UNRAVELLING THE ROLE OF DEFECTS IN HYBRID SEMICONDUCTOR MATERIAL: A HOLISTIC EXPLORATION OF THEIR INFLUENCE ON OPTO-ELECTRONIC DEVICE PERFORMANCE

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by

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Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

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Dedicated to

My Parents and Family….

CERTIFICATE

This is to certify that the thesis entitled, "**Unravelling the Role of Defects in Hybrid Semiconductor Material: a Holistic Exploration of their Influence on Opto-electronic Device Performance**", submitted by **Mr. Punit Sharma** to the Department of Energy Science and Engineering, Indian Institute of Technology Delhi, for the award of the degree of the **Doctor of Philosophy** is a record bonafide research work carried out by him under my supervision and guidance. The results contained in this thesis have not been submitted in part or full, to any other University or Institute for the award of any degree/diploma.

Date:

Place: New Delhi.

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Abstract

This study presents a comprehensive analysis of the synthesis and applications of phase-pure iron pyrite nanocrystals (FeS_2 NCs), focusing on defect states and their impact on optoelectronic properties. Two cost-effective chemical methods, hot injection and hydrothermal procedures, were used to synthesize FeS_2 NCs, revealing differences in crystallite size, optical band gap, and Urbach energy. The research examines charge carrier lifetimes and densities, influenced by surface defects or sulfur vacancies, and their effect on photovoltaic performance. Devices with FeS_2 NCs synthesized via the hydrothermal method showed ~50% lower power conversion efficiency compared to those using the hot-injection method.

Additionally, the study explores defects' effects on the optical properties of pristine, ionic liquid-treated, and Co-alloyed FeS_2 nanomaterials. Co-alloying shifts conductivity from p-type to n-type, enhancing electrical properties and nonlinear absorption coefficients, suggesting potential for advanced optoelectronic devices.

The investigation extends to FeS_2 NCs' role in improving the efficiency of hybrid bulk-heterojunction solar cells with a P3HT: $PC_{71}BM$ blend. Optimal doping concentration improves short-circuit current density and overall cell efficiency, with defect states aiding carrier generation and dissociation. Transient photocurrent and photovoltage studies reveal faster carrier extraction and longer recombination times, highlighting defect states' efficacy in performance enhancement.

The study also examines FeS_2 NCs' impact on organic photovoltaic cells (OPVs), focusing on trap states' energy distribution and their role in improving photovoltaic properties and mitigating trap-assisted recombination.

Further, FeS_2 NCs as hole transport material (HTM) in perovskite solar cells (PeSCs) based on $MAPbI_3$ show enhanced short-circuit current density and stability, suggesting FeS_2 NCs as a

cost-effective HTM alternative for air-processed PeSCs. Additionally, copper(I) halides (CuI and CuBr) are investigated for passivating defect states in $MAPbI_3$-based PeSCs, improving hole transport and reducing recombination. Optimized inverted PeSCs using CuI as a passivation agent achieved significant efficiency, reaching 14.1%.

In conclusion, this study offers significant insights into defect engineering in FeS_2 NCs and the use of p-type copper(I) halides in $MAPbI_3$ perovskite solar cells, contributing to advancements in sustainable energy research by enhancing the efficiency and durability of optoelectronic devices.

सारांश

यह अध्ययन चरण-शुद्ध आयरन पाइराइट नैनोक्रिस्टल्स (FeS_2 NCs) के संश्लेषण और अनुप्रयोगों का व्यापक विश्लेषण प्रस्तुत करता है, जिसमें दोष अवस्थाओं और उनके ऑप्टोइलेक्ट्रॉनिक गुणों पर प्रभाव पर ध्यान केंद्रित किया गया है। FeS_2 NCs के संश्लेषण के लिए दो किफायती रासायनिक विधियों, हॉट इंजेक्शन और हाइड्रोथर्मल प्रक्रियाओं का उपयोग किया गया, जिससे क्रिस्टलाइट आकार, ऑप्टिकल बैंड गैप और उरबाच ऊर्जा में अंतर सामने आया। यह शोध चार्ज कैरियर के जीवनकाल और घनत्व की जांच करता है, जो सतह दोष या सल्फर रिक्तियों से प्रभावित होते हैं, और उनके फोटोवोल्टिक प्रदर्शन पर प्रभाव का विश्लेषण करता है। हाइड्रोथर्मल विधि से संश्लेषित FeS_2 NCs वाले उपकरणों की पावर कन्वर्जन दक्षता, हॉट-इंजेक्शन विधि से बने उपकरणों की तुलना में लगभग 50% कम थी।

इसके अलावा, अध्ययन मौलिक, आयनिक लिक्विड-उपचारित और कोबाल्ट-एलॉयड FeS_2 नैनोमैटेरियल्स के ऑप्टिकल गुणों पर दोषों के प्रभाव का विश्लेषण करता है। कोबाल्ट-एलॉयिंग के कारण चालकता p-टाइप से n-टाइप में स्थानांतरित होती है, जिससे विद्युत गुणों और गैर-रैखिक अवशोषण गुणांकों में सुधार होता है, जो उन्नत ऑप्टोइलेक्ट्रॉनिक उपकरणों के लिए संभावनाएं सुझाते हैं।

अध्ययन P3HT: $PC_{71}BM$ मिश्रण वाले हाइब्रिड बल्क-हेटेरोजंक्शन सोलर सेल्स की दक्षता में सुधार में FeS_2 NCs की भूमिका की भी जांच करता है। अनुकूल डोपिंग सांद्रता से शॉर्ट-सर्किट करंट घनत्व और समग्र सेल दक्षता में सुधार होता है, जिसमें दोष अवस्थाएँ कैरियर जेनरेशन और असंतुलन में सहायता करती हैं। ट्रांजिएंट फोटोकरेन्ट और फोटोवोल्टेज अध्ययन तेज कैरियर निष्कर्षण और लंबा पुनर्संयोजन समय प्रकट करते हैं, जिससे प्रदर्शन सुधार में दोष अवस्थाओं की प्रभावशीलता स्पष्ट होती है।

अध्ययन FeS_2 NCs के ऑर्गेनिक फोटोवोल्टिक सेल्स (OPVs) पर प्रभाव की भी जांच करता है, जिसमें ट्रैप अवस्थाओं के ऊर्जा वितरण और फोटोवोल्टिक गुणों में सुधार और ट्रैप-सहायता प्राप्त पुनर्संयोजन को कम करने में उनकी भूमिका पर ध्यान केंद्रित किया गया है।

इसके अलावा, $MAPbI_3$ आधारित पेरोव्स्काइट सोलर सेल्स (PeSCs) में होल ट्रांसपोर्ट मैटेरियल (HTM) के रूप में FeS_2 NCs का उपयोग शॉर्ट-सर्किट करंट घनत्व और स्थिरता में सुधार दिखाता है, जिससे हवा में संसाधित PeSCs के लिए FeS_2 NCs को एक किफायती HTM विकल्प के रूप में सुझाया गया है। इसके अलावा, $MAPbI_3$ आधारित PeSCs में दोष अवस्थाओं को निष्क्रिय

करने के लिए कॉपर(I) हैलाइड्स (CuI और CuBr) के उपयोग की जांच की जाती है, जिससे होल ट्रांसपोर्ट में सुधार और पुनर्संयोजन में कमी आती है। CuI को दोष निष्क्रिय एजेंट के रूप में उपयोग करके निर्मित अनुकूलित उलटे PeSCs ने महत्वपूर्ण दक्षता सुधार प्राप्त किया, जो 14.1% तक पहुंची।

अंत में, यह अध्ययन FeS_2 NCs में दोष इंजीनियरिंग और $MAPbI_3$ पेरोव्स्काइट सोलर सेल्स में p-टाइप कॉपर(I) हैलाइड्स के उपयोग पर महत्वपूर्ण जानकारी प्रदान करता है, जो सतत ऊर्जा अनुसंधान में प्रगति में योगदान देते हुए ऑप्टोइलेक्ट्रॉनिक उपकरणों की दक्षता और स्थायित्व को बढ़ाने में सहायक है।

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Abbreviations and Symbols

A	Acceptor
a-Si	Amorphous Silicon
AFM	Atomic Force Microscopy
Ag	Silver
Al	Aluminium
AM	Air Mass
BTU	British Thermal Units
CdTe	Cadmium Telluride
CdS	Cadmium Sulphide
CIGS	Copper Indium Gallium Selenide
CNT	Carbon Nanotube
D	Donor
DC	Direct Current
DI	De-ionized
DSSC	Dye Sensitized Solar cell
ETL	Electron Transport Layer
FF	Fill Factor
GaAs	Gallium Arsenide
GWp	Giga Watt peak
HOMO	Highest Occupied Molecular Orbit
HTM	Hole Transport Material
IEA	International Energy Agency
IPA	Iso-Propyl Alcohol

IPCC	Intergovernmental Panel on Climate Change
kwh	kilo watt-hours
LUMO	Lowest Unoccupied Molecular Orbital
LiF	Lithium Floride
MTJ	Metric Tonne Joule
MPP	Maximum Power Point
NREL	National Renewable Energy Laboratory
OPVs	Organic Photovoltaic
OSC	Organic Solar cell
P3HT	Poly(3-hexylthiophene)
$PC_{71}BM$	[6,6]-Phenyl-C71-butyric acid methyl ester
PCE	Power Conversion Efficiency
PHJ	Planar heterojunction
PL	Photoluminescence
PSC	Perovskite solar cell
PV	Photovoltaic
r.m.s.	Root-mean-square
SEM	Scanning Electron Microscopy
SCLC	Space Charge Limited Current
Si	Silicon
TCO	Transparent Conducting Oxide
TWh	Tera Watt-hour
XRD	X-Ray Diffraction
e	Charge of electron
C	Capacitance

k_B	Boltzmann constant
ε_0	Free space permittivity
ε	Relative dielectric constant
μ	Mobility
η	Efficiency
eV	Electron volt
ml	Millilitre
µm	Micro-meter
mA	Milliampere
nm	Nano-meter
mg	Milligram
R	Resistance
V_{bi}	Built-in-voltage
J_{max}	Current density at MPP
V_{max}	Voltage at MPP
J_{sc}	Short circuit current density
V_{oc}	Open circuit voltage
Z’	Real impedance (resistance)
Z”	Imaginary impedance (reactance)
n	Ideality factor
τ	Time constant
Ω	Ohm