INVESTIGATION OF PEDOT:PSS/Si HETEROJUNCTIONS AND GRAPHENE/Si SCHOTTKY DIODES FOR POTENTIAL APPLICATION IN PHOTOVOLTAICS

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INVESTIGATION OF PEDOT:PSS/Si HETEROJUNCTIONS AND GRAPHENE/Si SCHOTTKY DIODES FOR POTENTIAL APPLICATION IN PHOTOVOLTAICS

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Certificate

We are satisfied that the thesis entitled “Investigation of PEDOT:PSS/Si Heterojunctions and Graphene/Si Schottky Diodes for Potential Application in Photovoltaics” submitted by Mr. Chandra Shakher Pathak is worthy of consideration for the award of the degree of Doctor of Philosophy and is a record of original and bonafide research work carried out by him under our supervision. The results contained in this thesis have not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

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Chandra Shakher Pathak
Abstract

Hybrid organic–inorganic materials play an important role in the field of optoelectronics. Now a days transparent conducting materials are needed to replace indium tin oxide as the transparent electrode for optoelectronic devices. Poly (3,4 ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is a promising candidate as a transparent electrode for optoelectronic devices. However as prepared PEDOT:PSS has less conductivity (less than 1 S/cm) and it is a major limiting factor for device applications. It is important to increase the conductivity of PEDOT:PSS. In this work the aim is to develop novel and effective methods for enhancement in electrical properties of PEDOT:PSS films, demonstrating the application of conducting and transparent PEDOT:PSS films in heterojunction diodes and solar cells.

In this thesis, the effect of various organic solvents on PEDOT:PSS films, PEDOT:PSS/Si heterojunction diodes and photovoltaic devices have been investigated. The conductivity of PEDOT:PSS films enhanced by two orders of magnitude and all films have transparency of more than 85%. The value of ideality factor improved from 9.6 in case of pristine to 1.9 and barrier height increased from 0.57 to 0.82 eV with organic solvent. We investigated how the doping of PEDOT:PSS films with co-solvents modifies the electrical and morphological properties of the films. The conductivity value is found to increase about 1000 times compared to its pristine value with co-solvents. The conductivity of PEDOT:PSS film increased from 0.16 for pristine to 194 S/cm with co-solvents. Value of ideality factor varies from 3.1 to 2.4 and polymer photovoltaic cells fabricated with the co-solvents show higher power conversion efficiency as compared to solvents doped PEDOT:PSS films.

The use of graphene oxide as a doping material increases the conductivity of PEDOT:PSS films by three orders of magnitude and all fabricated films are highly transparent. We proposed direct synthesis of graphene nanopowder and PEDOT:PSS for the formation of conducting and transparent nanocomposite materials and the application of nanocomposite materilas demonstrated in heterojunction diodes. The conducting and transparent nanocomposite materilas can be used in optoelectronics.

In addition of this, we fabricated graphene/n-Si Schottky diodes. To understand the transport mechanism in details, temperature dependent current-voltage
characteristics are carried out, which allow us to understand the different aspects of the conduction mechanism of graphene/$n$-Si Schottky diodes. At room temperature the value of ideality factor and barrier height are 2.0 and 0.84 eV, respectively. It is found that barrier height increases and ideality factor decreases with increase in temperature. Kelvin probe force microscopy (KPFM) and conductive atomic force microscopy (CAFM) are used to understand the electrical properties of graphene/$n$-Si Schottky diodes at nanoscale. Localized variations in surface contact potential difference are studied using KPFM while localized variations in current-voltage characteristics are studied using CAFM. Most of the value of ideality factor and barrier height is found to be in the range of 2.0–4.0 and 0.50–0.70 eV for the graphene/$n$-Si nanoscale Schottky nanoscale contact. The analysis of the temperature dependent transport properties in combination with nanoscale electrical properties will be important for their application in various electronic devices.
हाइब्रिड कार्बनिक-अकार्बनिक सामग्री ऑप्टोलेक्ट्रॉनिकस के क्षेत्र में एक महत्वपूर्ण भूमिका निभाती है। आजकल ऑप्टोलेक्ट्रॉनिक उपकरणों के लिए पारदर्शी इलेक्ट्रोड के रूप में इलेक्ट्रॉन ऑक्साइड को बदलने के लिए पारदर्शी संचालन सामग्री की आवश्यकता है। पांडी(3,4 थियोलीनडिऔक्सिथियोफेन)- पांडी (स्टडर्नर्नलकोबेट) (पीईडीओटी: पीएसएस) ऑप्टोलेक्ट्रॉनिक उपकरणों के लिए एक पारदर्शी इलेक्ट्रोड के रूप में एक आधारणक उपयोग वार्ड है। हालांकि तेघार पीईडीओटी:पीएसएस की चालकता (1 सीमेंट/सेमी) में कम है और वह उपकरण अनुप्रयोगों के लिए एक प्रमुख सीमित कारक है। पीईडीओटी:पीएसएस की चालकता बढाना महत्वपूर्ण है। इस काम का उद्देश्य पीईडीओटी:पीएसएस के विभिन्न गुणों में बुद्धि के लिए नया और प्रभावी तरीक़े विकसित करना है, चालक और पारदर्शी पीईडीओटी:पीएसएस फिल्मों का प्रदर्शन और उपयोग इलेक्ट्रॉनिक डायोड और सॉर बैटरी में करना है।

इस शोध प्रबन्ध में, विभिन्न कार्बनिक विलायकों का प्रभाव पीईडीओटी:पीएसएस फिल्म, पीईडीओटी: पीएसएस/सिलिकाइन्टेरनिक डायोड और सॉर उपकरण में जांच की गई है। पीईडीओटी:पीएसएस की चालकता परिमाण के 100 गुणा तक बढ़ाया गया और सभी फिल्मों में 85% से अधिक की पारदर्शिता है। कार्बनिक विलायक के साथ आदर्शता कारक का गुण 9.6 मूल से सूचार कर 1.9 और बाधा की ऊंचाई 0.57 से बढ़कर 0.82 ई. बॉल्ट हुआ है। हमने जांच की तो कैसे सह-विलायक ने पीईडीओटी:पीएसएस फिल्मों में मिलकर फिल्मों के विभिन्न और रुपायक गुणों को संभोगित किया। सह-विलायक के साथ अपने मूल की तुलना में चालकता लगभग 1000 गुणा बढ़ जाती है। पीईडीओटी:पीएसएस फिल्मों की चालकता 0.16 मूल से बढ़कर 194 सीमेंट/सेमी सह-विलायक के साथ हुई है। आदर्शता कारक का गुण 3.1 से 2.4 तक परिवर्तित हुआ है और विलायक पीईडीओटी:पीएसएस फिल्मों की तुलना में सह-विलायक के साथ निर्भर बहुत सी उपकरण उत्तर शक्ति प्राप्ती से दायीं है।

डोपिंग सामग्री के रूप में ग्राफिन ऑक्साइड का उपयोग पीईडीओटी:पीएसएस फिल्मों की चालकता को परिमाण के तीन आदेश तक बढ़ाता है और सभी बनाए फिल्मों में बहुत पारदर्शी हैं। हमने संचालन ऑर पारदर्शी अतिसुष्क मिश्र सामग्री के निर्माण के लिए ग्राफिन अतिसुष्क पाउडर और पीईडीओटी:पीएसएस के प्रत्येक संहिता का प्रस्ताव दिया। चालक और पारदर्शी अतिसुष्क मिश्र सामग्री का उपयोग ऑप्टोलेक्ट्रॉनिक में किया जा सकता है।

इसके अलावा, हमने ग्राफिन/एस-सिलिकाईन्ट शटर्ड डायोड का निर्माण किया है। विषय में संचालन प्रक्रिया को समझने के लिए, तापमान पर निर्भर विवरण प्रबाह - बॉल्टा विशेषताओं को पूरा किया गया, जो हमें ग्राफिन/एस-सिलिकाईन्ट
र्शाट्की डायोड के संवाहन प्रक्रिया के विभिन्न पहलुओं को समझने की अनुमति देता है। कमरे के तापमान पर आदर्शता कारक और बाधा ऊंचाई का गुण क्षमता 2.0 और 0.84 ईं. बोल्ट है। यह पाया गया है कि तापमान में वृद्धि के साथ बाधा की ऊंचाई बढ़ जाती है और आदर्शता कारक घट जाती है। केवलन प्रीब फॉर्स माइक्रोस्कोपी (कैपीएफएम) और केंडरिंग एटामिक प्रीब माइक्रोस्कोपी (सीएएफएम) का प्रयोग अतिसूक्ष्म पैमाने पर ग्राफीन/एन-सिलिकॉन शाद्दी डायोड के विद्युत गुणों को समझने के लिए किया जाता है। सतह संपर्क संभावित अंतर में स्थानीय विद्युत अतिसूक्ष्म के पीएफएम का उपयोग करके अध्ययन किया जाता है जबकि विद्युत व्यवस्था विशेषताओं में स्थानीय विद्युत अतिसूक्ष्म के सीएएफएम का उपयोग करके अध्ययन की जाती है। अधिकांश आदर्शता कारक और बाधा की ऊंचाई के गुण, ग्राफीन/एन-सिलिकॉन अतिसूक्ष्म शाद्दी अतिसूक्ष्म संपर्क के लिए 2.0-4.0 और 0.50-0.70 ईं. बोल्ट के वेंच में पाया गया है। अतिसूक्ष्म पैमाने पर विद्युत गुणों के साथ संयोजन में तापमान पर निर्भर संवाहन गुणों का विक्षेपण विभिन्न इलेक्ट्रॉनिक उपकरणों में उनके आवेदन के लिए महत्वपूर्ण होगा।
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List of symbols and abbreviations

**PEDOT:PSS** Poly (3,4 ethylenedioxythiophene):poly (styrenesulfonate)

**PVDF** Polyvinylidene fluoride

**Si** Silicon

**SiO$_2$** Silicon dioxide

**Al** Aluminum

**Au** Gold

**In-Ga** Indium-Gallium

**UV-Vis-NIR** Ultraviolet-visible near infra-red spectroscopy

**STM** Scanning tunneling microscopy

**SPM** Scanning probe microscopy

**AFM** Atomic force microscopy

**KPFM** Kelvin probe force microscopy

**CAFM** Conducting atomic force microscopy

**NMP** n-methyl-2-pyrrolidone

**DMF** Dimethyl formamide

**DMSO** Dimethyl sulfoxide

**EG** Ethylene glycol

**MeOH** Methanol

**DI** Deionized

**rpm** Rotation per minute

**VRH** Variable range hopping

**TE** Thermionic emission

**TFE** Thermionic field emission

**RMS** Root mean square

**RT** Room temperature
**CPD**  Contact potential difference

**SCLC**  Space charge limited current

**TCLC**  Trap charge limited current

**HOPG**  Highly oriented pyrolytic graphite

**BP**  Boiling point

**DC**  Dielectric constant

**Ar**  Argon

**PCE**  Power conversion efficiency

**CVD**  Chemical vapor deposition

**PMMA**  Poly (methyl methacrylate)

**GO**  Graphene oxide

**I-V**  Current-voltage

**I-V-T**  Temperature dependent current-voltage

**C-V**  Capacitance-voltage

**J-V**  Current density-voltage

**E_C**  Conduction band edge

**E_V**  Valance band edge

**q**  Elementary charge

**N_a**  Acceptor concentration

**V_{bi}**  Built-in-potential

**\varepsilon_0**  Permittivity of free space

**\varepsilon_s**  Permittivity of semiconductor

**n**  Ideality factor

**A**  Area

**T**  Temperature

**A^{**}**  Richardson coefficient

**k**  Boltzmann constant.

**\phi_{bi}**  Barrier height

**Pt-Ir**  Platinum-Iridium
<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>Co-Cr</td>
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<tr>
<td>$E_F$</td>
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