Low Cost Flexible Electronic Devices by use of Functional Nano-Inks

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by

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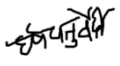
Certificate

This is to certify that this dissertation entitled ‘Low Cost Flexible Electronic Devices by use of Functional Nano-Inks’ towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Brijesh Meena, student at Indian Institute of Science Education and Research Pune, under the supervision of Professor Harsh Chaturvedi, IIT Guwahati, Assistant Professor, Centre for Energy, during the academic year 2017-2018.



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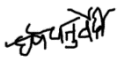
Declaration

I hereby declare that the matter embodied in the report entitled ‘Low Cost Flexible Electronic Devices by use of Functional Nano-Inks’ are the results of the work carried out by me at the Centre for Energy, IIT Guwahati and G Labs Innovation, Kolkata, under the supervision of Professor Harsh Chaturvedi and the same has not been submitted elsewhere for any other degree.

Brijesh Meena



Professor Harsh Chaturvedi

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Abstract

Printed Electronics is an emerging field providing fast manufacturing, low cost, flexible electronics for vast applications form healthcare, environment monitoring, IoT application, etc. Printing of such Electronics is done with Functionalised Inks. Printing methods that are compatible with the Functional Inks, are used for the fabrication of such Electronics.

This Thesis reports the development and characterization of carbon based Resistive Ink, and its use for the fabrication of a low voltage Flexible Heater (9 cm × 10 cm) on a PET substrate by Screen Printing method, which was test for its performance under different voltages and under different bend angles. This Heater was able to provide 45^{o}C with power consumption of 0.16 W/cm^{2} at 6 V.

Ammonia Gas Sensor was developed using Silicon Dioxide based dielectric Ink. Four different polymers were tried for development of this Ink, at four different concentration ratios of Silicon Dioxide and Polymer. Ammonia Sensor developed using each ink was tested for its sensing capacity and is being reported in this Thesis. Further, Tungsten oxide based Electrochromic Ink and study on its Electrochromic behaviour has been reported.

Chapter 1

Introduction

Printed Electronics is the umbrella term for technologies where various functionalized inks with compatible printing methods are used for the fabrication of Electronic Devices. Unlike colour pigment inks used for newspaper, magazine and book printing, functionalized inks have electrical properties depending upon the content of the ink; for e.g. Silver Nano-particles are the main component for the preparation of Conductive Inks which are used for printing circuits, electrodes and other conducting components[1]. Printing is fast, optimal method and being an additive process, wastage of materials is less when compared to other fabrication processes like photolithography and etching. This allows economical mass production of printed electronic devices in lesser time. With thickness of these devices ranging from tens of microns to less than a millimetre, they are light weight, flexible and comparatively low at cost. Because of all such novelties, Printed Electronics has become a huge area of investment, with market size valued at USD 3.02 billion in 2015 it is estimated to reach USD 19.15 billion by 2025[6].

As this devices are thin film and flexible, they can be fabricated not only on polymer substrates, but also on fabrics[7-9] and even on skin[10, 11]. Integrating printability with analysis of physical factors of body like motion, pressure, temperature, brain waves and heart beats, and electrochemical factors like chemical contain and biomarkers in sweat has enhanced the health monitoring capability[12-16]. This creates possibilities to develop wearable electronic products capable of continuous health monitoring, early diagnosis and tracking effects of therapies and treatments with less time and in an effortless manner.

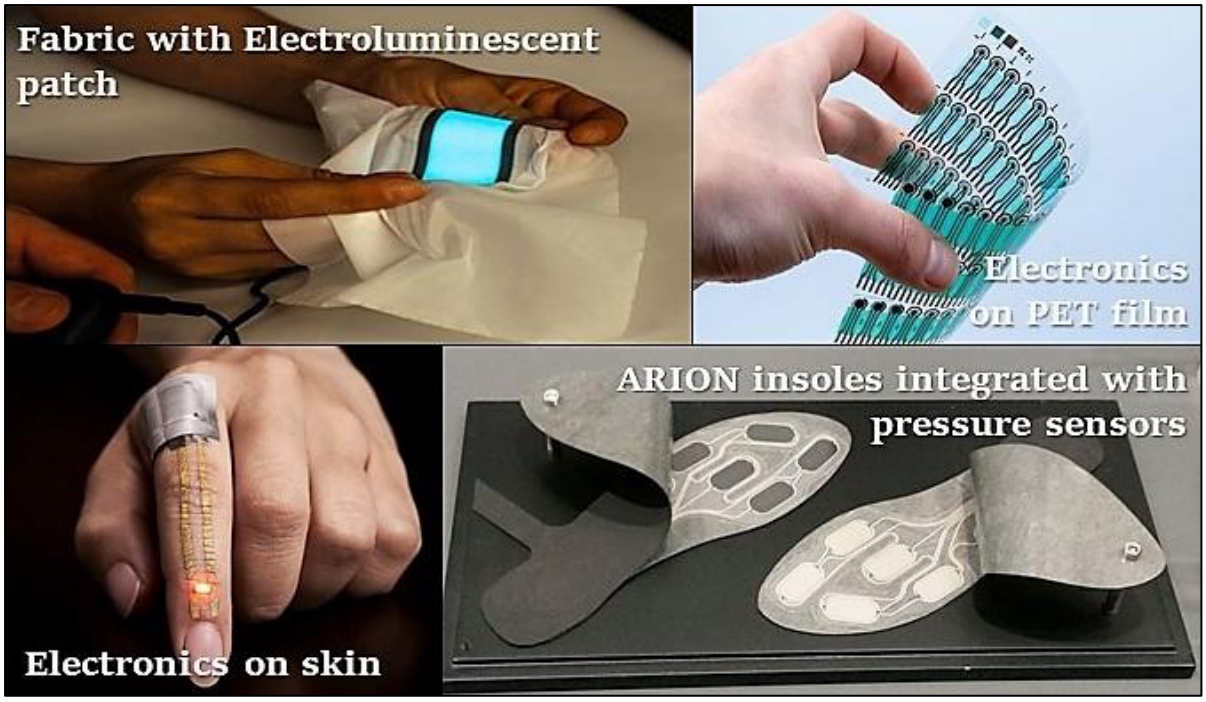

Figure 1: Health care and wearable Printed Electronics. Reference of images [17].

Radio Frequency Identification (RFID) tags are used as unique ID system devices for identification and tracking of various goods. As circuitry is involved in such tags, they cost more than other ID methods, such as barcode stickers, to serve the purpose of identification. But with new fabrication methods like printing, manufacturing cost of RFID tags can be reduced and are being developed by many groups[18, 19]. Further, such RFID tags can be used for many application like tracking and monitoring of good, parcels and food products, and for animal, vehicle and human situation tracking as well[20, 21].

Stacking of multiple layers due to printing process allows the possibility of creating products which have multi-layered structure. Thin film Transistors are being fabricated by printing layers of semiconducting inks, organic and/or inorganic, and electrodes on flexible substrates [22-27]. Various electric components, MEMS[28-30] and sensors have been developed such as gas sensors, pressure sensors, humidity sensors, photodetectors, etc[31-36]. Printing of thermochromic, electrochromic, electroluminescent layers and materials like OLEDs with conductive transparent substrates have led towards the development of foldable, light weight Displays, which have vast applications, such as luminescent labels, traffic sign boards, scale indicators and for light panels[37-42].

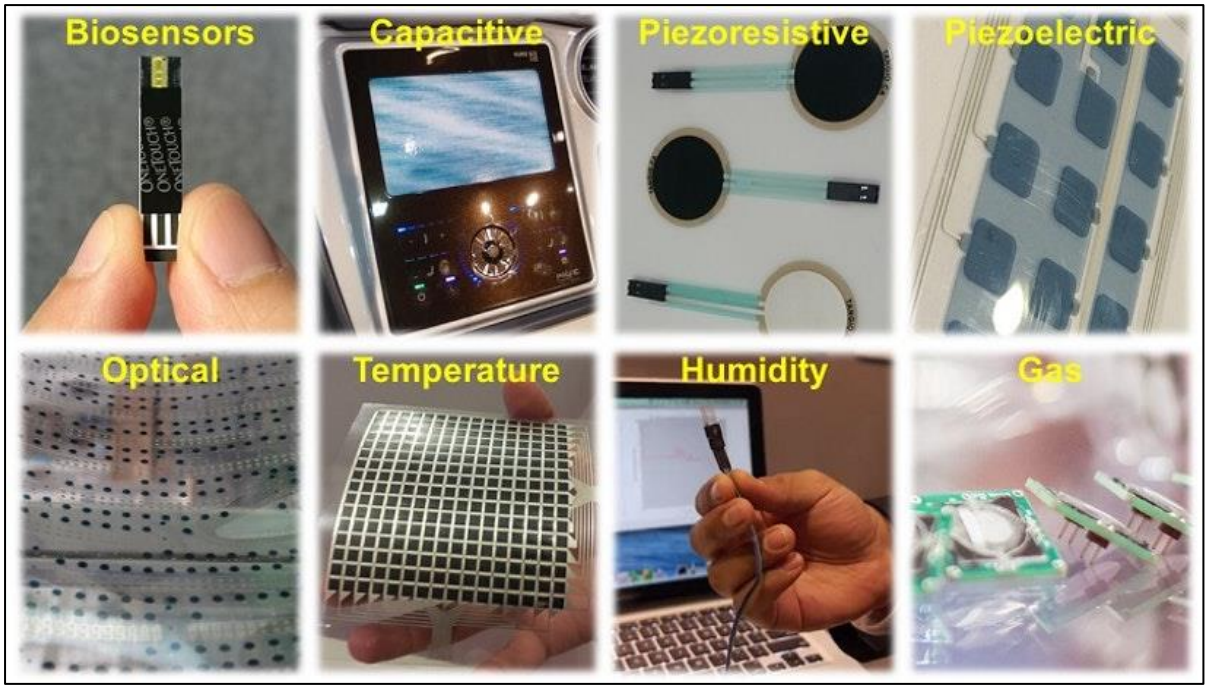

Figure 2: Different types of Printed Electronic Sensors. Reference[43].

All such electronic devices require energy to operate, and all their versatile properties are of no use if the batteries that provide energy are bulky and rigid. With advancement in electrolyte materials and electrode layer structure. Flexible, light weight batteries are being fabricated for powering printed electronics[44-46]. With research going on to further optimize the batteries, other energy storage devices are also being developed, such as Solar cells printed on flexible substrates, thin film supercapacitors for storage of energy [47-52].

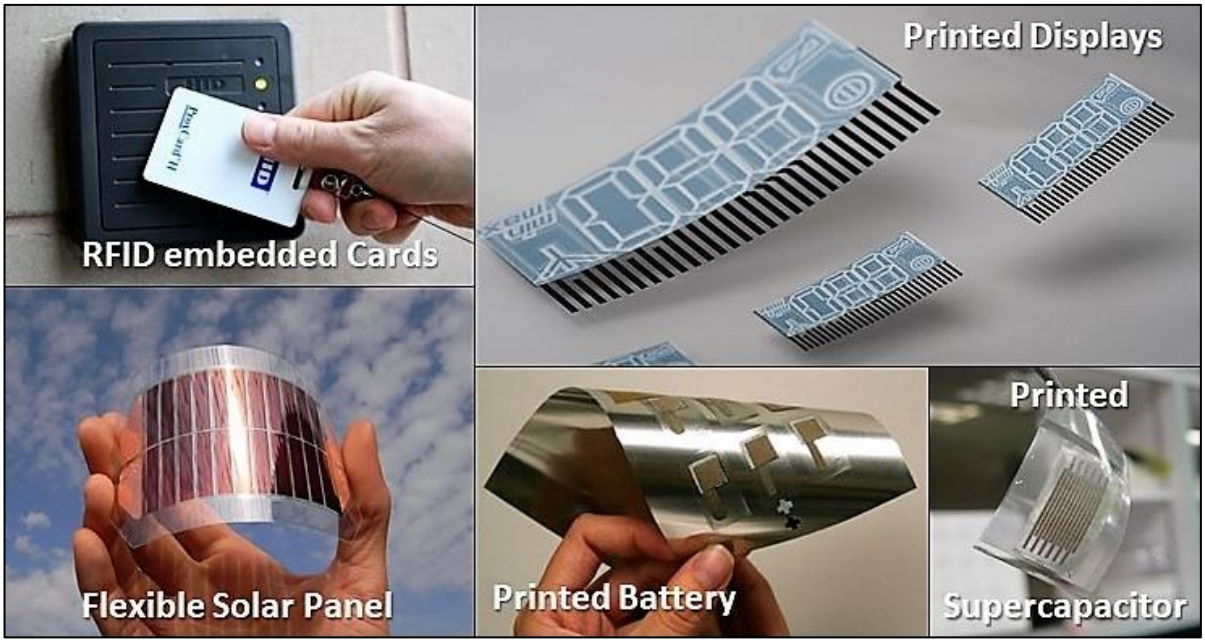

Figure 3: Various printed devices and components. References of images [49].

All these devices and components can be integrated together for many applications. Arrays of sensors installed at various location, or to various things can generate data for logistic purpose. Due to these low cost, easy and fast manufacturing of electronic devices by various printing techniques, many possibilities like the Internet of Things are on a peak.

Printing Techniques

From centuries, printing has been very useful techniques of representing information in form of visuals with associated design and colour. With the realization of printing of circuits and other electrical components, various printing techniques have been developed and customized for specific purpose of printed electronics. The key difference created between visual printing and printed electronics is due to the features of inks. Visual inks are developed with purpose to have colour and are made from colour materials, but inks used in development of electronics are functional with conductive, dielectric, semi-conductive properties.

There are many parameters associated with printing, such as substrate selection, ink materials, ink preparation method, ink viscosity, curing process, print resolution (typically range 50-500 μm), print density, printing speed, etc. Different techniques require/provide variance in these parameters which are interrelated. For e.g., with higher print resolution, highly dense printing can be achieved with use of less materials, but this precision affects the printing speed. Different printing method demand variation in ink viscosity and may or may not require curing process. Viscosity of ink depends on materials used and their concentrations.

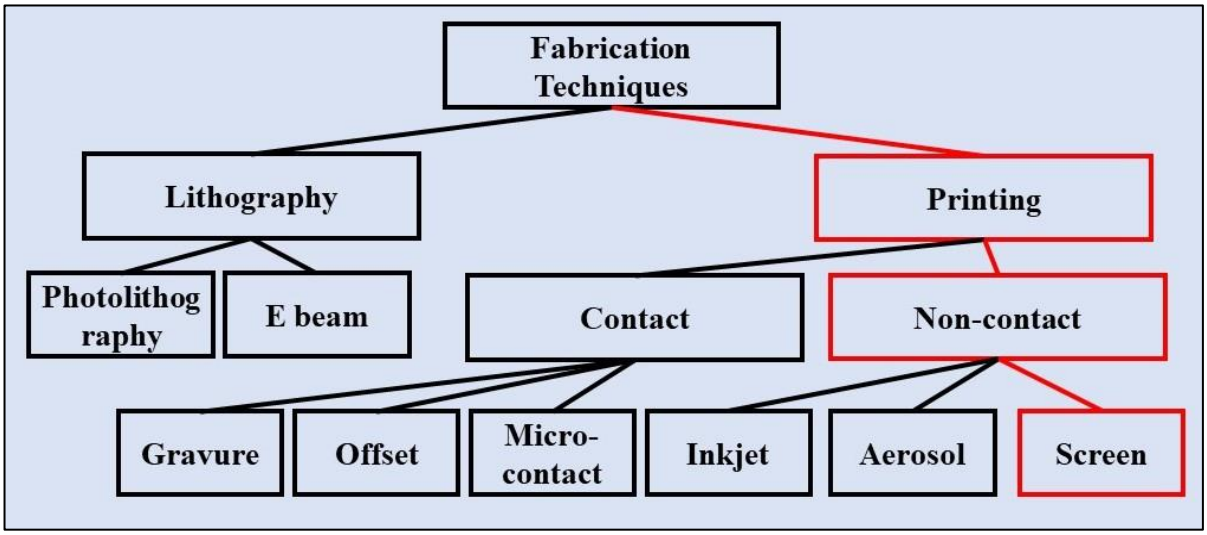

Figure 4: Classification of fabrication techniques for microelectronics. Technique significant to this thesis marked in red.

With less requirements for fabrication compared to photolithography, etching, etc, which are subtractive methods resulting in waste production, printing being an additive process becomes a favourable technique able to produce roll to roll and large area production. Due to its mass producibility with lesser time, using less materials, printing becomes a very cost-effective technique for microelectronic fabrication.

Design that has to be produced on substrate is fixed on a carrier. This carrier can be a software program or can be an actual image stencil. Carrier deposits the design by either coming in contact with substrate or without contacting to the substrate, which classifies the printing process in to Contact and Non-Contact Printing.

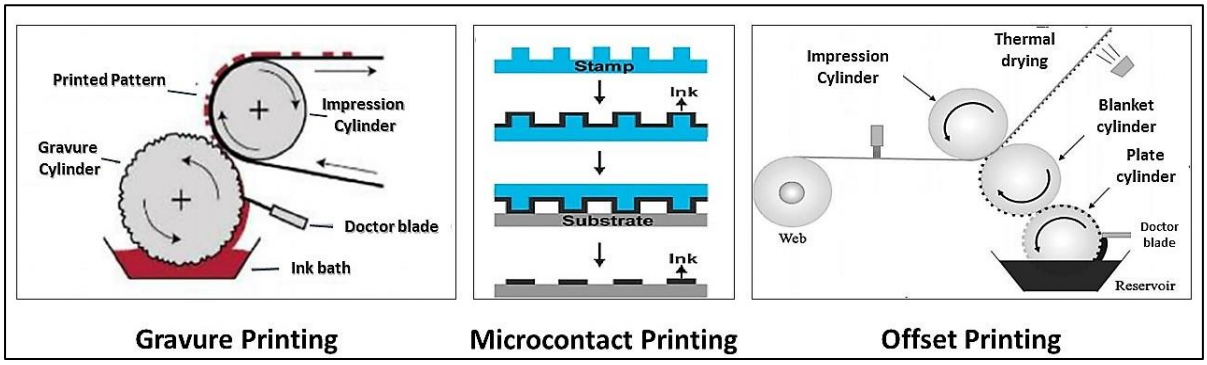

Figure 5: Schematics diagrams of Gravure, microcontact and Offset Printing. Reference[3].

Three main contact printing techniques includes Gravure, Offset and Microcontact Printing. In Gravure Printing, design is engraved on a plate which is attached to the outer surface of a cylinder. This cylinder is partially submerged in an ink bath form where ink gets stuck into cavities as the cylinder rolls. A doctor blade brushes with the cylinder removing excess ink of the surface leaving only the ink inside the cavity to pass ahead. After this, cylinder comes in contact with substrate with little pressure between both, causing ink inside the cavities to get printed onto substrate treated with adhesives. A similar process is used in Offset printing, but instead of printing directly on substrate, ink is first printed on a blanket cylinder which is in contact with the substrate and places the ink on it. In Microcontact Printing a soft stamp is used which stamps the ink on the adhesive substrate.

A low viscous ink is drop wise printed onto substrate from a nozzle (not in contact with substrate) which is controlled by computer program. This type of printing is called inkjet printing. In aerosol jet printing, aerosol of ink particles of size 1-5μm is passed through a nozzle producing high velocity aerosol stream which gets sprayed on substrate. Due to controlled spray, aerosol jet printing can achieve print resolution up to 10μm.

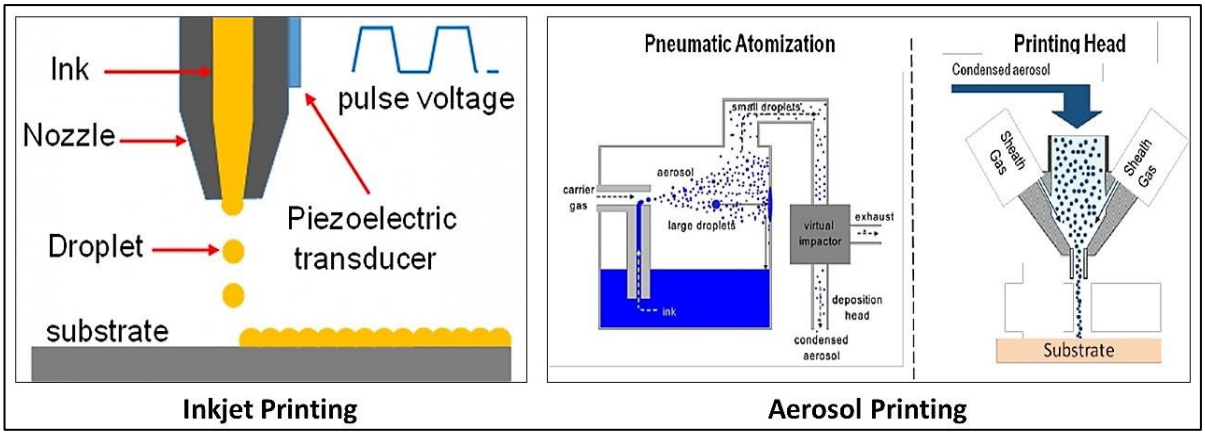

Figure 6: Schematic of Inkjet and Aerosol Printing process. Reference[5].

Screen Printing

Screen Printing is traditional printing technique used for mass printing of newspapers, decorative cards, posters on papers and even on fabrics, and can be adopted for printing electronics on flexible substrates such as PET films, paper substrates and fabrics. Devices explained in experimental section of this thesis were fabricated using screen printing.

Preparation of Screen

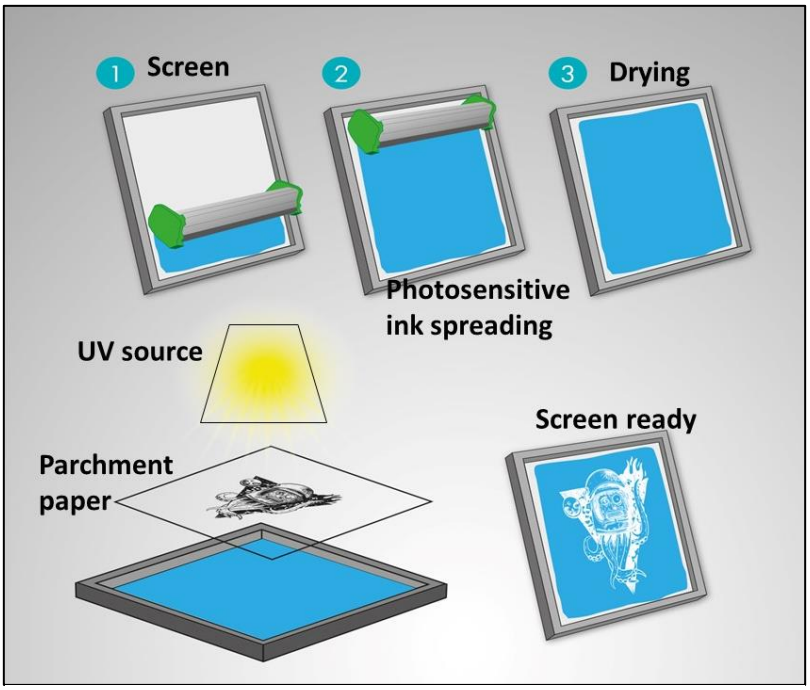

Figure 7: Schematic showing exposing of Screen. Reference[2].

Before printing of electronics, screen has to be developed which is known as screen exposing (as exposed to UV light in process). Screen consists of a mesh made of polyester fibbers or steel wires. A thin layer of photosensitive ink is spread on this screen and is kept for drying, which will work as stencil caring the image. Once the Screen is dry, design of interest is first printed on a parchment paper, this paper is place on the screen and together kept under UV light source. As Parchment paper is translucent, it will allow light to pass onto screen, photosensitive ink will react in presence of light and stick tightly to the mesh fabrics, only the area on parchment paper printed with design will not allow light to pass through. Ink area below the design will not react and will be soluble in water. After exposing to UV light, mesh is washed with the stream of water which will remove the soluble ink, leaving behind open area in the shape of desired design.

Printing using Exposed Screen

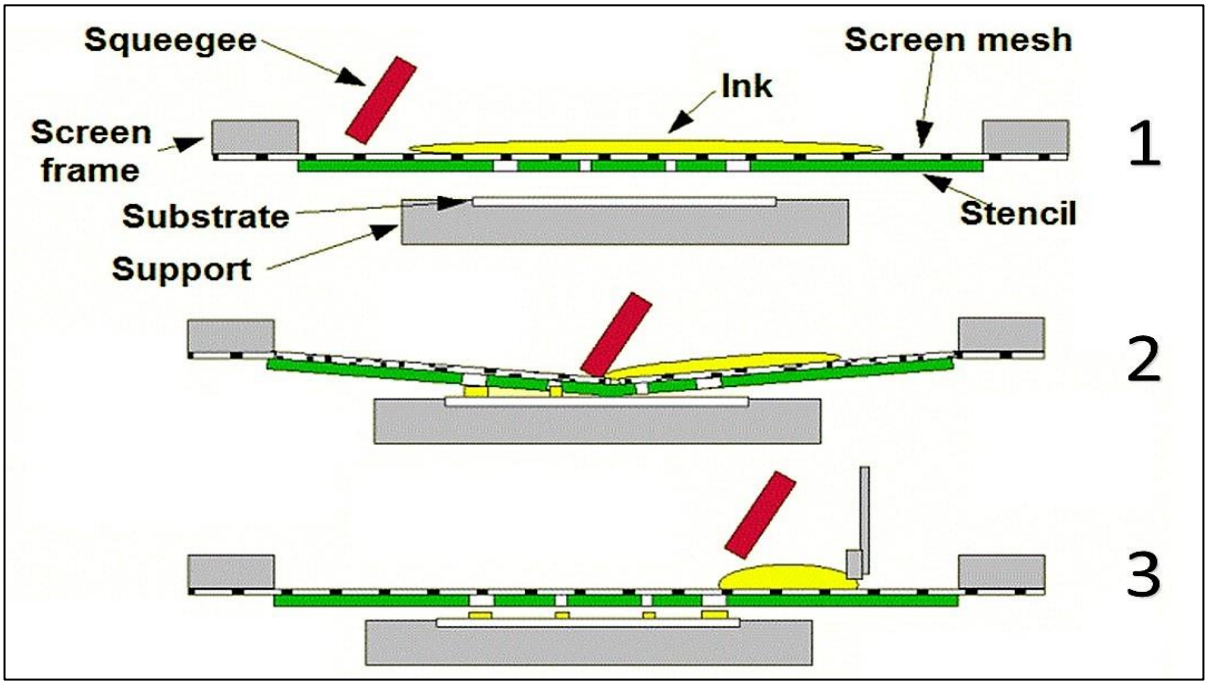

Figure 8: Schematic of screen printing. 1) Flooding. 2) pulling of squeegee. 3) print deposited on substrate. Reference[4].

Once the screen is exposed, it is ready for mass printing with life of 700-1000 prints depending upon the quality of photosensitive ink used for exposing. Functional ink is placed over one side of the screen as is pulled with the squeegee. This pulling of ink spreads it all over the screen and is known as flooding (as unexposed, open area of screen is now flooded with functional ink). Flooded screen is kept over the substrate with no contact to it,

maintaining a small gap between both, screen and substrate (part 1 in figure 8) Then with a squeegee screen is gently pressed on the substrate and pulled over (part 2 in figure 8). This pulling of squeegee forces ink to get deposited form the mesh to the substrate (part 3 in figure 8). Printed pattern on the substrate is still wet and requires curing process to dry the ink. After drying of ink by curing process, device is ready and has functionality as desired.

Some device fabrication requires multiple printing. For such devices design of each layer has to be exposed and printed layer by layer on each other after previous layer is completely cured.

Chapter 2

Experimental

Functional Inks have three main constituents.

1. Functional material
2. Polymer
3. Solvent

Functional material gives functionality to ink. For e.g. Conductivity of individual silver Nanoparticle gives conductivity to the ink prepared using it. Polymer provides the support to these particles. Nanoparticles are stable and stuck in the polymer matrix. Solvent provides the medium in which polymer is disentangled and homogenously mixed with functional material to create stable colloid.

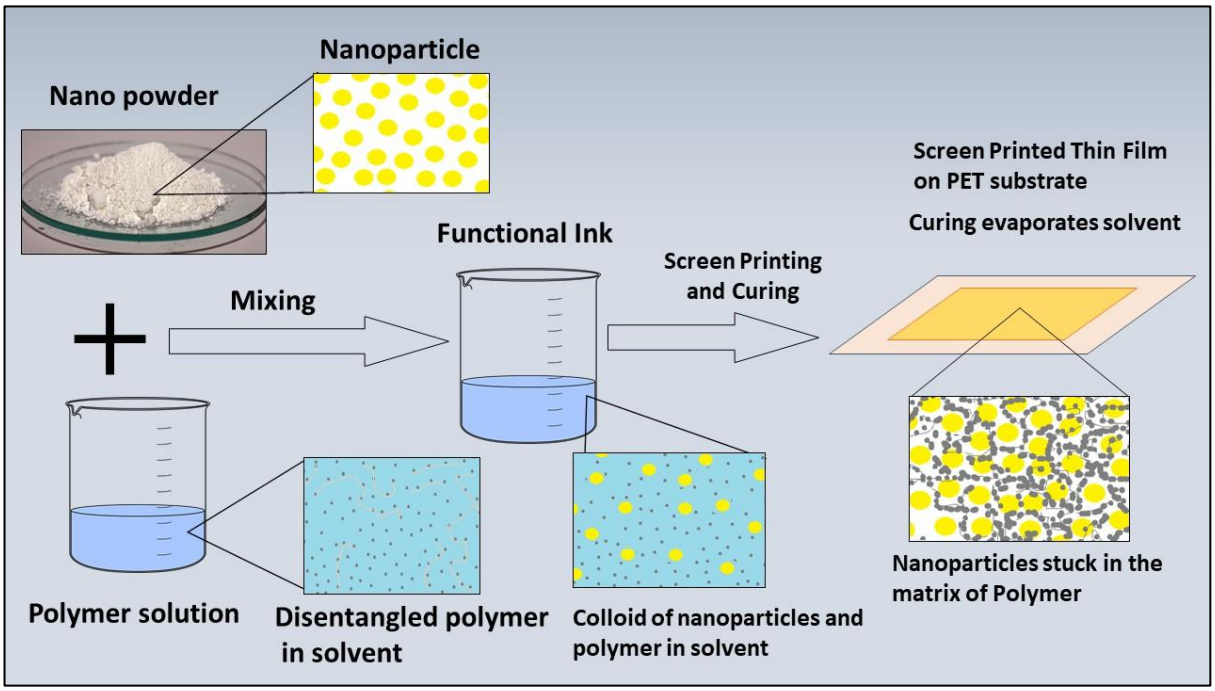

Figure 9: Schematic showing preparation of Functional Ink.

Functionality of ink increases with increase in concentration of the functional material. Adhesion required to hold the nanoparticles together and sticking of ink to substrate is depended on the concentration of polymer. viscosity is dependent up on the concentration of solvent. A balance between all three has to be maintained in order to have optimised ink suitable for printing. This thesis focuses on development of various functional inks, their characterization, use of these inks for fabrication of devices and testing of those devices.

Section A contains development of carbon-based ink, ink characterizations, fabrication and testing of Flexible Heater. Section B contains development of Silicon Dioxide based ink with 4 different polymers, ink characterizations, fabrication and sensing test of Ammonia Gas Sensor. Section C contains work that is under progress, development of Electrochromic ink and investigation done on of Protein sensing for development of Protein Sensors.

Section A

Printed Flexible Heater

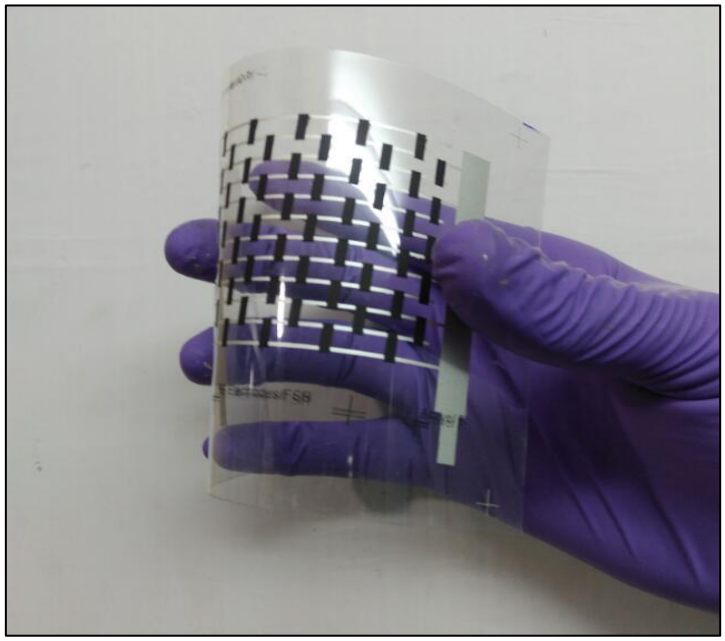

Figure 10: Image of Printed Flexible Heater

This section emphasises on the development of carbon-based ink and fabrication of flexible heater operating at low voltages using Screen Printing (Figure 10). Characterization of ink such as IV relation, viscosity of inks, SEM images and Raman Spectroscopy were performed. Temperature vs Time at different voltages and at different bend angles were measured for heater. Possible applications are discussed further.

Materials and Methods

Carbon ink was prepared by mixing carbon paste and Polyvinyl acetate solution. Carbon flakes of particle size 2-5 µm were the functional part of the carbon paste. Polymers used for the development of paste were Polyvinyle Pyrolidone (PVP) as the polymer matrix and Polyvinyl butyral (PVB) for enhancing binding in the paste, later for preparation of carbon ink Polyvinyl acetate (PVAc) was used as adhesive. Sodium Dodecyl Sulphate was used for better dispersion of carbon flakes. Ethanol was used as the solvent. Silver nanoparticle-based polymer composite paste was used for Interdigitated electrode printing. Polyethylene Naphthalate (PET) film was used as substrate.

For the preparation of carbon paste, two medium viscous solutions of PVB and PVP separately with ethanol were prepared (polymer/solvent ratio 1: 4 by weight), kept for stirring at 80^{o} C for 120 mins. Carbon paste constituents and there amount present in the paste are listed in the following table.

Constituent	Weight %
Carbon flakes	65%
Polyvinyl butyral solution	5%
Polyvinyl pyrrolidone solution	20%
Sodium dodecyl sulphate	10%

Table 1: constituents of Carbon paste.

To prepare Carbon ink using Carbon paste, a transparent dispersed Polyvinyl acetate (PVAc) solution with ethanol in ratio 1:2 by magnetic stirring for 30 min at 60^{o}C was prepared. Carbon ink of desired composition was prepared by mixing carbon paste and PVAc/ethanol solution at different ratios (weight) by magnetic stirring for 60 min at 60°C. Carbon Ink prepared with different ratio of Carbon Paste and PVAc solution are: **C (80)** (80% of Carbon Paste and 20% PVAc/Ethanol Solution) and **C (60)** (60% of Carbon Paste and 40% of PVAc/Ethanol Solution) and it is further inspected.

Ink Characterization

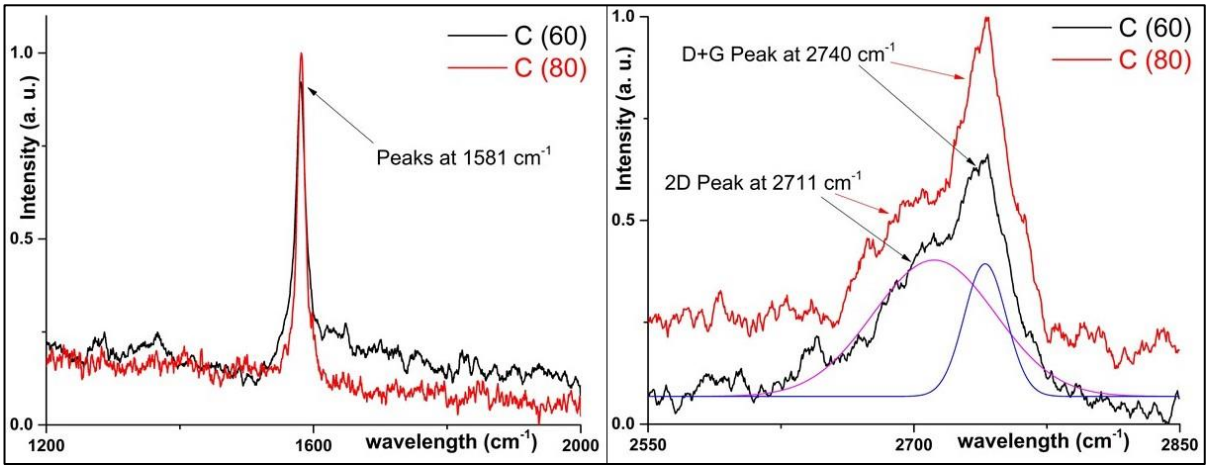

Figure 11: Raman Spectroscopy of Carbon Inks.

Raman spectroscopy for both carbon inks, C (60) and C (80) samples was performed. In Raman Spectra of the carbon inks, G Band peak at around 1581 cm^{-1} was observed, 2D band peak at 2711 cm^{-1} and D+G band peak at 2740 cm^{-1} (Figure 11). These peaks are similar to peaks observed for graphene indicating the presence of graphene in the inks. For Morphological study the carbon inks, C (80) and C (60) inks were printed in small patch on PET substrate with print thickness between 13 to 17 µm, and were used for SEM imaging using ZEISS SIGMA SEM. As polymer concentration is more in C (60) Ink compared to C (80) Ink, carbon flakes in C (60) Ink are more capped with polymer compared to C (80) Ink which can be seen in SEM Images (Figure 12).

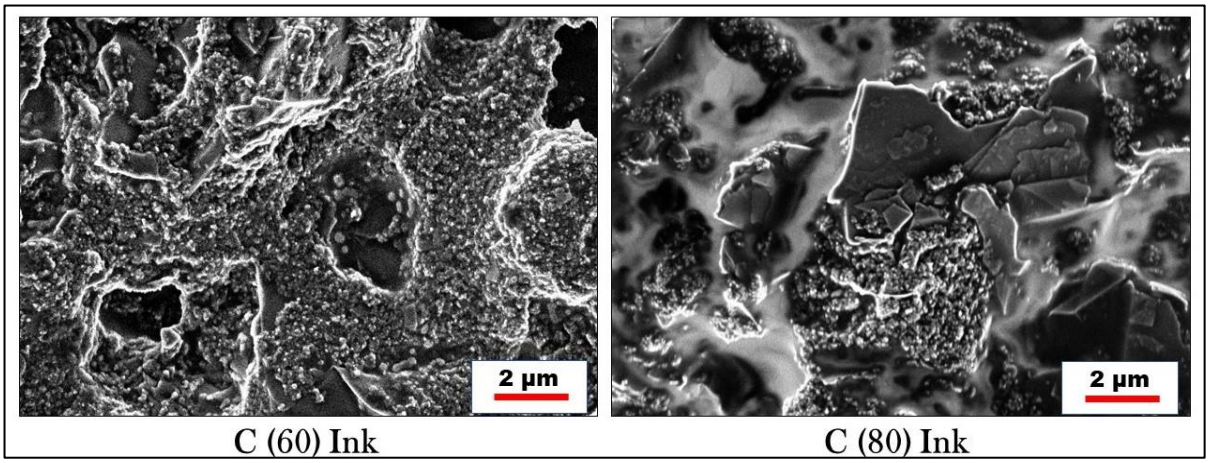

Figure 12: SEM Images of Carbon Inks.

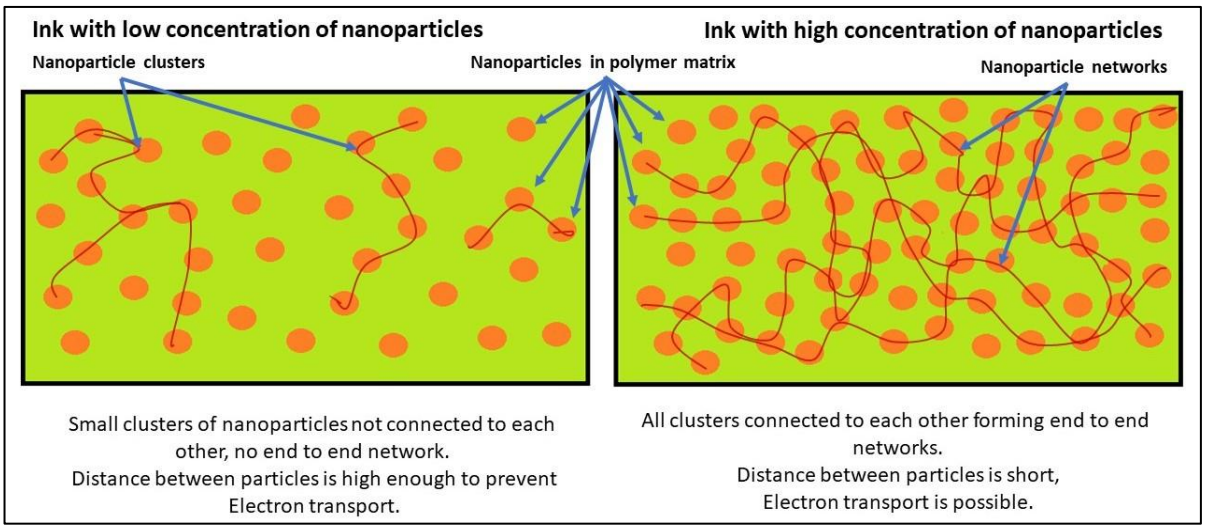

Figure 13: Schematic comparing high and low concentration inks.

Viscosity measurement was performed using Modular Compact Rheometer. Viscosity of C (60) Ink was found to be 7.2 ± 0.5 Pa-s and for C (80) Ink, 8.9 ± 0.4 Pa-s (at room temperature at 50 s^{-1} shear rate) which were suitable for Screen Printing.

To measure the electrical resistance offered by the carbon ink, identical patches of both C (60) and C (80) inks of different areas were screen printed, keeping the length and width constant by ratio 7:3. Resistance of these patches were measured by IV measurement using Keithley 2400 and was found to increase with increase in area (Figure 14).

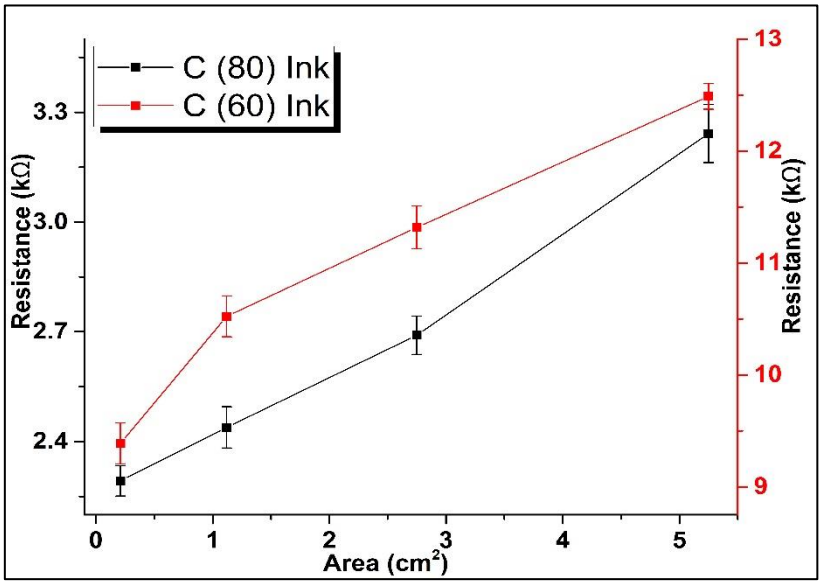

Figure 14: Graph of Resistance vs. Area for C (60) and C (80) Inks.

20 V DC voltage difference was applied across these patches to check there heating effect. In Figure 15 it can be seen that patches printed using C (80) ink are showing good heating effect compared to patches printed using C (60) ink. It can also be seen that heating is more as the area is decreasing.

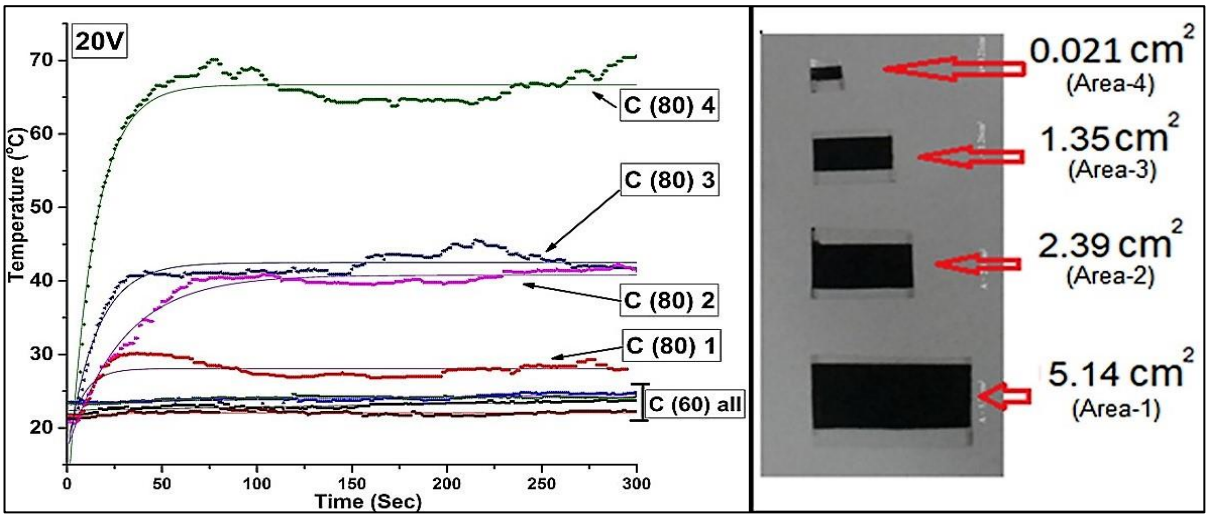

Figure 15: Temp. vs. Time for different area patches printed using C (60) and C (80) inks. Read C (80) 4 as patch of C (80) ink of Area-4 (0.21cm^2) from the image in right.

After a certain concentration of nanoparticles inside the polymer matrix of the nanoparticle/polymer composite, nanoparticles are close enough to each other that a continues conductive network is formed which can carry current. This concentration after which conductivity of nanoparticle/polymer composite increases is known as Percolation threshold.

As concentration is increased near percolation threshold, Electron Tunneling can be considered as a possible explanation for the initiation of conductivity in the composite[53]. And as concentration rises, gap between nanoparticles is reduced and few particles may even come in direct contact with each other, further increasing the conductivity (conductivity of C (80) ink is better compared to C (60) ink (Figure 14). Research for understanding electron transport in conductive composites highlight Electron Tunneling, variable range hoping of electrons and direct contact between nanoparticles as key electron transport mechanisms [54].

When area of carbon patches decreases, the size of network will decrease as there will be now less particles. Therefore, high amount of current will flow form the network, i.e. high amount of current through individual carbon particles, increasing electron phonon interaction, resulting in higher temperature for the carbon patch of smaller area compared to larger area. Therefore, C (80) 4 patch (read as patch using C (80) ink of size 4 as mentioned in Figure 15) has higher temperature output compared to C (80) 1 patch (Figure 15).

Device Fabrication

Screen printing technique were used for fabrication of Flexible Heater using Carbon Ink. Flexible Heater consist of two layers of printing. First Interdigitated electrodes (Figure 16 A), second, patches of C (80) ink (Figure 16 B), connecting the Interdigitated electrodes (Figure 16 D). C (80) ink was used because of its good conductivity and better output temperature compared to C (60) ink. Screen mesh consisted of 40 wires of polyester fibbers with 48 µm diameter per inch. Therefore, print resolution of 560 µm. Silver conductive paste with particle size in between 3-4 µm was used for printing Interdigitate electrodes. Polyethylene Naphthalate (PET) Film of thickness 125 microns was used as a substrate to provide mechanical base for the fabrication of heater.

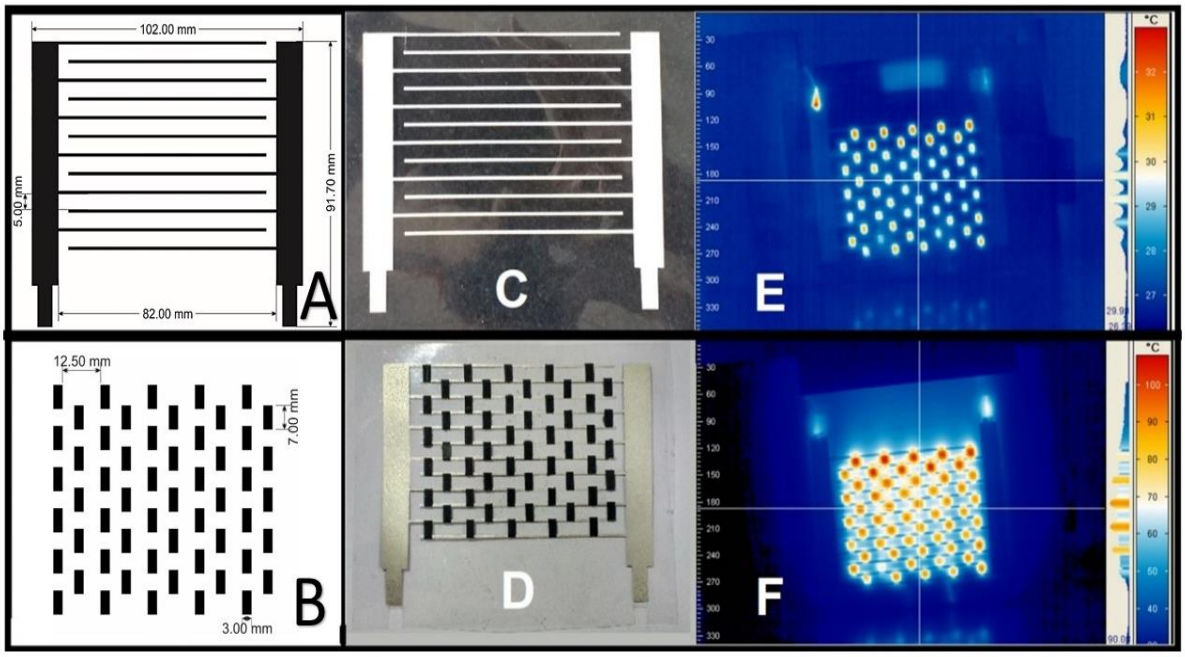

Figure 16 A: Design of Interdigitated Electrodes. Figure 16 B: Design of Thermal Active layer. Figure 16 C: Electrodes printed on PET film. Figure 16 D: Flexible Heater printed on PET film. Figure 16 E: Thermogram image of heater at the beginning of heating. Figure 16 F: Thermogram image of Heater when steady state Temperature is reached.

A grid like patches of C (80) ink is printed as the thermal radiant layer connecting the electrodes, as shown in the Figure 16 D. The inter electrode distance is kept at 5mm, each carbon patch is of size 21 mm^2 and the distance between two patches of carbon is 12.50 mm. over all area of heating is 90 cm^2. Wet ink on substrate is cured by keeping the sample at 140^o C in hot air oven after which Heater is ready.

Temperature profile of Heater

Temperature vs time measurement was performed at different supply voltages, shown in Figure 17. It can be seen in the graph that change in temperature is very high in the first 50 sec, after which Temperature reaching a steady state. As Voltage is increased, Stead state Temperature increases (Figure 17 A). With power consumption density 0.08 W/cm^2 at 34^o C, 0.16 W/cm^2 at 45^o C, 0.29 W/cm^2 at 58^o C and 0.4 W/cm^2 at 68^o C (Figure 17 B).

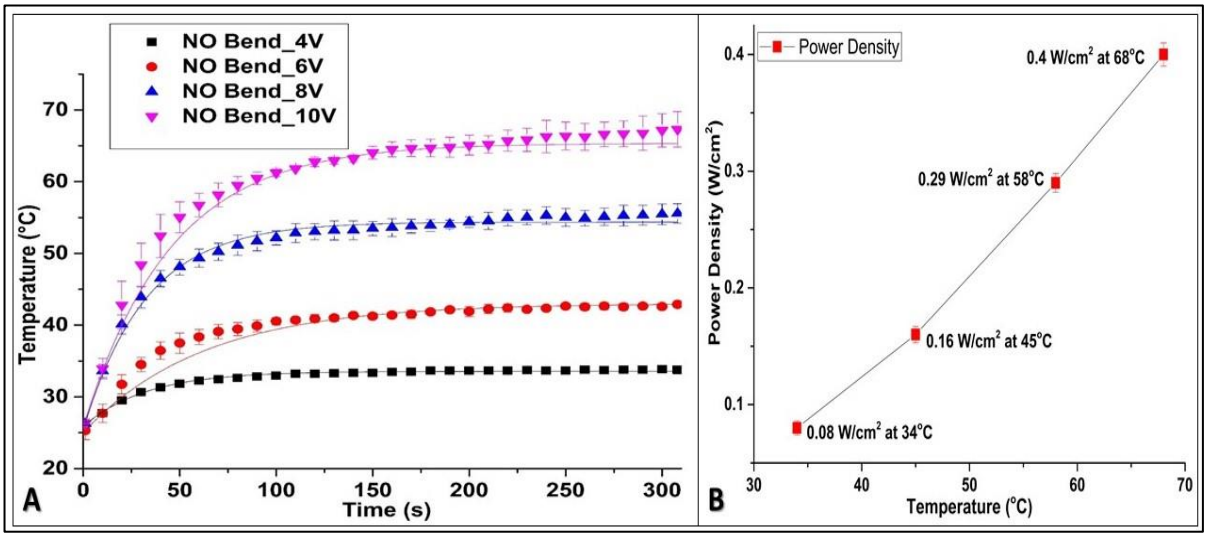

Figure 17 A: Temperature vs. Time at different voltages. Figure 17 B: Power consumption per area.

Temperature profile of heater on bending

Flexibility being a property of this heater, it becomes important to know that the functional property of this heater does not change. Therefore, variance in performance of heater when subjected to bending is studied. Heater was bend as shown in Figure 18, at different angles and Temperature with respect to time was measured.

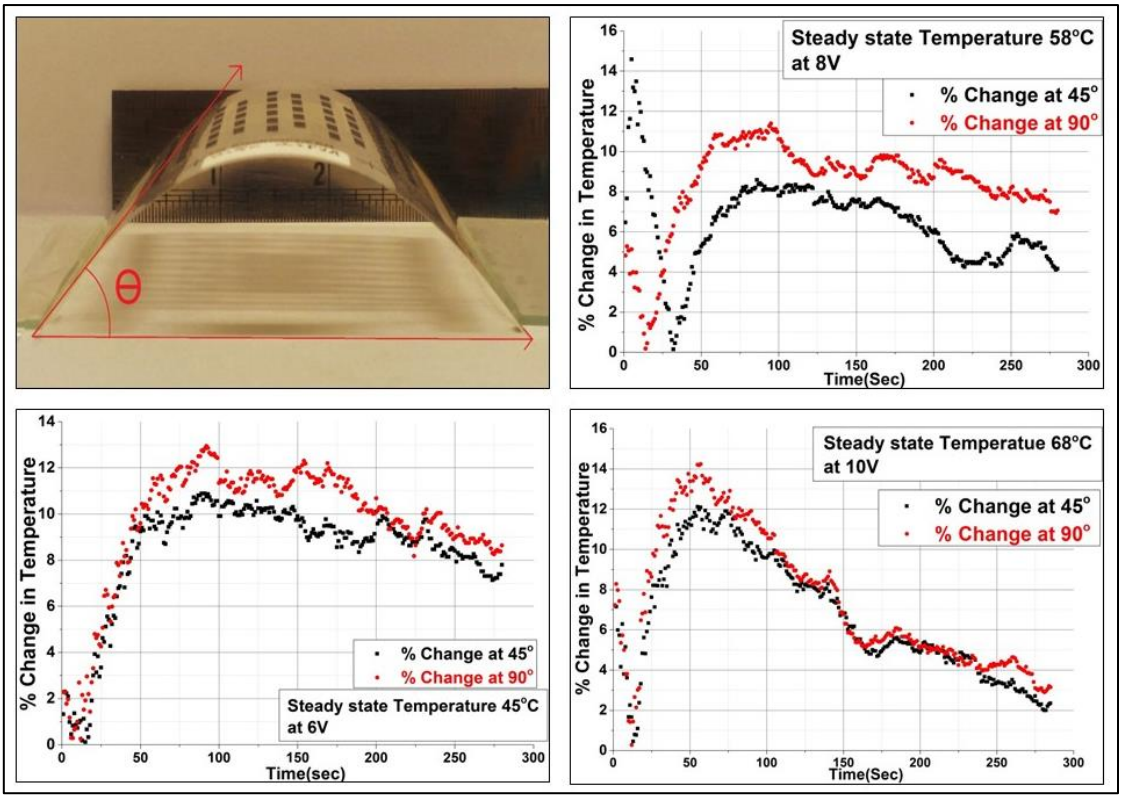

Figure 18: Bent test setup and Percent change in output temperature when subjected to bending.

Bend test was performed by bending the heater as shown in image in Figure 18, at 2 different angles, 45° and 90°, and measuring Temp. vs. Time at each bend for 6, 8 and 10V. Bend test show that the temperature output was increased by 10-14 % when compared with on bend temperature. A possible explanation for this change, can be the change in thickness of active layer on bending, resulting change in output temperature.

Conclusion and Applications

In Conclusion, carbon flakes-based carbon ink was developed and tested for its conductivity, viscosity and temperature output. Using this ink, low voltage flexible heater was fabricated on a PET substrate by using Screen Printing Technique. This heater was tested for its Temperature deliverance at different voltages. Initially, temperature raised quickly and was stable after a certain temperature was reached. This maximum temperature was dependent upon voltage applied. Performance under bending condition was checked by performing bend test which showed 10-14% change on bending. Due to its flexible, light weight, thin, and low voltage requirement nature, this Heater can be used as an essential component of wide range of applications, such as wearable electronics, health care products, etc.

Comparison of Printed Flexible Heaters with heaters available in market.

Heaters	Polyester Flexible Heater	Polyimide Thermofoil flexible heater	Printed Flexible Heater
Power consumption/Area	0.13 W/cm2	0.0078W/cm2	0.1W/cm2
Response Time	-	50 min	45-60 sec
Highest Temperature	110^{o}	52^{o}	120^{o}
Size	55*21 cm^2	300.257 cm^2	9*10 cm^2
Thickness	800µm	1mm	145µm
Cost	₹ 10,035	₹ 1196	₹ 80

Table 2: Comparison of Printed Flexible Heater with commercially available heaters[56]

This Heater was developed as one of the main component for products like Foldable Low-cost Neonatal Incubator (Figure 19), Low-cost baby packs for rural and urban needs, and for Smart Thermal Jackets which are under development at G-Labs Innovation Pvt Ltd, consulted and designed by Prof. Charu Monga (Dept. of Design, IIT Guwahati) and has been filed for provisional specification at the Patent Office for Indian Patent (**Application number 201831004095**).

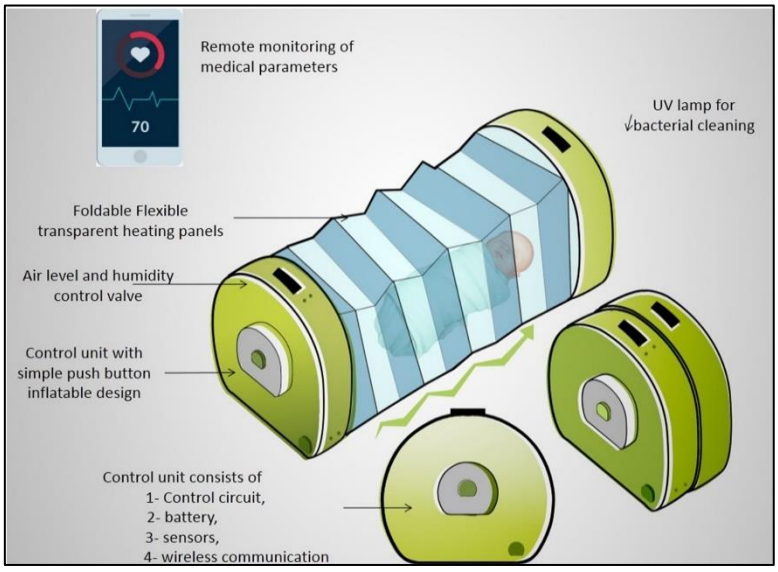

Figure 19: Foldable Low-cost Neonatal Incubator sketch

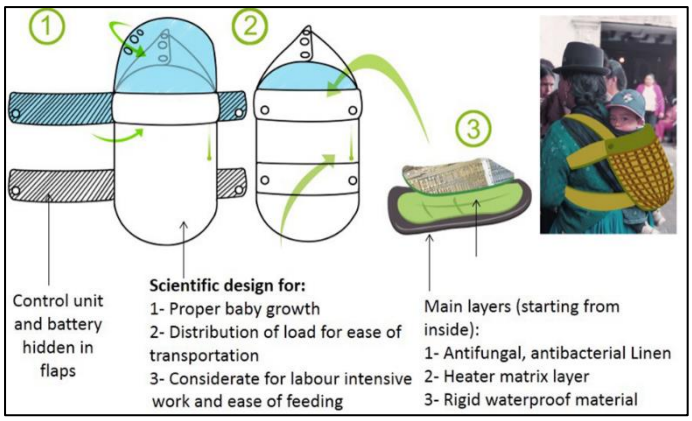

Figure 20: Low-cost baby packs for rural and urban needs

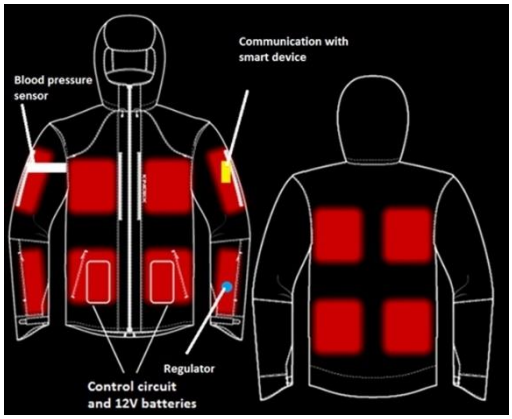

Figure 21: Schematic of Thermal Jackets installed with Heater

This Heater is highly applicable in wearable technology, especially for winter wears. It can be installed with textile sheets for making Radiant Heating Cloths which can be tailored for developing smart wearables such as Thermal Jackets (Figure 21) and baby packs (Figure 20).

Section B

Printed Reusable Ammonia Gas Sensor

This section consists of Flexible Ammonia Gas Sensor which was developed using Screen Printing Technique. It was fabricated by two-layer printing, first the interdigitated electrodes by using silver conductive paste and then an active layer by using Silicon Dioxide Ink. Silicon Dioxide Ink was prepared by mixing silicon dioxide with polymer. Four different polymer-based inks were prepared and tested. Ink with each polymer was developed at four different Polymer: SiO_2 ratios (by weight) and all were tested for printability and sensing response.

Materials and Methods

Silicon dioxide was used as the active material. Polymer such as Poly Methyl Methacrylate (PMMA), Polydimethylsiloxane (PDMS), Polyvinyl Alcohol (PVOH) and Polyvinyl Acetate (PVAc) were used for development of Silicon Dioxide Inks. Silver conductive paste was used for electrode printing. Polyethylene Terephthalate (PET) film was used as flexible substrate.

Polymer solutions were prepared by dissolving polymers into their respective solvents and keeping for magnetic stirring. Once the polymers were dispersed uniformly into solvent, this polymer solution was mixed with SiO_2 powder for development of Active Ink. Following table shows the concentration used for developing Polymer solutions.

Table 3: Polymer and solvent used for preparing polymer solution

Polymer	Solvent	Polymer: Solvent wt. Ratio	Mixing Time and Temperature
PVAc	Ethanol	1:4	40-45 min at 80-90^oC
PVOH	Di water	1:8	60 min at 70-80^oC
PDMS	Toluene	1:2	10 min to room temp
PMMA	Toluene	1:4	30 min at 40^oC

For e.g. PVAc Solution was prepared by mixing PVAc with Ethanol in ratio 1:4 for 40 to 45 mins at around 80^o C.

These stock solutions were further used for developing SiO_2 inks. SiO_2 powder was added to Polymer solution in four different ratios (1:4, 2:3, 3:2, 4:1) by weight and were kept for magnetic stirring for 60 min at Room Temperature.

Ink Characterization

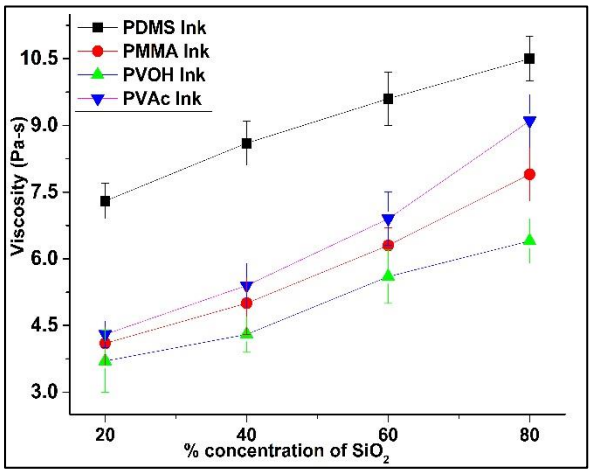

Figure 22: Viscosity with change in concentration

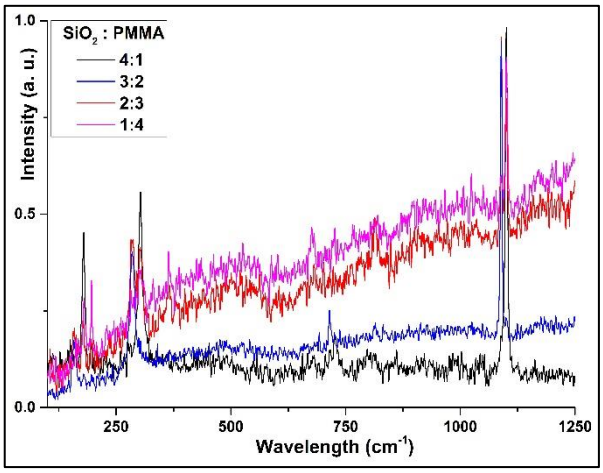

Figure 23: Raman Spectroscopy of PMMA inks

Viscosity of the ink was tested using Rheometer in order to have compatibility with Screen Printing. Raman spectroscopy was performed on PMMA polymer inks. Viscosity was found to increase with increase in concentration.

Fabrication of Device

First, Interdigitated electrodes were printed on flexible PET substrate using Screen printing and cured at 135^{o} C for 6 min. Later, active layer was screen printed on these electrodes using SiO_2 inks developed at four different ratios with each polymer solutions. Therefore, in total 16 samples were fabricated and further investigated.

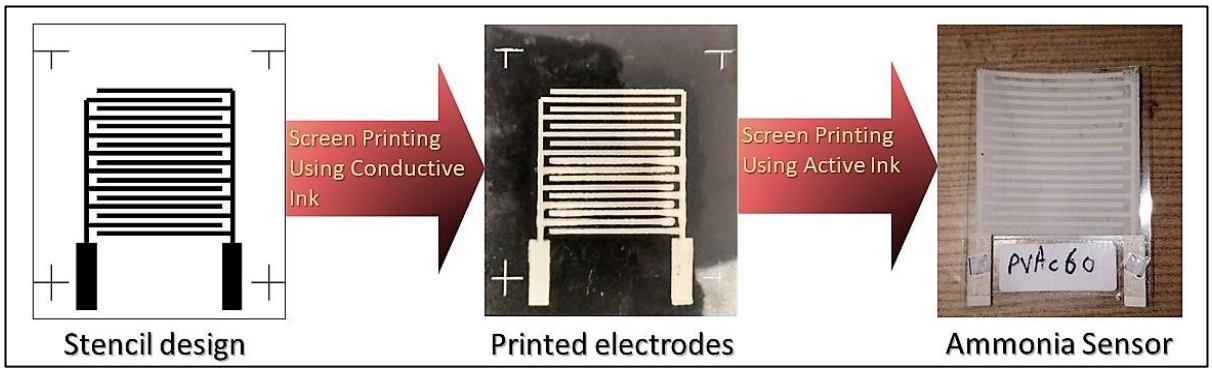

Figure 24: Fabrication of ammonia sensor 3.5×3.5 cm^2

Ammonia Sensing

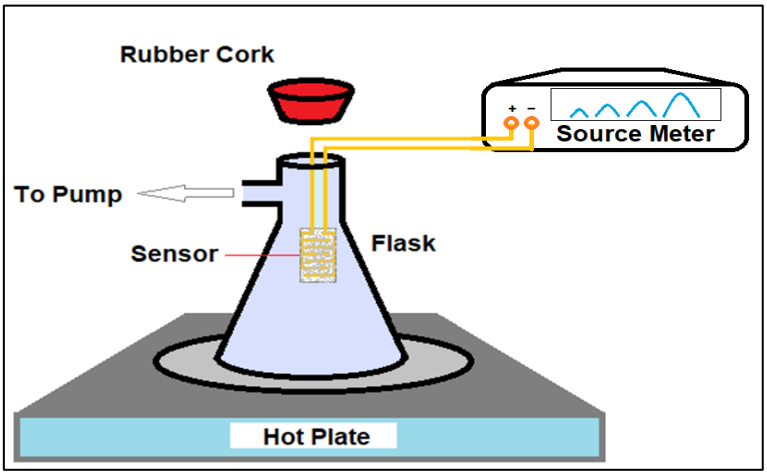

Fig 25. Experiment schematic for sensing Ammonia

Experiment setup was as shown in the above diagram. Ammonia sensor was suspended inside the flask and was connected to Source Meter. Constant 10 V DC was applied to the sensor and current was measured. Flask of volume 360 ml, which was attached to pump was kept on hot plate maintained at 130^{o}C. Ammonia in different amount was dropped directly to the floor of Flask (amounts mentioned in Table 1). Due to high temperature of floor, liquid ammonia dropped inside flask was vaporized (concentration of vapours in PPM mentioned in Table 1). Act of dropping ammonia into flask was done quickly and flask was immediately sealed with rubber cork.

Pump was turned on after 20 seconds were passed form the time of dropping ammonia and was kept on for 20 seconds. This helped in removing all the ammonia vapor present inside the flask. 10 second gap was maintained between turning off pump and dropping next ammonia amount.

Table 4: Relation between Peaks and amount of Ammonia dropped inside the flask.

Peak	Drop Amount	Vapour PPM
1	10 µl	28
2	20 µl	56
3	40 µl	111
4	60 µl	167
5	80 µl	222
6	100 µl	278

Result and Discussion

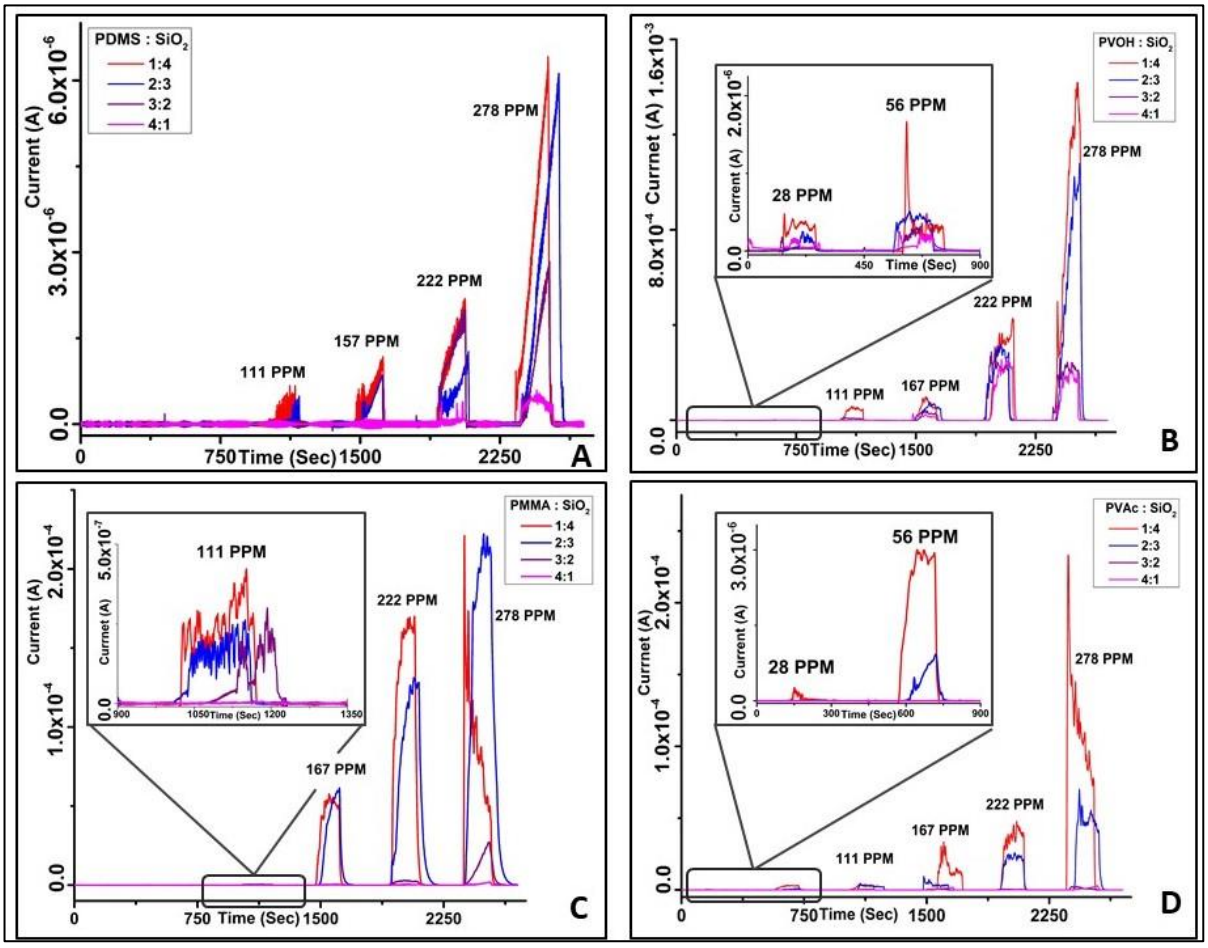

Figure 26: Current vs concentration of Ammonia fumes. A: Sensors developed using PDMS polymer. B: Sensors developed using PVOH polymer. C: Sensors developed using PMMA polymer. D: Sensors developed using PVAc polymer.

It can be seen in Figure 26, conductivity of the sensors increased in the presence of Ammonia fume. This increased conductivity was found to be dependent on the concentration of ammonia fumes, more current observed for 278 PPM compared to 111 PPM. Sensitivity of sensors was dependent on the concentration of SiO_2. Sensors developed using PVOH and PVAc were able to sense Ammonia at 28 PPM and 56 PPM concentrations with current in the range of microamperes. Sensors developed using PDMS and PMMA started sensing form 111 PPM concentration of Ammonia fumes.

For comparison of sensing, peaks at 278 PPM of sensors developed at polymer to SiO_2 ratio of 1:4 are compared (Figure 27). Sensor developed using PDMS had current in microampere, current observed for sensors of PVOH, PMMA and PVAc was in milliampere range.

Hypothesis of Mechanism: Metal oxide-based semiconductor sense a gas present in the surrounding environment based on electronic current variation, where external gas present donate or accept electrons from the sensing materials and accordingly there will be an increase or drop of electronic current. But due to band gap energy of about 8.9 eV, SiO_2 also

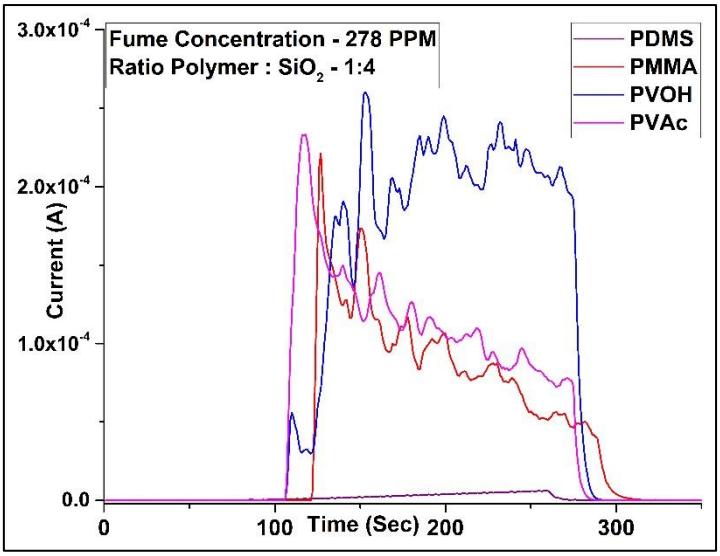

Figure 27: Comparison of current observed for sensors of different polymers at 278 PPM concentration

known as silica, shows good insulator characteristics. So, it is absurd to expect a sensing mechanism based on electronic current variation. Therefore, an ionic current variation mechanism is being proposed and has to be investigated further, which can be satisfactorily adopted where protons are transported through a Grotthuss like hoping process as well as by vehicle mechanism in a Hydrogen bonded network.

Surfaces of amorphous silica are covered by silanol unit and it can interact with the molecules present in the nearby environment through a Hydrogen bonding interaction where silanol group donates proton to the adsorbed molecules (ammonia in this case) [55]. Due to the delocalization of lone pare of oxygen of silanol group due to pi bonding interaction with vacant d orbitals of silicon atoms of both silanol group and adjacent silicon nonbonded atom, shifts the bonding electron towards oxygen resulting in more positive character protons (H in III more partially positive).

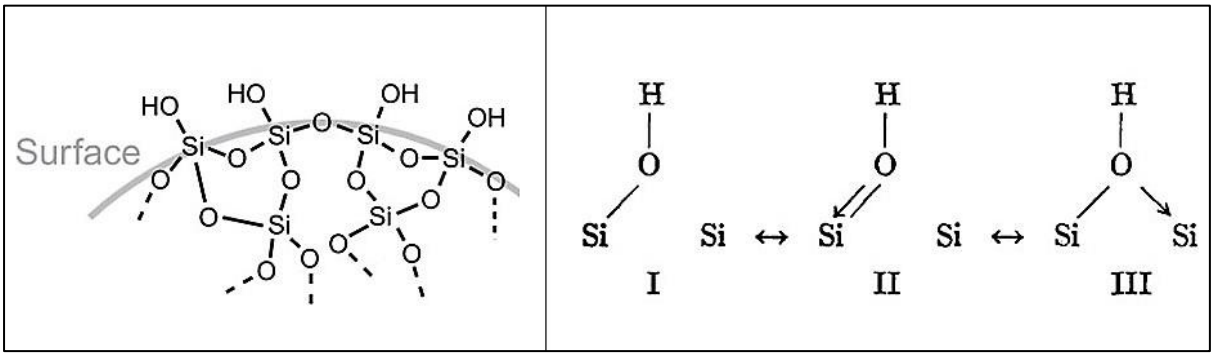

Figure 28: Presence of Silanol group at the surface of Silica. Resonance between silanol group and adjacent silicon atom (H in III is more partially positive compared to H in I.)

This makes an active site for H bonding with lone pare of Ammonia. Thus, Ammonia molecules are adsorbed on the silanol groups through H-bonding interaction and they are assumed to be present as $(NH3)_nNH_4^+$/SiOH adsorbates. The proton transport is assumed to result from proton diffusion along these $(NH3)_n$ chains by means of a Grotthuss like mechanism, proton hopping or rearranging from or with adjacent molecules.

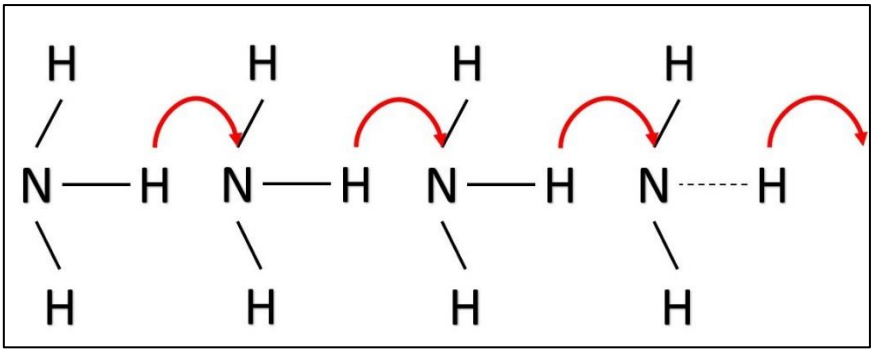

Figure 29: Grotthuss mechanism, proton hopping in chain of Ammonia molecules.

Proton in Silanol groups present near the anode gets more partially positive initiating hydrogen bonding with ammonia in surrounding resulting in flow of charge.

Future Scope

Ammonia sensing ability of sensors developed using four different polymers was studied, where sensors developed using PVOH showed good response compared to other polymers. An optimized balance between the viscosity of ink, concentration of SiO_2 and choice of polymer can be used for developing Ammonia Gas Sensors. Mechanism responsible for conductivity in presence of ammonia fumes has to be investigated by characterization of ink and surface analysis of sensor. Repeatability test by installing heater behind the ammonia sensor is under progress. The proposed mechanism presents a possibility of sensing not only ammonia but also moisture in the surrounding.

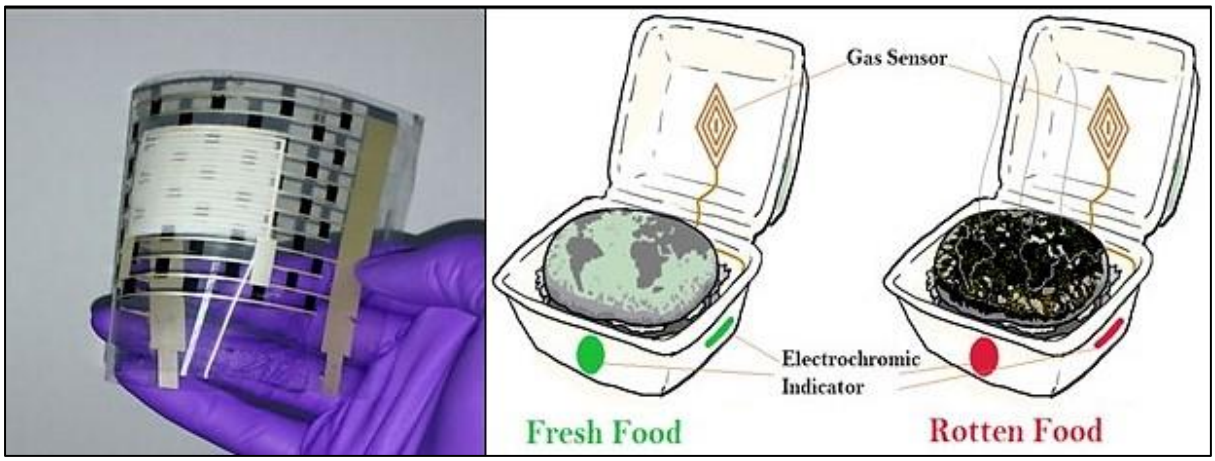

Figure 30: Ammonia sensor installed with Heater. And application in food packaging.

Mechanism of this sensor is under investigation in collaboration with Prof. Kalyan Raidongia (Dept. of Chemistry, IIT Guwahati). Study of area vs. sensing in order to optimise size of the sensor, and moisture sensing is being done at G-Labs Innovation Pvt Ltd for applications in industries, as component of IoT for environmental monitoring, and quantifying flow of gas in pipelines and in lab setups. Patent filing is under process for Ammonia Gas Sensor.

Section C

Development of Electrochromic Ink

This ink is being developed for applications such as smart windows which can control the light and solar energy passing through it, for Electrochromic displays and colour changing decorative sheets. This section presents the test performed and under progress for development of Electrochromic Display.

Materials and Methods

Tungsten Oxide was used for development of Electrochromic ink with Poly Methyl Methacrylate (PMMA) for polymer matrix. PMMA solution was prepared by mixing PMMA into Toluene in ratio 1:4 (by weight) for 30 min at 40^{o}C. Later, WO_3 powder was added in ratios, 3:7, 1:1 and 7:3 with PMMA solution.

Experiment

Strips of WO_3 Inks was screen printed in between two electrodes and were tested for change in colour under different pH environment.

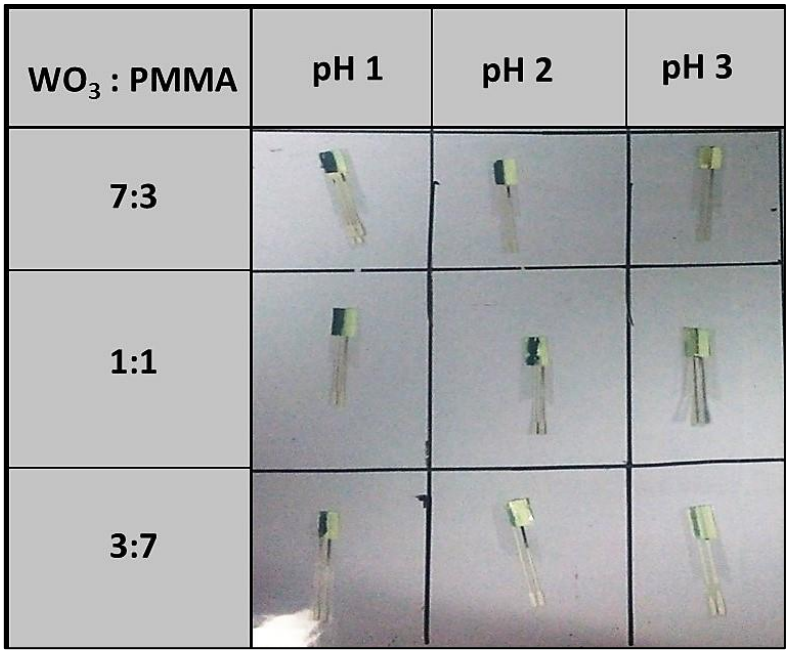

Figure 31: Strips after change in colour under different pH environment.

Many transition metal oxides show electrochromic and thermochromic behaviour. Reversible change of colour results from change in state when EC material goes under redox

reaction. For strip with higher concentration of WO_3, colour intensity is high. Also, colour intensity was found to be high for strips subjected to lower pH, which is because of increased ion presence in the surrounding.

Figure 30 shows snapshots of colour changing strip of WO_3: PMMA at 7:3 ratio, submerged into solution of pH 2 and 5 V DC applied across the electrodes.

Future Scope

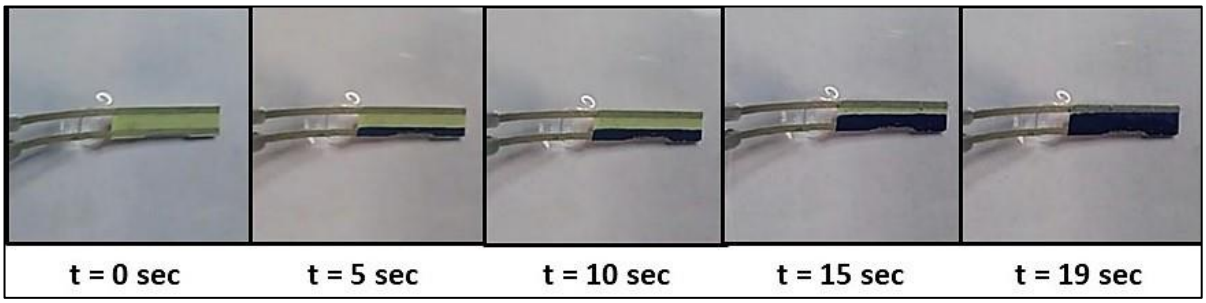

Figure 32: Snapshots of video showing colour change of a WO_3 strip under 1 pH at 5 V. https://youtu.be/3V5eLu9WZBc

Display device require reversibility in change of colour. Therefore, a layer mechanism similar to that of cell/battery has to be developed which may be beneficial for reversibility of colour. Difference in material characteristics among two states has to be studied for better understanding of colour change mechanism.

Annexure

1. A provisional patent at Indian Patent office, Pune has been filed for the Heater reported in this Thesis, **IP application number 201831004095** and patent for Gas sensor is under process.
2. Flexible heater was presented at Bright Idea Competition held in **Innovation and Entrepreneurship Exhibition and Workshop** organized by **DSIR-PRISM-TOCIC IIT Guwahati** and was awarded with **Second Prize** in the competition.
3. Flexible Heater was also honored with **1st prize in Model Presentation** at Research Conclave' 18, organised by Students' Academic Board, IIT Guwahati.
4. Poster presenting work done on Ammonia Gas Sensor was honored with **Best Poster presentation** at Research Conclave' 18, organised by Students' Academic Board, IIT Guwahati.

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