INVESTIGATION OF TRIBOELECTRIC EFFECT IN POLYMER DIELECTRIC AND INORGANIC SEMICONDUCTOR THROUGH ENGINEERED INTERFACE FOR ENERGY HARVESTING APPLICATIONS

SHAILENDRA KUMAR

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI

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Investigation of Triboelectric Effect in Polymer Dielectric and Inorganic Semiconductor Through Engineered Interface For Energy Harvesting Applications

by

Shailendra Kumar

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

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Dedicated to my beloved Parents, Uncle and Brothers

Shailendra Kumar

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CERTIFICATE

This is to certify that the thesis titled **Investigation of Triboelectric effect in Polymer Dielectric and Inorganic Semiconductor through Engineered Interface for Energy Harvesting Applications** , submitted by **Mr. Shailendra Kumar**, to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**, is a bonafide record of the research work done by him under our supervision and guidance. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Dr. Ankur Goswami
Professor
Department of Materials Science and Engineering
Indian Institute of Technology Delhi

New Delhi
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(Shailendra Kumar)

ABSTRACT

Triboelectric Nanogenerators (TENGs) are a cutting-edge technology that converts ambient mechanical energy into electrical energy, with enormous potential to use in self-powered gadgets, wearable electronics, and sustainable energy systems. Although significant progress has been achieved, issues remain in increasing energy conversion efficiency, durability, scalability for real-world applications. Further issues pertaining to efficiency and figure of merit is still not well structured in the existing literature. Hence, reporting the efficiency and the performance of TENG in majority of the cases are misleading. This thesis addresses the above issues by focussing on the design and manufacture of high-performance TENGs employing advanced nanostructured materials (both polymers and semiconductors), optimised surface engineering methods, using in house-built testing equipment.

The thesis is divided into three major components. The first component comprised of two sections. The first section focusses on the design and development of a horizontal contact-separation mode triboelectric nanogenerator (HCS-TENG), in which all input parameters (such as applied force, motor speed, tribo-plate separation, and operating frequency) were considered for performance evaluation and shed light on the efficiency and figure of merit of the proposed devices. The second section deals with the design, construction, and optimisation of a sliding contact photovoltaic triboelectric nanogenerator (SC-PTENG), an equipment that generates energy from mechanical friction and as well as in tandem external light.

The second component of the thesis to explore the opportunities to use polymer materials for the TENG applications for wearable devices. Using electrospun polyacrylonitrile (PAN) doped with multiwall carbon nanotube (MWCNT), to facilitate charge transfer, stacked in various combination of layers the triboelectric performance was investigated. Except PAN, inorganic polymer such as polydimethylsiloxane (PDMS) has been also explored for the above applications targeting flexible devices. Both polymers showed

significant increases in energy conversion efficiency and electrical output performance. Conductive fillers, such as MAX phase was used to improve overall electrical performance in PDMS.

The third component explores the synergistic effect of both tribo and photo voltaic effect in energy harvesting in two semiconductor (GaAs and Si p-n junction) and semiconductor metal junction (GaAs and Si with Cu/Al). A thorough examination of semiconductor bandgaps reveals the possibility for tailored nanostructures to increase TENG performance, indicating a possible route towards more efficient and sustainable energy harvesting systems.

Keywords: Triboelectric Nanogenerator, energy harvesting, Polyacrylonitrile, Multiwall Carbon Nanotube, Polydimethylsiloxane, MAX phase, Semiconductors, Self-Powered Wearable systems, Tactile sensing.

सारांश:

ट्राइबोइलेक्ट्रिक नैनोजेनरेटर (टीईएनजी) एक अत्याधुनिक तकनीक है जो परिवेशीय यांत्रिक ऊर्जा को विद्युत ऊर्जा में परिवर्तित करती है, जिसमें स्व-संचालित गैजेट, पहनने योग्य इलेक्ट्रॉनिक्स और टिकाऊ ऊर्जा प्रणालियों में उपयोग की भारी क्षमता होती है। यद्यपि महत्वपूर्ण प्रगति हासिल की गई है, वास्तविक दुनिया के अनुप्रयोगों के लिए ऊर्जा रूपांतरण दक्षता, स्थायित्व, स्केलेबिलिटी बढ़ाने में समस्याएं बनी हुई हैं। दक्षता और योग्यता के आंकड़े से संबंधित अन्य मुद्दे अभी भी मौजूदा साहित्य में अच्छी तरह से संरचित नहीं हैं। इसलिए, अधिकांश मामलों में TENG की दक्षता और प्रदर्शन की रिपोर्ट करना भ्रामक है। यह थीसिस उन्नत नैनोसंरचित सामग्रियों (पॉलिमर और अर्धचालक दोनों), अनुकूलित सतह इंजीनियरिंग विधियों, घर-निर्मित परीक्षण उपकरणों का उपयोग करके उच्च प्रदर्शन वाले टीईएनजी के डिजाइन और निर्माण पर ध्यान केंद्रित करके उपरोक्त मुद्दों को संबोधित करती है।

थीसिस को तीन प्रमुख घटकों में व्यवस्थित किया गया है। पहले घटक में दो खंड शामिल थे। पहला खंड एक क्षैतिज संपर्क-पृथक्करण मोड ट्राइबोइलेक्ट्रिक नैनोजेनरेटर (एचसीएस-टीईएनजी) के डिजाइन और विकास पर केंद्रित है, जिसमें सभी इनपुट मापदंडों (जैसे लागू बल, मोटर गति, ट्राइबो-प्लेट पृथक्करण और ऑपरेटिंग आवृत्ति) पर विचार किया गया था। प्रदर्शन मूल्यांकन और प्रस्तावित उपकरणों की दक्षता और योग्यता के आंकड़े पर प्रकाश डालना। दूसरा खंड एक स्लाइडिंग संपर्क फोटोवोल्टिक ट्राइबोइलेक्ट्रिक नैनोजेनरेटर (एससी-पीटीईएनजी) के डिजाइन, निर्माण और अनुकूलन से संबंधित है, एक उपकरण जो यांत्रिक घर्षण और बाहरी प्रकाश से ऊर्जा उत्पन्न करता है।

थीसिस का दूसरा घटक पहनने योग्य उपकरणों के लिए TENG अनुप्रयोगों के लिए पॉलिमर सामग्री का उपयोग करने के अवसरों का पता लगाता है। चार्ज ट्रांसफर की सुविधा के लिए, मल्टीवॉल कार्बन नैनोट्यूब (एमडब्ल्यूसीएनटी) के साथ डोप किए गए इलेक्ट्रोस्पून पॉलीएक्रिलोनिट्राइल (पैन) का उपयोग करके, परतों के विभिन्न संयोजनों में स्टैक्ड करके ट्राइबोइलेक्ट्रिक प्रदर्शन की जांच की गई। पैन को छोड़कर, लचीले उपकरणों को लक्षित करने वाले उपरोक्त अनुप्रयोगों के लिए पॉलीडिमिथाइलसिलोक्सेन (पीडीएमएस) जैसे अकार्बनिक पॉलिमर का भी पता लगाया गया है। दोनों पॉलिमर ने ऊर्जा रूपांतरण दक्षता और विद्युत उत्पादन प्रदर्शन में उल्लेखनीय वृद्धि दिखाई। पीडीएमएस में समग्र विद्युत प्रदर्शन को बेहतर बनाने के लिए मैक्स चरण जैसे प्रवाहकीय भराव का उपयोग किया गया था।

तीसरा घटक दो अर्धचालक (GaAs और Si p-n जंक्शन) और अर्धचालक धातु जंक्शन (Cu/Al के साथ GaAs और Si) में ऊर्जा संचयन में ट्राइबो और फोटोवोल्टिक प्रभाव दोनों के सहक्रियात्मक प्रभाव का पता लगाता है। सेमीकंडक्टर बैंडगैप की गहन जांच से TENG प्रदर्शन को बढ़ाने के लिए अनुरूपित नैनोस्ट्रक्चर की संभावना का पता चलता है, जो अधिक कुशल और टिकाऊ ऊर्जा संचयन प्रणालियों की दिशा में एक संभावित मार्ग का संकेत

देता है।

मुख्य शब्द: ट्राइबोइलेक्ट्रिक नैनोजेनरेटर, ऊर्जा संचयन, पॉलीएक्रिलोनिट्राइल, मल्टीवॉल कार्बन नैनोट्यूब, पॉलीडिमिथाइलसिलोक्सेन, मैक्स चरण, सेमीकंडक्टर, स्व-संचालित पहनने योग्य सिस्टम, स्पर्श संवेदन।

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AC	Alternating Current
AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflectance
Au	Gold
CB	Carbon Black
CFs	Cigarette Filters
CNT	Carbon Nanotube
CPD	Contact Potential Difference
CS	Contact Separation
DMF	Dimethylformamide
FEM	Finite Element Method
FOM	Figures of Merit
$\mathbf{FOM}_P$	Performance Figure of Merit
$\mathbf{FOM}_S$	Structural Figure of Merit
$\mathbf{FOM_m}$	Material Figure of Merit
$\mathbf{FOM_{nm}}$	Normalized Material Figure of Merit
FTIR	Fourier Transform Infrared Spectroscopy
GQD	Graphene Quantum Dots
HCS	Horizontal Contact Separation
HMI	Human Machine Interaction
HOMO	Highest Occupied Molecular Orbital

ICSD	International Crystal Structure Database
IoT	Internet of Things
KPFM	Kelvin Probe Force Microscopy
LED	Light Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
MDO	Mixed Domain Oscilloscope
MS	Metal Semiconductor
MWCNT	Multiwall Carbon Nanotube
n-GaAs	N-type Gallium Arsenide
NGs	Nanogenerators
P-TENG	Photovoltaic Triboelectric Nanogenerator
PAN	Polyacrylonitrile
PCB	Printed Circuit Board
PCE	Power Conversion Efficiency
Pd$_{max}$	Maximum Power Density
PDMS	Polydimethylsiloxane
PLC	Programmable Logic Controller
PMC	PAN-MWCNT Composite
PMxC	PDMS-MAX Phase Composite
PTFE	Polytetrafluoroethylene
PV	Photovoltaic
PVAc	Polyvinyl Acetate
rGO	Graphene Oxides
SCS	Sliding Contact Separation
TEGs	Triboelectric Generator
TEM	Transmission Electron Microscopy
TENG	Triboelectric Nanogenerator

TGA	Thermogravimetric Analysis
TiO_2	Titanium Dioxide
TVNG	Tribovoltaic Nanogenerator
XRD	X-ray Diffraction

List of Symbols

I_{sc}	Short circuit current
Q	Transferred free charge
S	Contact area
$\varepsilon_{r1}, \varepsilon_{r2}$	Relative permittivity of tribo layers
ε_0	Air permittivity
$x(t)$	Separation distance
$v(t)$	Vibrational speed
σ_T	Tribo charge density
ϕ	Work function
V_{OC}	Open circuit voltage
D	Displacement current
Al	Aluminum
Cu	Copper
σ	Surface charge
Q_{SC}	Charge density
ε'	Dielectric constant
ε''	Dielectric loss
κ'	Conductance
ε	Permittivity of material
I_{drift}	Drift current
I_{diff}	Diffusion current
E	Electric field
q	Electric charge
n	Electron doping density
D_n	Diffusion constant

c	Capacitance
Z	Impedance
R_L	Output resistive load
X_C	Capacitive reactance
ε_0	Permittivity of vacuum
x_{max}	Maximum gap between the TENG layers
E_m	Maximum input energy
m	Mass
V	Velocity
σ_s	Surface charge density
D	Electric flux density
ρ_v	Volumetric charge density
$P_{d\mathrm{max}}$	Maximum power density

List of Materials Properties

Physical Properties	Materials					
	PDMS	MWCNT	MAX phase	PAN	Silicon	n-GaAs
Chemical Formula	$(C_2H_6OSi)n$	C_xH_y	Ti_3AlC_2	$(C_3H_3N)n$	-	-
Molecular Weight (g/mol)	95,000	12.01	194.60	83.12	28.0	145
Dielectric Constant	3-40	200-290	8-15	4.2-5.5	11.7	12.85
Electrical Conductivity (S/m)	10^{-14}-10^{-16}	2.73×10^{-3}	3.2×10^{6}	10^{-2}	10^{3}	10^{-6}
Density (g/cm^3)	0.965	1.7–2.1	2.36	1.184	2.3	5.3