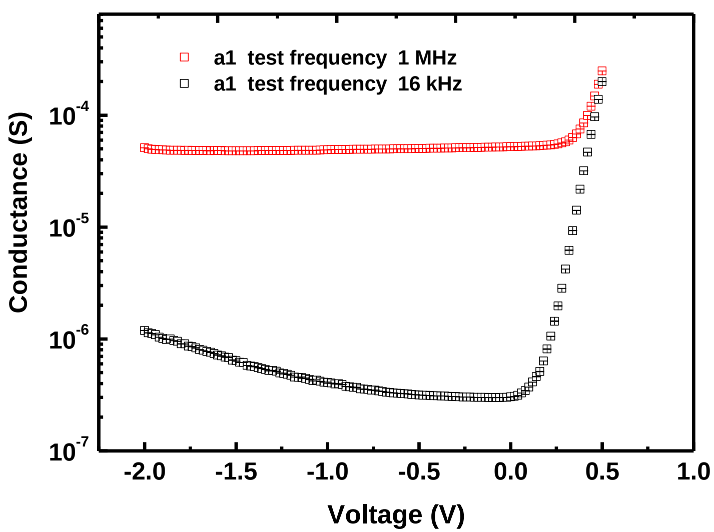
layers grown by D. Snigurenko



- Up to 5 orders in rectification achieved (-2 V, +2V range).
- Low series resistance ~ 19 – 21 Ω.

Schottky diode C-V and G-V characteristics





- Possible to reduce the carrier concentration down to ~1- 4 · 10^{17} cm^{-3}.
- Low on/off conductance (G) ratios and high reverse bias values of G at 1 MHz.
- G in reverse bias condition should not exceed ~10^{6} S for performing DLTS measurements.
- Alternative ways to reduce G are under investigation (introduction of a thin insulating layer, growth conditions and substrate effects).

Conclusions

- *N-ZnO/p-4H-SiC* heterostructures with 10^9 rectification ratio, ~1.2 ideality factor, very low leakage current density (~6 10^{-8} A/cm^2), ~10^3 light to dark reverse current ratio and relatively fast photoresponse (~2 ms) have been demonstrated.

- The possibility of tuning the *n-ZnO/p-Si* conduction band alignment by introducing Mg and its effect on the photovoltaic response of the device has been experimentally verified.

- A maximum ~7.1% efficiency for a *n-ZnMgO(Mg=2. at.4%)/p-Si* based solar cell has been demonstrated.

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*M. Guziewicz, R. Schifano, E. Przezdziecka, J. Z. Domagala, W. Jung, T. A. Krajewski, and E. Guziewicz, Appl. Phys. Lett. **107**, 101105 (2015)*

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and K. Goscinski

Thanks for your attention!