http://www.jctjournals.com ISSN(ONLINE):2278 – 3814

Volume-08, Issue-10, October 2019
JOURNAL OF COMPUTING TECHNOLOGIES (JCT)
International Journal
Page Number: 01-05

Electrical Conductivity Enhancement in Polymer Thin Films by Iodine Doping

Milind Bhaskarrao Nawarkhele
Lecturer in Physics
Government Polytechnic Hingoli, M.H., INDIA
Email: meetmbn@gmail.com

***Abstract*— Polymer thin films have attracted considerable attention in recent years due to their lightweight nature, mechanical flexibility, and potential applications in electronic and optoelectronic devices. However, their inherently low electrical conductivity limits their practical use in advanced functional materials. In this study, the effect of iodine doping on the electrical conductivity of polymer thin films is systematically investigated. Thin films were prepared using a suitable deposition technique and subsequently exposed to iodine under controlled conditions to induce chemical doping. The interaction between iodine molecules and the polymer matrix leads to the formation of charge transfer complexes, resulting in an increased density of mobile charge carriers and improved charge transport pathways. Electrical characterization revealed a significant enhancement in conductivity after doping compared to the undoped films. The degree of conductivity improvement was found to depend on factors such as film morphology, doping time, iodine concentration, and polymer structure. In addition to conductivity enhancement, iodine doping may also influence the optical and structural properties of the films, indicating its multifunctional role in tuning material performance. The findings demonstrate that iodine doping is an effective and economical approach for modifying the electrical behavior of polymer thin films, thereby expanding their applicability in flexible electronics, sensors, energy devices, and other polymer-based electronic systems.**

***Keywords*— Polymer thin films, iodine doping, electrical conductivity, charge transfer complex, flexible electronics, conductive polymers.**

I. INTRODUCTION

Polymer thin films have attracted significant attention in recent years due to their lightweight nature, mechanical flexibility, low-cost fabrication, and potential applications in modern electronic and optoelectronic devices [1]. These materials are widely used in sensors, flexible electronics, photovoltaic devices, antistatic coatings, and organic semiconductors. However, the inherently low electrical conductivity of most pure polymers limits their direct use in advanced electronic applications[2]. Therefore, various strategies have been explored to improve the electrical properties of polymer thin films, among which chemical doping has emerged as one of the most effective and practical approaches. Iodine doping is a well-known and widely studied method for enhancing the electrical conductivity of polymeric materials. Iodine acts as an electron acceptor and interacts with the polymer backbone through charge-transfer mechanisms, resulting in the formation of mobile charge carriers such as polarons, bipolarons, or radical cations [3]. This process significantly reduces the resistivity of the polymer and improves charge transport within the thin film structure. The extent of conductivity enhancement depends on several factors, including the chemical structure of the polymer, degree of conjugation, film morphology, thickness, doping concentration, exposure time, and environmental stability [4].

In polymer thin films, the interaction between iodine molecules and the polymer matrix can induce substantial modifications in both electrical and optical properties. The doping process may alter the band gap, increase carrier density, and improve intermolecular charge hopping, thereby making the material more suitable for electronic applications. In addition, iodine doping is relatively simple, cost-effective, and can be performed through vapor-phase or solution-based methods, which makes it attractive for large-scale fabrication processes. Several studies have reported remarkable increases in conductivity in polymers such as polyacetylene, polyaniline, polypyrrole, polysilanes, and other conjugated or semi-conjugated systems after iodine treatment [5] [3].

The enhancement of electrical conductivity through iodine doping is not only important from a practical application standpoint but also from a scientific perspective, as it provides insight into the charge transport mechanisms in polymeric systems. Understanding how iodine interacts with different polymer structures helps in designing high performance materials with tunable electrical characteristics[1] [4].

The thin film geometry offers additional advantages such as controlled thickness, uniform surface coverage, and compatibility with microelectronic device architectures, which further strengthens the importance of studying iodine-doped polymer thin films[7] .

Iodine-doped polymer thin films have several important applications:

- Flexible electronic devices
- Antistatic coatings
- Gas and chemical sensors
- Organic photovoltaic devices
- Thin-film transistors
- Electromagnetic interference (EMI) shielding
- Energy storage electrodes
- Wearable electronics.

II. LITERATURE REVIEW

Yuhan Zhong et.al (2019) - In this research work author presented an effective design strategy of polymer thermoelectric materials based on structural control in doped polymer semiconductors. The strategy is illustrated for two archetypical polythiophenes e.g. poly(2,5-bis(3-dodecyl-2-thienyl)thieno[3,2-b]thiophene) (C12-PBTTT) and regioregular poly(3-hexylthiophene) (P3HT). $FeCl_3$ doping of aligned films results in charge conductivities up to 2. 105 S/cm and metallic-like thermopowers similar to iodine-doped polyacetylene. The films are almost optically transparent and show strongly polarized near-infra-red polaronic bands (dichroic ratio > 10). The comparative study of structure-property correlations in P3HT and C12-PBTTT identifies three conditions to obtain conductivities beyond 105 S/cm: i) achieve high in-plane orientation of conjugated polymers with high persistence length, ii) ensure uniform chain oxidation of the polymer backbones by regular intercalation of dopant molecules in the polymer structure without disrupting alignment of π-stacked layers and iii) maintain a percolating nano-morphology along the chain direction [01].

Dogan Mansuroglu et.al (2018)- In this research work author presented iodine doped plasma-polymerized biphenyl thin film is investigated in this study. Iodine atoms lead to increase the charge transfer complexes and change the electronic equilibrium in the polymer structure due to their high electro negativity. Therefore, the iodine doped films show significant improvements in the electrical characteristics as compared to the undoped ones. The results of Raman spectroscopy verify the presence of the iodined groups in the structure of deposited thin films. The number density of the iodine groups increases with increasing the radio frequency input power. The ID/IG ratio changes in a range from 0.40 to 0.72 for the undoped thin films while it decreases from 0.74 to 0.58 for the iodine doped thin films which can be due to the rearrangement in the structure. Photoluminescence spectra show a broad red emission band at about 630 nm as well as unclear bands placed like small shoulders at 580 nm and 731 nm. These bands become to seem clearly after the iodine doping process. The conjugation length of the polymer thin films increases with iodine doping as well as increasing the power values. All depositions are produced using a capacitively coupled plasma system with 13.56 MHz radio frequency source. During the doping process, the vaporized iodine material is directly exposed to the plasma discharge and mixed with the biphenyl polymer material. All results are characterized in detail [02].

Teresa Hernández de la Cruz et.al (2018) - In this research work author presented the chemical structure, morphology, electromagnetic absorption and electric conductivity of thin films. The electrochemical synthesis of polypyrrole/surfactant (PPy/SDS) films doped with iodine is carried out by glow discharge plasma in aqueous solution, at different reaction times. The morphology shows agglomerations of particles dispersed in the surface. Infrared spectroscopic analysis shows absorption on the wavenumbers 2915, 2362 and 2082 cm^{-1} corresponding to chemical groups C-H, C=O and R/N=C=S, respectively. The electromagnetic absorption had higher response sensitivity between 340 to 800 nm in the visible region, and the electric conductivity of samples oscillated between 5.0×10^{-6} and 2.0×10^{-5} S/cm. The thickness films significantly increased when doping with iodine, reaching values up to 50 μm [03].

Omer Naji Ali et.al (2017) - A bridged compound from Tetrapyrazinoporphrazine Venadyloxide and p- Dicyano benzene was synthesized. A thin surface film from the bridged compound and the complex were cast on a glass substrate and its dc electrical conductivity was measured. The two thin surface films from the two complexes were doped with Iodine vapour for one night. The excess iodine was removed by heating at 110 0C for one hour and their dc electrical conductivity were measured and compared. The electrical measurement shows that the iodine doped thin film have higher conductivity than the undoped due to the oxidation of the complex by the Iodine. The bridged complex with p-Dicyano benzene has lower dc conductivity than the unabridged, which could be attributed to the separation gap between the ring groups by p-Dicyanobenzene [04].

Choon-Sang Park et.al (2016) - In this research work author presented nanostructured conductive polymer synthesis method that can grow the single-crystalline high-density plasma-polymerized nanoparticle structures by enhancing the sufficient nucleation and fragmentation of the pyrrole monomer using a novel atmospheric pressure plasma jet (APPJ) technique. Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and field emission scanning electron microscopy (FE-SEM) results show that the plasma-polymerized pyrrole (pPPy) nanoparticles have a fast deposition rate of 0.93 $\mu m\cdot min^{-1}$ under a room-temperature process and have single-crystalline characteristics with porous properties. In addition, the single-crystalline high-density pPPy nanoparticle structures were successfully synthesized on the glass, plastic, and interdigitated gas sensor electrode substrates using a novel plasma polymerization technique at room temperature. To check the suitability of the active layer for the fabrication of electrochemical toxic gas sensors, the resistance variations of the pPPy nano-particles grown on the interdigitated gas sensor electrodes were examined by doping with iodine. As a result, the proposed APPJ device could obtain the high-density and ultra-fast single-crystalline pPPy thin films for various gas sensor applications. This work will contribute to the design of highly sensitive gas sensors adopting the novel plasma-polymerized conductive polymer as new active layer [05].

Lina Fan et.al (2015) - In this research work author presented Iodine-doping is used to develop the high-conductivity carbon nanotube (CNT) -polymer composites. We prepared three kinds of CNT-polymer composites by in-suit polymerization, and obtained iodine-doped samples by mechanical mixing. A series of research about electrical conductivity proves iodine doping is an effective way to get high-conductivity composites with heteroatom in the polymer matrix. The conductivity could increase up to 4 orders of magnitude compared to the undoped samples. Based on Hall-effect, Raman and XPS spectra, we propose the synergistic effect between CNT and iodine results in the superior property. When the heteroatom is N, the synergistic effect of iodine and CNT helps to form stronger p-π conjugate system. The N cation radical (as a kind of carriers) increase with the enhanced conjugate, resulting in the improved conductivity. When the heteroatom is S, CNT and iodine form π-π conjugate system and charge-transfer complex with S separately. The combination of the two interaction induced the boost of the carrier concentration, as well as the conductivity [06].

K Sreelatha et.al (2015) - In this research work author presented an attempt has been made to dope Low Density Polyethylene (LDPE) with iodine and to study the effect of iodine doping on the optical band gap of LDPE films. The DC conductivity measurements and UV/Vis spectral studies are employed to characterize the samples. Iodine treatment induces colour change in the polymer film which supports the interaction between iodine molecules and polyethylene chains. I2 molecule links the polymer chains electronically and provides conducting path ways by forming DA complexes. The absorption band of complex films has extended to the visible and near infrared region of the spectrum. Further there are discernible shifts found in the energy gap and band edge towards lower energies on doping with iodine. This is essentially due to the formation of strong DA complexes upon iodine doping which improves the conducting behaviour [07].

Table-1 Compression Table of Pervious Method

Authors & Year	**Material System**	**Doping Type**	**Key Techniques**	**Conductivity Range**
Yuhan Zhong et al. (2019)	P3HT, C12-PBTTT	$FeCl_3$ doping	Structural control, alignment studies	~10^5 S/cm
Dogan Mansuroglu et al. (2018)	Plasma-polymerized biphenyl thin film	Iodine doping	Raman, PL spectroscopy	Not specified (improved vs undoped)
Teresa Hernández de la Cruz et al. (2018)	PPy/SDS thin films	Iodine doping	IR spectroscopy, morphology, EM absorption	5×10^{-6} – 2×10^{-5} S/cm
Omer Naji Ali et al. (2017)	Tetrapyrazino porphrazine complexes	Iodine vapor doping	DC conductivity measurement	Not specified (increase observed)
Choon-Sang Park et al. (2016)	Plasma-polymerized pyrrole (pPPy)	Iodine doping	TEM, FTIR, XPS, FE-SEM	Not specified (enhanced sensitivity)
Lina Fan et al. (2015)	CNT–polymer composites	Iodine doping	Raman, Hall effect, XPS	Up to 10^4× increase
K. Sreelatha et al. (2015)	LDPE films	Iodine doping	UV-Vis, DC conductivity	Not specified (enhanced conductivity)

III. MATERIALS AND METHODS

A. *Materials*

The materials used in this study may include:

- Base polymer (e.g., Polyaniline (PANI), Polypyrrole (PPy), Polyvinyl Alcohol (PVA), PMMA, or Polysilane)
- Solvent (e.g., chloroform, tetrahydrofuran, DMF, distilled water depending on polymer type)
- Iodine crystals (I_2) as dopant
- Glass substrates / quartz substrates
- Acetone and ethanol for substrate cleaning

B. Preparation of Polymer Thin Films

Polymer thin films can be prepared using one of the following methods:

(a) Solution Casting Method

1. Dissolve a known amount of polymer in a suitable solvent.
2. Stir the solution continuously until a homogeneous mixture is obtained.
3. Pour the solution onto a clean glass substrate or Petri dish.
4. Allow the solvent to evaporate slowly at room temperature or under controlled heating.
5. Peel off the formed film or use directly on substrate.

(b) Spin Coating Method

1. Prepare a polymer solution of desired concentration.
2. Deposit a few drops of the solution onto the cleaned substrate.
3. Spin the substrate at a controlled speed (e.g., 1000–3000 rpm) for 30–60 seconds.

4. Dry the coated film in an oven to remove residual solvent.

C. Iodine Doping Process

The polymer thin films are doped by **iodine vapor exposure**.

Procedure:

1. Place iodine crystals in a sealed glass chamber.
2. Suspend the polymer thin film above the iodine crystals without direct contact.
3. Expose the film to iodine vapor for different durations (e.g., 5 min, 10 min, 20 min, 30 min).
4. Remove the film and store in a desiccator before characterization.

IV. CHARACTERIZATION TECHNIQUES

A. Thickness Measurement

Film thickness can be measured using:

- Micrometer screw gauge
- Surface profilometer
- Ellipsometry

B. Structural Characterization

Fourier Transform Infrared Spectroscopy (FTIR)

Used to identify functional groups and confirm interactions between iodine and polymer chains.

X-ray Diffraction (XRD)

Used to determine crystallinity changes after doping.

Scanning Electron Microscopy (SEM)

Used to observe surface morphology and microstructural change.

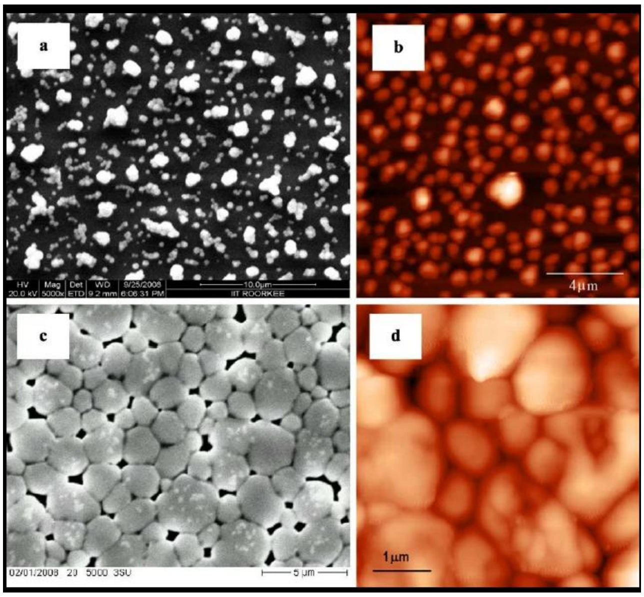

Fig:1 SEM Image of Compact Granular Morphology in Thin Film Structure

C. Optical Characterization

UV–Visible Spectroscopy

Used to study:

- Optical absorption changes
- Band gap variation
- Formation of charge transfer complexes after iodine doping.

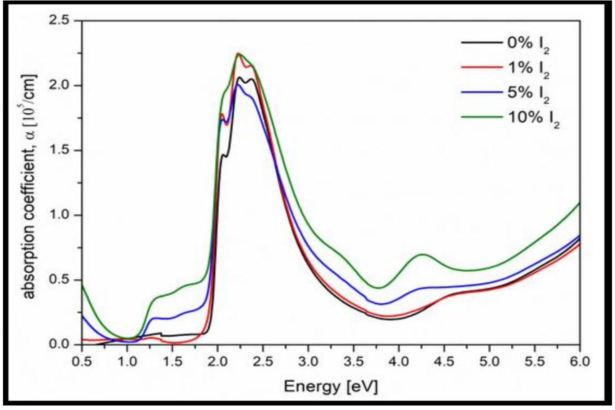

Fig: 2 Comparative UV–Vis Absorption Analysis of Iodine-Doped Polymer Thin Films

D. Properties

Increased Electrical Conductivity

The most significant property observed after iodine doping is the substantial increase in electrical conductivity of polymer thin films.

Charge Transfer Interaction

Iodine doping introduces a charge-transfer complex between the polymer chains and iodine molecules. This interaction partially removes electrons from the polymer backbone, generating mobile positive charges, which enhance the conductive behavior of otherwise insulating or semiconducting polymers.

Improved Carrier Mobility

Iodine-doped polymer films often show higher carrier mobility due to better hopping conduction between adjacent polymer chains. The dopant modifies the electronic structure and reduces barriers for charge transfer, allowing charges to move more efficiently across the thin film.

Optical Property Modification

Iodine doping affects the optical properties of polymer films, including:

- Shift in UV–Visible absorption peaks
- Increase in absorbance intensity
- Possible red shift due to extended conjugation or charge-transfer states

These optical changes indicate successful doping and correlate with enhanced electrical behavior.

V. Conclusion

This study demonstrates that iodine doping is an effective technique for enhancing the electrical conductivity of polymer thin films. By exposing polymer films to iodine vapor, charge transfer complexes are formed, generating mobile charge carriers that significantly improve electrical transport. The conductivity increases with doping time up to an optimum level, beyond which saturation or film degradation may occur. In addition to electrical improvement, iodine doping also modifies the structural and optical properties of the polymer films, which can be confirmed using FTIR, UV–Vis, XRD, and SEM analyses. Due to its simplicity, affordability, and strong impact on conductivity, iodine doping remains a valuable method for developing advanced polymer-based conductive materials. The results suggest that iodine-doped polymer thin films have excellent potential for applications in flexible electronics, sensors, antistatic materials, and energy-related devices. Future work may focus on improving the long-term stability of iodine-doped films and exploring hybrid doping approaches for even higher conductivity and durability.

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