Earth abundant oxynitrides alloys for tandem solar cells

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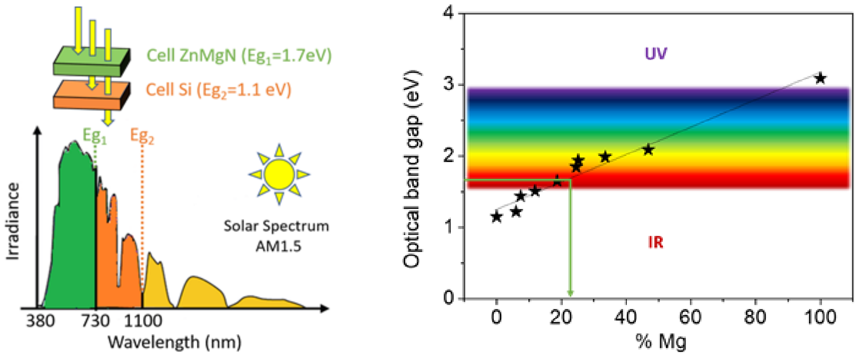
Owing to the increasing energy demand due to the rising population, there is a crucial need for sustainable energy resources. Government regulations focus on the reduced dependency on fossil fuels and gases, but also on the control of environmental pollution. This promotes the demand for renewable energy sources such as solar energy, thus driving the photovoltaic (PV) energy development. Different PV devices are being developed, including high-efficiency tandem cell devices but also lower cost thin films alternatives. However, these devices are often made of materials whose elements are considered scarce, like indium, or toxic, like lead.

The studies of earth-abundant nitrides started a decade ago, guided by the desire to replace critical materials in III-nitrides technology. Semiconducting earth-abundant nitrides are therefore an emerging group of materials, opening the way to a wide range of key technological devices, including solar cell absorbers. Among them, the nitrides Zn_3N_2 and Mg_3N_2 are both earth abundant and non-toxic semiconductors. Recently, we successfully grew by molecular beam epitaxy these two binary materials and we determined room temperature direct bandgap energies around 1.0 eV and 2.9 eV for Zn_3N_2 and Mg_3N_2, respectively, thanks to transmission measurements . Besides, we analyzed their electrical properties, both carrier concentration and electronic mobilities, in view of developing absorber materials for tandem solar cells[1, 2, 3].

In this context, and based on these two materials, we aim to develop a top cell based on indium free, earth abundant and non-toxic quaternary nitride alloy, namely the $(Zn_{1-x}Mg_x)_3(N_{1-y}O_y)_2$ alloy, compatible with bottom crystalline Si technology. The targeted tandem cell architectures rely on a gap stacking of 1.7 eV/1.1 eV, which provides the maximum theoretical power conversion efficiency with Silicon as a bottom cell [4] (*Figure 1*).

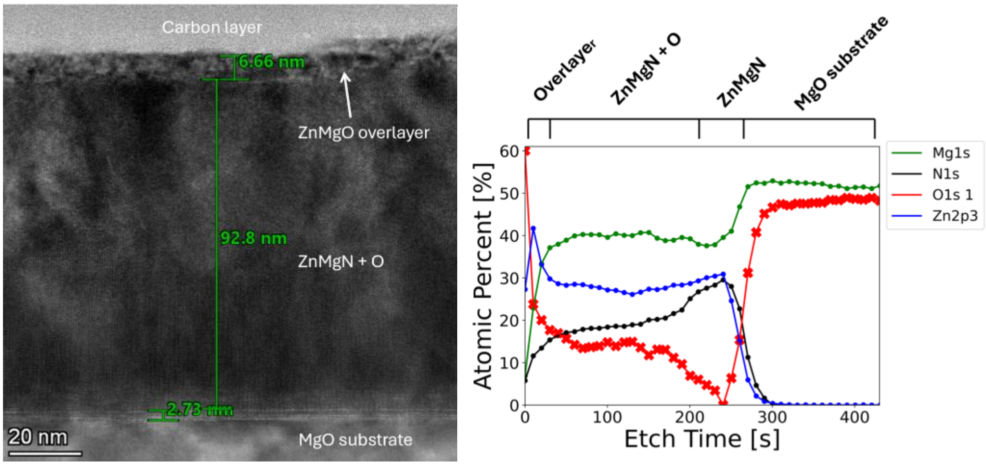
In this work, we will discuss the epitaxial growth of ZnMgON thin films, which was performed by plasma assisted molecular beam epitaxy (PA-MBE) in order to stabilize monocrystalline epitaxial layers on insulating MgO(100) substrate. The crystalline quality was characterized by X-ray diffraction and transmission electron microscopy on cross sections. STEM of epitaxial ZnMgNO on MgO substrates confirms a homogenous crystallinity along the layer. (fig 3). The Zn/Mg ratio was evaluated by energy dispersive X-ray analysis. The proof of the incorporation of oxygen was revealed by measuring the element profiles extracted from

XPS measurements through successive in-situ etchings with an argon ion gun as well as EDX-STEM mapping. The atomic profiles show that oxygen has been incorporated across the entire ZnMgN thickness (fig 2). The optical band gaps were measured by transmission while the carrier densities and the mobilities of the newly synthesized quaternary alloys were extracted from Hall effect measurements. By adjusting the growth conditions, in particular substrate temperature, N_2 flow, presence of O_2 during growth and the temperature of the Mg cell, we achieved monocrystalline layers of (Zn,Mg)(O,N) with the targeted 1.7 eV band gap, a carrier density around 4-5x10^{19} [cm^{-3}] and a mobility of 45-50 [cm^2/V/s].



(a) (b)

Figure 1. a) Absorption of the ZnMgN solar cell combined with a silicon bottom cell in the solar irradiance spectrum. b) Band gap of ZnMgN as a function of Mg concentration.



(a) (b)

Figure 2. a) TEM image of ZnMgNO on MgO substrate. b) XPS atomic profil of ZnMgON with a control ZnMgN control layer and the MgO substrate.

[1] P. John, et al., Phys. Rev. Materials 4, (2020) 054601

[2] P. John, et al., J. Appl. Phys. 130, (2021) 065104

[3] P. John, et al., J. Appl. Phys. 129, (2021) 095303

[4] A. Marti and G.L. Arujo, Solar Energy materials and Solar Cells, 43 (1996) 203

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