



## **LANTHANUM-DOPED ZNO NANORODS AS ELECTRON TRANSPORT LAYER IN PEROVSKITE SOLAR CELL**



**MASTER OF SCIENCE IN ELECTRONIC ENGINEERING**

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**Faculty of Electronics and Computer Technology and  
Engineering**

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**Nurul Aliyah Binti Zainal Abidin**

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

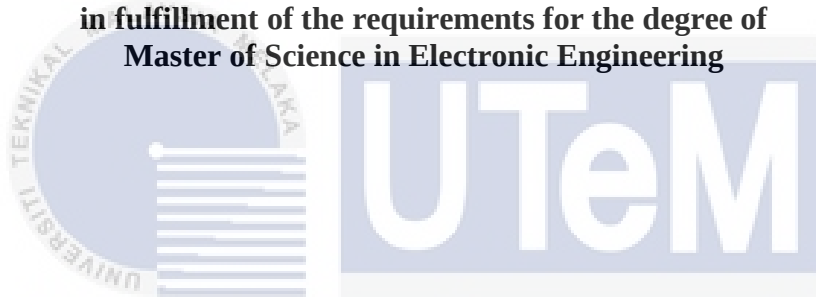
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**NURUL ALIYAH BINTI ZAINAL ABIDIN**

**A thesis submitted  
in fulfillment of the requirements for the degree of  
Master of Science in Electronic Engineering**



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**2024**

## DEDICATION

To my beloved supervisor, my family, my team and my cats  
whose constant guidance, love and encouragement have been my strength throughout this  
academic journey.

Thank you for your support and always believing me.



## ABSTRACT

Conventional Electron Transport Layer (ETL)  $\text{TiO}_2$  (Titanium dioxide) has been widely used in Perovskite Solar Cells (PSCs) which have produced encouraging Power Conversion Efficiency (PCE), allowing the technology to be highly regarded and propitious. Nevertheless, the recent high demand for energy harvesters in wearable electronics, aerospace and building integration has led to the need for flexible solar cells. However, the conventional  $\text{TiO}_2$  ETL layer is less preferred, where a crystallization process at a temperature as high as  $450^\circ\text{C}$  is required, which degrades the plastic substrate. Zinc Oxide nanorods (ZnO NRs) is yet simple and low-cost fabrication may lead the task as ETL, but still suffer from low PCE due to atomic defects vacancy. To delve into the issue, Lanthanum (La) dopant has been introduced as an additive to passivate or substitute the  $\text{Zn}^{2+}$  vacancies. Pure ZnO nanorods and La-doped ZnO nanorods with different growth time (3,5,7,9 hours) and concentration (1 mol%-4 mol%) were synthesized by hydrothermal method with  $90^\circ\text{C}$  of annealing temperature. The influence of different growth time and La concentration as dopant in terms of structural, optical and electrical properties have been investigated. Scanning electron microscopy (SEM) revealed that La-doped ZnO produced smooth and stable morphology with less pore of nanorods compared to pure ZnO. From Raman-spectroscopy, La-doped ZnO at 1 mol% produced the best peak intensity with fewer defect peak. X-ray diffraction (XRD) revealed that the size of the crystal structure reduced, ranging from 23.626 nm to 27.089 nm when introducing La into ZnO lattice. The optical measurement from ultraviolet visible spectrometer (UV-Vis) indicates an enhancement of absorption in La-doped ZnO with transmittance value lies between 18.03% to 79.7% and direct bandgap between 2.90 eV to 3.39 eV. According to IV-measurement, 1 mol% of La-doped ZnO at 9 hours of growth time produced the best conductivity with 5.46 S/m making it the ideal concentration and growth time of La doped into ZnO. Following this, 1 mol%-9 hours was chosen as the ETL for SCAPS-1D study by applying its bandgap and absorption coefficient parameters obtained from the experiment.  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (methylammonium lead iodide) was used as the absorber layer,  $\text{Cu}_2\text{O}$  (copper (I) oxide) as Hole Transport Layer (HTL), Indium Tin Oxide (ITO) and platinum as front and back contact. The investigation was determined by varying various parameters within each tuned layer including layer thickness, doping concentration, defect density, electron affinity, bulk density, operating temperature and metal work function. From the simulation, the fully optimized device structure, ITO/La-ZnO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ / $\text{Cu}_2\text{O}$ /Pt attained a PCE of 30.70%, proving a drastic improvement over the initial PCE of 19.21% by 59.81%. Therefore, this study proposes a low-cost hydrothermal synthesis method with a low operating temperature, and emphasizes novel doping techniques for efficient, lead-free PSC.

## ROD NANO ZNO DOPAN LANTHANUM SEBAGAI LAPISAN PENGANGKUTAN ELEKTRON DALAM SEL SOLAR PEROVSKITE

### ABSTRAK

Lapisan Pengangkutan Elektron Konvensional (ETL)  $\text{TiO}_2$  telah digunakan secara meluas dalam Sel Surya Perovskite (PSC) yang menghasilkan Kecekapan Penukaran Kuasa (PCE) yang menggalakkan, membolehkan teknologi itu dipandang tinggi. Namun begitu, permintaan tinggi baru-baru ini untuk penuai tenaga dalam elektronik boleh pakai, aeroangkasa dan integrasi bangunan telah membawa kepada keperluan untuk sel solar yang fleksibel. Walau bagaimanapun, lapisan  $\text{TiO}_2$  ETL konvensional kurang dipilih, di mana proses penghabluran pada suhu setinggi  $450^\circ\text{C}$  yang diperlukan, merosakkan substrat plastik. Zinc Oxide nanorods (ZnO NRs) yang mudah dengan kos fabrikasi rendah mungkin dipilih sebagai ETL, tetapi masih mengalami PCE yang rendah kerana kekosongan kecacatan atom. Untuk menyelidiki isu ini, Lanthanum (La) dopan telah diperkenalkan sebagai bahan tambahan untuk memasifkan atau menggantikan kekosongan  $\text{Zn}^{2+}$ . Nanorod ZnO tulen dan ZnO terdop La dengan masa pertumbuhan (3,5,7,9 jam) dan kepekatan (1 mol%-4 mol%) berbeza telah disintesis melalui kaedah hidroterma dengan  $90^\circ\text{C}$  suhu penyepuhlingdapan. Pengaruh masa pertumbuhan yang berbeza dan kepekatan La sebagai dopan dari segi sifat struktur, optik dan elektrik telah disiasat. Pengimbasan mikroskop elektron (SEM) mendedahkan bahawa ZnO terdop La menghasilkan morfologi licin dan stabil dengan liang nanorod yang lebih kecil berbanding ZnO tulen. Daripada spektroskopi raman, ZnO terdop-La pada 1 mol% menghasilkan keamatan puncak terbaik dengan kecacatan yang lebih sedikit. Difraksi sinar-X (XRD) mendedahkan bahawa saiz struktur kristal berkurangan, antara 23.626 nm hingga 27.089 nm apabila memasukkan La ke dalam kekisi ZnO. Pengukuran optik ultraungu daripada spektrometer (UV-Vis) menunjukkan peningkatan penyerapan dalam ZnO terdop La dengan nilai transmisi di antara 18.03% hingga 79.7% dan jurang jalur antara 2.90 eV hingga 3.39 eV. Mengikut pengukuran IV, 1 mol% ZnO berdop La pada masa pertumbuhan selama 9 jam menghasilkan kekonduksian terbaik dengan 5.46 S/m menjadikan kepekatan dan masa pertumbuhan tersebut adalah ideal bagi pengedopan La ke dalam ZnO. Berikutan ini, 1 mol% selama 9 jam telah dipilih sebagai ETL untuk kajian SCAPS-1D dengan menggunakan jurang jalur dan parameter pekali penyerapan yang diperoleh daripada eksperimen.  $\text{CH}_3\text{NH}_3\text{PbI}_3$  digunakan sebagai lapisan penyerap,  $\text{Cu}_2\text{O}$  sebagai HTL, ITO dan platinum sebagai sentuhan depan dan belakang. Penyiasatan ditentukan dengan memvariasikan pelbagai parameter dalam setiap lapisan termasuk ketebalan lapisan, kepekatan dopan, ketumpatan kecacatan, pertalian elektron, ketumpatan pukal, suhu operasi dan fungsi kerja logam. Daripada simulasi, struktur peranti yang dioptimumkan sepenuhnya, ITO/La-ZnO/ $\text{CH}_3\text{NH}_3\text{SnI}_3$ / $\text{Cu}_2\text{O}$ /Pt mencapai PCE sebanyak 30.70%, membuktikan peningkatan drastik berbanding PCE awal sebanyak 19.21% dengan peningkatan sebanyak 59.81%. Oleh itu, kajian ini mencadangkan kaedah sintesis hidroterma kos rendah dengan suhu operasi yang rendah, dan menekankan teknik pengedopan baharu untuk PSC yang cekap dan bebas plumbum.

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*Nurul Aliyah*

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## LIST OF ABBREVIATIONS

|                  |   |                                    |
|------------------|---|------------------------------------|
| ETL              | - | Electron transport layer           |
| HTL              | - | Hole transport layer               |
| PCE              | - | Power conversion efficiency        |
| PSC              | - | Perovskite solar cell              |
| TiO <sub>2</sub> | - | Titanium dioxide                   |
| ITO              |   | Indium Tin Oxide                   |
| ZnO              | - | Zinc Oxide                         |
| NRs              | - | Nanorods                           |
| La               | - | Lanthanum                          |
| SEM              | - | Scanning Electron Microscopy       |
| XRD              | - | X-ray diffraction                  |
| UV-Vis           | - | UV-visible spectroscopy            |
| IEA              | - | International Energy Agency        |
| PV               | - | Photovoltaic                       |
| DSSCs            | - | Dye-sensitized solar cells         |
| QD               | - | Quantum dots                       |
| AgNPs            | - | Silver nanoparticles               |
| MEA              | - | Monoethanolamine                   |
| CuI              | - | Copper (I) iodide                  |
| HOMO             | - | Highest occupied molecular orbital |
| LUMO             | - | Lowest occupied molecular orbital  |
| SnO <sub>2</sub> | - | Tin Oxide                          |

|                                                                      |                                            |
|----------------------------------------------------------------------|--------------------------------------------|
| BaSnO <sub>3</sub>                                                   | - Barium Stannate                          |
| WO <sub>3</sub>                                                      | - Tungsten Oxide                           |
| In <sub>2</sub> O <sub>3</sub>                                       | - Indium Oxide                             |
| ALD                                                                  | - Atomic layer deposition                  |
| CB                                                                   | - Conduction band                          |
| VB                                                                   | - Valence band                             |
| Zn                                                                   | - Zinc                                     |
| Al                                                                   | - Aluminium                                |
| Ag                                                                   | - Silver                                   |
| rGO                                                                  | - Reduced graphene oxide                   |
| I                                                                    | - Iodine                                   |
| LAR                                                                  | - Low aspect ratio                         |
| Zn(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O | - Zinc acetate dihydrate                   |
| NaOH                                                                 | - Sodium hydroxide                         |
| (CH <sub>2</sub> ) <sub>6</sub> N <sub>4</sub>                       | - Hexamethylenetetramine                   |
| Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O                 | - Zinc nitrate hexahydrate                 |
| DI                                                                   | - Deionized water                          |
| La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O                 | - Lanthanum nitrate hydrate                |
| SLG                                                                  | - Soda lime glass                          |
| SCAPS 1D                                                             | - Solar Cell Capacitance Simulator Program |
| CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub>                     | - Methylammonium lead halide               |
| CH <sub>3</sub> NH <sub>3</sub> SnI <sub>3</sub>                     | - Methylammonium tin halide                |
| Cu <sub>2</sub> O                                                    | - Copper(I) oxide copper                   |
| CuSCN                                                                | - Copper(I) thiocyanate                    |

|      |                                |
|------|--------------------------------|
| P3HT | - Poly 3-Hexylthiophene        |
| Pt   | - Platinum                     |
| TO   | - Transverse optical phonons   |
| LO   | - Longitudinal optical phonons |
| FWHM | - Full width at half maximum   |
| Voc  | - Open circuit voltage         |
| Jsc  | - Short-circuit voltage        |
| FF   | - Fill Factor                  |
| CBO  | - Conduction band offset       |
| VBO  | - Valence band offset          |
| VBM  | - Valence band maximum         |
| Vbi  | - Built-in potential           |
| SRH  | - Shockley-Read Hall           |
| QE   | - Quantum efficiency           |
| Ni   | - Nickel                       |
| In   | - Indium                       |
| Ga   | - Gallium                      |
| Ce   | - Cerium                       |
| Dy   | - Dysprosium                   |
| Nd   | - Neodymium                    |
| Er   | - Erbium                       |
| DFT  | - Density Functional Theory    |

## LIST OF SYMBOLS

|                       |   |                                                        |
|-----------------------|---|--------------------------------------------------------|
| $J_e$                 | - | Electron current density                               |
| $q$                   | - | Elementary charge                                      |
| $D_e$                 | - | Diffusion coefficient of electron                      |
| $J_h$                 |   | Hole current density                                   |
| $D_h$                 | - | Diffusion coefficient of hole                          |
| g/mol                 | - | Molecular mass                                         |
| $^{\circ}\text{C}$    | - | Temperature                                            |
| mol%                  | - | Mole percent concentration of a component in a mixture |
| $E_g$ (eV)            | - | Bandgap energy                                         |
| $X$ (eV)              | - | Electron affinity                                      |
| $\epsilon/\epsilon_0$ | - | Dielectric permittivity                                |
| $N_c$                 | - | Effective density of states of conduction band         |
| $N_v$                 | - | Effective density of states of valence band            |
| $V_e$                 | - | Thermal velocity of electron                           |
| $V_h$                 | - | Thermal velocity of holes                              |
| $\mu_e$               | - | Electron Mobility                                      |
| $\mu_h$               | - | Hole mobility                                          |
| $N_D$                 | - | Density of donor                                       |
| $N_A$                 | - | Density of acceptors                                   |
| $\mu\text{m}$         | - | Micrometer                                             |
| $\lambda$             | - | X-ray wavelength                                       |

|                   |                                                               |
|-------------------|---------------------------------------------------------------|
| $\beta$           | - Full width at half maximum                                  |
| $2\theta$         | - Bragg diffraction angle                                     |
| $\varepsilon$     | - Lattice strain                                              |
| $\delta$          | - Dislocation density                                         |
| $A$               | - Absorbance                                                  |
| $T$               | - Transmittance                                               |
| $\rho$            | - Average resistivity                                         |
| $\sigma$          | - Average conductivity                                        |
| $\alpha$          | - Absorption coefficient                                      |
| $d$               | - Film thickness                                              |
| $\sigma_n$        | - Capture cross-sections for electrons                        |
| $\sigma_p$        | - Capture cross-sections for holes                            |
| $v$               | - Electron thermal velocity                                   |
| $N_T$             | - Atomistic defect concentration                              |
| $n_i$             | - Intrinsic carrier density                                   |
| $n_1$             | - Concentrations of electrons in trap defect and valence band |
| $p_1$             | - Concentrations of holes in trap defect and valence band     |
| $R^{SH}$          | - Shockley-Read Hall recombination                            |
| $\tau_{lifetime}$ | - Carrier lifetime                                            |
| $K_B$             | - Boltzmann constant                                          |
| $\mu$             | - Mobility of the charge carriers                             |
| $q$               | - Fundamental unit charge                                     |
| $L$               | - Diffusion length                                            |
| $E_a$             | - Activation energy                                           |