INVESTIGATION AND TEMPERATURE RELIANT ON ELECTRICAL CONDUCTIVITY RECITAL AND DIODE CARACTERISTICS OF POLYANILINE BY CHEMICAL OXIDATIVE METHOD

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Abstract: This study consume virtuous phenomenon has happened here due to the rheological change. That miraculous occurrence can be originate in the compendium underneath. Polymer diodes are the very fantastic issues of this research field. Commonly saying, water and oil under no circumstances combination collected. Now as chemist, one empowers to 'bond' both aqueous (water) and aromatic (oil) molecules through the intermediary called surfactant (detergent) to have gigantic applications scattering a broad focus of fascinating fields. Let us arrival at the following further down. The interfacial coating of immaculate or pristine polyaniline (PANI) polymer was prepared exhausting chemical oxidative method with 0.1 M concentration previously, aniline hydrochloride was oxidized with ammonium peroxydisulfate 0.25 M in aqueous medium at 1-2 °C next to aniline, stirring time and polymerization temperature are significant causing parameters of polymerization reaction, harmoniously metal polymer- semiconductor (MPS) constructions of Cu/PANI/n-Si Schottky barrier diodes with dissimilar acids (HCl, acetic acid, nitric acid and sulfuric acid) be there invented. This research work carried out in the present thesis pertains to the study of effect of surfactant (organic detergent) on synthesis, morphology and crystalline structural aspects of conjugated polymers Furthermost applications of conjugated polymers demand exceedingly ordered structures for the best maternal enactment For example, the morphology ranges from highly crystalline (conducting) to totally amorphous (no conducting), depending on polymer and its synthetic route The properties of these polymers heavily depend on molecular chain orientation and crystalline structures. The structural scrutinizes of XRD sizes of the rudiments revealed that the crystal structure of distortion and converted into amorphous nature and FE-SEM revealed that the morphology of pristine PANI powders. The FT-IR spectra confirmed that ammonium peroxydisulfate with pristine PANI along with band establishment. The optical property of PANI was scrutinizes using UV-vis spectra and deliberate with minimum band gap 3.1 eV by resources of HCl. The electrical property I -V temperature ranges 30 °C to 120 °C represents that the maximum average conductivity obtains as 0.80×10^{-2} S/cm for 0.1 M HCl. The lowest ideality factor (η) and minimum barrier height (Φ B) values were achieved for HCl of Cu/PANI/n-Si Schottky barrier diode (SBDs) under the explanation disorder.

Keywords: PANI, COM, band gap, FESEM, Electrical property, MPS category SBDs.

1. INTRODUCTION

Steering Polymers has largely been investigated in energy stockpiling application since long time. Polyaniline is a conductive polymer showing a simplicity of affidavit on terminal, synthetic specificities, ecological security, and redox conductivity. Numerous alluring properties which make leading polymers an entirely reasonable material for the utilization of energy stockpiling gadgets comprise of its high conductivity, electro action, doping levels, amazing ecological dependability and explicit capacitance. Conductive polymers must stayed the subject of the robust whole number of requests during most recent twenty years in view of their remarkable assets like mechanical strength, electrical conductivity, erosion, steadiness and plausibility of both oxidative and electrochemical combination. Henceforth PANI is helpful in wide territory of utilization: like sun powered energy transformation, battery-powered batteries, electro chromic shows, electrochemical sensors, capacitors and dynamic erosion defender [1,2]. Attributable to prosperity of amalgamation, preparing natural solidness and low manufactured expense, so polyaniline is likely the main mechanical directing polymer today [3,4] Various procedures have been created for combination and portrayal of nanocomposite materials to improve the particular Leading polymers have a place with an unconventional group of mixtures made out of monomer units with formed substance bonds that, under specific conditions (doping), guarantee the electron conductivity of the poly mer. From the business perspective, these polymers show guarantee for the creation of materials for a few applications; they can supplant metals and semiconductors, since they highlight conductivity, low thickness, and simple cycle

capacity. Polyaniline (PANI) a councils from the group of directing polymers is recognized by simple combination and high ecological steadiness. Since this polymer contains just benzene and amino gatherings, leucoemeraldine gradually oxidizes in air and isn't electrically leading. Leucoemeraldine might be oxidized in an acidic medium to the leading emeraldine salt (p doping). Pernigraniline is made out of substituting amino benzene and quinonediimine pieces. Since the quinonediimine bunch is temperamental within the sight of nucleophiles, explicitly water, pernigraniline and its salts promptly disintegrate in air. The emeraldine salt of PANI is framed during protonation of the emeraldine base with natural and inorganic acids. Generally speaking, this cycle is alluded to as doping. At the point when PANI as the emeraldine base is treated with acids, protons fundamentally connect with the imine molecules of nitrogen; accordingly, polycaptions show up. Since positive charges limited on adjoining nitrogen molecules increment the all-out energy of the polymer framework, electron thickness will in general go through reallocation; as a result, "unpairing" of the solitary electron pair of nitrogen particles happens with no adjustment in the measure of electrons in the framework [5-9]. In a chain, cation revolutionaries show up; they are delocalized over a specific formation length and give the electron conductivity of the polymer. The electron conductivity of polyaniline as emeraldine relies upon its protonation and increments by ten significant degrees as the level of protonation is expanded from 0 to 20% [10]. Note that this conduct is commonplace for polyaniline exclusively. The delocalization of PANI cation extremists may happen by means of the intramolecular system as well as through the intermolecular invention. For this situation, chains of the leading polymer ought to be arranged one way with the goal that the exchange of π electrons starting with one polymer chain then onto the next is guaranteed [11]. This cycle happens generally speaking by means of van der Waals collaborations among benzene and quinoid rings of PANI (π stacking) [12,13]. The electron conductivity of a particularly organized polyaniline might be pretty much as high as $(1.1-1.2) \times 10-3$ S/cm.

In the accessible writing various approaches to deliver PANI have been illustrated, notwithstanding, aniline is traditionally picked as the beginning monomer In past works, [14,15] a strategy to create polyaniline in the EB structure beginning from the aniline dimer (DANI), which on the in opposition to aniline is non-poisonous and ease, was created. As of late, the improvement of inorganic polymer half breed materials on nanometres scale has gotten huge consideration because of a wide scope of likely applications in optoelectronic gadgets [16, 17]. As a rule, the union of a mixture polymer inorganic material plans to acquire another composite material with synergetic or corresponding practices between the polymer and inorganic material. It is a most examined polymer on account of its general simplicity in arrangement, great natural steadiness [18, 19] and tuneable conductivity. It has been pulled in different electronic gadgets, for example, electromagnetic obstruction protecting, against electrostatic coatings, batterypowered light weight batteries, high-thickness data stockpiling material [20] and Leading polymers are finishing various applications in different electronic gadgets, for example, electromagnetic impedance safeguarding, hostile to electrostatic coatings, battery-powered batteries and substance sensors [21-26]. PANI has been broadly contemplated, because of its ecological soundness, redox properties and reversible nature of its electrical conductivity [27, 28]. The polymer/inorganic nanocomposites join numerous properties of the inorganic segments, for example, nature of the taxability's, improved process ability of polymers and especially appealing modulus, straightforwardness, surface hardness and warmth obstruction properties [29]. Thusly, expanding research interests have been centred on polyaniline/inorganic nanocomposites [30]. The readied unadulterated PANI powder utilizing various acids were incorporated by synthetic oxidative strategy. The I-V qualities of these composites at room temperature and furthermore as a component of temperature ranges [300-393K], voltage ranges [1-10V] have been examined. At last the readied unadulterated PANI powders were portrayed by optical [FT-IR, UV-vis], underlying [FE-SEM, XRD], and electrical properties [I-V].

2. EXPERIMENTAL DETAILS

2.1. Chemicals

TABULARIZATION 1: Extraordinary information of these used resources

	Acetone	Ammonium peroxydisulfate	Aniline	HCL	Acetic acid	Nitric acid	Sulfuric acid
Assay	99.5%	≥98%	≥99%	36.5 to 38%	≥99.7%	69-71%	95-97%
Residue after evaporative	≤ 0.0001%	-	-	-	≤ 0.001%	-	≤ 0.0005%
Heavy metal	-	≤ 50ppm	-	≤1ppm	≤0.5ppm	≤0.2ppm	≤ 2ppm
Titrable base	≤ 0.0006meg/g	-	-	-	≤ 0.0004meg/g	-	-
Titrable acid	≤0.0003meg/g	\leq 0.04 meg/g	-	-	-	-	-
Trace analysis	-	Fe ≤10ppm Mn ≤ 0.5ppm	_	$\begin{array}{ll} {\rm Br} & \leq \\ {\rm 50ppm} \\ {\rm So}_4 & \leq \\ {\rm 1ppm} \\ {\rm So}_3 & \leq \\ {\rm 1ppm} \end{array}$	Cl ≤ 1ppm So₄≤1ppm Fe ≤0.2ppm	$\begin{array}{l} Cl \leq 0.5 ppm \\ AS \leq 0.01 ppm \\ Fe \leq 0.2 ppm \\ So_4 \leq 1 ppm \end{array}$	No3≤1ppm Cl ≤0.5ppm AS≤0.9ppm Fe≤0.5ppm
Melting point	-94°	-	-6.3°	-35°	16°-17°	-42°	10°
Boling point	56°	-	181°- 185°	57°	117°-118°	122°	290°

Freezing	-20°	-	76°	-	40°	-	-
point							

	Acetone	Ammoniu	Aniline	HCL	Acetic	Nitric	Sulfuric acid
		m			acid	acid	
		peroxydis					
		ulfate					
Company Name	Spectrum	Nice	Merck	Rank	Spectrum	Nice	Merck
				em			
m.w(g/mL)	58.08	228.18	93.13	36.46	60.05	63.01	98.08
Density(g/mL)	_	1.98	1.0217	1.29	1.05	1.51	1.42
Concentration(M)	_	0.25	0.1	0.1	0.1	0.1	0.1
Formula	(CH3)2CO	(NH4)2S2	C6H5N	HC1	CH3CO	HNO3	H2SO4
		O8	H2		OH		
Quality range	L.R	L.R.	G.R.	.L.R.	L.R.	A.R.	G.R.
pH(power of	-	2	6	2	4	<2	2
hydrogen)							

TABULARIZATION 2: Particulars of chemicals used in the amalgamation of pristine polyaniline (PANI) polymers

2.2. PANI preparation

The raw chemicals used for grounding anticipated concentration of PANI with 0.1 M aniline hydrochloride, acetic ANI, nitric ANI, sulfuric ANI and 0.25 M ammonium peroxydisulfate (APS) were prepared (Table-1). Placid astonishing information roughly these chemicals (table- 2). All the paraphernalia's were eviscerated with double deionized water advantageous acetone. A 50 mL of double deionized water with volumetric flask also placed on the ice bath, then added 0.25M ammonium peroxydisulfate in this flask, Another 50 mL of deionized water in volumetric flask and kept on the ice-bath (0-2 °C), added 0.1 M HCl and 0.1 M aniline. Now both solutions were kept disjointedly for 1 h at 0-2 °C. After 1 h, 50 mL of aniline HCl in a beaker, 50 mL of ammonium peroxydisulfate solution was added by sluggishly dewdrops by dewdrops to 50 mL of aniline HCl solution with unremitting magnetic stirring. Continued the rousing for 30 min and during this process, the solution color was changed to dark green. Subsequently the solution was covered by aluminium foil and kept in the freezer for 24 h. Now, PANI hurried was filtered using Whatman filter leaf and washed quite a lot of times with the help of distilled water in order to jettison unreacted salts and finally trace with acetone. The precipitate was transferred to the watch glass and dried in a furnace for 5-6 h at 60-80 °C. In the progression of grinding, the achieved polyaniline with the help of mortar and festal, we got ultra-pure fine pristine PANI deep green powder (Table-3). The same practice was shadowed by using acetic acid, nitric acid and sulfuric acid to prepare ultra-pure fine pristine PANI.

TABULARIZATION 3: Gotten weightiness of manufactured pristine polyaniline polymers consuming dissimilar acids

Weight conc. (M)	PANI HCl (g)	PANI acetic acid (g)	PANI nitric acid (g)	PANI sulfuric acid (g)
0.1M	2.315g	1.771g	2.3098g	1.0787g

2.3. Spring-cleaning technique of silicon wafer:

One side sophisticated n-type silicon wafer (100) with a width of $279 \pm 29 \,\mu\text{m}$ was used as an electrode for the manufacture of SBDs. The new-fangled silicon wafer may has assertive supplementary impurities, such as dust, lubricant and metallic impurities on its surface and prime to low efficiency of Schottky barrier diode (SBDs). The Cu/PANI/n-Si structures were fabricated on a 2inch chunkiness n-type (P-doped) solitary crystal silicon wafer with (111) surface orientation, 0.7 Ω cm resistivity and 3.5 μ m thick- ness. So, some cleaning ladders of Si wafers be located required [31] as:

(a) Level with the procurements of new paraphernalia's, we usage it only after the clean-up. This is for the reason that there is a lot of dust and dirt. It's unquenchable law of cleaning process.

(b) The wafer was condensed for 10 min in steaming acetone and ethanol;

(c) Eradicating organic residues from the substrate using piranha solution ($H_2SO_4 + H_2O_2$ in the ratio of 3:1);

(d) The inherent oxide layer since Si wafer was detached by the diluted hydrofluoric acid ($HF + H_2O$ in the ratio of 1:10);

(e) Finally, in each step, the silicon wafers were rinsed with quality of pure double distilled.

2.4. Characterization

The morphologies of the products were scrutinized with JEOL JSM-6701F field-emission scanning electron microscope (FE-SEM) and JEOL JEM-1011 transmission electron microscope (FESEM). The samples for FESEM were mounted on aluminium stubs without sputter-coating of gold. Samples for FESEM measurements were dispersed in ethanol and coated on copper micro grids with a carbon support film. Fourier transformer Infrared spectra in the range 400–4000 cm⁻¹ on sample pellets made with KBr were measured by means of an infrared spectrophotometer (Perkin Elmer Tensor 100). UV-visible spectra of the products were recorded from 300 to 1000 nm using Perkin Elmer 750 spectrophotometer. X-ray scattering of the samples was carried out on Xray diffraction instrument (with radiation). Electrical characterization of the doped polyanilines was performed by four-probe

method, under collinear contact geometry on top of compressed pallet. The data was collected at temperatures ranging from 100 to 300 K, in low vacuum ambient ($\sim 10^{-3}$ mbar). The electrical conductivity was determined from the conductance measurements multiplied by the geometrical factor. The two-probe method eliminates the inspiration of leads resistance or contact resistance, providing a better accuracy for measuring conductance. Samples were pelletized to a diameter of 13 mm and a thickness of 0.4 mm using a vacuum press at 8 MPa for 5 min.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

The X- ray diffractometer (XRD) (XPERT-Genius) With Cuk α 1 radiation of frequency 1.5406 Å at a maker area of 30 mA and 40 kV in the 2 θ territory from 10° to 90° was utilized. XRD example of PANI with different acids is appeared in Fig. 1. Unadulterated PANI is normally shapeless nature and it has just wide top at 27.20° from its XRD design it's adjusts the PANI present in the example.



Fig. 1. Powder diffraction pattern of PANI with different acids

There no significant pinnacles present in the example which mean no glasslike materials this outcomes proposing to shapeless nature for the PANI material. This outcomes very much coordinated with G. Pradeesh et.al an endeavour has been made to combination polyaniline composites with molybdenum oxide through synthetic oxidative technique [32]. S. Ramanathan the joining of aniline onto chitosan regarding diverse monomer fixation has been concentrated acceptable event our outcomes. This obvious at the point 20° is reflected to be the hold between two hills in the 2-D mounding readiness of polymer chain with abrogating fuse particles [33]. Totally coordinated with HCl corrosive utilized example very much coordinated in writing results.

3.2. FT-IR analysis

FT-IR range: The polymer tests for FTIR examination were blended and trudge with KBr fine particles and dense dependent on pellets, in which the example powder was reliably protected. At the point when a powdered example is situated in the pillar, it retains singular frequencies, so their focuses are abbreviated in the inferogram and the succeeding Fourier change is the infrared ingestion range of the sample.



Fig. 2. FT-IR spectrum of PANI with different acids

Fig.2 shows the FT-IR range of PANI utilizing various acids. FTIR spectroscopy was utilized to clarify the covalent joining and to affirm the change in useful gatherings during each progression. The GO shows ingestion groups at 3200 and 1734 cm-1, which match to O–H, C=O in COOH [34]. It very well may be likewise seen that there are groups around 1605 and 1376, which are because of the intercalated water and disfigurement vibrations of C–O in C–OH and C–O–C useful gatherings. For unadulterated PANI noticeable ascribed assimilation tops are seen at 1630 and 1394 cm-1, having a place with C=C extending disfigurement of quinoid and C=N extending of optional fragrant amine, uncovering the presence of emeraldine salt state in PANI. The groups at 1184 and 805 cm-1 relate to–C–N extending vibration and of plane twisting vibrations of C–H in the benzene ring. Around 3281 cm-1, it was noticed an ingestion band for N–H extending of the amine group. The FTIR range of the GO/PANI composite was indistinguishable from that of PANI, which affirmed that the GO surface was wrapped by PANI [35]. There is no pinnacle seen at 3200 and 1734 cm-1 (–OH and C=O vibrations, individually), demonstrating the decrease of GO occurred because of the polymerization of aniline, notwithstanding the affirmation that PANI has been covalently joined onto the outside of the GO sheets. The FTIR groups were dislodged, showing a covalent bond and uprooting because of the atom plan. Utilitarian gatherings answerable for adjustment of gold nanoparticles showed up in the band at 3300 cm-1 comparing to N–H vibrations [36].

3.3. UV-Vis analysis

Fig. 3 demonstrations the Ultra-violet absorption spectrum of polyaniline with 0.1 M using four different acids such as. HCl, acetic acid, nitric acid and sulfuric acid in the discernible spectrum. The UV-visible spectrum of PANI depends on the wavelength (nm) and absorption (a.u). The absorption at 295 nm arises from the π - π * excitation of benzenoid ring segments and the absorption at 600 nm arise from the excitation of quinone diamine edifice [37,38].





The presence of strong absorption bands of closely 299-325 nm. But HCl is the utmost rejoinder of absorption peaks in the region 325 nm which relates to the π - π * changeover of the benzenoid ring segments. The high absorption peak observe HCL sample it's more sympathetic to better-quality MPS device recital.

Fig 4 shows the transmittance graph of PANI with various acids transmittance also HCl sample observed high value due to generally HCL modified surface of samples and atoms ailment is corrected compared with other acids. The high transmittance is electron renovations metal to semiconductor is appropriate fast, these results suggest that hug barrier height and minimum ideality factor of device. Fig 5 displays 0.1 M PANI with different acids reflection graph The high reflection is observed from HCL samples this results more loyal to enhanced MPS device performance diode.



Fig. 4. Transmittance graph of PANI with different acids.



Fig. 5. Reflection graph of PANI with different acids.

Band gap:

Theory Behindhand calculations: UV Vis Spectroscopy absorption peak means the electrons are absorbing the energy at some specific wavelength.



Fig. 6. Band gap graph of PANI with different acids.

Electrons are absorbing energy earnings the electrons are profitable to excited state from its ground state. Electrons are going to excited state from its ground state means the material is having band gap, thus which can be control by absorption wavelength.

Energy Equation of Quantum Mechanics: is given Equation (1). Energy (E) = Planks Constant (h) * Speed of Light (C) / Wavelength (λ) $E = h * (c)/(\lambda)$ (1) Where, Energy (E) = Band gap, Planks constant (h) = 6.626×10^{-34} Joules sec, Velocity of Light (C) = 2.99×10^8 meter/sec and Wavelength (λ) = Absorption peak value. Also $1eV = 1.6 \times 10^{-19}$ Joules (Conversion factor) by this formula band gap can be calculated easily, from UV Vis spectroscopy absorption peak. The calculated HCl, acetic acid, nitric acid and sulfuric acid having same concentration (0.1 M) the HCL acid observed minimum band gap 3.6 eV compared with other acids. Fig. 6. Displays 0.1 M PANI with different acids band gap graph the spickand-span band gap is observed from HCL sections this penalties supplementary loyal to discriminating MPS device concert diode.

3.4. FE-SEM

The morphologies of PANI and PANI/acids nanocomposite with different HCL, Acetic acid, Nitric acid and Sulfuric acid contents are also observed by FESEM micrographs (Fig. 7). Pure PANI has a micro-plates structure with diameter around 30-40 nm. The micro-plates structure of PANI is also observed in PANI/acids nanocomposites. This morphology of as-synthesized PANI agrees with several reports in the literature, which used in situ chemical oxidative polymerization method in acid media. The formation of agglomerated particles on the thin films can be explained by nucleation- aggregation- agglomeration and growth mechanism: (i) Aggregation of elemental nanocrystals are formed due to the physical attractions, (ii) The nucleation and growth forms crystallites in nanometric size range, (iii) Further the crystal growth is possible at constant residual supersaturation state.

FESEM is the gorgeous clear organization. It accurately stratagems apiece prearrangement. Conversely, forward-looking cohort Field Emission Scanning Electron Microscopy (FESEM) established studies recommended significant advantages like: focusing with higher resolution, ability to measure structural and micromechanical properties and the potential of imaging in well accuracy manner [39–41].

FESEM fruitages clearer, a smaller amount electrostatically misleading imageries with altitudinal steadfastness depressed to 1 1/2 nm. That's 3 to 6 times better than unadventurous SEM. Less significant-area contagion acnes container stand scrutinized at electron hastening voltages harmonious through Energy Dispersive X-ray Spectroscopy. Abridged permeation of truncated kinetic energy electrons probes more rapidly to the instantaneous quantifiable surface. High quality, low voltage images are obtained with trifling electrical alleging of samples. (Accelerating voltages range from 0.5 to 30 kV.) Prerequisite for enlisting conducting coatings on insulating materials is virtually jettisoned. Intrinsically smaller beam gives enhanced tenacity. The FESEM utilizes smaller emission garbage dump with a much smaller diameter (100-1000nm). FESEM as well hand-me-down for superior superficial morphology technique can be used segregate bio continuous commencing dewdrop category micro-emulsions. The images spectacles each one have poles apart types. It shows up as cloud Assemblages, fungi, boiled rice and cauliflower.

We pragmatic that the morphology of PANI is strongly influenced by HCl acid. The densely arranged particles, indicate the large agglomeration of grains at HCL. It is palpable that HCL strongly encouragements the surface morphology of PANI. It should mention that the PANI nanoparticles prepared at HCL has mixed particles is strongly influenced by MPS diode applications.



Fig. 7 FE-SEM images of PANI nanoparticles prepared at various acids

3.5. EDAX



Fig. 8 EDX spectrum for PANI nanoparticles with different acids

The EDAX spectrum is used to identify the elemental composition of the formed nanoparticles. The EDAX spectrum of PANI nanoparticles is shown in Fig. 8. The EDAX spectrum indorses the obtainable oxygen (O), cadmium (Cd) and a small amount of cerium (Ce) in the nanoparticles. PANI plays an important role in MPS (SBDs) and it increases the barrier height.

3.6. DC electrical Conductivity measurements using two probe method:

The DC conductivity test is measured using two probe method. Now the sample powder was change to a pellet form for DC conductivity test. Then increase the temperature ascending order 303 K to 393 K, calculate the conductivity for all four samples. Fig 9 shows the conductivity for PANI used acetic acid, sulfuric acid, nitric acid, HCL with 0.1M. The DC electrical conductivity of samples is observed to be frequency as well as temperature dependent. The frequency dependent conductivity for disordered materials such as polymer can be due to interfacial polarization at contacts and grain boundaries of the samples [42].

The conductivity of pure PANI exhibits metallic behaviour in which conductivity decreases slightly with increasing temperature or frequency. It was measured at room temperature by a two probe method using keithley [6517B] electrometer. The current values were measured at different applied voltages from 1-10V. The DC electrical conductivity (o-) for pure PANI powder was calculated using the given Eq-2

$$\sigma = (I/V)X(d/A)$$

(2)

Where, I- current, V - applied voltage, d - inter probe distance, A- cross sectional area of the sample. The dc electrical conductivity of the prepared NPs were measured using Keithley electrometer by applying voltage 1-10 V. The conductivity of the samples was measured using a two probe method as a function of the temperature range from 30 to 120 °C.

The dc electrical conductivity of the PANI prepared from different acids (A, H, N and S) with 0.1 M were measured using two probe setup with the function of temperature from 30 to 120 °C as shown in Fig. 9. From Fig. 9, as voltage increases, the current increases. The maximum current value obtained for higher temperature (120 °C). The electrical conductivity (σ) was calculated (Eq. 4) and it shows that there is an increase in conductivity for hydrochloric acid (H). The high conducting countryside was obtained for H compare to other acids and their values were listed in Table 4.



Fig. 9 I-V characterization of PANI nanoparticles prepared for different acids

$\sigma_{dc} = \frac{t}{RA}$	(3
$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right)$	(4

Where t is the thickness, R is the resistance and A is the active area. σ_0 , E_a and k_B are called as pre exponential factor, activation energy and Boltzmann constant. From Arrhenius plot, the inverse temperature escalations with increasing in conductivity for HCL solution as shown in Fig. 9 [43]. Another more acid solution was gained at inverse temperature increases with decreasing in conductivity. The activation energy was calculated using the equation (4). From the relation (4), the minimum average activation energy is obtained for HCL and maximum average activation energy is attained for A of PANI as shown in Table 4.



Fig. 10. Arrhenius plot for PANI nanoparticles prepared with different acids of (HCL, acidic acid, nitric acid and sulfuric acid)

Fig. 10 unveils samples versus average conductivity, resistivity and activation energy of various acids with PANI nanoparticles. The resistivity of the PANI was calculated using the equation (5)

(5)

$$\rho = \frac{RA}{L}$$

Where ρ is the resistivity, R is the resistance, A is the area and t is the thickness. Fig. 10 shows the variation of the electrical resistivity with the different acids of PANI. The larger crystallite size of the samples acquired at HCL helped to reduce their electrical resistivity. The reduction in the sample resistivity with HCL is due to the increase in mobility of the charge carriers. The lower ρ can improve the current transport properties of the film thereby enhancing the rectification behaviour of SBDs. This behaviour can create the MPS diodes to perform with superior efficiency.



Table 4 Electrical parameters of PANI nanoparticles for different acids

Samples	Conductivity σ _{dc} (S/cm)	Resistivity ρ (Ω/cm)	Activation energy (E _a) (eV)
A 0.1M	7.355×10 ⁻⁹	2.8640×10 ⁸	0.25096
H 0.1M	4.1443×10 ⁻⁸	5.5698×10 ⁷	0.0389
N 0.1M	5.8322×10 ⁻⁹	2.6365×10 ⁸	0.04002
S 0.1M	4.5058×10 ⁻⁹	4.2053×10 ⁸	0.00808

3.7. Fabrication of metal polymer semiconductor (MPS) diodes

The diode parameters such as n and Φ_B of the fabricated Cu/PANI/p-Si diodes were analysed at light intensity using portable solar simulator (PEC-L01). Fig. 11 shows the current-voltage (I-V) characteristics for PANI of Cu/PANI/n-Si type diodes. The measurement conditions of the fabricated MPS diodes are summarized in Table 5. The I_D and I_{Ph} of the prepared MPS diodes were measured by applying a constant bias voltage from -4 to +4 V (step of 0.4 V) using Keithley source meter. Fig. 11 indicates that the forward current values of the device increase exponentially with the applied bias voltage confirming the Schottky diode nature of the fabricated device. The I_{Ph} values of the Cu/PANI/n-Si diodes varied from 10⁻⁹ to 10⁻⁴ A with the light intensity which is due to the swept charge separation in the depletion region after light absorption. Both I_D and I_{Ph} conduction mechanism of the Cu/PANI/n-Si diode was described by thermionic emission theory (TET) using the following relation [44].

$$J = J_0 \exp\left[\frac{qv}{(nk_BT)} - 1\right]$$

(6)

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Where J_o is the reverse leakage current density, q is the electron charge, V is the applied voltage, n is the ideality factor, k is the Boltzmann constant and T is the absolute temperature. The semi-logarithmic plot of current density (ln J) versus voltage (V) is displayed in the Fig. 12. The ideality factor of the Cu/PANI/n-Si SBDs is determined from the slope and the intercept of the semi-logarithmic forward bias of J–V plot for V > 3kT/q using Eq. (6). The ideality factor (n) and barrier height (Φ_B) can be calculated by the following Eqs. (7, 8) [45].

$$\mathbf{n} = \frac{q}{(K_BT)} \left[\frac{dV}{(d(lnJ))} \right]$$
(7)
$$\Phi_B = \frac{K_BT}{q} \ln \left(\frac{AA^*T^2}{J_0} \right)$$
(8)



Fig. 12 I-V characteristics of Cu/PANI/p-Si SBDs fabricated with various acids

Where A* is the effective Richardson constant for p-type Si. The Φ_B and n prices were summarized in Table 5. From this Table, hefty n values were achieved in the ailment of together in darkness and under the light condition for S of PANI content on SBDs. The effective Schottky barrier heights (SBHs) and ideality factors conquered since the current–voltage (*I–V*) characteristics devour fluctuated from diode to diode. The minimum ideality factor (n = 2.9) with corresponding barrier height (Φ_B = 0.54) value obtained for H of Cu/PANI/n-Si diode is under the light illumination circumstance. Moreover, it increases to 3.2 in darkness. The proposed motives owing to both renovation proficiency of Si and absorption of the PANI layer, which includes film thickness [46]. The n value is more than one, which exhibited a non-idealities owing to the bias dependent barrier height, the existence of interfacial thin native SiO₂ layer between the metal (Cu) contact and semiconductor (Si) wafer and may be owing to the generation of recombination of currents within the space charge region [47]. Also, the other reasons may be owing the states associated with the defects near the surface of the semiconductor [48], chemical reactions and barrier in homogeneities.



Fig. 13 Semi-logarithmic plots of MPS structured SBDs with different acids

From Fig. 13 shows the Semi-logarithmic plots of MPS structured SBDs with different acids. The Cu/PANI/n-Si SBDs under the illumination condition provide a large number of photo-generated charge carriers, which increase the current and in darkness, the current is suddenly decreased owing to the decreasing of charge carriers. From these results, the prepared Cu/PANI/n-Si SBDs express a good photo-conducting nature [49, 50]. The decreasing of the Schottky barrier height by image forces and thermionic field emission at the interface state are explained by the acid level dependence of PANI samples [51].

	Barrier heigh	t (Φ _B) (eV)	Ideality factor (n)		
Samples	Dark	Light	Dark	Light	
A 0.1M	0.61	0.60	4.7	3.6	
H 0.1M	0.57	0.54	3.2	2.9	
N 0.1M	0.68	0.66	5.3	5.2	
S 0.1M	0.75	0.75	5.8	5.5	

Table 5: The Cu/PANI/p-Si (MPS) SBDs parameters for different acids

CONCLUTION:

A pristine PANI polymers were synthesized using chemical oxidative method having 0.1 M concentration of diverse four acids (HCl, acetic acid, nitric acid and sulfuric acid) and characterized by FT-IR, UV-visible, SEM, XRD, etc. The FT-IR analysis long-established the chemical structure of PANI. UV-vis studies confirmed the π - π * transitions of aniline radical and π - π * transitions of Quinone-imine groups. FE-SEM unveiled the cloudy like structure of the polymer, while XRD revealed that it is amorphous in nature. The electrical conductivity behaviour of polyaniline was also analysed, when increased the applied voltage, the conductivity also increases. This performance of the voyage of I-V curves appears as an idiosyncrasy with respect to the conventional behaviour of SBDs. On the basis of the described above results, the PANI could be important materials for technological points of view in terms of morphology, size, and electrical conductivity. HCL Obtained lowest ideality factor and Minimum barrier height under the dark and light illumination condition. Among all the pristine PANI polymers, HCl prepared polymer is found to be effective conductivity as compared to polymers prepared from other three acids.

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