

**STUDIES ON THE MORPHOLOGICAL AND  
OPTOELECTRONIC PROPERTIES FOR ULTRASONIC SPRAY  
DEPOSITED SCALABLE ORGANIC SOLAR CELLS**

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DEPARTMENT OF ENERGY SCIENCE AND ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY DELHI

AUGUST, 2022



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DEPOSITED SCALABLE ORGANIC SOLAR CELLS**

*by*

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Submitted

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

to the



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*Dedicated to  
My Family....*



## CERTIFICATE

This is to certify that the thesis entitled, “**Studies on the Morphological and Optoelectronic Properties for Ultrasonic Spray Deposited Scalable Organic Solar Cells**”, submitted by **Ms. Sobia Waheed** to 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 her 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.

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## ABSTRACT

Organic semiconducting materials have attracted huge attention from the electronics industry by providing flexible, light weight and cheaper devices. These materials have gained considerable popularity in the field of photovoltaic devices. This thesis highlights the various features of organic semiconductors and organic solar cell (OSC) devices. In addition to that, the need for their commercialization and the basic requirements for the purpose have also been discussed. This thesis deals with the OSC fabrication process where the Ultrasonic spray coating process has been used for active layer deposition. This technique meets the requirements of scalable device fabrication along with being easily controllable, high throughput, least material wasting technique.

The systematic study of the formation of Bulk Heterojunction (BHJ) of poly (3-hexylthiophene) and phenyl-C<sub>71</sub> butyric acid methyl ester (P3HT:PC<sub>71</sub>BM) deposited by ultrasonic spray coating subjected to in-situ annealing has been done and the results have been compared with spin deposited films. The attempts have been made via structural, morphological, and optoelectronic characterizations to probe the behaviour of film crystallization and its effect on electron and hole mobility of the BHJ layer. It has been found that spray coating at moderate substrate temperature, well below the boiling point of the solvent, results in film characteristics comparable to spin-coated ones.

Furthermore, an attempt has been made to correlate the performance of ultrasonic spray deposited organic photovoltaic (OPV) devices with the imposition of acoustic vibration on the substrate. A systematic study has been performed to understand the role of acoustic vibration applied on the substrate and the effect of different frequencies on spray deposited OSC device parameters and thin-film properties. The best performance OPV device was obtained at an acoustic vibration frequency of 15 kHz, with almost 68% increment in short-circuit current density, compared to the device with no vibration condition. The power conversion efficiency and Fill Factor (FF) obtained for this device were about 3.5% and 40%, respectively. We observed that a threshold is present in acoustic vibration frequency beyond which the substrate vibration becomes detrimental for the film. The surface morphology investigation reveals that there is a visible improvement in droplet spreading and coalescence due to acoustic vibration till 15 kHz, with a reduction in r.m.s. roughness, reaching 10 nm for 15 kHz sample. However, beyond this point, higher frequencies were found to have a detrimental effect on film formation. The performance enhancement is mainly attributed to the improved film morphology due to

uniform and homogenous droplet spreading and coalescence under the influence of acoustic vibration.

To alleviate the chances of establishing a scalable spray deposition method, a detailed understanding of the influence of changes in deposition conditions over device performance is required. Therefore, Impedance spectroscopy, Mott-Schottky analysis, Urbach energy analysis, and trap-state density calculation have been done to get a better understanding of the fundamental contribution of ultrasonic spray deposition and the impact of substrate temperature and substrate vibration on charge carrier dynamics. The correlation between charge transport behaviour and device performance has been identified for the ultrasonic spray deposition of P3HT:PC<sub>71</sub>BM organic solar cell. The reduction in surface roughness and droplet boundaries leads to a significant decrease in overall device resistance by 50% and in diffusion time by 75%. An Increase in effective lifetime suggests strong bimolecular recombination in the in-situ-vibration annealed spray device. Trap and defect-state densities have also been quantified for ultrasonic spray deposited devices under various conditions.

To understand the scalability and its limitations in the case of spray deposition, the as optimized ultrasonic spray deposition process is been used to investigate the effect of the increasing area over OSC device performance. The performance seems to be degrading with increasing electrode dimensions. The short circuit current density observed for the 0.04 cm<sup>2</sup> area device got reduced with the increasing active area and for the large-area device of 1.5 cm<sup>2</sup>, it got reduced by more than 70%. The FF has also decreased to 27% for large-area devices in comparison to small area devices having 40% FF. The overall device resistance increased by more than 10 times and the global charge carrier mobility was found to get decreased from  $8.28 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$  to  $1.83 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$  for the large-area device in comparison to small-area one. This also leads to reduction in overall charge generation as the maximum carrier generation rate has decreased from  $4.77 \times 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$  for small-area device to  $1.92 \times 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$  for large area device.

## सार

कार्बनिक अर्ध-चालक पदार्थों ने लचीले, हल्के वजन और सस्ते उपकरण प्रदान करके इलेक्ट्रॉनिक्स उद्योग का बहुत ध्यान आकर्षित किया है। इन सामग्रियों ने फोटोवोल्टिक उपकरणों के क्षेत्र में काफी लोकप्रियता हासिल की है। यह थीसिस कार्बनिक अर्ध-चालक और कार्बनिक सोलर सेल (OSC) उपकरणों की विभिन्न विशेषताओं पर प्रकाश डालती है। इसके अलावा उनके व्यावसायीकरण की आवश्यकता और उद्देश्य के लिए बुनियादी आवश्यकताओं पर भी चर्चा की गई है। यह थीसिस ओएससी निर्माण प्रक्रिया से संबंधित है जहां सक्रिय परत जमाव के लिए अल्ट्रासोनिक स्प्रे कोटिंग प्रक्रिया का उपयोग किया गया है। यह तकनीक आसानी से नियंत्रित, उच्च थ्रूपुट, कम से कम सामग्री बर्बाद करने वाली तकनीक होने के साथ-साथ स्केलेबल डिवाइस फैब्रिकेशन की आवश्यकताओं को पूरा करती है। इन-सीटू एनीलिंग के अधीन अल्ट्रासोनिक स्प्रे कोटिंग द्वारा जमा पॉली (3-हेक्सिलथियोफेन) और फिनाइल-सी71 ब्यूटिरिक एसिड मिथाइल एस्टर (P3HT:PC<sub>71</sub>BM) के बल्क हेटेरोजंक्शन (BHJ) के गठन का व्यवस्थित अध्ययन किया गया है और परिणामों की तुलना स्पिन जमा फिल्मों से की गई है। क्रिस्टलीकरण के व्यवहार और BHJ परत के इलेक्ट्रॉन और होल गतिशीलता पर इसके प्रभाव की जांच के लिए संरचनात्मक, रूपात्मक और ऑप्टोइलेक्ट्रॉनिक लक्षण वर्णन के माध्यम से प्रयास किए गए हैं। यह पाया गया है कि मध्यम सबस्ट्रेट तापमान पर स्प्रे कोटिंग, विलायक के क्वथनांक से काफी नीचे, स्पिन कोटिंग की तुलना में फिल्म विशेषताओं में परिणाम होता है।

इसके अलावा, सबस्ट्रेट पर ध्वनिक कंपन लगाने के साथ अल्ट्रासोनिक स्प्रे जमा कार्बनिक फोटोवोल्टिक (ओपीवी) उपकरणों के प्रदर्शन को सहसंबंधित करने का प्रयास किया गया है। सबस्ट्रेट पर लागू ध्वनिक कंपन की भूमिका और स्प्रे जमा ओएससी डिवाइस पैरामीटर और पतली फिल्म गुणों पर विभिन्न आवृत्तियों के प्रभाव को समझने के लिए एक व्यवस्थित अध्ययन किया गया है। सबसे अच्छा प्रदर्शन ओपीवी डिवाइस 15 kHz की ध्वनिक कंपन आवृत्ति पर प्राप्त किया गया था, जिसमें बिना कंपन स्थिति वाले डिवाइस की तुलना में शॉर्ट-सर्किट धारा घनत्व में लगभग 68% की वृद्धि हुई थी। इस उपकरण के लिए प्राप्त शक्ति रूपांतरण दक्षता और फिल-फैक्टर (FF) क्रमशः लगभग 3.5% और 40% थे। हमने देखा कि ध्वनिक कंपन आवृत्ति में एक थ्रेशोल्ड मौजूद होता है जिसके आगे सबस्ट्रेट कंपन फिल्म के लिए हानिकारक हो जाता है। सतह आकारिकी जांच से पता चलता है कि 15 kHz तक ध्वनिक कंपन के कारण बूंदों के प्रसार और सहसंयोजन में सुधार हुआ है, आर.एम.एस खुरदरापन में कमी के साथ, 15 kHz नमूने के लिए 10 nm तक पहुंचना। हालांकि, इस बिंदु से परे, उच्च आवृत्तियों का फिल्म निर्माण पर हानिकारक प्रभाव पाया गया। प्रदर्शन में वृद्धि मुख्य रूप से ध्वनिक कंपन के प्रभाव में वृद्धि और समरूप बूंदों के प्रसार और सहसंयोजन के कारण बेहतर फिल्म आकारिकी के लिए जिम्मेदार है।

एक स्केलेबल स्प्रे जमा करने की विधि स्थापित करने की संभावना को बढ़ाने के लिए, डिवाइस के प्रदर्शन पर बयान की स्थिति में बदलाव के प्रभाव की एक विस्तृत समझ की आवश्यकता है। इसलिए, अल्ट्रासोनिक स्प्रे जमाव के मौलिक योगदान और चार्ज वाहक गतिकी पर सबस्ट्रेट तापमान और सबस्ट्रेट कंपन के प्रभाव की बेहतर समझ प्राप्त करने के लिए प्रतिबाधा स्पेक्ट्रोस्कोपी, Mott-Schottky विश्लेषण, Urbach ऊर्जा विश्लेषण, और Trap-state density की गणना की गई है। P3HT:PC<sub>71</sub>BM ऑर्गेनिक सोलर सेल के अल्ट्रासोनिक स्प्रे डिपोजिशन के लिए चार्ज ट्रांसपोर्ट बिहेवियर और डिवाइस परफॉर्मेंस के बीच सहसंबंध की पहचान की गई है। सतह खुरदरापन और छोटी बूंदों की सीमाओं में कमी से समग्र डिवाइस प्रतिरोध में 50% और प्रसार समय में 75% की उल्लेखनीय कमी आती है। प्रभावी जीवनकाल में वृद्धि इन-सीटू-वाइब्रेशन एनील्ड स्प्रे डिवाइस में मजबूत द्वि-आणविक पुनर्संयोजन का सुझाव देती है। विभिन्न परिस्थितियों में अल्ट्रासोनिक स्प्रे जमा उपकरणों के लिए जाल और defect-state घनत्व भी निर्धारित किया गया है।

स्प्रे डिपोजिशन के मामले में मापनीयता और इसकी सीमाओं को समझने के लिए, ओएससी डिवाइस के प्रदर्शन पर बढ़ते क्षेत्र के प्रभाव की जांच के लिए अनुकूलित अल्ट्रासोनिक स्प्रे डिपोजिशन प्रक्रिया का उपयोग किया गया है। इलेक्ट्रोड आयामों में वृद्धि के साथ प्रदर्शन कम होता जा रहा है। बढ़ते सक्रिय क्षेत्र के साथ 0.04 cm<sup>2</sup> क्षेत्र डिवाइस के लिए मनाया गया शॉर्ट सर्किट धारा घनत्व कम हो गया और 1.5 cm<sup>2</sup> के बड़े क्षेत्र के उपकरण के लिए यह 70% से अधिक कम हो गया। 40% FF वाले छोटे क्षेत्र के उपकरणों की तुलना में बड़े क्षेत्र के उपकरणों के लिए FF भी घटकर 27% हो गया है। समग्र उपकरण प्रतिरोध में 10 गुना से अधिक की वृद्धि हुई और बड़े क्षेत्र के लिए वैश्विक चार्ज वाहक गतिशीलता 8.28 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> से 1.83 × 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> तक घट गई। छोटे क्षेत्र की तुलना में डिवाइस। इससे समग्र चार्ज जनरेशन में भी कमी आती है क्योंकि छोटे क्षेत्र के डिवाइस के लिए अधिकतम वाहक उत्पादन दर 4.77 × 10<sup>21</sup> cm<sup>-3</sup> s<sup>-1</sup> से घटकर बड़े क्षेत्र के डिवाइस के लिए 1.92 × 10<sup>21</sup> cm<sup>-3</sup> s<sup>-1</sup> हो गई है।

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## ABBREVIATIONS AND SYMBOLS

A	Acceptor
a-Si	Amorphous Silicon
AFM	Atomic Force Microscopy
Ag	Silver
Al	Aluminum
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
HTL	Hole Transport Layer
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
OSC	Organic Solar cell

P3HT	Poly(3-hexylthiophene)
PC <sub>71</sub> 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 <sub>B</sub>	Boltzmann constant
ε <sub>0</sub>	Free space permittivity
ε	Relative dielectric constant
μ	Mobility
η	Efficiency
eV	Electron volt
ml	Millilitre
μm	Micrometer
mA	Milliampere
nm	Nanometer
mg	Milligram
R	Resistance
V <sub>bi</sub>	Built-in-voltage
J <sub>max</sub>	Current-density at MPP
V <sub>max</sub>	Voltage at MPP
J <sub>sc</sub>	Short circuit current density
V <sub>oc</sub>	Open circuit voltage

$Z'$	Real impedance (resistance)
$Z''$	Imaginary impedance (reactance)
$n$	Ideality factor
$\tau$	Time constant
$\Omega$	Ohm

