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ALD grown ZnMgO:Al on Si for photovoltaic applications: test solar cells performances for Mg content up to ~12% at.

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Motivation

Heterojunction solar cells based on ZnMgO and Si employed as an emitter and absorber, respectively, have a potential theoretical efficiency of ~24% if the conduction band offset between ZnO and Si is eliminated by Mg alloying [1]. This approach has been experimentally tested and has shown that an efficiency increase from ~3,7% to ~6% can be achieved following this route [2]. However, as discussed in Ref. 2, further improvements in efficiency are hindered by the increase in resistivity of the ZnO-based layer when the Mg content overcomes ~2-3 at.%. In the presented work the possibility of increasing the Mg content above ~2-3 at.%, while maintaining a low resistivity by Al doping, has been investigated.

Samples

The n-ZnMgO/ZnMgO:Al /AZO layers deposited by ALD on p-Si substrate

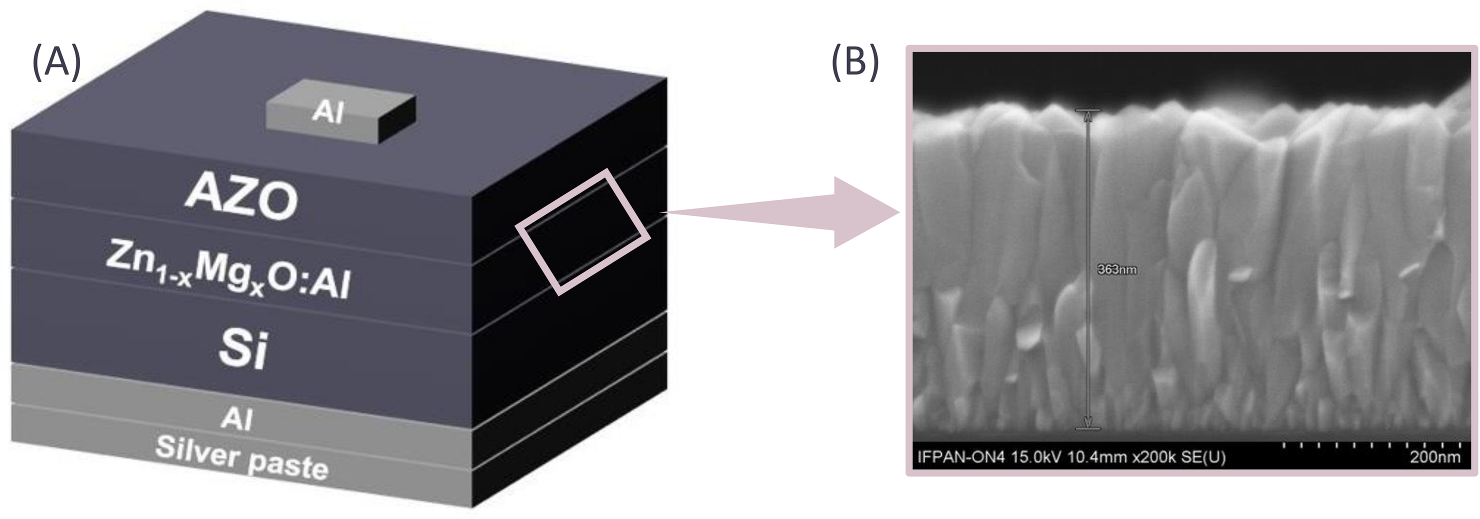


Fig. 1 (A): The schematic draw of the studied structures (not scaled).
(B): Cross section view of a ZnMgO film from set A (see Tab.1).

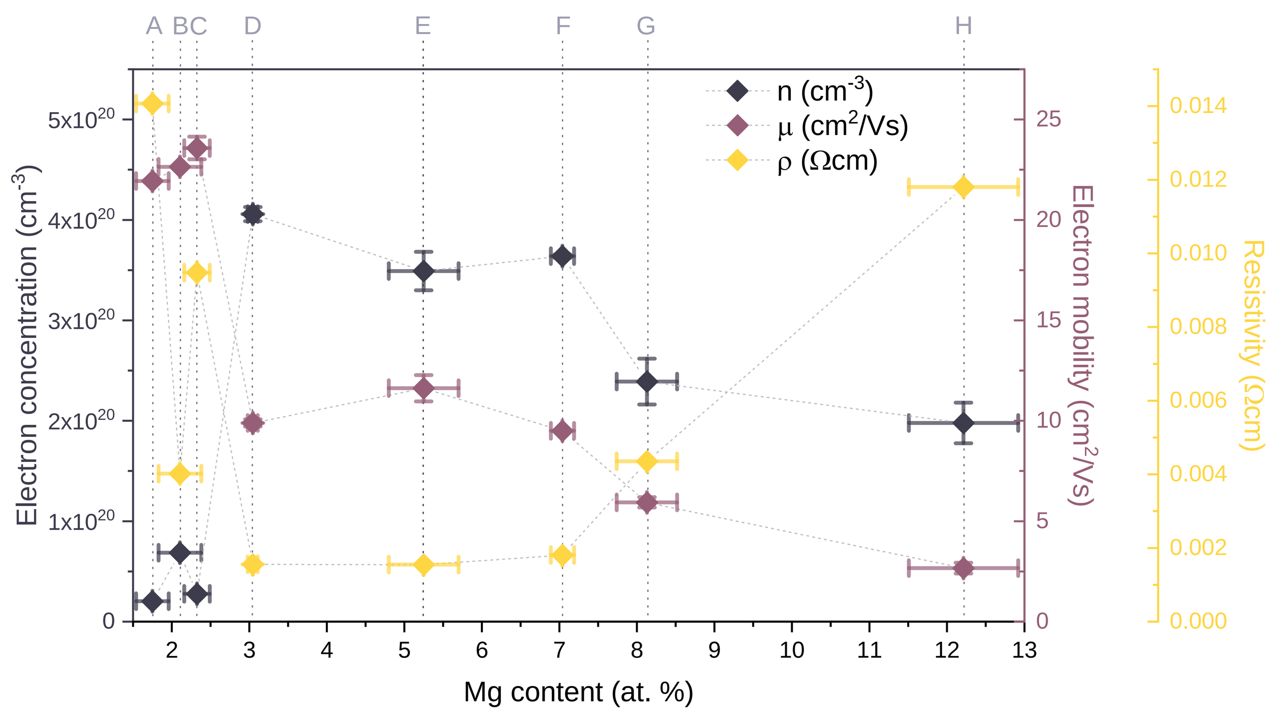
Experimental techniques

- Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM+EDX)
  - Thickness and composition of the ZnMgO/ZnMgO:Al layers
- Hall measurements of ZnMgO/ZnMgO:Al layers
  - Electron concentration (n), electron mobility (μ), resistvity (ρ)
- Capacitance and conductance vs voltage (C-V and G-V, respectively) measurements
  - Built-in potential (V_{bi}), effective acceptor concentration (N_{eff})
- Current vs voltage (I-V) measurements in dark and under standard illumination
  - Open circuit voltage (V_{oc}), short circuit current density (J_{sc}), efficiency (η), fill factor (FF), series resistance (R_s)
- External quantum efficiency (EQE) measurements of the ZnMgO:Al/Si heterostructures
  - Optical band gap, J_{sc}^{EQE}

Results

Table 1. **Composition** and **thickness** of the examined ZnMgO:Al layers

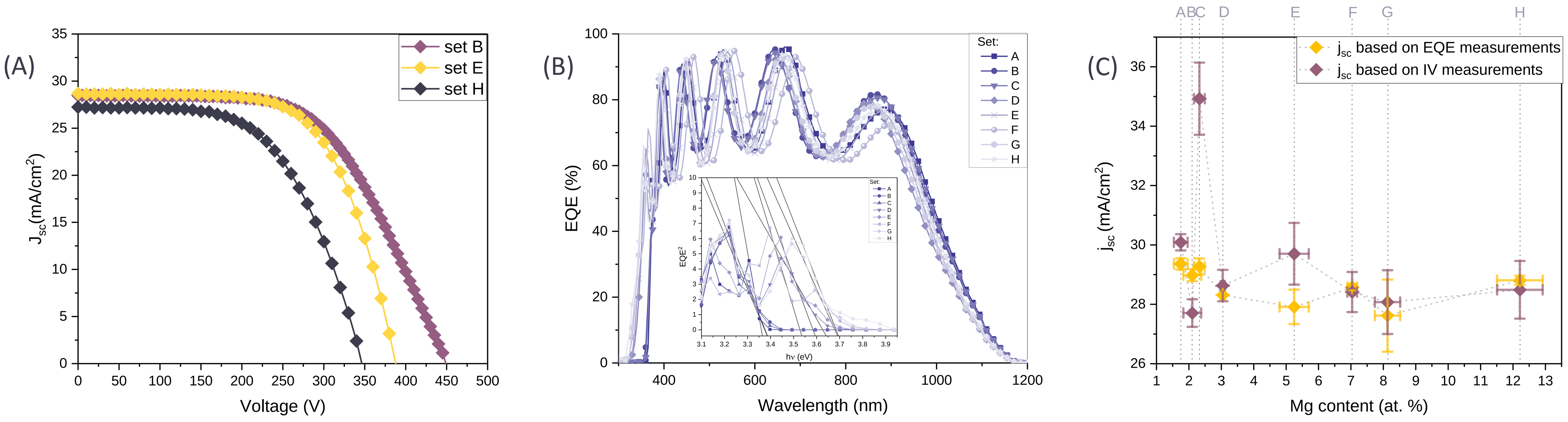
Set of samples	Mg (% at.)	Al (% at.)	Thickness (nm)
A	1,8 ± 0,2	0	470 ± 13
B	2,1 ± 0,3	0	448 ± 9
C	2,3 ± 0,2	0	406 ± 34
D	3,0 ± 0,1	2,4 ± 0,1	474 ± 2
E	5,3 ± 0,5	2,4 ± 0,1	499 ± 7
F	7,0 ± 0,2	2,3 ± 0,1	503 ± 3
G	8,1 ± 0,4	2,8 ± 0,2	453 ± 20
H	12,2 ± 0,7	2,5 ± 0,3	464 ± 24



(see Table 1 for the labels – the dashed lines are a guide to the eye)

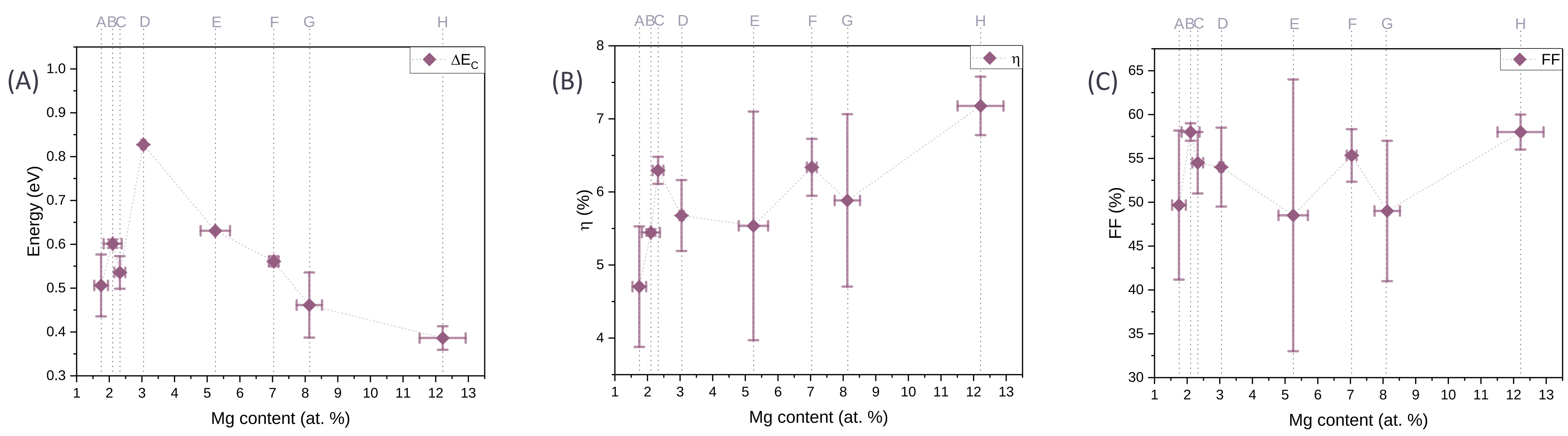
Fig. 2: **Hall measurements**: electron concentration, mobility and resistivity versus Mg content. A visible increase in the concentration of electrons (by an order of magnitude), with a simultaneous decrease in the resistivity of the layer to 0,001 Ωcm with Al introduction (set D) proves that the difficulties described in Ref. 2, have been overcome, that is, this approach permits to increase the Mg content up to ~12 at.% while maintaining the required electrical characteristics of the layers.

Fig. 3 (A): **I-V measurements under illumination** for 3 samples with different Mg contents.
(B): **External quantum efficiency** for the whole series of examined samples. A shift of the EQE edge towards higher energies with increasing Mg content is clearly visible. A Tauc-like plot (inset) permits to estimate a ZnMgO band gap increase from ~3,34 eV (~2,1 Mg at.%) to 3,76 eV (~12,2 Mg at.%).
(C): J_{sc}^{I-V} and J_{sc}^{EQE} versus Mg content. The values are found to be very close to the maximum expected (~30 mA/cm²) for an equivalent AZO layer). $J_{sc}^{I-V} \sim J_{sc}^{EQE}$ suggests a limited density of microshunts in the ZnMgO/ZnMgO:Al layers.



(see Table 1 for the labels – the dashed lines are a guide to the eye)

Fig. 4 (A): The **conduction band offset** (ΔE_c) versus Mg content in the ZnMgO:Al/Si heterostructures. ΔE_c increased up to ~0,83 eV after introducing Al. The initial increase of ΔE_c from ~0,3 eV is consistent with band gap narrowing previously reported in highly doped ZnO:Ga layers [3].
(B) **Efifciency** versus Mg content. A beneficial effect of further reducing the conduction band misalignment by introducing larger amount of Mg (maximum $\eta \gtrsim 7\%$ for Mg ~12 at.%) is observed.
(C) **Fill factor** versus Mg content. The fill factor is fluctuating around ~55% independently of the Mg content, thus suggesting other causes than Mg introduction as limiting factors (metallization, cell design, as an example).



(see Table 1 for the labels – the dashed lines are a guide to the eye)

Summary

It has been found that, as expected, by keeping the Al content ~2 at.%, up to ~12 at.% Mg can be incorporated into the ZnO layers with the films still maintaining excellent electrical properties:

- $n = (2{,}0\pm0{,}2)\cdot10^{20}$ cm^{-3}
- $\mu = (2{,}7\pm0{,}3)$ cm²/Vs
- $\rho = (11{,}08\pm0{,}01)$ mΩcm

For the test solar cell with the Mg content equal to (12,2±0,7)%:

- Reduction of the conduction band misalignment from (0,5±0,1) eV to (0,38±0,03) eV
- $V_{oc} = (430\pm16)$ mV
- Efficiency (7,2±0,4) %.

References

[1] K. E. Knutsen , R. Schifano et al. Phys. Status Solidi A 210, No. 3, 585–588 (2013).
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[3] Y. Wang, W. Tang et al. Thin Solid Films 565 (62-68) (2014).

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