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

NURUL ALIYAH BINTI ZAINAL ABIDIN

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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) 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 TiO_2 ETL layer is less preferred, where a crystallization process at a temperature as high as 450 °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 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 °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 microspcopy (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. $CH_3NH_3PbI_3$ (methylammonium lead iodide) was used as the absorber layer, Cu_2O (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/$CH_3NH_3SnI_3$/Cu_2O/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) TiO_2 telah digunakan secara meluas dalam Sel Suria 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 TiO_2 ETL konvensional kurang dipilih, di mana proses penghabluran pada suhu setinggi 450 ℃ 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 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 ℃ suhu penyepuhlindapan. 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. $CH_3NH_3PbI_3$ digunakan sebagai lapisan penyerap, Cu_2O 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/$CH_3NH_3SnI_3$/Cu_2O/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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ETL	-	Electron transport layer
HTL	-	Hole transport layer
PCE	-	Power conversion efficiency
PSC	-	Perovskite solar cell
TiO_2	-	Titanium dioxide
ITO		Indium Tin Oxide
ZnO	-	Zinc Oxide
NRs	-	Nanorods
La	-	Lanthanum
SEM	-	Scanning Electron Mircoscopy
XRD	-	X-ray diffraction
UV-Vis	-	UV-visible spectroscopy
IEA	-	International Energy Agency
PV	-	Photovoltaic
DSSCs	-	Dye-sensitize 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_2	-	Tin Oxide

$BaSnO_3$	-	Barium Stannate
WO_3	-	Tungsten Oxide
In_2O_3	-	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
$Zn(O_2CCH_3)2.2H_2O$	-	Zinc acetate dihydrate
NaOH	-	Sodium hydroxide
$(CH_2)6N_4$	-	Hexamethylenetetramine
$Zn(NO_3)2.6H_2O$	-	Zinc nitrate hexahydrate
DI	-	Deionized water
$La(NO_3)_3.6H_2O$	-	Lanthanum nitrate hydrate
SLG	-	Soda lime glass
SCAPS 1D	-	Solar Cell Capacitance Simulator Program
$CH_3NH_3PbI_3$	-	Methylammonium lead halide
$CH_3NH_3SnI_3$	-	Methylammonium tin halide
Cu_2O	-	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

Je	-	Electron current density
q	-	Elementary charge
De	-	Diffusion coefficient of electron
Jh		Hole current density
Dh	-	Diffusion coefficient of hole
g/mol	-	Molecular mass
°C	-	Temperature
mol%	-	Mole percent concentration of a component in a mixture
Eg (eV)	-	Bandgap energy
X (eV)		Electron affinity
$\varepsilon / \varepsilon_o$	-	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
μ_e	-	Electron Mobility
μ_h	-	Hole mobility
N_D	-	Density of donor
N_A	-	Density of acceptors
µm	-	Micrometer
λ	-	X-ray wavelength

β	-	Full width at half maximum
2θ	-	Bragg diffraction angle
ε	-	Lattice strain
δ	-	Dislocation density
A	-	Absorbance
T	-	Transmittance
ρ	-	Average resistivity
σ	-	Average conductivity
α	-	Absorption coefficient
d	-	Film thickness
σ_n	-	Capture cross-sections for electrons
σ_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
μ	-	Mobility of the charge carriers
q	-	Fundamental unit charge
L	-	Diffusion length
E_a	-	Activation energy