ALD Grown ZnMgO:Al on Si for Photovoltaic Applications: Effect of High Mg Alloying and Al Doping

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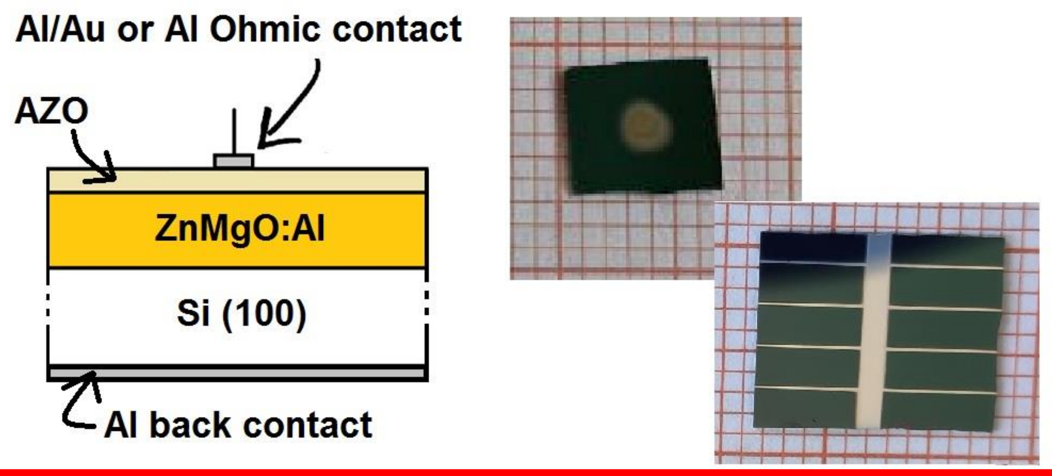
A potential theoretical efficiency of ~24% has been predicted by PC1D simulations in the case of solar cells based on ZnO/Si if the conduction band gap misalignment (ΔE_C) between ZnO and Si is eliminated while keeping an interfacial recombination as high as 10^6 cm s^{-1} [1]. Such an effect in the case of ZnO can be achieved, at least partially, by alloying the material with Mg since this is up-shifting the conduction band. Indeed, following this approach it has been experimentally shown that an increase in efficiency from ~4% to ~7% can be achieved [2]. However, at the same time Mg alloying increases the ZnO based layer resistivity, thus limiting to ~2 at.% the actual amount of Mg that can be incorporated without hindering the heterojunctions photovoltaic performances in the case of the suggested device structure [2]. In the present case we have investigated the effect of combining Mg alloying in the 3-12 at.% range with Al doping (~2 at.%) on the electrical properties of the films, band alignment, and overall optoelectronic properties of test devices. It has been found that introducing Al into the ZnMgO matrix permits to obtain films with excellent electrical properties even in the case of the highest Mg content investigated; that is, for a Mg content ~12 at.% a resistivity, carrier concentration and mobility equal to ~2×10^{-2} Ωcm, ~2×10^{20} cm^{-3} and ~2 $cm^2 V^{-1} s^{-1}$, respectively could be achieved. This suggests that they can be used as an *n*-type emitter layer for ZnO/Si based solar cells. An increase of the open circuit voltage from ~0.37 V (without Al doping) to ~0.45 V was found to occur as a consequence of the Mg and Al introduction in the test heterojunctions realized. Furthermore, the solar cells with the optimized Mg and Al content exhibited an open circuit voltage, short circuit current density, efficiency, and fill factor up to ~0.44 V, ~29 mA cm^{-2}, ~7.5%, and ~63%, respectively. However, also in this case capacitance vs voltage characterization evidenced a type II band alignment at the interface between the *n*-ZnMgO:Al and *p*-Si with ΔE_C ~0.6 eV despite Mg being ~12 at.%.

Experimental details

- Substrate: boron doped *p*-type silicon wafers with (100) orientation (ρ~5-10 Ω cm, thickness ~250 μm, Al back contact) or glass/SiO_2.
- *n*-side of the heterojunction: ZnMgO:Al (Mg~3-12 at.%, Al~2 at.%) deposited by ALD (thickness ~400 nm, T_G = 280 °C).
- AZO as a top collecting layer deposited by ALD (thickness ~200 nm, T_G = 280 °C).
- Top contacts: Al/Au on test heterostructures and on layers grown on glass/SiO_2, Al on test solar cells (see figure below).

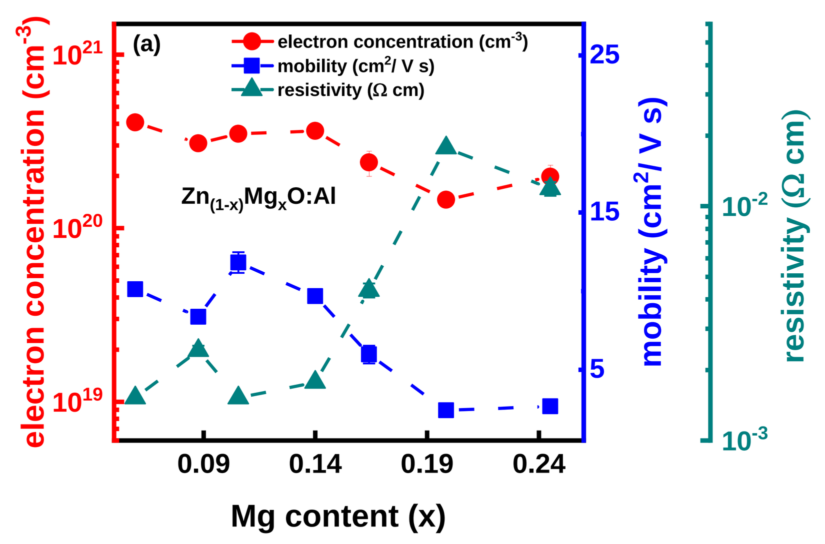
The resulting devices



Characterization techniques used

- SEM and EDX measurements for determining the Mg/Al at.% and cross sectional overview (here not shown).
- RT Hall measurements of the layers deposited on glass/SiO_2 to determine carrier concentration (**n**), mobility (μ) and resistivity (ρ).
- RT Current vs Voltage (**I-V**) and Capacitance vs Voltage (**C-V**) measurements for determining heterojunctions characteristics i.e. diode series resistance (**R_S**), diode ideality factor (η) and conduction band misalignment (ΔE_C).
- **I-V** under standard illumination conditions (STD) to determine the short circuit current (**I_{SC}**), open circuit voltage (**V_{OC}**), fill factor (**FF**) and efficiency (**Eff**) of the test devices.
- STEM measurements performed with a monochromated FEI Titan G2 60-300 microscope operated at 200 kV to analyze the ZnMgO:Al/Si interface.

Electrical characteristics of the layers and realized devices



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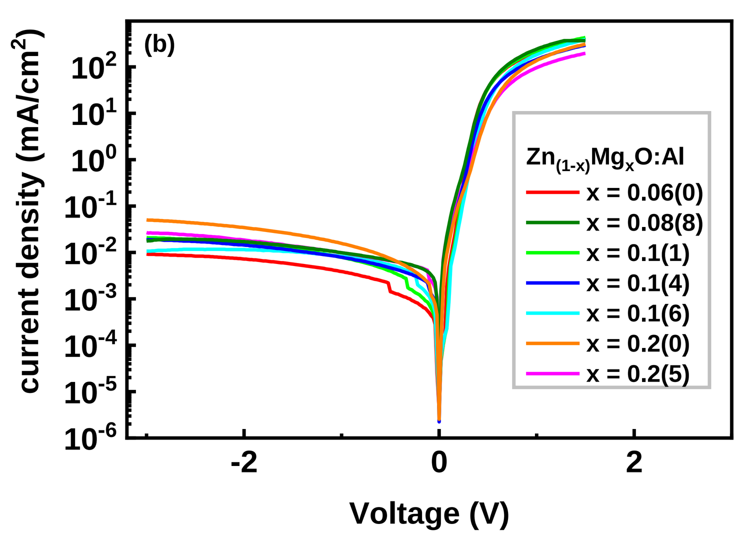
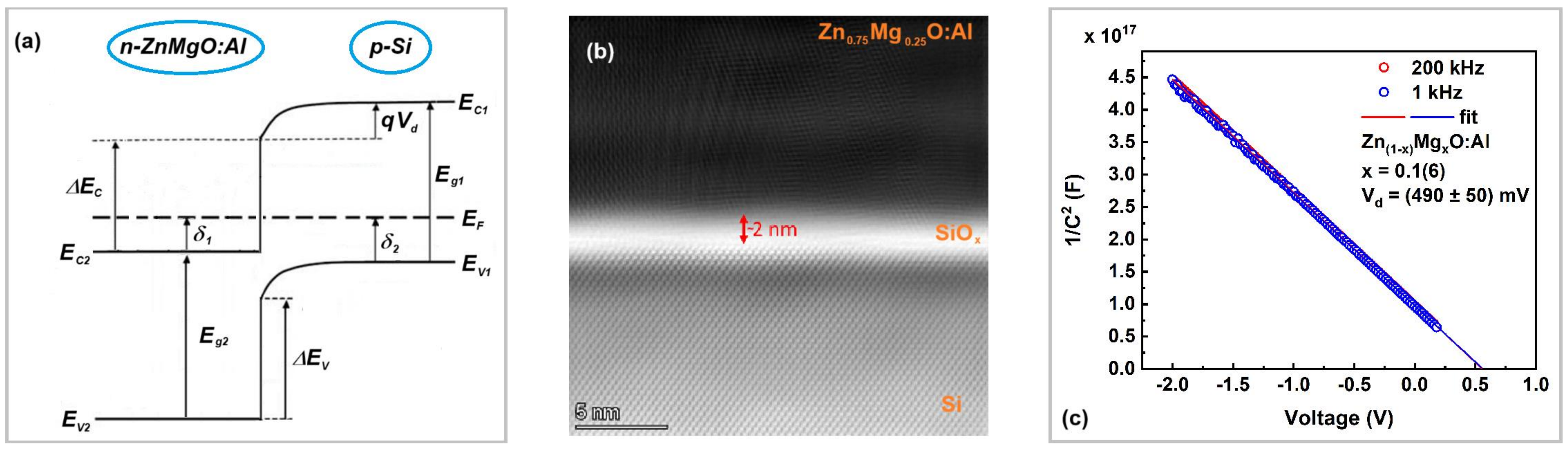
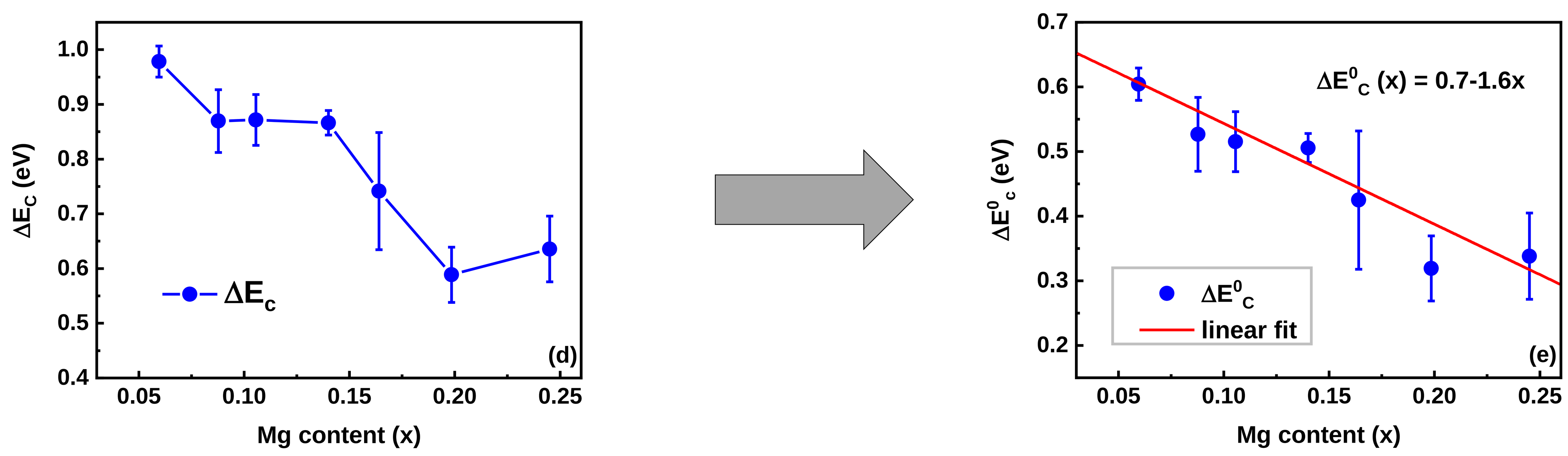


- (a) Al doping permits to achieve films with **n** up to ~3×10^{20} cm^{-3}, ρ ~10^{-3} Ωcm and μ ~10 cm/Vs; significant variations are not observed for Mg up to 7 at.%. For higher Mg contents ρ increases to ~10^{-2} Ωcm, due to a combined factor ~2 and ~5 decrease of **n** and μ, respectively, however the deposited films are degenerate over the whole investigated Mg content.
- (b) About 4 orders of magnitude in rectification for all the test heterostructures. No significant variations in η (in the 1-2 range) and R_S are found vs Mg content for [Mg]<0.25 at.%.

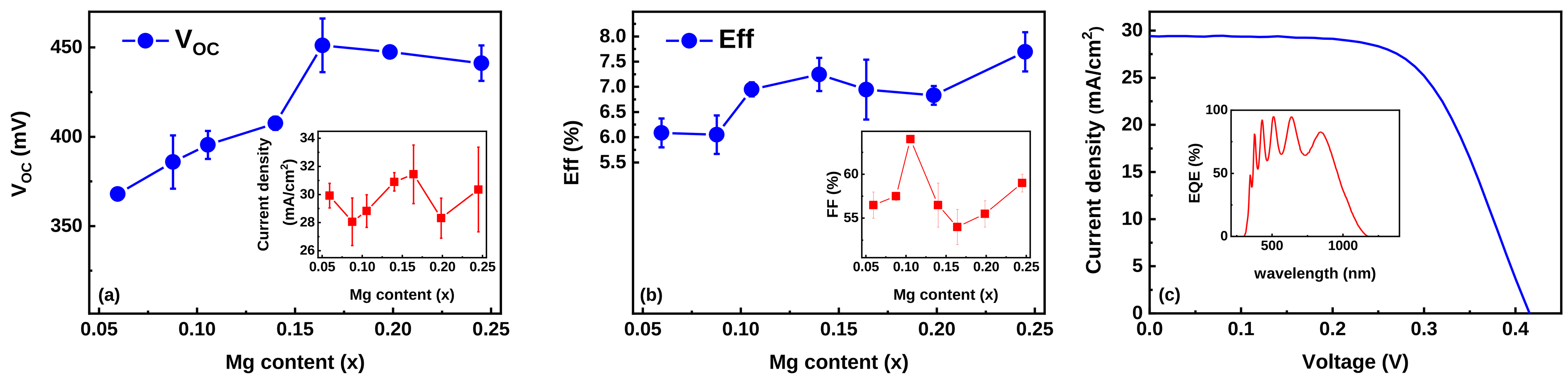
Conduction band misalignment between ZnMgO:Al and Si



- As shown in (a) by measuring V_d (the diffusion potential), δ_1 and δ_2 (the Fermi level in the ZnMgO:Al film and Si, referred to the respective conduction/valence band) the conduction band misalignment (ΔE_C) can be evaluated as $\Delta E_C = E_{g1} - qV_d - \delta_2 + \delta_1$ (where E_{g1} is the Si bandgap).
- Due to the ZnMgO:Al layer degeneracy the heterojunctions can be modeled as Schottky contacts to p-Si with a SiO_x interlayer ~2-3 nm thick with its presence confirmed by STEM measurements (see (b)).
- The expected linear dependence of $1/C^2$ vs V has been observed in all the examined samples independently of the *ac* probing voltage frequency varied in the 1-200 kHz range (see (c) for an example).



- In (d) ΔE_C extracted from the Hall and RT C-V measurements vs Mg content.
- In (e) the conduction band misalignment in the low doping limit (ΔE^0_C). ΔE^0_C has been obtained by correcting ΔE_C for the many body effects and interactions of the electrons with the donors. Both effects contribute to lower the conduction band and should be taken into account to determine the low doping limit (see Ref. [3] for more details).
- From ΔE^0_C within the interface-gap states approach branch point energies referred to the valence band edge equal to (2.7 ± 0.1) eV and (3.7 ± 0.3) eV are obtained for ZnO and MgO, respectively under the assumption of a linear variation of the ZnMgO:Al branch point between the respective values of the two binary compounds ZnO and MgO.
- The values obtained are in very good agreement with other experimental estimates (see for example Ref.[4]).



- **I-V** measurements under STD reveal a constant **I_{SC}** ~ 30 mA/cm^2, while **V_{OC}** and **Eff** increase with Mg content from ~330 mV to ~450 mV and from ~6.0 % to 7.7 % as shown in (a) and (b). No clear dependence of **FF** on the Mg content is observed. These trends are consistent with the observed dependence of ΔE_C and published simulations (see Ref.[1]).
- As shown in (c) test solar cells with the highest Mg contents (~10 at.%) exhibit **V_{OC}**, **I_{SC}**, **Eff** and **FF** up to ~0.44 V, ~29 mA cm^{-2}, ~7.5%, and ~63%, respectively.

Conclusions

- ALD deposited ZnMgO:Al layers exhibit suitable electrical characteristics (ρ ~10^{-2} Ωcm, **n** ~2 x 10^{20} cm^{-3} μ ~2 $cm^2 V^{-1} s^{-1}$) for acting as *n*-type electrodes for heterojunctions based on *p*-Si even at the highest Mg contents (≲12 at.%).
- The test solar cells exhibited promising characteristics: **V_{OC}**, **I_{SC}**, **Eff** and **FF** up to ~0.44 V, ~29 mA cm^{-2}, ~7.5%, and ~63%, respectively, however ΔE_C is still ~0.6 eV even for the highest Mg contents (~12 at.%) thus impeding a full exploitation of the heterojunctions potentialities for photovoltaic applications.

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