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HETEROSTRUCTURILE ITO/$Zn_{1-x}Mg_xO$:Al/Si CU DIFERITE CONFIGURAȚII PENTRU APLICAȚII ÎN CELULE SOLARE

VARIOUS DESIGN OF ITO/$Zn_{1-x}Mg_xO$:Al/Si HETEROSTRUCTURES FOR SOLAR CELLS APPLICATIONS

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Rezumat. *Acest studiu prezintă fabricarea și optimizarea heterostructurilor n-ITO/n-$Zn_{0.9}Mg_{0.1}O$/p-Si pentru aplicații fotovoltaice. Filmele de $Zn_{0.9}Mg_{0.1}O$ și n-ITO au fost depuse prin piroliză prin pulverizare, variindu-se sistematic grosimea stratului de ITO pentru a investiga compromisurile dintre transparență și conductivitate. Caracterizarea electrică și optică a arătat că creșterea grosimii stratului de ITO îmbunătățește conductivitatea și reduce rezistența serie, menținând în același timp o transparență acceptabilă. Celulele solare cu o configurație în două contacte au prezentat o eficiență maximă (η) de 0,31%, un factor de umplere (FF) de 32% și o putere maximă (P_{max}) de 6,12 μW. Introducerea electrozilor de tip grilă a îmbunătățit η la 1,15%, FF la 36,7% și P_{max} la 91 μW, demonstrând o colectare superioară a purtătorilor de sarcină și o calitate mai bună a joncțiunii. Proprietățile optice, inclusiv indicele de refracție și banda interzisă, au depins puternic de grosimea filmelor, subliniind rolul parametrilor structurali în performanța dispozitivului. Aceste rezultate indică faptul că heterostructurile ITO/ZnMgO/Si reprezintă o platformă promițătoare pentru celule solare transparente și conductive.*
Cuvinte-cheie: *Bandă interzisă, Caracteristici I-V, Parametri fotovoltaici, Indice de refracție, Transparență.*

1. INTRODUCTION

The global demand for sustainable energy has accelerated the development of solar cell technologies, making photovoltaics one of the most promising alternatives to fossil fuels. Traditional silicon-based solar cells continue to dominate the market, offering high efficiencies of 15–24% for monocrystalline and 15–18% for polycrystalline devices, while maintaining long-term stability and relatively low production costs [1]. In parallel, emerging technologies such as perovskite solar cells have shown laboratory efficiencies above 25% and rapid improvement rates, although stability issues under environmental stress remain a major challenge [2]. Thin-film technologies, including cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), also provide efficiencies of 15–23% and present advantages such as lightweight flexibility and reduced material usage for large-scale deployment [3,4]. At the cutting edge, multi-junction and tandem cells have surpassed 40% efficiency in laboratory settings by employing bandgap engineering to capture a broader solar spectrum, though their high costs and complex fabrication limit widespread terrestrial applications. To further improve device performance, researchers are focusing on advanced transparent conductive oxides (TCOs), which play a crucial role in balancing optical transparency and electrical conductivity in solar cells. Among these, zinc magnesium oxide ($Zn_{1-x}Mg_xO$) has gained significant attention due to its tunable band gap (3.3–7.8 eV) and potential use as a customizable window layer in photovoltaic devices [5, 6].

Since pure ZnMgO suffers from poor conductivity, aluminum doping has been widely employed to introduce donor states that improve carrier concentration and mobility while preserving high optical transparency [7,8]. Related studies have also demonstrated the effectiveness of aluminum-doped zinc oxide (AZO) [9] and aluminum-doped tin oxide (ATO) [10] as cost-effective alternatives to conventional indium tin oxide (ITO) [11]. Building on these advances, this study focuses on the synthesis of Al-doped ZnMgO films and ITO as a transparent conductive layer and the achievement of heterostructures with different configurations, whose performance will be evaluated through current-voltage characterization.

2. MATERIALS AND METHODS

Oxide thin films were deposited on commercial p-type silicon (Si) substrates with a resistivity of 10^6 Ω·cm and crystallographic orientation [100], which were cut into 1.5 cm² pieces to ensure uniform deposition. Prior to film growth, the wafers underwent a rigorous cleaning process involving immersion in an $NH_4OH/H_2O_2/H_2O$ (1:1:8) solution, rinsing with distilled water, drying by centrifugation, and heat treatment at 120 °C for 10 minutes to remove residual moisture. Al-doped zinc magnesium oxide ($Zn_{1-x}Mg_xO$:Al) thin films were synthesized on the cleaned Si substrates by spray pyrolysis, a scalable method for producing uniform oxide layers. The precursor solution was prepared using zinc acetate dihydrate, magnesium acetate tetrahydrate, and aluminum chloride hexahydrate dissolved in a methanol + water + acetic acid mixture, adjusted to 0.25 M concentration, stirred for 60 minutes in an ultrasonic bath at 50 °C, and aged for 24 hours. $Zn_{1-x}Mg_xO$ thin films with magnesium concentrations of $x = 0.05$ to 0.15 were initially synthesized, after which $Zn_{0.90}Mg_{0.10}O$ films were selected as the base material for (Al) aluminum doping at concentrations of 0.0025, 0.01, 0.03, and 0.05. Deposition was performed at 500 °C with a spray rate of 1.2 mL/min, a nozzle-to-substrate distance of 4 cm, and oxygen as the carrier gas at 1 Bar, resulting in films 200 – 850 nm thick depending on spray duration. After deposition, the films were cooled to room temperature and stabilized on a hot plate for subsequent processing. To form the transparent conductive electrode, indium tin oxide (ITO - 90 wt.% In_2O_3 and 10 wt.% SnO_2) was deposited via spray pyrolysis using $SnCl_4 \cdot 5H_2O$ and $InCl_3$ precursors in an alcohol-based solvent, stirred under similar conditions as $Zn_{1-x}Mg_xO$:Al, with a spray rate of 1.5 mL/min and oxygen flow at 1 Bar. The ITO layer, approximately 200 nm thick, was optimized to provide a sheet resistance of ~70 Ω while maintaining ~95% optical transparency. Finally, silver (Ag) contacts were deposited on the ITO surface by high-vacuum thermal evaporation (1.5×10^{-4} Torr) using two electrode configurations: two-point contacts and grid-type metallic contacts (see Figure 1).

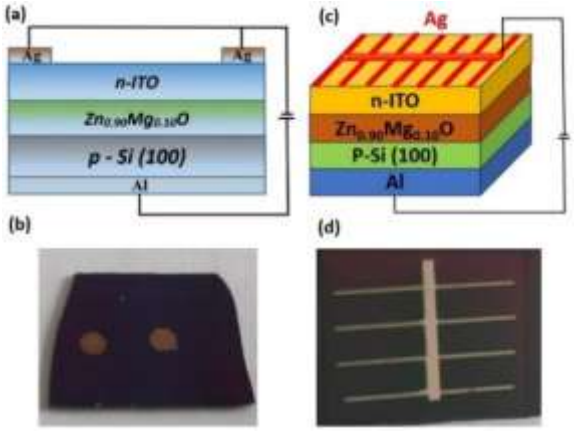


Figure 1. Design configurations of Ag/n-ITO/n-$Zn_{1-x}Mg_xO$:Al/p-Si/Al heterostructures: two-point configuration (a,b) and grid-type metal contacts (c,d).

3. RESULTS AND DISCUSSIONS

Following the optimization of the technological parameters for obtaining n-ITO films through aerosol deposition, special attention was given to achieving a balance between conductivity, transparency, and antireflection properties. The deposited films exhibited a clear dependence of their optoelectronic behavior on thickness. Films with an average thickness of approximately 200 nm demonstrated about 95% transparency and a sheet resistance of 70 Ω, while thicker layers (≈850 nm) showed reduced transparency (89%) but significantly improved conductivity (12 Ω). This correlation highlights the critical influence of deposition parameters on the microstructural and electronic properties of the ITO films. Figure 2 demonstrates the reflectance and transmittance of n-ITO films at different thicknesses. The optical analysis, based on reflection spectra, revealed a linear increase in the refractive index (see Figure 3a) from 1.7 to 2.05 across the 1.0 – 4.0 eV photon energy range, with thicker films exhibiting higher values. This behavior is attributed to enhanced interband electronic transitions as the photon energy increases, as well as to structural factors such as carrier concentration, microstructure, and crystallinity influenced by the spray pyrolysis deposition at 500 °C. Furthermore, the optical bandgap (Eg) of the ITO films was found to vary slightly with thickness, ranging between 3.37 eV and 3.41 eV (see Figure 3b). This smooth change in bandgap energy with increasing thickness indicates that structural and electronic modifications within the films play a critical role in determining their optical properties.

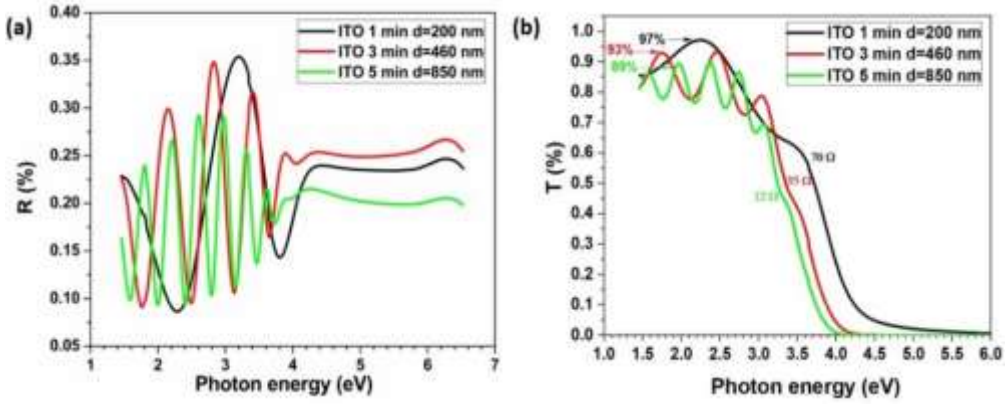


Figure 2. The reflectance (a) and transmittance (b) of the n-ITO films obtained by aerosol deposition method.

Such behavior is typical for transparent conducting oxides, where small changes in microstructure or carrier density significantly influence the bandgap energy.

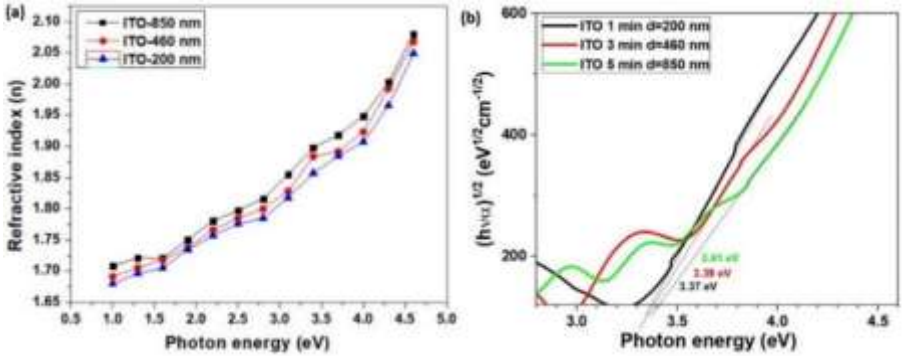


Figure 3. The refractive index (n) (a) and bandgap (b) at different thickness of the n-ITO films obtained by aerosol deposition method.

For the fabrication of n-ITO/n-$Zn_{1-x}Mg_xO$:Al/p-Si heterostructures, $Zn_{0.9}Mg_{0.1}O$ layers doped with 1% Al were deposited for 3 minutes, followed by ITO coatings with varied deposition times. The aim was to explore the correlation between ITO layer thickness and the resulting electrical and photovoltaic performance of the heterostructures. Two representative samples with different contact configuration, Ex.115 (ITO – 460 nm) and Ex.118 (ITO – 460 nm), were analyzed through current-voltage (I–V) measurements and extracted the photovoltaic parameters.

The electrical characterization of sample Ex.115 with two-point configuration (Figure 4a) revealed features essential for solar cell operation. The short-circuit current (Isc) reached 71 μA, while the open-circuit voltage (Uoc) was 0.27 V. The maximum output power was 6.12 μW, corresponding to a power conversion efficiency (η) of 0.31%. The series resistance remained relatively low (2.7 kΩ), ensuring efficient charge transport, while the parallel resistance (4.8 kΩ) indicated some internal recombination or leakage effects. The fill factor (FF) was approximately 32%, suggesting a reasonably good diode quality and stable junction behavior.

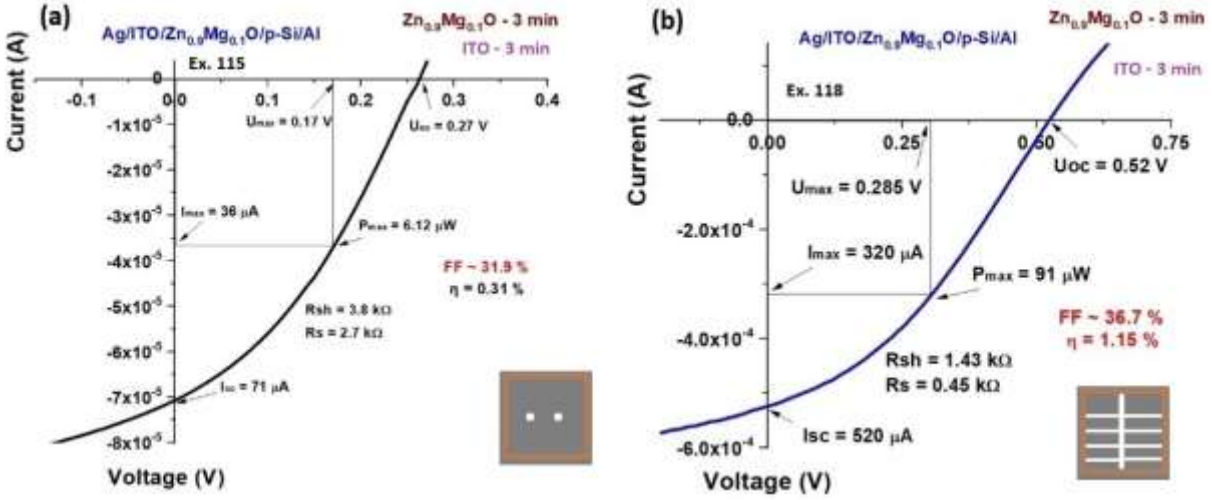


Figure 4. Load characteristic of the Ag/n-ITO/n-$Zn_{1-x}Mg_xO$:Al/p-Si/Al heterostructures (Ex. 115) with two-point configuration (a) and grid-type metal (Ag) contacts (Ex. 118) (b).

To further enhance device performance, the ZnMgO layer was more effectively doped with aluminum to increase conductivity, and grid-type contacts were implemented to improve charge carrier collection over a larger surface area. These optimizations were integrated into sample Ex.118, which exhibited the most efficient photovoltaic behavior in the series (Figure 4b). For this sample, the short-circuit current (Isc) increased significantly to 520 μA, and the open-circuit voltage (Uoc) reached 0.52 V. The maximum output power rose to 91 μW, while the efficiency (η) improved to 1.15%, representing a more than sevenfold increase compared to Ex.115. The series resistance decreased further to 0.45 kΩ, indicating excellent charge transport, whereas the parallel resistance decreased to 1.43 kΩ, suggesting an increase in internal leakage or recombination phenomena. Despite this, the overall performance clearly confirms the positive impact of optimized doping and electrode architecture on the photovoltaic response.

The comparative analysis of Ex.115 and Ex.118 reveals a substantial enhancement in electrical and photovoltaic characteristics driven by structural and compositional optimization. The evolution of the optical bandgap with film thickness, combined with improved carrier mobility and interface engineering,

demonstrates that both material structure and device architecture play crucial roles in determining the efficiency of n-ITO/n-$Zn_{1-x}Mg_xO$:Al/p-Si heterojunction solar cells. All photovoltaic (PV) parameters investigated and mentioned in the text are represented in Table 1.

Table 1. All photovoltaic (PV) parameters investigated.

Samples	I_{sc}, µA	U_{oc}, V	I_{max}, µA (at P_{max})	U_{max}, V (at P_{max})	P_{max}, µW	Rs, KΩ	Rsh, KΩ	FF, %	η, %
Ex.115	71	0.27	36	0.17	6.12	2.7	4.8	31.9	0.31
Ex.118	520	0.52	320	0.285	91	0.45	1.43	36.7	1.15

4. CONCLUSIONS

The optimization of n-ITO films via spray pyrolysis demonstrates a clear trade-off between transparency and conductivity, with thicker films improving conductivity but slightly reducing transparency. Increasing ITO thickness reduces series resistance and improves short-circuit current, as evidenced by the superior performance of sample Ex.115. Implementing grid-type contacts further boosted the solar cell efficiency sevenfold, achieving 1.15% while maintaining low series resistance. The heterostructures exhibit good rectifying behavior, indicating high junction quality and suitability for photovoltaic applications. Optical measurements reveal that the refractive index and bandgap are strongly influenced by film thickness, reflecting the material's structural and electronic properties. The results highlight the critical role of precise control over layer thickness and interface quality in optimizing device performance. Overall, the combination of ITO, ZnMgO, and silicon provides a promising approach for transparent and conductive solar devices.

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