# Development of Bio-FET sensor for the detection of boron

A Thesis

Submitted in the partial fulfilment of the requirement for

Award of the degree of

MASTER OF SCIENCE

IN

BIOTECHNOLOGY

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

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JULY 2019

# DECLARATION

I, the under designed, hereby declare that the research work presented in the thesis entitled “Development of Bio-FET sensor for the detection of Boron” in partial fulfilment of the requirement for the award of the degree of Masters of Science in Biotechnology, Department of Biotechnology (DBT), Thapar Institute of Engineering and Technology, Patiala, is an authentic record of my work during the period of six months from January 2019 to July 2019 under the supervision and guidance of Moushumi Ghosh, Professor and Head of the Department of Biotechnology & Arun Kumar Chatterjee, Assistant Professor, ECED, Thapar Institute of Engineering and Technology, Patiala. Further, I declare that no part of this dissertation has been submitted for a degree or any other qualification of any university or examining body in India/elsewhere.

Sayantani.

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Place: - Patiala

# CERTIFICATE

This is to certify that dissertation entitled, “Development of Bio-FET sensor for the detection of Boron” submitted by Ms Sayantani Bhattacharya in partial fulfilment of the requirements for the award of M.Sc. Biotechnology at Thapar Institute of Engineering and Technology, Patiala is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this dissertation has not been submitted to any other university/institute for award of any Degree or Diploma.

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# ACKNOWLEDGEMENT

I would first like to thank my thesis advisor Prof. Moushumi Ghosh of the Department of Biotechnology at Thapar Institute of Engineering and Technology, Patiala. The door to Prof. Ghosh office was always open whenever I ran into a trouble spot or had a question about my research or writing. I am indebted to Prof. Ghosh for being Supportive to my career goals and worked actively to provide me with the protected academic time to pursue those goals. As my teacher and mentor, she has taught me more than I could ever give her credit for here. She has shown me, by her example, what a good scientist (and person) should be.

I would also like to thank my co-guide who helped me in the validation survey for this research project: Arun Kumar Chatterjee, Assistant Professor, and Madhu K Chatterjee, Lecturer, of the Department of Electronics and Communication Engineering, Thapar Institute of Engineering and Technology, Patiala. They helped and encouraged me during my dissertation period in research as well as in thesis writing.

I am grateful to all of those with whom I have had the pleasure to work during this. Each of the members of my Dissertation Committee has provided me extensive personal and professional guidance and taught me a great deal about both scientific research and life in general.

Nobody has been more important to me in the pursuit of this project than the members of my family. I must express my very profound gratitude to my parents for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

I am indebted to laboratory staff Mr Babban for his kindly help and assistance while completing this project.

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# Abstract

Boron is an essential micronutrient for the plants and plays a major role in development of animals and human. The rise in industry of glass, ceramic, cosmetic, soaps, and detergent caused emission of larger amount of boron into the atmosphere, soil, and water. On exposure to this excess boron, the living beings are suffering from serious health hazards and this is also causing death of the plants. Several methods have been implemented to determine their concentration such as spectrophotometric methods, but these methods suffer as they’re not very sensitive and precise, require large sample volume, sophisticated instrument, and are expensive. This lead to develop a sensor that will overcome the drawbacks of earlier method of boron determination. Bio-FET sensor was then designed on SILVACO TCAD tool based on the doping concentration of boric acid into different biopolymers to check for small change in dielectric and large change in threshold voltage of the sample solution.

**Keywords: -** Bio-FET, Capacitance, Dielectric Constant, JL-MOSFET, Threshold Voltage

# List of Symbols

| | |
|---|---|
| ºC | Degree(s) Celsius |
| hr | Hour |
| ml | Millilitre |
| mg/ml | Milligram per litre |
| µl | Microliter |
| nm | Nanometre |
| pF | Pico Farad |
| g/l | Gram per litre |
| mg/l | Milligram per litre |
| $\varepsilon$ | Permittivity |
| $\varepsilon_{\circ}$ | Permittivity of Free space |
| k | Dielectric Constant |
| A | Area |
| d | Thickness |
| µS | Micro Siemens |
| cm$^3$ | Cubic Centimetre |
| B | Boron |
| pH | Power of Hydrogen |
| mg/kg | Milligram per kilogram |
| mM | Milli Molar |

# List of Abbreviations

| | |
|---|---|
| BIS | Bureau of Indian Standards |
| PVA | Polyvinyl alcohol |
| JL | Junctionless |
| MOSFET | Metal Oxide Semiconductor Field Transistor |
| ED | Electronic Dialysis |
| CMOS | Complementary Metal Oxide Semiconductor |
| ISFET | Ion Sensitive Field Effect Transistor |
| DMFET | Dielectric Modulated Field Effect Transistor |
| AES/AAS | Atomic Emission/Absorption Spectrometric |
| TIMS | Thermal ionization mass spectrometry |
| SIMS | Secondary ion mass spectrometry |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| FET | Field Effect Transistor |
| hs-CRP | High-sensitivity C-reactive protein |
| TNF-α | Tumour necrosis factor α |
| SOD | Superoxide dismutase |
| SAM-e | *S*-adenosyl methionine |
| $NAD^+$ | Nicotinamide adenine dinucleotide |
| GSH | Glutathione |
| MDA | Malondialdehyde |
| CAT | Catalase |
| TAS | Total antioxidant status |
| MTT | 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide |
| CPs | Conductive Polymers |
| PS | Polystyrene |
| DVB | Divinylbenzene |
| NMDG | *N*-methyl-D-glucamine |

| | |
|---|---|
| DIBL | Drain-induced barrier lowering |
| AC | Alternating Current |
| DC | Direct Current |
| EDLC | Electric double-layer capacitors |
| mins | Minutes |
| IM | Inversion Mode |
| $MP_1$ | Microbial Polymer 1 ($X_4$) |
| $MP_2$ | Microbial Polymer 2 ($W_1b$) |

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# Chapter 1

# Introduction

## BORON

Boron is a trace micronutrient mineral which is ubiquitous in the environment in the form of tetraborates of sodium or calcium. Boron has a vital role in metabolism of plants, animal, and human health. Commonly occurring boron compounds include boron oxide, boric acid, borax, borides, boron hydrides, boron nitrides, polyhedral boranes, and boron halides (e.g., boron trichloride and boron trifluoride).

### Sources of boron in environment

Water: - There are two sources of Boron in water: -

a) **Natural Source: -** Boron is present in water due to weathering of rocks, mineralization of boron in silts, volatilization of seawater, volcanic and geothermal activity, etc.

b) **Anthropogenic Source: -** Boron contamination in water is due to discharge of effluents from several glass, ceramic, soaps and detergent industry, etc.

Soil: - Boron is taken up by the plants in the form of: -

1) Boric acid and borate ions in soil solution.

2) Adsorption of boron to the soil particles such as clay minerals, organic matter, oxides of aluminium or iron.

3) As a mineral component.

Plants and Animals: - Plants are exposed to boron by means of: -

1) Agricultural fertilizers.

2) Directly release into the soil by the decomposition of dead parts of plants which has fallen off in the soil.

Animals get exposed to boron by means of fruits, vegetables, water, air, and animals that feed upon plants. Consumption of large quantities of boron may cause serious health hazards like failure of the vital organs consequently leading to death of the organism.

Due to emerging industry of glass, ceramic, combustion of coal etc. the boron emission into the environment has increased. The excess boron then enters the food cycle, and cause serious diseases to plants, animals and humans. To check for the rise in levels of boron in the atmosphere several methods has been implemented.

Boron has been quantified using spectrophotometric methods such as plasma-source spectrometric, nuclear reaction and atomic emission/absorption spectrometric (AES/AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), Thermal ionization mass spectrometry (TIMS) and secondary ion mass spectrometry (SIMS) methods. Spectrophotometric methods work on the principle of colorimetric reactions of boron with azomethine-H, curcumin, or carmine, besides several colorimetric and fluorometric methods were also been used to some extent. These above mentioned methods have several drawbacks like low sensitivity and precision, require large sample volume, highly sophisticated equipment, time consuming and require extensive sample preparation and purification etc.

This lead to develop a sensor that overcomes all the drawbacks of above mentioned boron detecting instrument.

### Metal Oxide Semiconductor Field Effect Transistor

MOSFET is a device which has 4 terminals i.e. source, gate, drain, and body. MOSFET resembles field effect transistor when its body is connected to the source terminal. It works on the principle of varying the channel width electronically when charge carriers flow in the form of electrons or holes. The charge carriers enter the channel via source and exit through drain. The channel width is regulated at the gate terminal present in between the source and drain by the voltage applied on gate. Gate terminal is separated from the channel region by a thin layer of metal oxide. The MOSFET can function in two ways**:-**

(1) **Depletion Mode: -** Channel shows maximum conductance, when voltage is not applied on the gate terminal. The channel conductivity decreases, as the gate voltage is positive or negative.

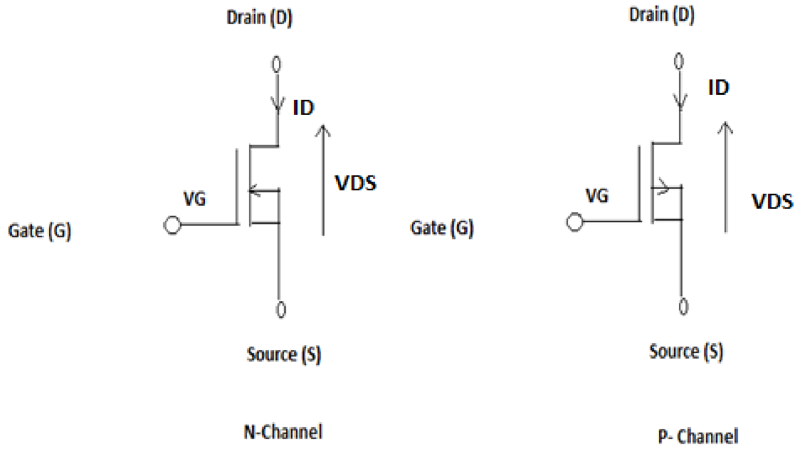


Fig 1.1:- Depletion mode MOSFET. [1]

(2) **Enhancement Mode**: - The device does not conduct when gate voltage is not applied. The device conduct well when there is maximum voltage applied on the gate terminal.

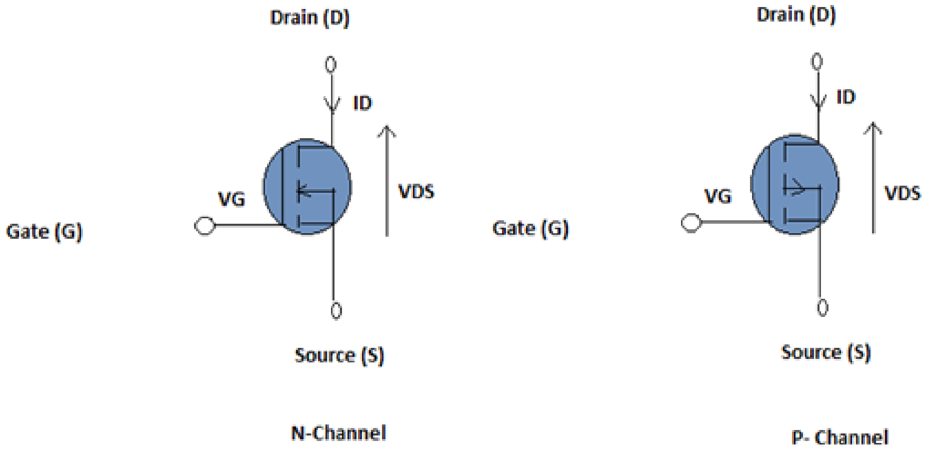


Fig 1.2: - Enhancement mode MOSFET. [1]

**Working: -** The principle of MOSFET device is to regulate current flow and gate voltage in the channel region. Working of MOSFET requires MOS capacitor which has a below oxide layer in the channel region. It can be inverted back by changing the positive or negative voltage applied to the gate terminal into p-type or n-type. When positive gate voltage is applied, holes that is present under the oxide layer starts moving down with repulsive forces along with substrate.

## Junction less MOSFET

It is a device without source/ drain junctions and extension regions by appropriate design of the thickness of the silicon body and can switch on and off under control of the gate biases. The major differences between JL MOSFETs and conventional inversion mode MOSFETs are the body doping type (n-type body doping for n-type JL MOSETs and p-type body doping for conventional n-type MOSFETs) and the conduction mode. (Jin et al., 2013)

A junctionless transistor is basically an accumulation mode device in which the channel doping concentration is equal to that on the source and drain. The electrical characteristics of both conventional ($N^+$-P-$N^+$) and junctionless ($N^+$-$N^+$-$N^+$) devices were simulated using the Atlas 3-D device simulator. (Lee et al., 2009)

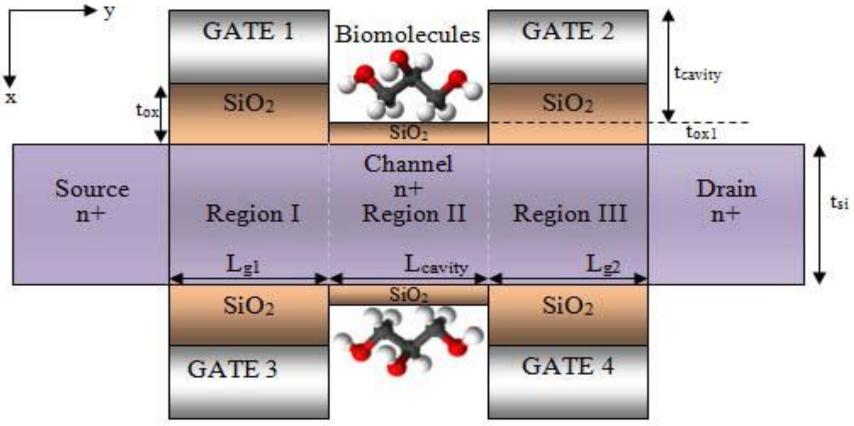


Fig 1.3: - Setup of a Bio-FET. [34]

Bio-FET is a device that is based on detecting changes in electrostatic potential due to binding of an analyte. The choice of reference electrode (liquid gate) or back-gate voltage determines the carrier concentration within the field effect transistor, and thereby its region of operation, therefore the response of the device can be optimized by tuning the gate voltage. The response is often reported as the change in current on analyte binding divided by the initial current ($\Delta I/I_0$). One optimization of Bio-FET may be to put a hydrophobic passivation surface on the source and the drain to reduce non-specific biomolecular binding to regions which are not the sensing-surface.

## Parameters of MOSFET sensor

In MOSFET sensor, scaling of channel length shows increasing opposition as, leakage current and short channel currents increases when control efficiency of the gate decreases on the channel of the device. JL transistor is a resistor having a uniform doping concentration across the source, channel, and drain. The lack of doping concentration gradient eradicates impurity diffusion and sharp doping profile formation. Electrical parameters of MOS devices (e.g., threshold voltage shift, increase of leakage current, and reduction of mobility) are varied when there is increase in temperature. All DG-MOSFETs are either un-doped or lightly counter-doped are junctionless when channel doping is of same type as source and drain. When junctionless device is fabricated with high impurity concentration in the channel and source/drain regions have many advantages such as nearly ideal sub-threshold slope, high ON/OFF current ratio, low source/drain series resistance, and small DIBL.

The Junctionless transistor is doped constantly and uniformly throughout SOI resistor in the range of $10^{17}$ to $10^{23}$ $cm^{-3}$ respectively with a MOS gate that controls current flow. DG JL MOSFET works on bulk conduction instead of surface channel region. The sub-threshold region having the highly doped channel is depleted fully; thereby holding a large electric field. When the gate voltage is increased, and becomes equal to flat band voltage, electric field in the channel is reduced until neutral channel region is achieved in the underlap region. During the onset of increasing voltage, bulk current reaches up to maximum peak. On further, increasing the gate voltage, negative charges gets accumulated on the channel surface. These charges results in surface current, similar to n-channel DGL FET. Though, surface current for bulk current flows at higher gate voltage than the gate voltage.

## Scope of the study:

The above deliberation indicates that an approach using biological materials especially polymers from microbial sources may be important in designing sensors. The biopolymers however should have qualifying attributes such as conductivity, stability and most importantly capability of binding with boron. Accordingly, the main objectives of the present study were framed as follows:

## Objectives

The main objectives of this study are

1) Screening of suitable conducting microbial polymers from Biopolymer Library.
2) Design of Bio-FET for detection of Boron.
3) Optimization of parameters for boron doping on Biopolymer matrix in simulated system.
4) Predictive modeling of Boron chelation by biopolymer for evaluation of efficacy of designed sensor.

# Chapter 2

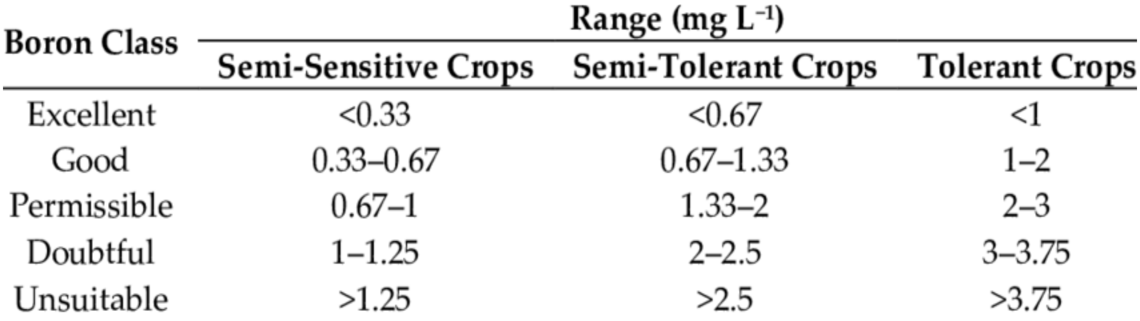
# Review of Literature

Boron dissolved in surface and ground water is present in the concentration levels of 0.3–100 mg/L and maybe higher, depending upon anthropogenic and geothermal activity. The boron concentration recommended for drinking water according to the World Health Organization guidelines is up to 2.4 mg/L (*Kluczka* et al. 2018).

## 2.1 Importance of Boron in Plants

Boron is involved in the structural and functional integrity of the cell wall and membranes, ion fluxes ($H^+$, $K^+$, $PO_4^{3-}$, $Rb^+$, $Ca^{2+}$) across the membranes, cell division and elongation, nitrogen and carbohydrate metabolism, sugar transport, cytoskeletal proteins, and plasmalemma-bound enzymes, nucleic acid, indoleacetic acid, polyamines, ascorbic acid, and phenol metabolism and transport. Boron starvation dramatically inhibits root elongation, with deformed flower and fruit formation due to impaired cell division in the meristematic region, whereas adequate boron supply promotes advantageous root development (*Shireen* et al. 2018)

The adequacy range for boron in leaf tissue is from 10 to 50 mg/kg (ppm) of the dry weight. It has been observed that boron accumulates in the leaf margins at concentrations 5 to 10 times that in the whole leaf blade. Average boron content in the soil is considered to be 30ppm. Consequently plants need trace amounts of boron but it becomes toxic at 20 ppm or greater for most plants. (*Gupta,* 2013)



| Boron Class | Range (mg $L^{-1}$) | | |
|---|---|---|---|
| | Semi-Sensitive Crops | Semi-Tolerant Crops | Tolerant Crops |
| Excellent | <0.33 | <0.67 | <1 |
| Good | 0.33–0.67 | 0.67–1.33 | 1–2 |
| Permissible | 0.67–1 | 1.33–2 | 2–3 |
| Doubtful | 1–1.25 | 2–2.5 | 3–3.75 |
| Unsuitable | >1.25 | >2.5 | >3.75 |

Fig 1.4:- Permissible limits of Boron in irrigation water for crops. [57]

### 2.1.1 Boron Toxicity in Plants

Boron (B) is unique among the micronutrients because of the narrow range of soil B levels between deficiency and excess (toxicity). A fraction of one part per million in the soil solution is all that is required for sufficiency, and several parts per million can be toxic. (*Dixon*, 1988)

Typical visible toxicity symptoms are generally restricted to older leaves as a yellowing, spotting, or drying of leaf tissue at the tips and edges. In boron-immobile species, these symptoms then spread among the lateral veins toward the midrib because of B accumulation transported through the transpiration stream. (Nable et al., 1997; Reid et al., 2004; Reid and Fitzpatrick, 2009)

Fig 1.5:- Effect of Boron Toxicity on Plants. [9]

### 2.1.2 Boron Deficiency in Plants

**Conditions leading to deficiency**: - Boron is more easily percolated from the soil than other trace elements and its deficiencies are normally related to high rainfall areas as well acid soil conditions. As boron is more water soluble, it can therefore be leached below the root zones of plants by rainfall or irrigations. Because of these sandy or free-draining lightly textured soils in high rainfall areas are more likely to be deficient. Moreover, availability of B decreases under drought conditions and as a consequence of a rising alkalization of the soil. Soil lows in organic matters are more prone to boron deficiency because available boron is released from organic matter as it breakdowns.

Boron deficiency symptoms are an expression of sugar deficiency in the cambia, stem tips, root tips, flowers and fruits. Death of terminal buds directly affects the growth of lateral shoots, the tips of which may also be deformed or die leaving a rosette on the plant called “witches broom” condition. Leaves usually become thick, have a coppery texture and become curled and brittle and the growth of young leaves is inhibited. Tissue of boron deficient plants often breaks down prematurely, causing brown flecks, necrotic spots, cracking and corky areas in fruit and tubers. Hampers flowering and fruiting by retarding pollen germination and pollen tube development processes. B deficiency reduces fertility and fruit development becomes slow or non-existent. B deprivation harms numerous processes like cell wall synthesis, lignification, cell wall structure, mitosis and cell elongation, along with of cell differentiation and development is badly affected and eventually brings about cell death due to boron deficiency. (*Gupta*, 2013)

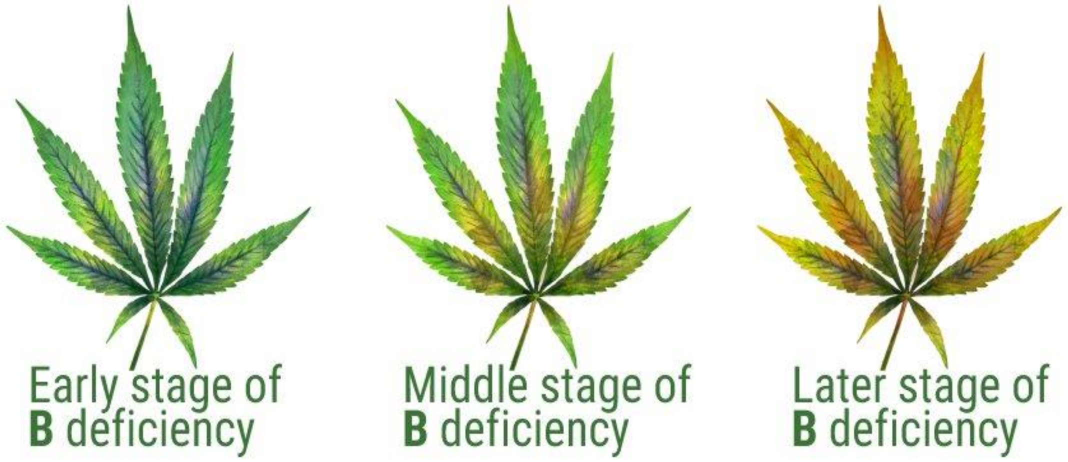


Fig. 1.6:- Stages of Boron deficiency in *Cannabis* leaf. [8]

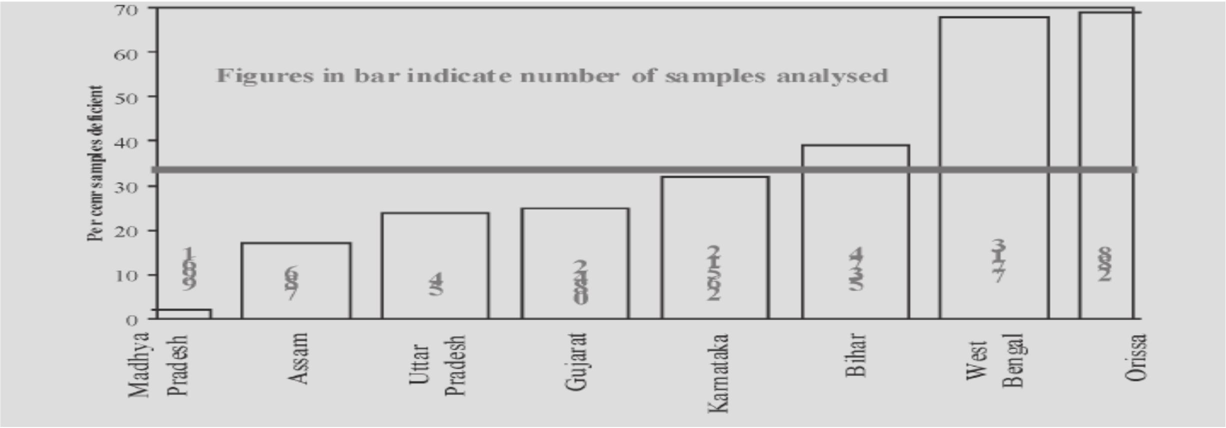


Fig. 1.7:- Extent of Boron deficiencies in different states. [45]

## 2.2 Importance of Boron in Humans & Animals

Boron has been proven to be an important trace mineral because it:-

(1) Is essential for the growth and maintenance of bone;
(2) Greatly improves wound healing;
(3) Beneficially impacts the body’s use of estrogen, testosterone, and vitamin D;
(4) boosts magnesium absorption;
(5) Reduces levels of inflammatory biomarkers, such as high-sensitivity C-reactive protein (hs-CRP) and tumor necrosis factor α (TNF-α);
(6) Raises levels of antioxidant enzymes, such as superoxide dismutase (SOD), catalase, and glutathione peroxidase;
(7) Protects against pesticide-induced oxidative stress and heavy-metal toxicity;
(8) improves the brains electrical activity, cognitive performance, and short-term memory for elders;
(9) Influences the formation and activity of key biomolecules, such as *S*-adenosyl methionine (SAM-e) and nicotinamide adenine dinucleotide ($NAD^+$);
(10) Has demonstrated preventive and therapeutic effects in a number of cancers, such as prostate, cervical, and lung cancers, and multiple and non-Hodgkin’s lymphoma; and
(11) May help ameliorate the adverse effects of traditional chemotherapeutic agents.

Animal studies published in 2008 and 2009 found that healing of the alveolar bone—a ridge of compact bone that contains the tooth sockets on the maxillae and mandible (i.e., the bones that hold teeth)—was inhibited in boron-deficient rats. Boron was determined to induce mineralization of osteoblasts by regulating the expression of genes related to tissue mineralization and the actions of key hormones (17β-estradiol [$E_2$], testosterone, and vitamin D) involved in bone growth and turnover.

Application of a 3% boric acid solution to deep wounds reduced the time required in intensive care by two-thirds. In 2000, in vitro research using human fibroblasts showed that a boric-acid solution improved wound healing through action on the extracellular matrix. In vitro studies published in 2002 revealed that these beneficial effects of boron were due to direct actions on specific enzymes found in fibroblasts: elastase, trypsin-like enzymes, collagenase, and alkaline phosphatase. (*Pizzorno*, 2015)

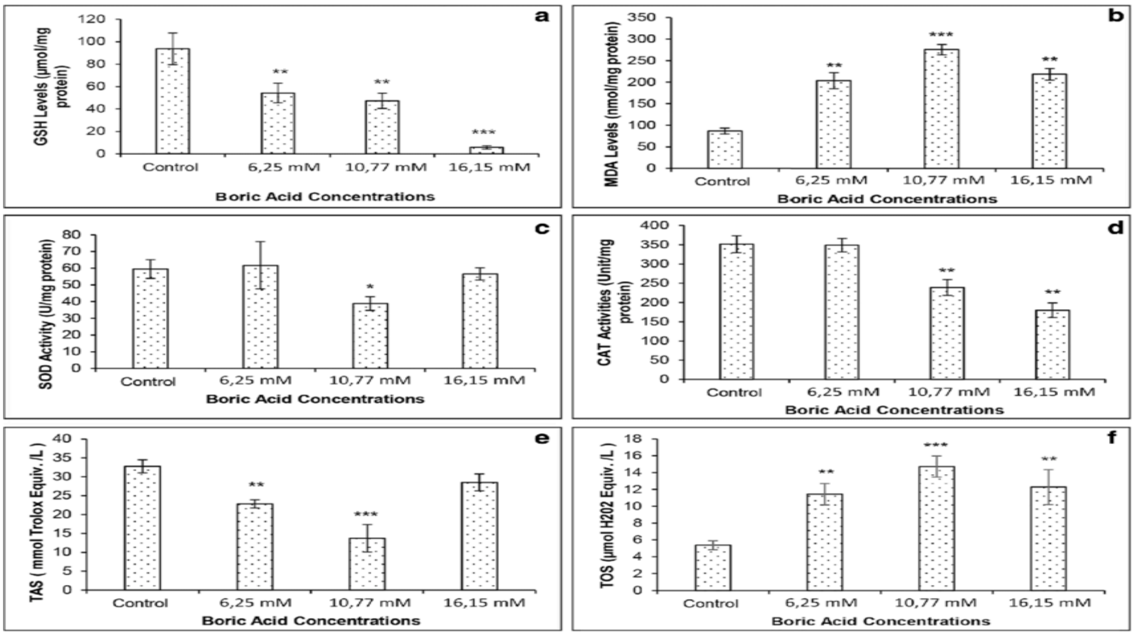


Fig 1.8: - Antioxidant and oxidant molecule levels in DU-145 prostate cancer cell treated with boric acid. A) Glutathione (GSH) levels. B) Malondialdehyde (MDA) levels. C) Superoxide dismutase (SOD) activity. D) Catalase (CAT) activity. E) Total antioxidant status (TAS). F) Total oxidant status (TOS). [21]

### 2.2.1 Impact of Boron toxicity on Humans & Animals

The acute lethal dose of boric acid is 3000-6000 mg for infants and 15,000-20,000 mg for adults. Clinical effects include irritability, seizures and gastrointestinal disturbances. Inflammation, congestion, exfoliation of the Mucosa, exfoliative dermatitis, findings of cloudy swelling and granular degeneration of renal tubular cells and oedema. Boron compounds are toxic to all species tested at high doses, but they are not mutagenic or carcinogenic. The major chronic toxicities are developmental and reproductive. The reported developmental toxicities occurring after boron exposure include high prenatal mortality, reduced foetal body weight, cardiovascular system, central nervous system, malformations of the eyes, cardiovascular system, and axial skeleton**.** (*Bakirdere et al.* 2010).

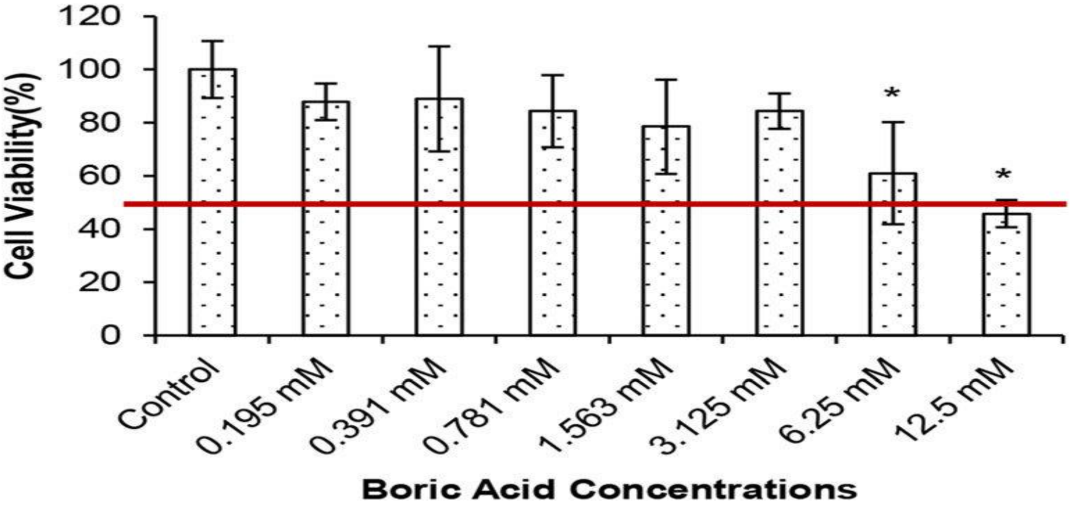
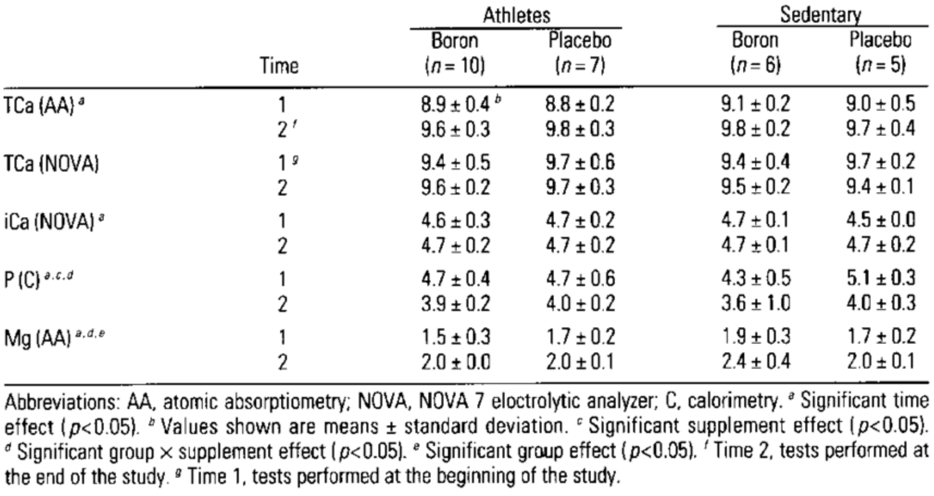


Fig 2.1: - Cell viability percentages v/s ascending boric acid concentrations according to the MTT assay results. [21]

### 2.2.2 Boron deficiency in Humans & Animals

Boron deficiency symptoms have been seen in rats, chickens, and humans. Boron deprivation in animals leads to impaired growth and abnormal bone development. Deprivation in humans and animals causes increased urinary calcium excretion. Other boron deficiency symptoms may result from an altered macro mineral status. For example, **boron deficiency exacerbates the signs of vitamin D3 deficiency** (e.g., abnormal bone formation and poor growth). A low-magnesium diet exacerbated the deficiency symptoms of boron in rats, resulting in reduced growth and enlarged kidney and spleen as determined by ratio of organ to body weight.

Table 1:- Pre-and post-test blood calcium (mg/ DI) [35]



| | | Athletes | | Sedentary | |
|---|---|---|---|---|---|
| | Time | Boron (*n* = 10) | Placebo (*n* = 7) | Boron (*n* = 6) | Placebo (*n* = 5) |
| TCa (AA) [a] | 1 | 8.9 ± 0.4 [b] | 8.8 ± 0.2 | 9.1 ± 0.2 | 9.0 ± 0.5 |
| | 2 [f] | 9.6 ± 0.3 | 9.8 ± 0.3 | 9.8 ± 0.2 | 9.7 ± 0.4 |
| TCa (NOVA) | 1 [g] | 9.4 ± 0.5 | 9.7 ± 0.6 | 9.4 ± 0.4 | 9.7 ± 0.2 |
| | 2 | 9.6 ± 0.2 | 9.7 ± 0.3 | 9.5 ± 0.2 | 9.4 ± 0.1 |
| iCa (NOVA) [a] | 1 | 4.6 ± 0.3 | 4.7 ± 0.2 | 4.7 ± 0.1 | 4.5 ± 0.0 |
| | 2 | 4.7 ± 0.2 | 4.7 ± 0.2 | 4.7 ± 0.1 | 4.7 ± 0.2 |
| P (C) [a,c,d] | 1 | 4.7 ± 0.4 | 4.7 ± 0.6 | 4.3 ± 0.5 | 5.1 ± 0.3 |
| | 2 | 3.9 ± 0.2 | 4.0 ± 0.2 | 3.6 ± 1.0 | 4.0 ± 0.3 |
| Mg (AA) [a,d,e] | 1 | 1.5 ± 0.3 | 1.7 ± 0.2 | 1.9 ± 0.3 | 1.7 ± 0.2 |
| | 2 | 2.0 ± 0.0 | 2.0 ± 0.1 | 2.4 ± 0.4 | 2.0 ± 0.1 |

Abbreviations: AA, atomic absorptiometry; NOVA, NOVA 7 electrolytic analyzer; C, calorimetry. [a] Significant time effect ($p<0.05$). [b] Values shown are means ± standard deviation. [c] Significant supplement effect ($p<0.05$). [d] Significant group × supplement effect ($p<0.05$). [e] Significant group effect ($p<0.05$). [f] Time 2, tests performed at the end of the study. [g] Time 1, tests performed at the beginning of the study.

- Increase in oxidative system, DNA damage, impairment of DNA repair systems and membrane functions, or the inhibition of protein folding, protein function and activities.
- Boron deprivation results in impairment of growth, abnormal bone development, decrease in blood steroid hormone levels, increase in urinary calcium excretion, and changes in macro-mineral status in humans and animals.
- In animals and humans, boron deficiency is also related to the decrease in the electrical activity of brain, short term memory, and decrease in skills in performing tasks whereas the boron supplementation increases brain functions.
- Humans consume boron daily, mostly from fruits and vegetables. When consumed at high doses, it can cause developmental and reproductive abnormalities.

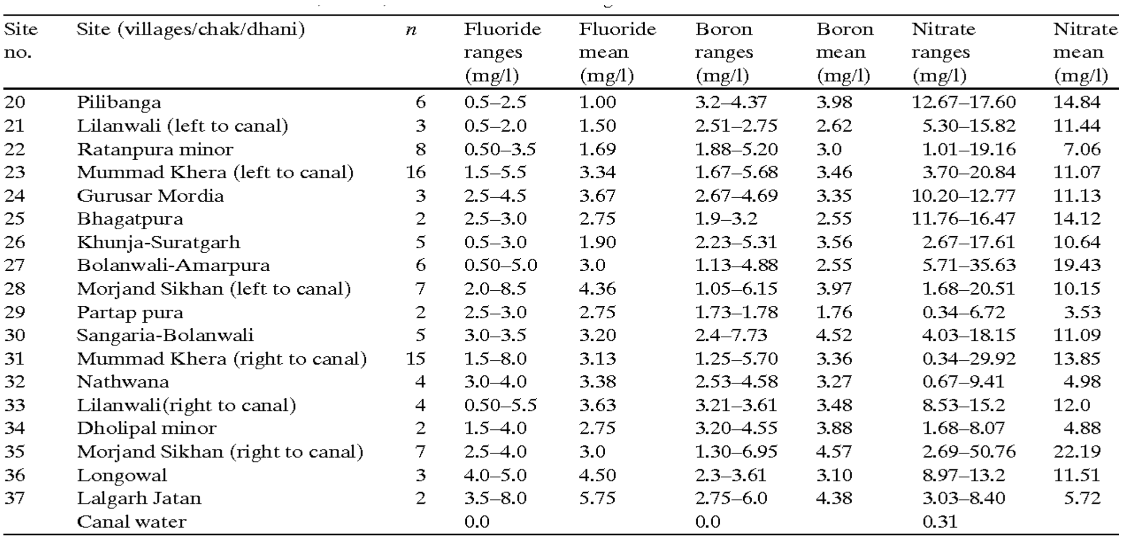
### 2.3 Boron Contamination

Fig 2:- Boron Contamination in River Yamuna and Groundwater in Parts of Delhi in 2014. [48]

- The re-sampling of some of the isolated patch of high Boron levels in 2014 revealed that the high Boron concentration has generally persisted.
- Hence, it can be suggested that the anomalously high Boron concentration in Palla is most likely a localized phenomenon.

- One of the possible reasons for this could be attributed to infiltration of contaminant enriched flood waters entering aquifer through gravel packing of some of the tube wells.
- However, Boron contamination was also reported from other parts of active flood plain areas of the Yamuna River beside Palla.

Table 2:- Concentration of fluoride, boron, nitrate in different villages of Bhakra canal catchment area. [12]



| Site no. | Site (villages/chak/dhani) | *n* | Fluoride ranges (mg/l) | Fluoride mean (mg/l) | Boron ranges (mg/l) | Boron mean (mg/l) | Nitrate ranges (mg/l) | Nitrate mean (mg/l) |
|---|---|---|---|---|---|---|---|---|
| 20 | Pilibanga | 6 | 0.5–2.5 | 1.00 | 3.2–4.37 | 3.98 | 12.67–17.60 | 14.84 |
| 21 | Lilanwali (left to canal) | 3 | 0.5–2.0 | 1.50 | 2.51–2.75 | 2.62 | 5.30–15.82 | 11.44 |
| 22 | Ratanpura minor | 8 | 0.50–3.5 | 1.69 | 1.88–5.20 | 3.0 | 1.01–19.16 | 7.06 |
| 23 | Mummad Khera (left to canal) | 16 | 1.5–5.5 | 3.34 | 1.67–5.68 | 3.46 | 3.70–20.84 | 11.07 |
| 24 | Gurusar Mordia | 3 | 2.5–4.5 | 3.67 | 2.67–4.69 | 3.35 | 10.20–12.77 | 11.13 |
| 25 | Bhagatpura | 2 | 2.5–3.0 | 2.75 | 1.9–3.2 | 2.55 | 11.76–16.47 | 14.12 |
| 26 | Khunja-Suratgarh | 5 | 0.5–3.0 | 1.90 | 2.23–5.31 | 3.56 | 2.67–17.61 | 10.64 |
| 27 | Bolanwali-Amarpura | 6 | 0.50–5.0 | 3.0 | 1.13–4.88 | 2.55 | 5.71–35.63 | 19.43 |
| 28 | Morjand Sikhan (left to canal) | 7 | 2.0–8.5 | 4.36 | 1.05–6.15 | 3.97 | 1.68–20.51 | 10.15 |
| 29 | Partap pura | 2 | 2.5–3.0 | 2.75 | 1.73–1.78 | 1.76 | 0.34–6.72 | 3.53 |
| 30 | Sangaria-Bolanwali | 5 | 3.0–3.5 | 3.20 | 2.4–7.73 | 4.52 | 4.03–18.15 | 11.09 |
| 31 | Mummad Khera (right to canal) | 15 | 1.5–8.0 | 3.13 | 1.25–5.70 | 3.36 | 0.34–29.92 | 13.85 |
| 32 | Nathwana | 4 | 3.0–4.0 | 3.38 | 2.53–4.58 | 3.27 | 0.67–9.41 | 4.98 |
| 33 | Lilanwali(right to canal) | 4 | 0.50–5.5 | 3.63 | 3.21–3.61 | 3.48 | 8.53–15.2 | 12.0 |
| 34 | Dholipal minor | 2 | 1.5–4.0 | 2.75 | 3.20–4.55 | 3.88 | 1.68–8.07 | 4.88 |
| 35 | Morjand Sikhan (right to canal) | 7 | 2.5–4.0 | 3.0 | 1.30–6.95 | 4.57 | 2.69–50.76 | 22.19 |
| 36 | Longowal | 3 | 4.0–5.0 | 4.50 | 2.3–3.61 | 3.10 | 8.97–13.2 | 11.51 |
| 37 | Lalgarh Jatan | 2 | 3.5–8.0 | 5.75 | 2.75–6.0 | 4.38 | 3.03–8.40 | 5.72 |
|  | Canal water |  | 0.0 |  | 0.0 |  | 0.31 |  |

In natural conditions, Boron exists as boric acid or borate ions in groundwater. Its major controlling factors for speciation in water include pH, temperature and specific cation concentrations. In soil, it commonly occurs as borates of Calcium (Ca) and Sodium (Na), resulting from the slow dissolution from minerals such as tourmaline. It has also been noted that Boron in soils could be associated to organically bound and clay- and mineral-fixed fractions. The anthropogenic sources for Boron include effluents from glass manufacturing, ceramics, and cosmetics industries along with borate components that are used both as fertilizers to accommodate Boron deficiencies in soil and detergent industry in which Sodium Perborate (NaBO3) is added to washing powders.

Presence of dissolved Boron in high concentration can cause several problems, including phyto-toxitcity and unsuitability of water source for irrigation.

High Boron intake in human directly affects the central nervous system and is associated with symptoms such as nausea, camps, convulsions, coma etc. Realizing the potential concern related to Boron contamination, the Bureau of Indian Standards (BIS) had recently modified the maximum permissible limits for Boron concentration in drinking water from 5 to 1 mg/L. The desirable limit of Boron in drinking water was also lowered from 1 to 0.5 mg/L.(*Sarkar et al.*, 2016)

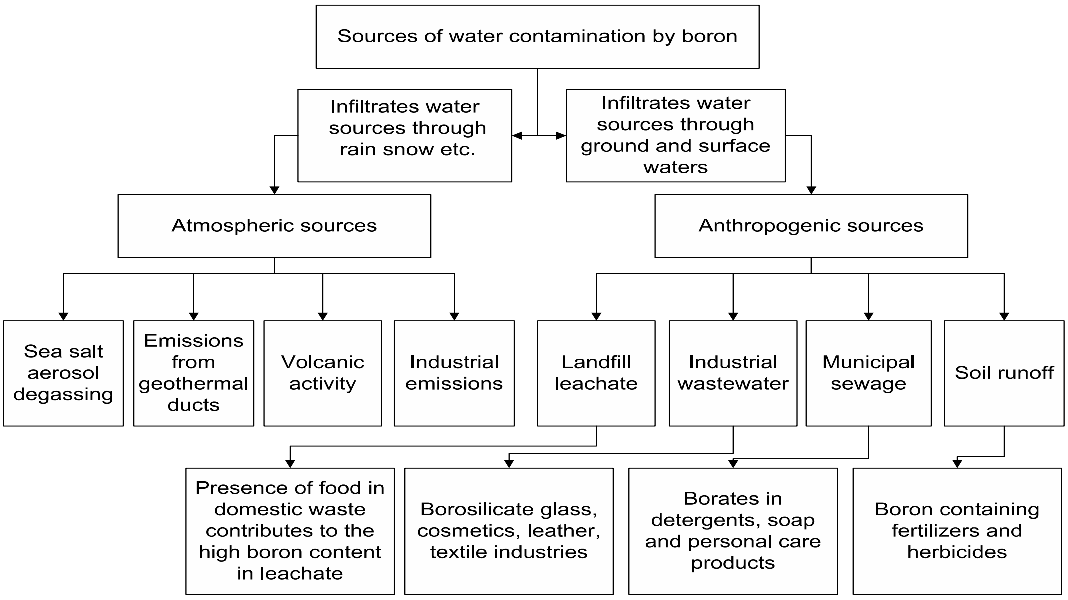


Fig 2.1:- Various sources of water contamination by Boron. [38]

## 2.4 Need for Novel Sensor for Detection of Boron

### 2.4.1 Conduction Polymers

Conductive polymers (CPs) are used in chemical and biological sensors as an immobilizing matrix for probe materials, such as enzymes, DNAs and antibodies. Conductive polymers have good compatibility with biomaterials. If conductive polymers could be combined with silicon substrate, then mass production and miniaturization of a sensing device could be possible; however, direct immobilization of a conductive polymer on a silicon Substrate is difficult because the surface of an unmodified silicon wafer is too smooth and too chemically hydrophobic to permit effective immobilization of the conductive polymer. Therefore, a metallic layer is commonly deposited on the silicon Substrate as an intermediate layer between the substrate and the conductive polymer when fabricating silicon-based sensors with conductive polymer lawns. There is a need for electro-polymerization of con ducting polymers directly on the silicon Substrate without any deposition of a metallic layer. It is therefore an object of the present disclosure to provide an improved silicon Substrate bound to a conducting polymer for use in a conduct metric assay as a biosensor. It is further an object to provide a reliable and economic assay. The advantage of using conducting polymers compared to more traditional sputtered metal coatings is that the polymer is soluble, enabling a non-destructive analysis of the specimens. (Sharifirad, 2014)

The composite material comprises: (a) a p-doped silicon Substrate comprising a porous Surface; (b) a lawn of a conductive polymer bound to the porous Surface; and (c) a binding pair member bound to the conductive polymer. In a more specific embodiment, the composite material comprises: (a) a p-doped silicon Substrate comprising a porous Surface and a boron dopant; (b) a lawn of a conductive polymer bound to the porous Surface, the conductive polymer comprising one or more of an electrolyte-doped polypyrrole, polyaniline, and polythiophene; and (c) a probe DNA (pDNA) oligonucleotide electrostatically bound to the conductive polymer. (Jin et al., 2009)

### 2.4.2 Various boron detection methods

Inductively coupled plasma optical emission spectrometry (ICP-OES) has recently been used in boron determination because of its simplicity, sensitivity, and multi-element capability. Though, this method is not very sensitive for some nutritional and biological system that is having low boron concentration. All methods involving the measurement of B isotopic composition require a mass spectrometer. Thermal ionization mass spectrometry (TIMS) and secondary ion mass spectrometry (SIMS) have been used to measure isotopic composition of B; however, these methods are time consuming and require extensive sample preparation and purification. (Sah, 2002).

Development of inductively coupled plasma mass spectrometry (ICP-MS) not only overcame most of the drawbacks of earlier methods, but also its capability of measuring boron isotopes made possible; However it requires larger sample volume up to 5 ml ,very sophisticated and expensive. (Kmiecik et al., 2016)

Azomethine-H has high selectivity and can be directly applied to aqueous acidic medium. (Zenki, 1989)

The determination of boron in an alcoholic solution of curcumin in the presence of oxalic acid has been described. Spectrophotometric methods, in general, suffer interferences from several species. Many elements such as Fe, Ti, V, Ta, Nb, Zr, W, Ge and Be interfere with the determination of boron with curcumin, since they form similarly coloured complexes with the reagent. Nitrate and fluoride are the main interferents since the former oxidises curcumin and the latter masks the element (in acidic medium) as well as destroys the curcumin complex. The existing spectrophotometric procedures used to eliminate nitrate interference by chemical treatment are tedious and complicated. The method previously used for the determination of boric acid in boron powder involves the titration of boric acid in water slurry after formation of mannitol–boric acid complex. This procedure requires a large size of sample when low levels of boric acid are present. (Thangavel et al., 2003)

Colorimetric based assays using curcumin or Azomethine-H dyes can be used for the routine analysis of boron in all laboratories with access to a spectrophotometer that can measure absorbance at 550 nm. (Mohan, 2018)

## 2.5 Microbial Polymer as Sensor Matrix

### 2.5.1 Biosensor

A microbial biosensor is an analytical device that couples biological sensing element with a transducer to produce a signal proportional to the analyte concentration and enable rapid, accurate and sensitive detection of target analytes in fields as diverse as medicine, environmental monitoring, defence, food processing and safety. (Lie et al., 2006)

A biosensor is an analytical device that combines a biological sensing element with a transducer to produce a signal proportional to the analyte concentration. The transducer converts this biological signal into a measurable response such as current, potential or absorption of light through electrochemical or optical means, which can be further amplified, processed and stored for later analysis. Microorganisms have been integrated with a variety of transducers such as amperometric, potentiometric, calorimetric, conductimetric, colorimetric, luminescence and fluorescence to construct biosensor devices. Enzymes are the most widely used biological sensing element in the fabrication of biosensors. Although purified enzymes have very high specificity for their substrates or inhibitors, their application in biosensors construction may be limited by the tedious, time-consuming and costly enzyme purification, requirement of multiple enzymes to generate the measurable product or need of cofactor/coenzyme. Microorganisms provide an ideal alternative to these bottle-necks. The many enzymes and co-factors that co-exist in the cells give the cells the ability to consume and hence detect large number of chemicals; however, this can compromise the selectivity. They can be easily manipulated and adapted to consume and degrade new substrate under certain cultivating condition. Additionally, the progress in molecular biology/ recombinant

DNA technologies has opened endless possibilities of tailoring the microorganisms to improve the activity of an existing enzyme or express foreign enzyme/protein in host cell. All of these make microbes excellent biosensing elements. Fabrication of a microbial biosensor requires immobilization on transducers with close proximity. Since microbial biosensor response, operationalstability and long-term use, to some extent, immobilization technology plays a very important role and the choice of immobilization technique is critical. Microorganisms can be immobilized on transducer or support matrices by chemical or physical methods. Chemical methods of microbe immobilization include covalent binding and cross-linking which includes, formation of a stable covalent bond between functional groups of the microorganism's cell wall components such as amine, carboxylic or sulphydryl and the transducer such as amine, carboxylic, epoxy or tosyl. This is carried out by exposing the whole cells to harmful chemicals and harsh reaction condition, which may damage the cell membrane and decrease the biological activity. Cross-linking involves bridging between functional groups on the outer membrane of the cells by multifunctional reagents such as glutaraldehyde and cyanuric chloride, to form a network. Because of the speed and simplicity, the method has found wide acceptance for immobilization of microorganisms. The cells may be cross-linked directly onto the transducer surface or on a removable support membrane, which can then be placed on the transducer. (Lie et al., 2006)

Various physiochemical and biological treatments have been used for the removal of boron from water and wastewater. These treatments include techniques such as precipitation, ED, phytoremediation, and ion exchange.

Precipitation is capable of removal percentage up to 95%, which cannot be used independently to meet the new wastewater discharge regulations. Thus, it is integrated with boron-selective polymers such as polyvinyl alcohol (PVA), a poly-1,3-diol able to form a complex with boric acid or monoborate compounds under basic conditions. Boron can be effectively removed from various streams using boron-selective (chelating) resins. These resins contain functional hydroxyl groups in the 1-2 or 1-3 positions, thus enabling boron capture by the formation of borate-diol complexes. The removal efficiency of boron with ion exchange methods depends heavily on the type of resin/adsorbent used. Commercially available BSRs normally possess a macroporous polystyrene (PS) matrix cross-linked with divinylbenzene (DVB) and loaded with diol-bearing compounds such as *N*-methyl-D-glucamine (NMDG) functional group, which has a tertiary amine and polyol ends. A typical example of BSRs that is early reported is Amberlite IRA 743, prepared by the condensation of *N*-methylglucamine with cross-linked chloromethylated PS. This resin was reported to have a boron sorption capacity of 0.37 mmol/g (at pH 8.5, 25ºC). (Nasef et al., 2014)

### 2.5.2 Characteristics of Microbial Polymer

Chitosan is a natural linear polysaccharide having a cationic charge which makes it different from other polysaccharides as they’re either neutral or negatively charged in acidic environment; which allows it to form electrostatic complexes with negatively charged polymers. (Cheung et al, 2015)

Starch Corn is soluble in hot water. They bear a neutral formal charge. Corn Starch is sparingly soluble in water at room temperature. The Corn starch solution is heated up to solubilize it.  Starch is renewable material having good biocompatibility, inexpensive, plentiful in the environment. (Liew, 2015)

Xanthan Gum is a fast hydrating water-soluble hydrocolloid. Long chain xanthan polymer are slowly hydrated and easily dispersed. Hydration is related to ionic strength, which means high ionic strength tends to have slow hydration. (Jindal, 2018)

Locust Bean Gum and Guar Gum resemble each other but is sparingly soluble and has less viscosity due to few galactose subunits than Guar Gum. It is soluble in hot water. It differs from Guar Gum by forming thermally irreversible weak gels. (Doublier, 1981)

Pectin bears a negative charge and controls net charge in terms of degree of methyl esterification and maintains local charge density in terms of degree of blocking. (Sperber, 2009)

Carboxymethyl cellulose is a weak polyelectrolyte whose dissociation constant depends upon the electric charges on the neighbouring chain and in the medium. The electric field intensity and concentration of $H_3O^+$ ions increases in the presence of other negative charges in vicinity of Carboxyl groups of CMC chains. Electrical properties of CMC as polyelectrolyte are determined by the dissociation of carboxylic groups in aqueous medium. (Zhivkov, 2013)

Gelatin ion is positively charged ampholyte protein, which is neutral at isoelectric point. Addition of neutral salts into gelatin solution increases ionisation of gelatin as they produce highly dissociated complexes. (Thimann, 1930)

## 2.6 Biopolymer Field Effect Transistor

### 2.6.1 JL-MOSFET

An analytical model has been developed for a split gate junctionless (JL) MOSFET, which works as a bio-transistor to detect the analytes (biomolecules), such as protein, DNA, enzyme, cell, and so on, using the dielectric modulation technique.

Advantages of Junctionless MOSFET such as simple fabrication process, low gate leakage current and low DIBL than conventional MOSFET. Junctionless MOSFET is a heavily doped silicon film and it has same type of doping in source, channel, and drain regions. Since there is no doping concentration gradient hence it has no abrupt junctions between source/drain and channel which simplifies the fabrication of Junctionless MOSFETs in comparison to conventional MOSFET. One such application facilitated by the fact that JL-MOSFETs experience changes in the electrical properties when channel region is exposed to neutral and charged analytes. Therefore, the biosensing application has been investigated of n-type split gate Junctionless MOSFET for label free electrical detection of bio targets. It has been assumed that the analytes detect under the dry environment conditions. In the dry environment the electrical signal of biosensors does not depend on the Debye length whereas in watery environment screening depends on the Debye length. Therefore, dry environment provides Debye-screening-free sensing. (Narang et al., 2017)

BIOSENSOR is an analytical device used to detect biological elements, harnessing the exquisite sensitivity and binding specificity of biomolecules such as proteins, enzymes, antibodies, and nucleotides. FET based biosensors have been studied extensively owing to their various advantages over other methods including direct transduction, high sensitivity, mass production, miniaturization and compatibility with the standard complementary metal-oxide semiconductor. (Narang et al., 2017)

FET based biosensor where the gate material was replaced by an ion-sensitive membrane, an electrolyte solution and a reference electrode i.e., ion sensitive field effect transistor (ISFET). The biomolecules diffuse towards the gate oxide insulator where they bind with receptors, disorganizing the charge density on top of the gate oxide and thus modify the threshold voltage and the drain current of FET. (Bergveld, 1970)

An ISFET gives good performance with high sensitivity for charged biomolecules, but in the case of neutral biomolecules it has poor detection capability.

### 2.6.2 DM-FET

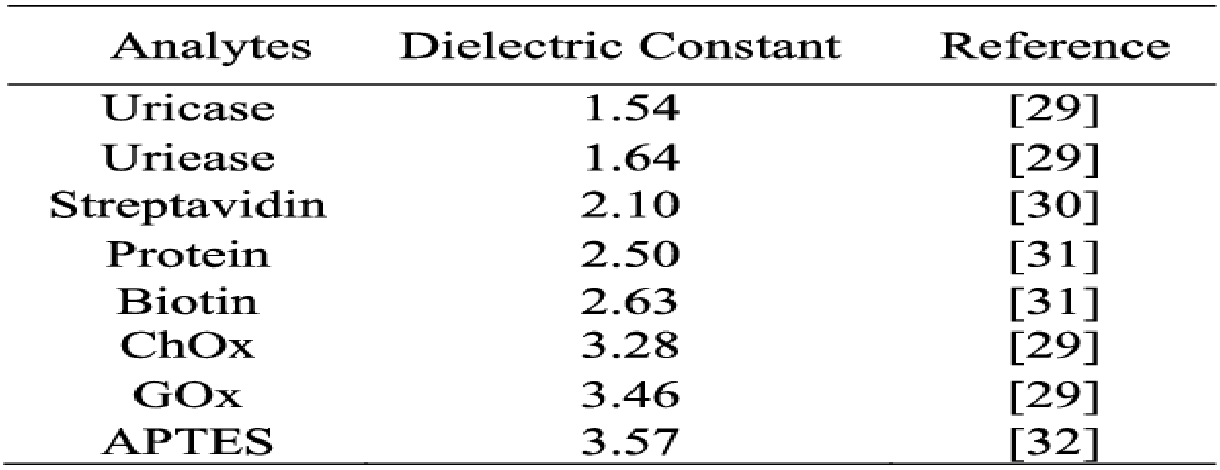
Where gate oxide layer was etched to carve out a vertical Nano gap underneath the gate material, DM-FET is capable of detecting the neutral biomolecules and also shows great compatibility with standard CMOS process.

DM-FET has few limitations such as low structural stability stemming from the mechanically suspended Nano gap structure, high cost, and low binding probability in carved cavity region.

Structural modification of the conventional MOSFET, another type of DM-FET was demonstrated, which is gate underlap DM-FET.

In underlap DM-FET, the gate material and the gate oxide layer are both etched from the conventional MOSFET to make the gate underlap region which is used for binding of biomolecules. (Narang et al., 2017)

Table 3: - Dielectric Constants of Analytes. [37]



| Analytes | Dielectric Constant | Reference |
|---|---|---|
| Uricase | 1.54 | [29] |
| Uriease | 1.64 | [29] |
| Streptavidin | 2.10 | [30] |
| Protein | 2.50 | [31] |
| Biotin | 2.63 | [31] |
| ChOx | 3.28 | [29] |
| GOx | 3.46 | [29] |
| APTES | 3.57 | [32] |

### 2.6.3 MOSFET

Generally, there are optical, spectrometric, electrochemical, and SPR measurement as the method to analyse biological molecules. However, all these methods involve time consuming, and multi-stage processes that are expensive and unsuitable for on-line monitoring. To overcome these disadvantages, recently some papers proposed the field effect transistor (FET) type biosensor that was fabricated by using standard semiconductor-processing technology. In case of using the FET type sensor for application as a biosensor, it is likely to get standardization, miniaturization, and mass production because its configuration effectively integrates both a sensor and a measurement circuit. Fabrication of FET type biosensor, that is able to detect both protein and DNA simultaneously. It is possible because protein and DNA have a positive charge and a negative charge, respectively. In the operation of a FET, the channel current characteristics are controlled based on the electric field established by applying a voltage between the gate and the body of the semiconductor. Likewise the response of FET type biosensors can be obtained by the electric field on the gate which is established by biomolecules, such as protein and DNA with a charge. Up to now to get the response for bio molecules, the FET type biosensor generally adopt the amperometric method that obtains the current variation as the response. With amperometric, stable response is not generated, for this reason potentiometry is implemented that is able to get voltage variations as response. Potentiometry method in a FET type sensor has various advantages that are related to miniaturiazation for their capability of measuring different species on same silicon chip, & their large scale production capabilities of microelectronic industry. Especially, it is able to directly convert the charge variations caused by bio molecules on the gate surface to the response that is recognized as biomolecules. The most important step in the fabrication of the FET type protein and DNA sensor is the immobilization of the bio sensing material on the gate surface to capture proteins and DNA. Thus, to capture proteins and DNA effectively, we used the gold gate that is chemically modified by immobilized molecular receptors, so called self-assembly mono-layer (SAM), which is able to combine with protein and DNA specifically. In addition, this is very useful because the SAM is favourably formed on the FET’s gate (Au) based on the attachment of a thiol group. In this research, we will use two different kinds of SAMs, such as 11-Mercaptoundernoic acid and 3- mercaptopropionic acid which are able to capture protein and DNA, respectively. Generally, the drain current of a conventional MOSFET is varied by the gate potential.(Park et al.)

### 2.6.4 DM-JLTFET

Recently human interventions and bioterrorism have created problems related to the pollution of ecosystem, because pollution monitoring and supervision of biological pathogens have become a challenge for early-stage detection and diagnosis of systems. Therefore, enlargement of extremely responsive handheld biosensors with greater life, robustness, and effectiveness is the need of the current generation. They can act as a competent device for the cost-effective supervision of diseases and inspection of biohazards in the ecosystem. A tunnel FET-based biosensor has been extensively explored and emerged as a potential sensor due to its ability to provide better sensitivity, improved response time, and energy efficient due to low leakage, and is proficient to overcome larger detection time due to $kT/q$ limit, short channel effects, drain-induced barrier lowering, low $I$ON/$I$OFF ratio, high power consumption due to leakage, and limitations related to scaling of threshold voltage with supply voltage. Investigate a charge-plasma-based dielectric-modulated junctionless tunnel field-effect transistor (DM-JLTFET) that can be utilized to sense the biomolecules. For this purpose, p+ source and n+ drain regions are induced by suitable metal work-function electrodes. Furthermore, a nanogap is created within the gate dielectric to accumulate the biomolecules. For this purpose, the device performance has been analyzed in terms of energy band diagram, e− tunneling rate, surface potential, drain current ($I$ds), SS, and sensitivity. (Singh et al., 2017)

## 2.7 Capacitance Measurement

### 2.7.1 Capacitor

The capacitor is a component which has the ability or “capacity” to store energy in the form of an electrical charge producing a potential difference (*Static Voltage*) across its plates, much like a small rechargeable battery. Capacitors consists of two or more parallel conductive (metal) plates which are not connected or touching each other, but are electrically separated either by air or by some form of a good insulating material such as waxed paper, mica, ceramic, plastic or some form of a liquid gel as used in electrolytic capacitors. The insulating layer between capacitors plates is commonly called the dielectric. Due to this insulating layer, DC current cannot flow through the capacitor as it blocks it allowing instead a voltage to be present across the plates in the form of an electrical charge.

The conductive metal plates of a capacitor can be either square, circular or rectangular, or they can be of a cylindrical or spherical shape with the general shape, size and construction of a parallel plate capacitor depending on its application and voltage rating. When used in a direct current or DC circuit, a capacitor charges up to its supply voltage but blocks the flow of current through it because the dielectric of a capacitor is non-conductive and basically an insulator. However, when a capacitor is connected to an alternating current or AC circuit, the flow of the current appears to pass straight through the capacitor with little or no resistance. The flow of electrons onto the plates is known as the capacitors Charging Current which continues to flow until the voltage across both plates (and hence the capacitor) is equal to the applied voltage $V_c$. The strength or rate of this charging current is at its maximum value when the plates are fully discharged (initial condition) and slowly reduces in value to zero as the plates charge up to a potential difference across the capacitors plates equal to the source voltage. The amount of potential difference present across the capacitor depends upon how much charge was deposited onto the plates by the work being done by the source voltage and also by how much capacitance the capacitor has and this is illustrated below.

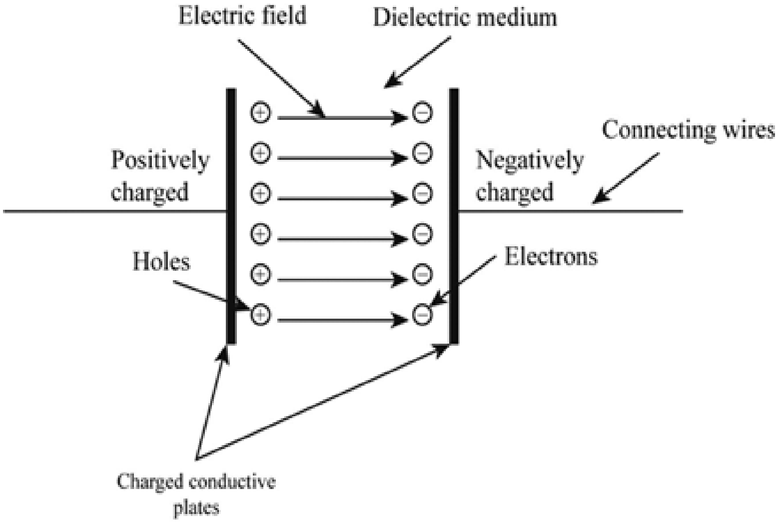


Fig 2.4: - Normal Parallel Plate Capacitor. [10]

In a normal capacitor, the two parallel conducting plates are electrodes which allow the conduction. Whereas, the medium between two parallel conducting plates is purely insulating dielectric material which does not allow conduction.

When a voltage or potential difference is applied across a capacitor the charges accumulates at the electrodes. The voltage will not move through the dielectric. But the dielectric medium will allow an electric field to flow through it when huge number of charges accumulates at the electrodes. However, the electrodes are able to store electric charge. This ability of storing electric charge is known as capacitance.

When reverse bias voltage applied across a PN junction diode, the two regions P and N behaves as electrodes (with less resistance) and the depletion region between two regions acts as dielectric medium (with more resistance). The P, N regions (electrodes) and depletion region (dielectric medium) allows the storage of charge in electric field. This ability of storing the charge is nothing but capacitance which in fact is termed in PN junction diode as junction capacitance or transition capacitance or depletion capacitance.

Capacitors store the energy of the electrons in the form of an electrical charge on the plates the larger the plates and/or smaller their separation the greater will be the charge that the capacitor holds for any given voltage across its plates. In other words, larger the plate area, smaller is the distance and more will be capacitance.

### 2.7.2 Biopolymer composites as supercapacitor

Biopolymers and their composites are emerging materials for supercapacitor because they are conducting additive or support for materials with pseudocapacitance properties. Conducting polymers have been shown to possess high capacitance and conductivity, plus that they are low cost compared to carbon-based electrode materials. Conducting polymer electrodes have been shown to have the greatest potential energy and power densities. For material to function as a supercapacitor material, it has to be conductive and have increased surface area which can enhance the efficiency of the supercapacitor.

# Chapter 3

# Materials and Methods

For screening of conducting microbial polymer, different polymers were used and their electrical properties were studied. Biopolymers are used to design Bio-FET, due to their abundance, biocompatibility, high selectivity, sensitivity, reversibility of biopolymer based sensor. Wide range of polymers are taken such as chitosan, carboxymethyl cellulose, pectin, gelatin, locust bean gum, guar gum, starch corn, xanthan gum, $MP_1$, $MP_2$.

Doping of boric acid was done in to different polymers, to study the effect of boric acid on polymer; they were then coated on butter-paper for further electrical analysis of the polymer doped mixture.

Stock solutions of different polymers and boric acid were prepared in water. The mixture was then taken in ratio, polymer was taken in the ratio of 1:1 to 10:1, and boric acid was taken in the ratio of 1:1 to 1:5.

**3.1 (a) Stock solution of polymer: -** Polymer stock concentration: - 50 mg in 100 ml.

Table 4: - Concentration of polymer prepared.

| Volume of polymer in solution | Concentration of polymer (mg/ml) |
|---|---|
| 100 µl | 0.05 |
| 200 µl | 0.1 |
| 300 µl | 0.15 |
| 400 µl | 0.2 |
| 500 µl | 0.25 |
| 600 µl | 0.3 |
| 700 µl | 0.35 |
| 800 µl | 0.4 |
| 900 µl | 0.45 |
| 1000 µl | 0.5 |

### (b) Stock Solution of Boric Acid

Boric Acid Stock Concentration: - 400 mg in 20 ml

Table 5: - Concentration of boric acid prepared.

| **Dilution of Boric Acid (ml)** | **Distilled Water (ml)** | **Volume of Boric Acid taken (µl)** |
|---|---|---|
| 2 | 18 | 100 |
| 4 | 16 | 200 |
| 6 | 14 | 300 |
| 8 | 12 | 400 |
| 10 | 10 | 500 |

### (c) Composition of mixture taken

Table 6: - Proportion of polymer and boric acid used.

| **Volume of Boric Acid** → | 100 µl | 200 µl | 300 µl | 400 µl | 500 µl |
|---|---|---|---|---|---|
| **Volume of Polymer** ↓ | Ratios | | | | |
| 100 µl | 1:1 | 1:2 | 1:3 | 1:4 | 1:5 |
| 200 µl | 2:1 | 2:2 | 2:3 | 2:4 | 2:5 |
| 300 µl | 3:1 | 3:2 | 3:3 | 3:4 | 3:5 |
| 400 µl | 4:1 | 4:2 | 4:3 | 4:4 | 4:5 |
| 500 µl | 5:1 | 5:2 | 5:3 | 5:4 | 5:5 |
| 600 µl | 6:1 | 6:2 | 6:3 | 6:4 | 6:5 |
| 700 µl | 7:1 | 7:2 | 7:3 | 7:4 | 7:5 |
| 800 µl | 8:1 | 8:2 | 8:3 | 8:4 | 8:5 |
| 900 µl | 9:1 | 9:2 | 9:3 | 9:4 | 9:5 |
| 1000 µl | 10:1 | 10:2 | 10:3 | 10:4 | 10:5 |

## 3.2 Methodology of sensing

### (a) Capacitance measurement and dielectric constant of biopolymer

The capacitance of biopolymer was measured using parallel plate capacitor made of aluminium sheet. Butter paper was used as a platform to coat the varying concentration of biopolymer with varying doping concentration of boric acid.

These coated butter paper was used as dielectric material in the parallel plate capacitor. The capacitance was measured in LCR meter (inductance (L), capacitance(C), resonance(R). For capacitance measurement various ratios of polymer (ranging from 100µl to 1ml) with varying boric acid concentration (ranging from 100µl to 500µl) was prepared. This mixture was then vortex and coated on butter paper with the help of a paint brush. Capacitance was measured once the butter paper was dried.

Dielectric Constant of the biopolymer is calculated from the formula;

$$\boldsymbol{C = \frac{\varepsilon A}{d}} \qquad (1)$$

Where, C= Capacitance in pF

ε= Dielectric constant of Polymer

A= Area of Plate

d= Distance between two plates

$$\boldsymbol{K = \frac{\varepsilon}{\varepsilon_{\circ}}} \qquad (2)$$

Where, k= Dielectric Constant

ε= Dielectric Constant of Polymer

$\varepsilon_{\circ}$= Dielectric Constant of free space = $8.854 \times 10^{-12}$ F/m

### (b) Design of Bio-FET

Split gate junctionless (JL) MOSFET, which is working as the bio-transistor device is used to detect the bio molecules or biopolymer such as protein, DNA, enzymes etc. This device has been fabricated and its electrostatic properties of the device have been simulated by the TCAD tool. Here the underlap region which is also known as the open cavity region is etched with small part of oxide material in the gate. This open cavity region is generated for the immobilization of the bio-polymer. Here the changes in the threshold voltage of the device and transfer characteristics are used as the sensing parameter to detect the biopolymer in its dry environment. Here, by varying the thickness of the device and comparing their threshold voltage and the sensitivity that which one is better device.

In this chapter two devices are formed by

1) **Scaling of the device**. One is according to the change in the concentration of the device and other is by
2) Changing the thickness of silicon substrate of the device. According to both the concentration and from the scaling method, which is better sensitive to biopolymer is going to find out.

### (c) Simulation of Bio-FET

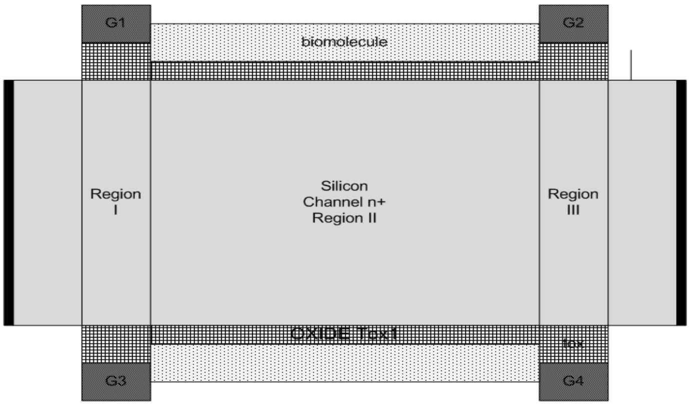


Fig 2.6: - Schematic structure of the n-type split gate JL MOSFET with varying thickness and varying doping concentration in the substrate

Here the n-type channel region is going to be fabricated in the split gate junctionless MOSFET. Channel doping and its thickness is selected in such a way so that device should be in fully depleted in it's OFF state [27-]. Here the channel region is divided into three regions (region I, region II and region III). Dimension of the region I and III are same i.e. Lg1 and Lg2 are 25nm. Region I and region III are known as the gate overlap region because in both of the region the oxide layer is covered with the gate. Although the region II is known as the gate underlap region (i.e. where the biomolecule communicate with the device) and sense the changes in the threshold voltage of the device according to the variation in the dielectric constant. The length of the underlap region is defined by Lc which is taken as 50nm. Thickness of the channel region (i.e. tsi) is 20nm and 30nm. Here the source, drain and channel region has the invariable doping (i.e. ND=1X 1018 cm-3 and ND=1X1017cm-3). Here the tox1and tox are defined as the width of the oxides of the underlap region and overlap region, although tc is define as the width of the cavity region where the biomolecule is placed.

In this device, 0.05V drain voltage is applied and -1 V gate voltage is applied to the device at the G1, G2, G3 and G4. Gate voltage is varied from -2V to 1V for noticing the variation in drain current of the device. This device is going to be stimulated on the n-type DG JL MOSFET. Device simulation are presented according to the experimental results

### 3.3 Conductance of Boric Acid

Table 7: - Dilution of Boric Acid for measuring conductance.

| Dilution of Boric Acid (ml) | Distilled Water (ml) |
|---|---|
| 1 | 29 |
| 2 | 28 |
| 3 | 27 |
| 4 | 26 |
| 5 | 25 |

Conductance of various concentration of Boric acid was measured in Conductivity meter of Spectralab. Dilutions were made from stock solution of Boric Acid ranging from 100µl to 500µl and the final volume was made up to 10 ml with Distilled Water.

# Chapter 4

## Results and Discussion

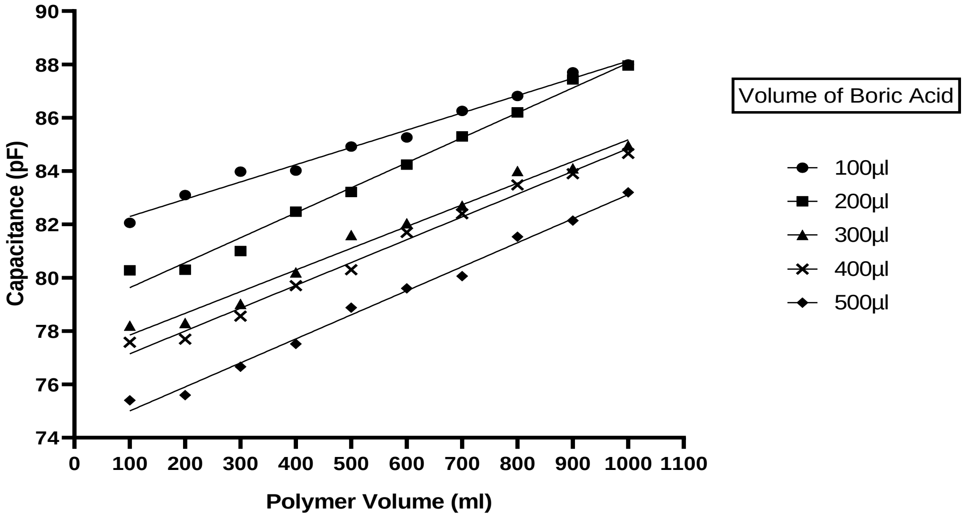
Capacitance of parallel plate capacitor using different polymers doped with boric acid as dielectric material was calculated using LCR meter. There are various factors affecting the observations for capacitance of biopolymers such as overlapping plate area, average spacing between aluminium plates, dielectric material, and ambient conditions etc. To overcome these, a sensing technique using MOSFET has also been proposed here.

Different polymers were used such as; Chitosan, Starch Corn, Xanthan Gum, Locust Bean Gum, Pectin, Guar Gum, Carboxymethyl Cellulose, $MP_1$, $MP_2$, Gelatin.

### 4.1 **Capacitance of Polymer**

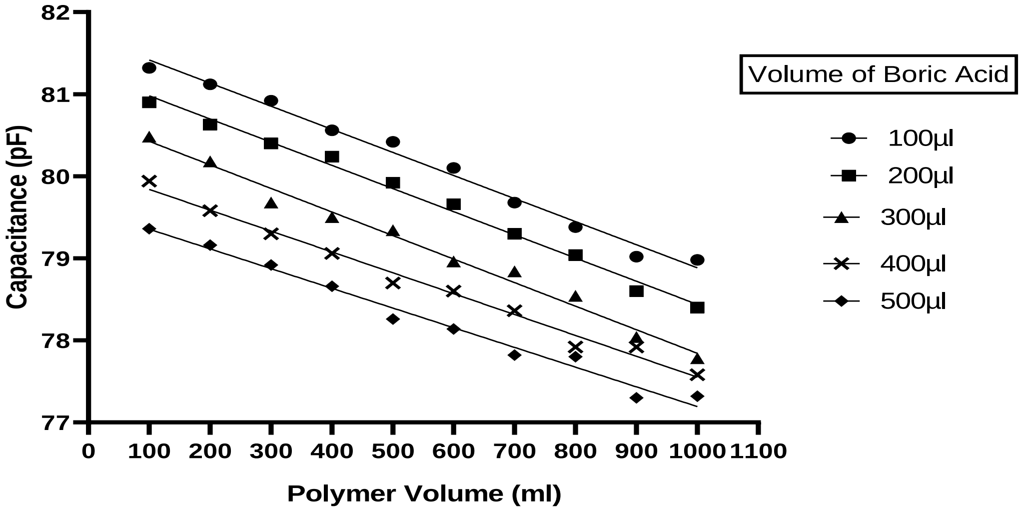
Capacitance of various polymers was measured in LCR meter and readings were noted down for each polymer. Individual graph of capacitance were plotted for each polymer in ratio with boric acid.

Fig. 2.4 (a to j) show capacitance (in picofarad) of different polymers against boric acid.



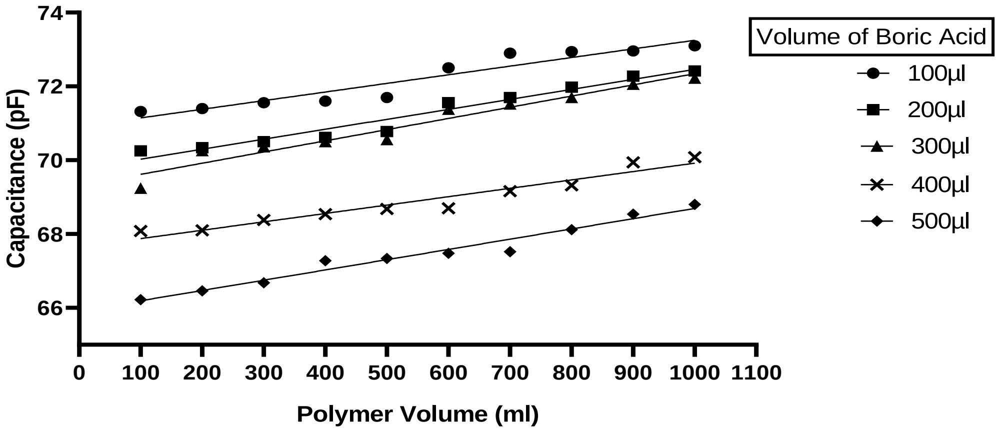
(a) Capacitance at different concentration of chitosan.

In Fig 2.4 (a) this graph of chitosan polymer shows varying trends of boric acid with increase in capacitance as the polymer concentration increases down the lane from 100 µl to 1000 µl. As the Boric acid concentration increases from 100 µl to 500 µl, the capacitance decreases from higher to lower. There is a net linear increase in capacitance value of each boric acid concentration. The reason of increasing capacitance with increasing concentration of polymer doped with boric acid is due to interface developed between conducting capacitor plates and butter paper coated with liquid polymer doped boric acid acts as electrical double layer. Charges are developed in the boundary of butter paper with opposing polarity, one at the surface of the capacitor plate, and one in butter paper coated with Polymer doped boric acid. There is a separation of charges between the electrons of capacitor plates and ions formed on the surface of butter paper with coating. When a voltage is applied to the capacitor plates, two layers of polarized ions are generated at the interface. The other layer, with opposite polarity, formed from dissolved and solvated ions distributed in the electrolyte that have moved towards the polarized electrode. Polarized ions get adhered to capacitor plate surface and separates oppositely polarized ions from each other.



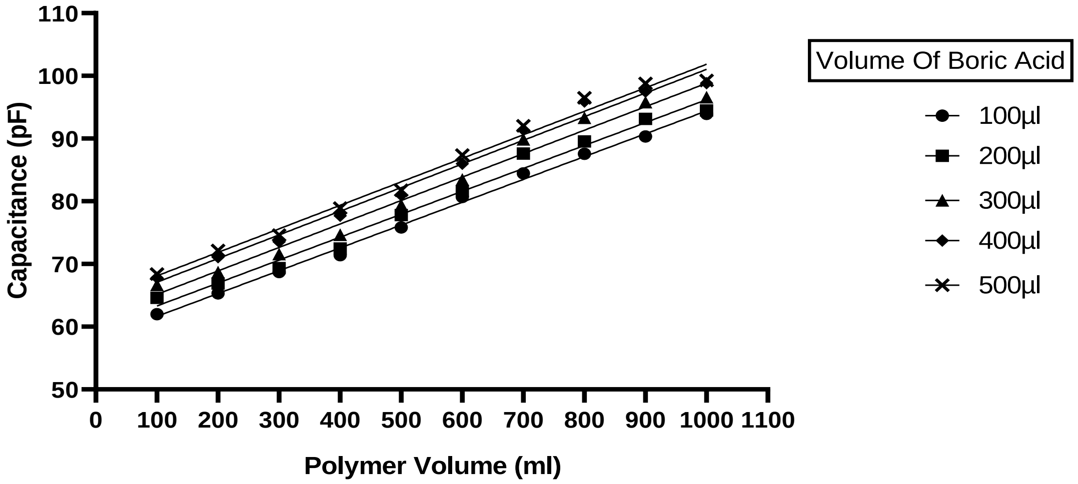
(b) Capacitance at different concentration of $MP_2$ polymer.

In Fig. 2.4 (b) the polymer $MP_2$ shows decrease in capacitance with increasing polymer doped boric acid concentration. Capacitance value is maximum when small amount of polymer mixture is taken. The capacitance decreases when addition of polymer increases from left to right. Capacitance is related to electrostatic field between the capacitor plates, more closely the plates stronger are the electrostatic field. This maybe the reason that capacitance decreases with increasing concentration due to increase in plate distance.



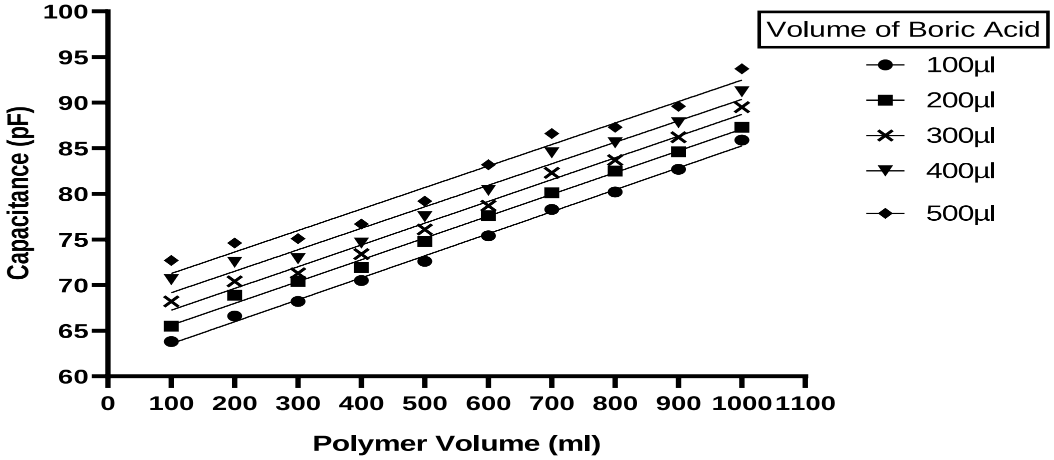
(c) Capacitance at different concentration of $MP_1$ polymer.

In Fig. 2.4 (c) The capacitance of $MP_1$ polymer is almost constant given concentration of boric acid. 100µl of boric acid has highest values of capacitance and 500µl of boric acid has lowest capacitance value. Though, there is an increasing trend of capacitance of each boric acid concentration. There is very slightest increase in capacitance with increasing polymer concentration. From which it can be concluded that, in this polymer the capacitance change along different polymer concentration is almost constant.



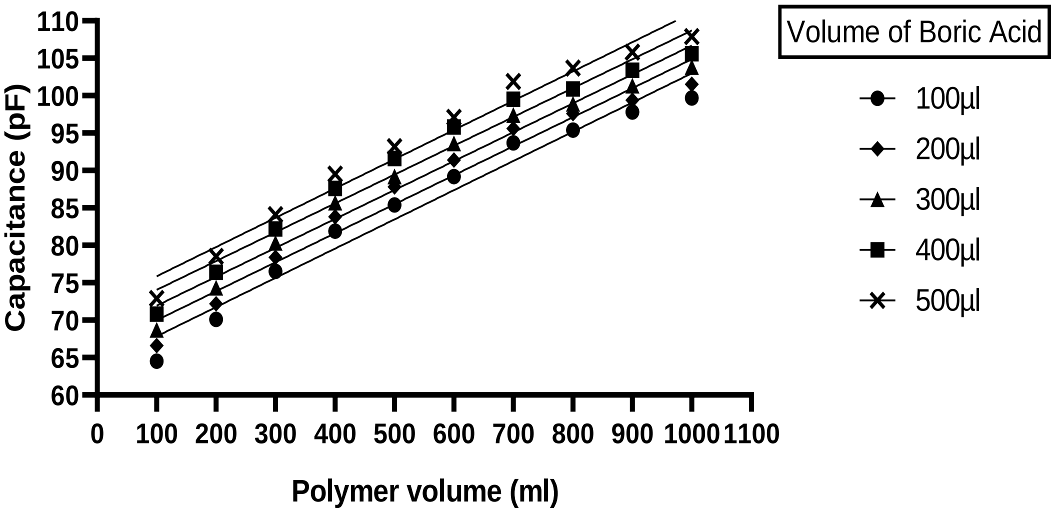
(d) Capacitance at different concentration of Xanthan gum polymer.

In Fig. 2.4 (d) the capacitance of xanthan gum increases with increasing boric acid concentration into different polymer concentration. There is no significant difference in the degree of capacitance change from which it can be concluded that with increase in boric acid concentration with regards to different polymer concentration is showing very small increase i.e. there is no direct correlation between capacitance and concentration of polymer when boric acid is doped with it.



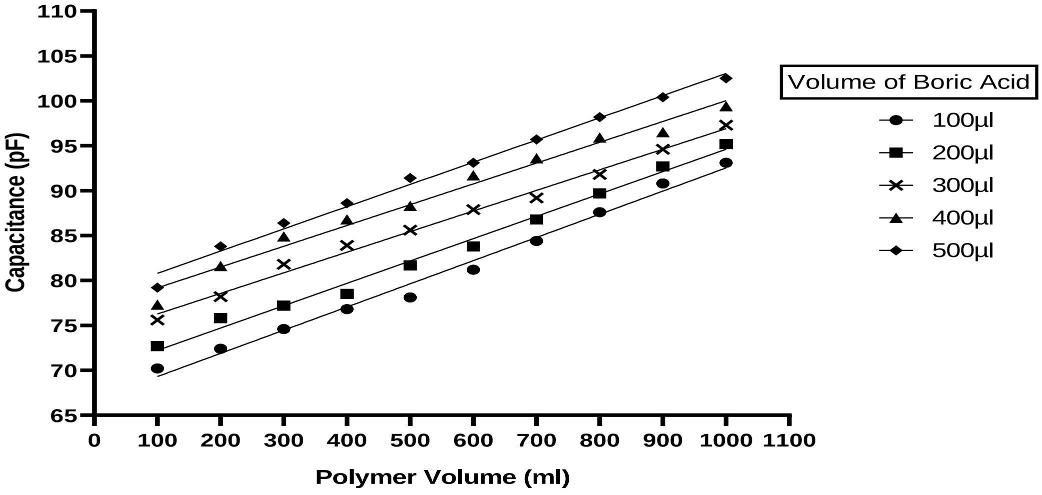
(e) Capacitance at different concentration of guar gum polymer.

In Fig. 2.4 (e) there is increase in capacitance as boric acid concentration is increased from 100µl to 500µl which shows direct correlation of concentration with capacitance. This polymer almost shows linear trend when polymer concentration increases from 100µl to 1000µl, which can be concluded by a direct relation between capacitance and polymer concentration. Reason is explained above in Fig. 2.4 (a)



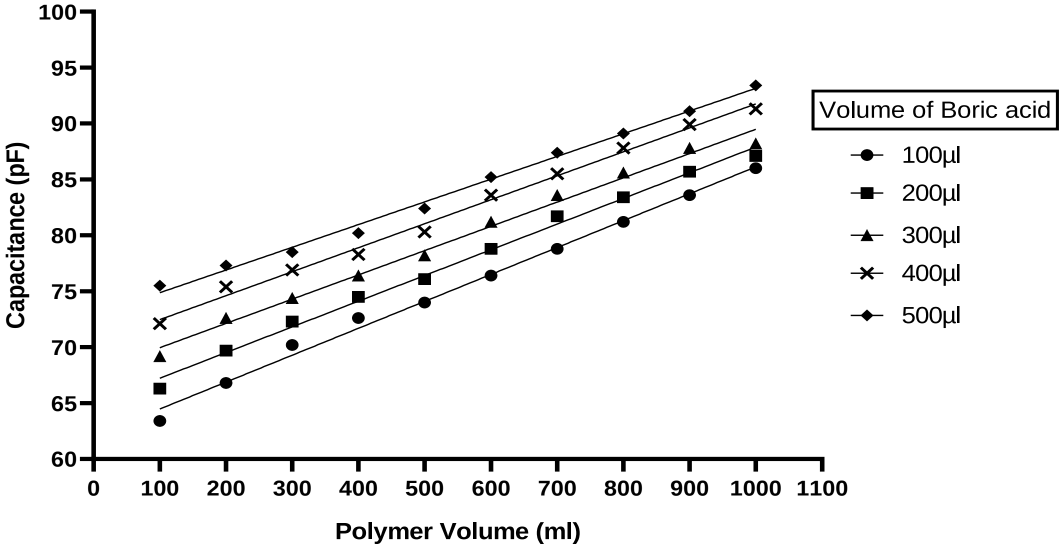
(f) Capacitance at different concentration of Starch Corn polymer.

Starch based electrolyte has low ionic conductivity which can be approved by addition of mixed salt systems, additives in the form of ionic liquids, blending it with polymer mixed in a solvent system. Ionic liquids such as boric acid has wide electrochemical potential window, decomposition temperature range, negligible vapour pressure, intoxic, inflammable, involatile and high conductivity. The ionic conductivity of biopolymer electrolyte increases due to strong plasticizing effect of ionic liquids resulting in softening of polymer backbone thereby, increase in the flexibility of the polymer chain as well as the polymer chain also improvement in the mobility of polymer subunits, which in turn helps in ionic transport in the polymer complexes.



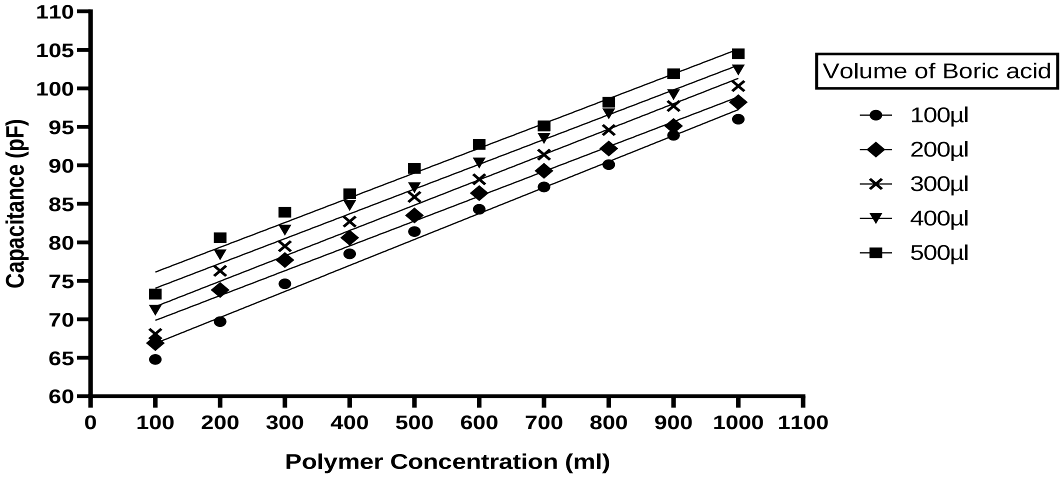
(g) Capacitance at different concentration of Locust Bean Gum polymer.

In Fig. 2.4(g) Locust bean gum being a hydrocolloid are either viscous or forms gels when dispersed in water. Large number of hydroxyl groups is present that increases the affinity for binding water molecules by giving them hydrophilic compounds.



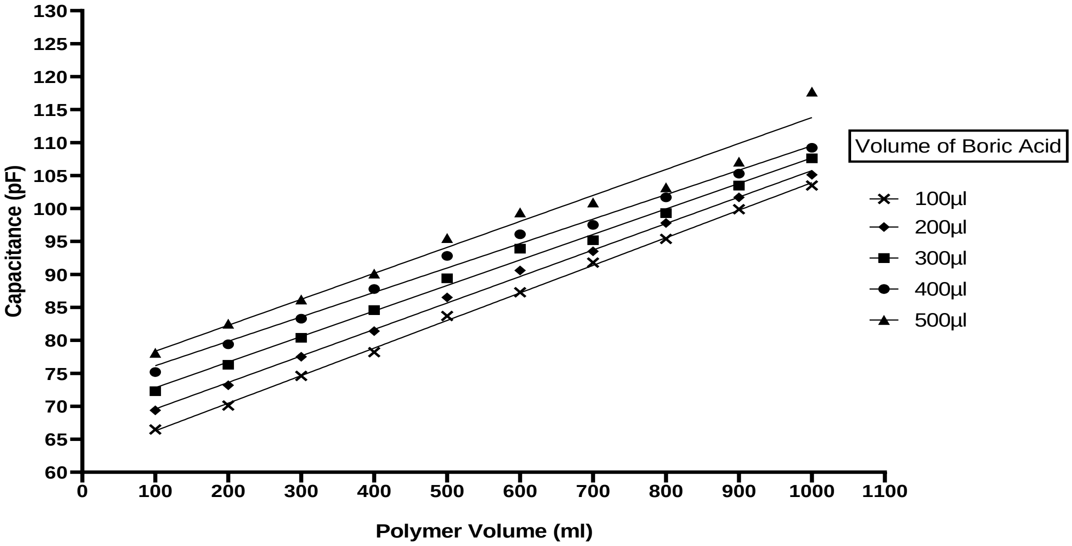
(h) Capacitance at different concentration of cellulose polymer.

Sodium salt of CMC is an anionic polymer i.e. bears a negative charge, when it is in combination with a positively charged ion of boric acid. Reason of increase in capacitance with respect to polymer and boric acid concentration is explained in Fig 2.4 (a).



(i) Capacitance at different concentration of Pectin polymer.

In Fig 2.4 (i) Pectin polymer being negatively charged colloid, when it comes in contact with sugar, the equilibrium between water and pectin breaks down and a fibrous network is established that supports liquid in gel formation.

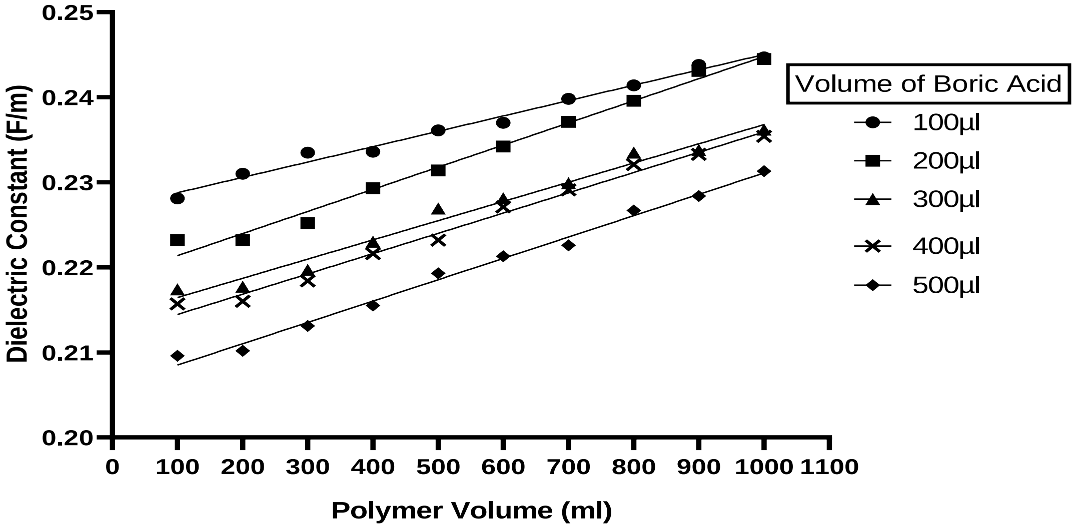


(j) Capacitance at different concentration of Gelatin.

In Fig. 2.4 (j) Gelatin being a weak polyvalent ampholyte when reacts with boric acid shows an increasing trend as we go from 100µl to 500µl, the reason for increase in capacitance with respect to concentration is explained above in Fig 2.4 (a).

Fig 2.4: - (a-j) Capacitance of varying concentration of polymers with respect to boric acid concentration as parameter.

## 4.2 **Dielectric Constant of Polymers**

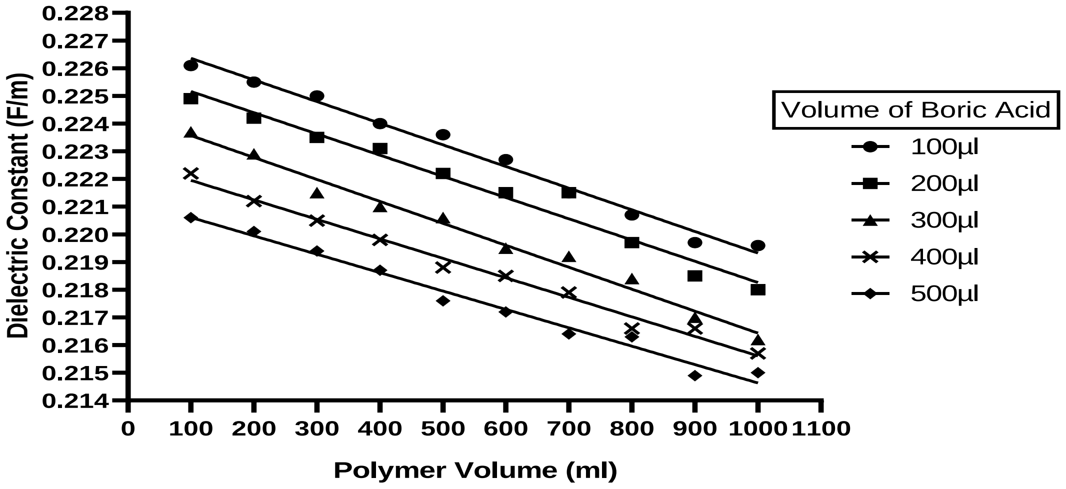


(a) Dielectric constant at different concentration of chitosan polymer

In Fig. 2.5 (a) Chitosan polymer showed an increasing trend which infers that with the increase in concentration of boron doping on chitosan polymer, the capacitors charge holding capacity has increased. The dielectric constant tells about electronic polarization of the dielectric medium in the presence of electric field that separates the alignment of electric charges. Physically it means the greater the polarisation developed by any material in applied field of known strength the greater will be its dielectric constant.

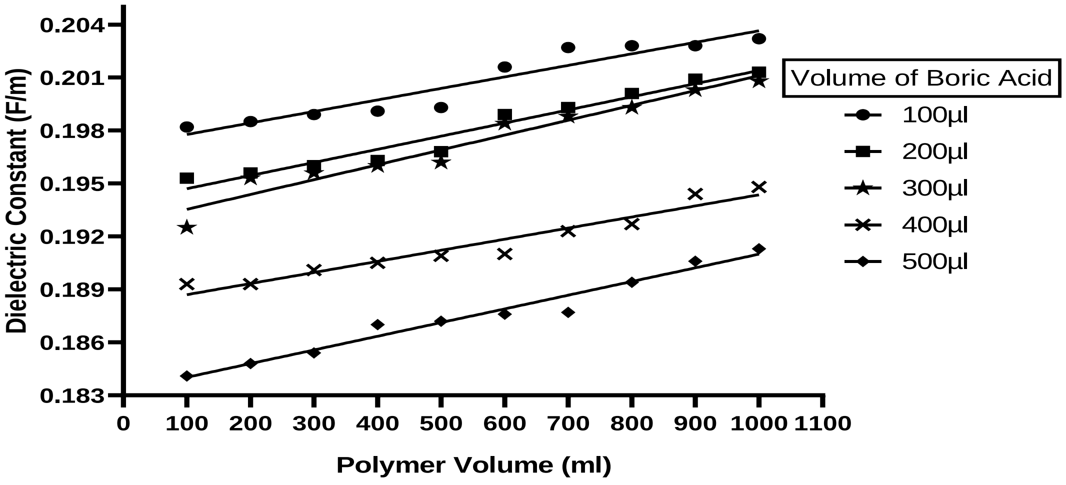
Polarisability is induced when electric field is applied onto the materials. Without electric field, the electrons are disseminated uniformly around the cores of nuclei. At the point when the electric field is applied the electron cloud gets displaced from the nuclei toward the path opposite to the applied field. Resulting in division of positive and negative charges and the particles carry on like an electric dipole.

Relative permittivity decreases with increasing temperature, which means the temperature was optimum as there is an increase in dielectric constant value.



(b) Dielectric constant at different concentration of $MP_2$ polymer.

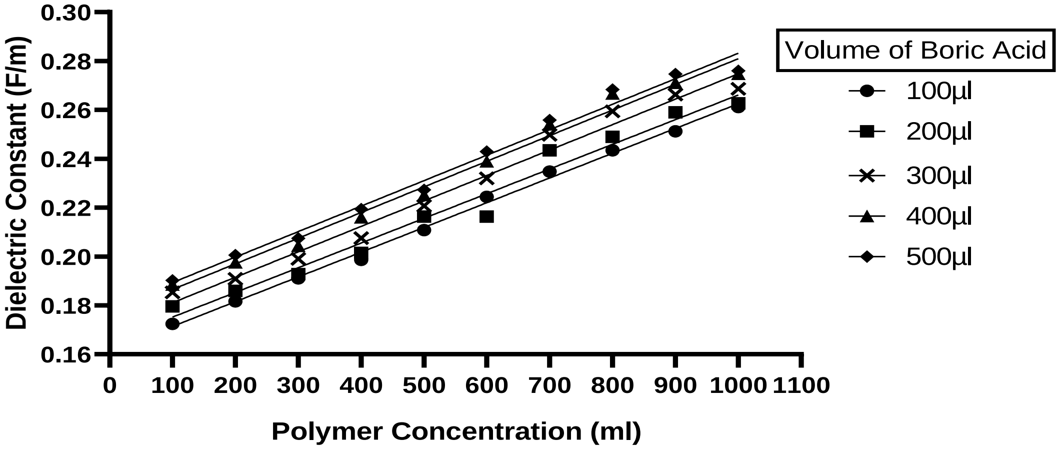
In Fig. 2.5 (b) $MP_2$ polymer shows a decreasing trend as polymer concentration increases from 100µl to 1000µl similar trend was seen when boric acid concentration increased from 100µl to 500µl. The change in dielectric constant is not that much significant, which may be due to less binding affinity of polymer with boric acid. When the dielectric constant of the material is higher, the force of attraction between the plates is decreased.



(c) Dielectric constant at different concentration of $MP_1$ polymer.

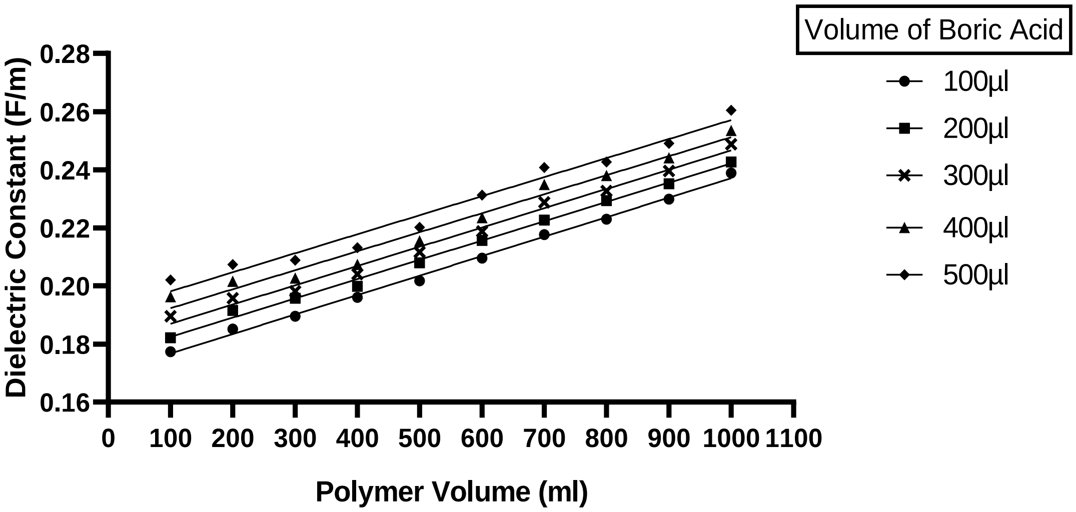
In Fig. 2.5 (c) The polymer MP1 shows an increasing dielectric constant value, though it gets almost constant in 200µl and 300µl and then gradually decreases in

400µl and 500µl. The reason may be due to weak binding of the two or distance between the plates is disturbed, temperature in the surrounding etc.



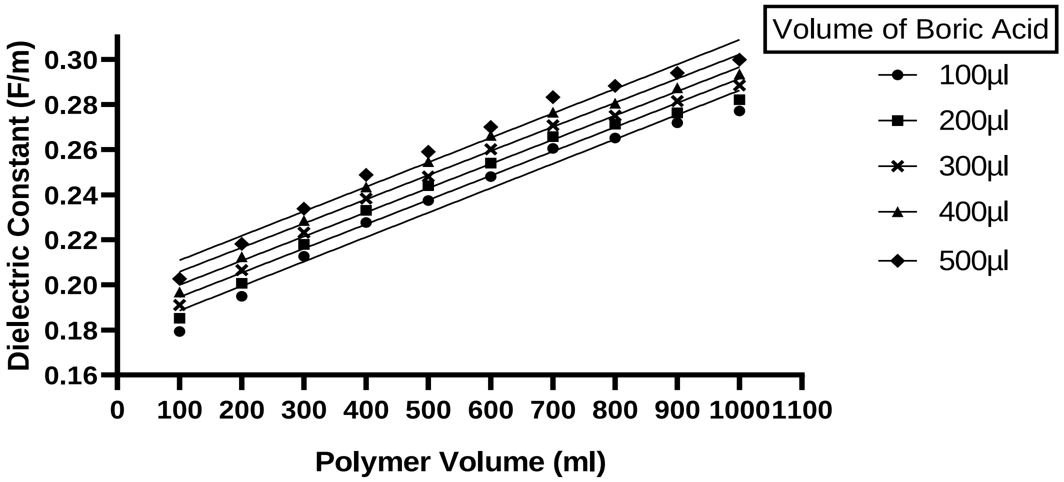
(c) Dielectric constant at different concentration of Xanthan Gum polymer.

In Fig. 2.5 (d) Xanthan Gum polymer shows direct correlation with boric acid concentration. There is no significant change in dielectric constant value with increase in polymer concentration with respect to boric acid. This shows, on increasing concentration of polymer and boric acid the dielectric constant has no specific effect on this polymer.



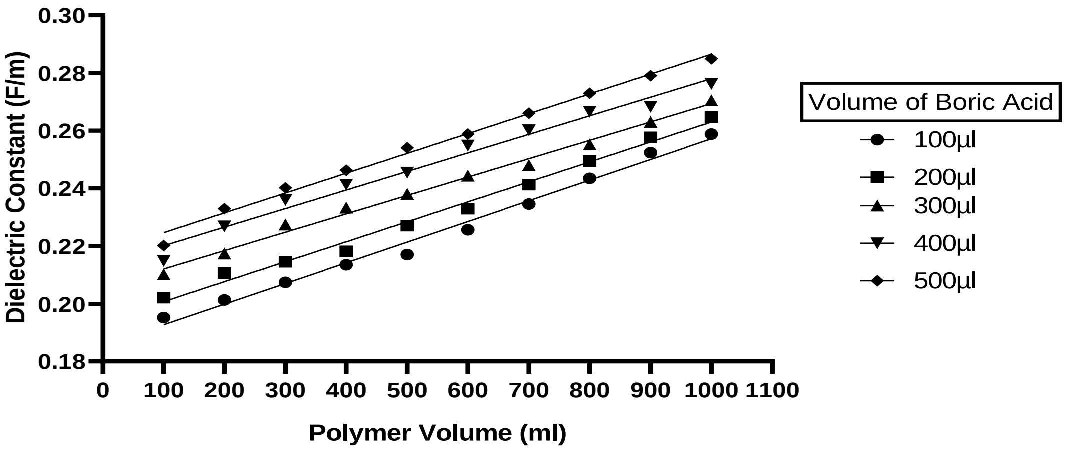
(e) Dielectric constant at different concentration of Guar Gum.

In this Fig. 2.5 (e) guar gum shows a linear increase in dielectric constant values as we go from 100µl to 1000µl. Similarly, there is increase in dielectric constant when boric acid concentration increases from 100µl to 500µl, from which it can be concluded that on increasing boric acid concentration the binding affinity of polymer with boric acid increases.



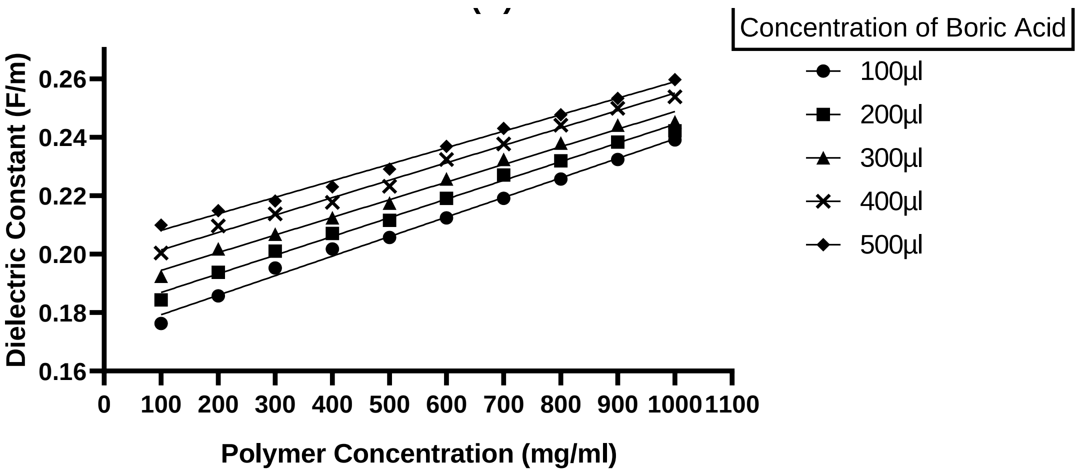
(f) Dielectric constant at different concentration of Starch Corn polymer.

In this Fig. 2.5 (f) Starch Corn shows a gradual increase in dielectric constant values due to high dielectric permittivity of ionic liquids that plays a significant role in separating the ion pairs or aggregating the ions having high self-dissociating properties.



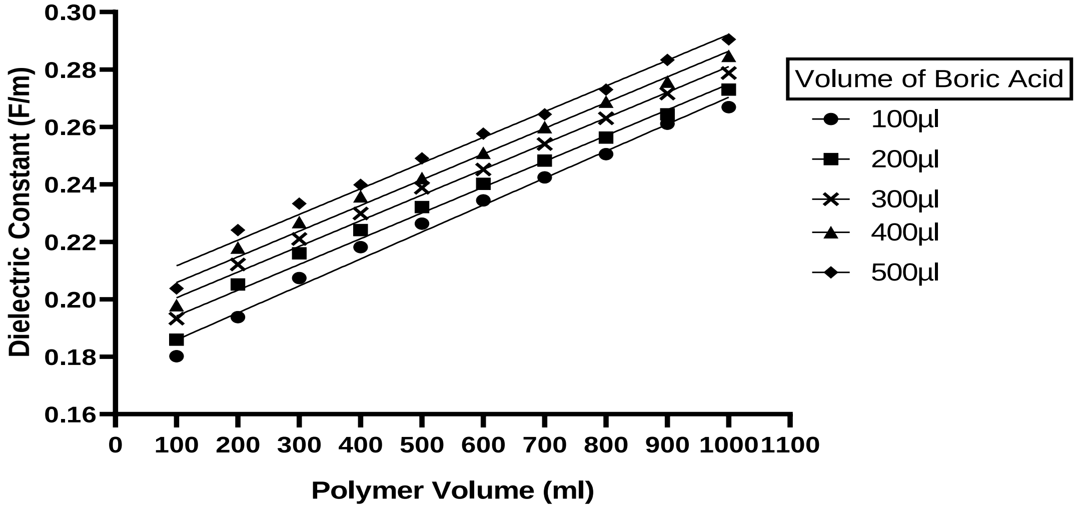
(g) Dielectric constant at different concentration of Locust Bean Gum polymer.

In this Fig. 2.5 (g) the dielectric constant increases from 100µl to 500µl of boric acid. Similarly there is increase from left to right as we go from 100µl to 1000µl. The reason of increase in trend is explained above in Fig. 2.5 (a)



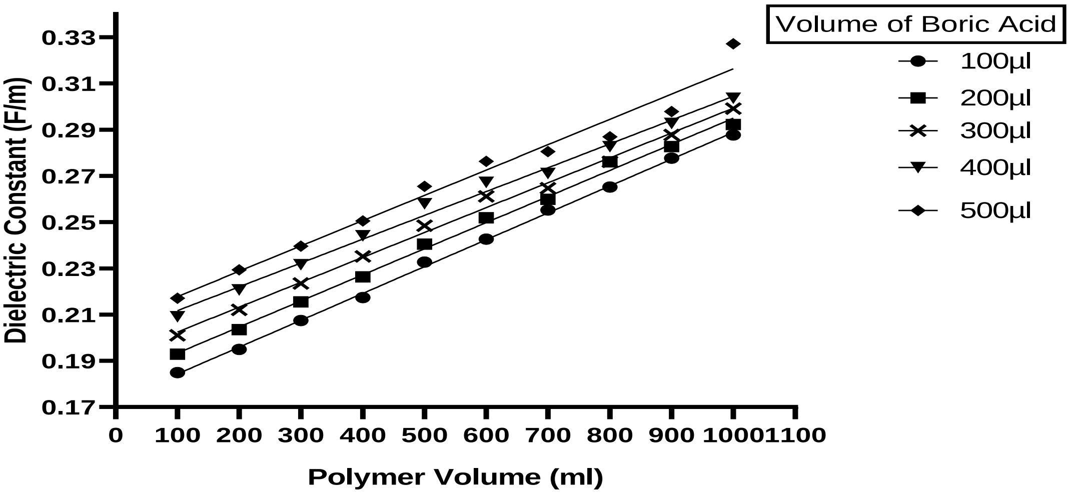
(h) Dielectric constant at different concentration of Cellulose polymer.

In Fig. 2.5 (h) Dielectric increase of the sodium salt of CMC increases with increase in ionization of the salt. As we go from 100µl to 1000µl there is an increase in dielectric value, which tells that it increases with increase in dilution.



(i) Dielectric constant at different concentration of Pectin polymer.

In this Fig. 2.5 (i) Pectin polymer shows increase in dielectric constant down the lane from 100µl to 500µl as well as left to right from 100µl to 1000µl. The reason for increase in dielectric constant values is explained above in Fig. 2.5 (a)



(j) Dielectric constant at different concentration of Gelatin polymer.

In this Fig. 2.5 (j) Gelatin being the weal polyvalent ampholyte shows increase in dielectric constant as we go from 100µl to 1000µl of polymer concentration with respect to 100µl to 500µl of boric acid concentration.

**Fig. 2.5**: - Dielectric constant of different concentration of biopolymers.

Table 8: - Capacitance and dielectric constants of different polymers.

| Polymer | Capacitance (pF) | | Dielectric constant | |
|---|---|---|---|---|
| | Minimum | Maximum | Minimum | Maximum |
| Chitosan | 55.6 | 88 | 0.2281 | 0.2447 |
| $MP_2$ | 77.3 | 81.3 | 0.2149 | 0.2261 |
| $MP_1$ | 74.5 | 125 | 0.1841 | 0.2032 |
| Xanthan Gum | 73.1 | 84.5 | 0.1724 | 0.276 |
| Guar Gum | 73.3 | 89.3 | 0.1774 | 0.2605 |
| Starch Corn | 74.3 | 105.7 | 0.1793 | 0.3000 |
| Locust Bean Gum | 75.2 | 107.2 | 0.1952 | 0.28496 |
| Cellulose | 74.9 | 109.6 | 0.1763 | 0.2597 |
| Pectin | 75.2 | 121.8 | 0.1802 | 0.2905 |
| Gelatin | 75.9 | 130.7 | 0.1849 | 0.3272 |

The maximum and minimum value of capacitance and dielectric constant is written here. Different polymers exhibit different capacitance value and dielectric constant.

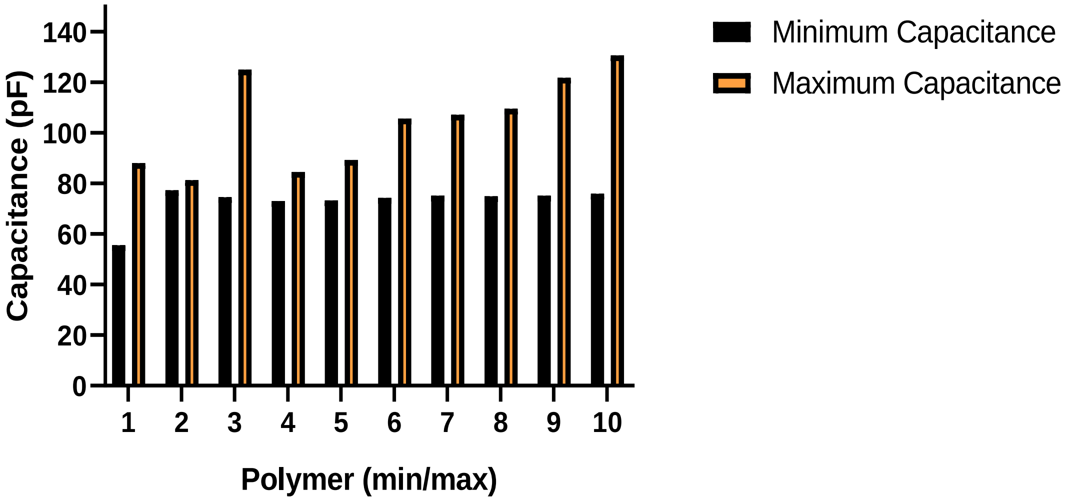


**Fig 2.6**: - Capacitance (min/max) of different polymers.

Maximum and minimum value of capacitance of each polymer is plotted in graph. This graph depicts the range between which capacitance of any given polymer will come. Based on the value obtained, the concentration of polymer as well as boric acid can be determined.

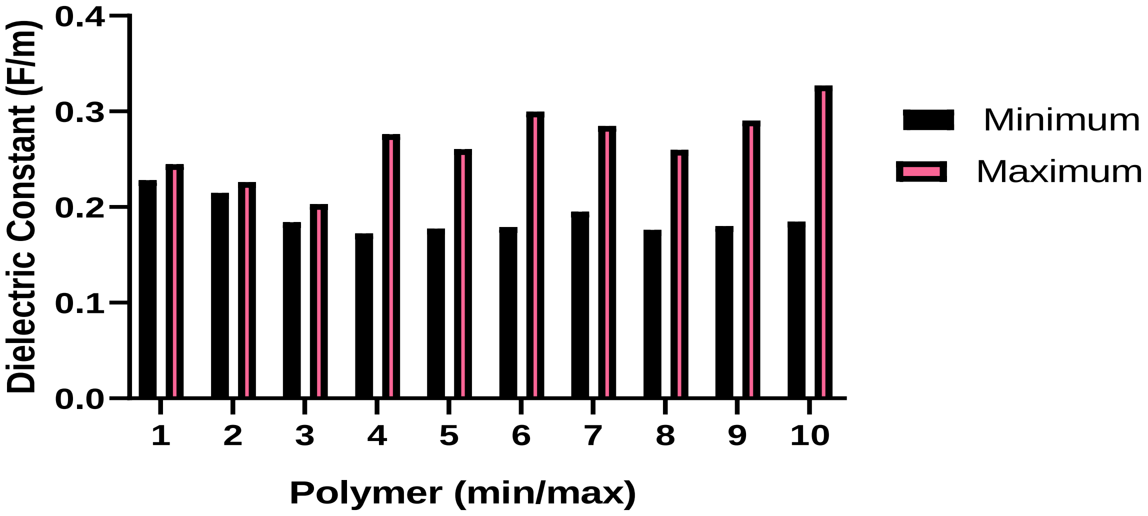


**Fig 2.7**: - Dielectric constant of different polymers

Different polymer had different dielectric constant, the maximum and minimum value of it gives a range between which dielectric constant is varying. For an unknown sample whose dielectric constant is known, its concentration can be calculated.

## Simulation results of MOSFET biosensor

In this thesis work, Double Gate Junctionless MOSFET biosensor as shown in Fig. 1.4 has been designed using SILVACO TCAD tool. In the designed structure the underlap cavity region can be filled with a biopolymer doped with boron ions. The dielectric constant of this biopolymer mixture varies when boron ion concentration is changed. This change in dielectric constant due to change in boron concentration can easily be detected by observing the change in drain current and change in threshold voltage of the MOSFET. The following sections discuss the results obtained from simulation of proposed Bio-FET on SILVACO TCAD tool.

### 4.3 $I_D$ v/s $V_G$

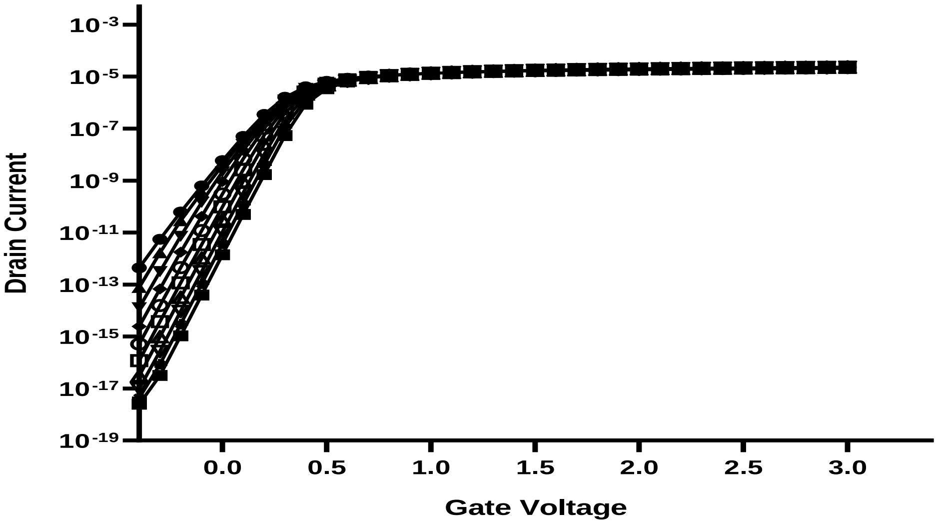


**Fig 2.8**: - Drain Current v/s Gate Voltage of varying dielectric constant.

Fig 2.8 shows samples having different dielectric constant ranging from K=1 to K=10. As the dielectric constant is varied, the amount of drain current increases in the underlap region.

Table below shows the different dielectric constant values of biopolymers.

Table 9: - Dielectric Constant of different polymers.

| Polymer | Dielectric Constant |
|---|---|
| Guar Gum | 2.91 |
| Xanthan Gum | 2.85 |
| Locust Bean Gum | 2.42 |
| Carboxymethyl Cellulose | 3.3 |
| Chitosan | 5.5 |
| Pectin | 3.2 |
| Gelatin | 1.24 |
| Starch Corn | 1.7 |

The effect of neutral and charged analytes appearance and non-appearance on the channel current of n-type split entryway JL MOSFET demonstrates the channel current variation when the different analytes are bound in the open cavity region. The off-current of the device diminishes when the dielectric constant of the under lap region increases, though the on-current stays unaltered. The off-current decreases for the negative analytes though it increased for positive analytes. The cavity of the device is loaded up with biopolymer. The amount of current that is flowing through Silicon is increased when doping of boric acid is gradually increased in the polymer.

## 4.4 K vs $V_T$

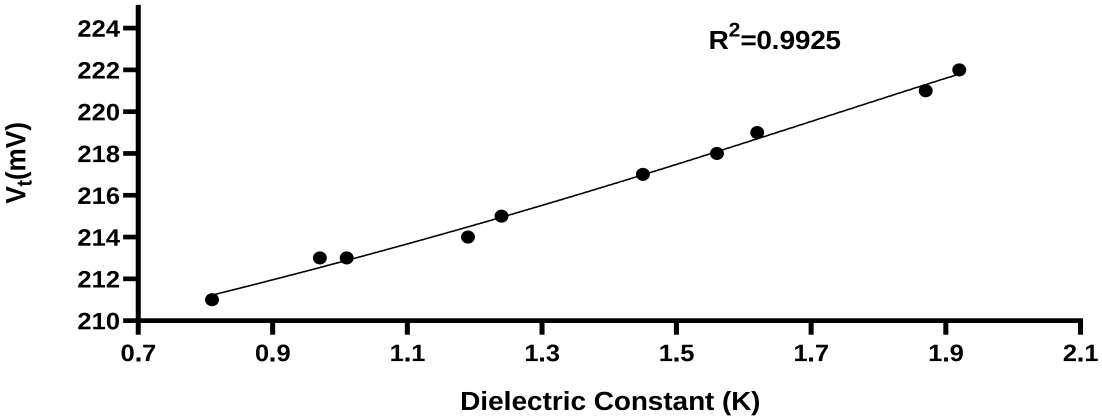


**Fig 2.9**: - Dielectric Constant vs $V_t$ graph of different polymers. (Where solid lines represents best fitted linear curve)

Fig 2.9 shows the varying threshold voltage with respect to dielectric constant of different polymers. This graph depicts the direct relation of dielectric constant of different material and the threshold voltage of the material. So, for any sample whose threshold voltage is known, its dielectric constant can be evaluated. That means, concentration of boron ions can be calculated from the value of dielectric constant.

## 4.5 **Sensitivity**

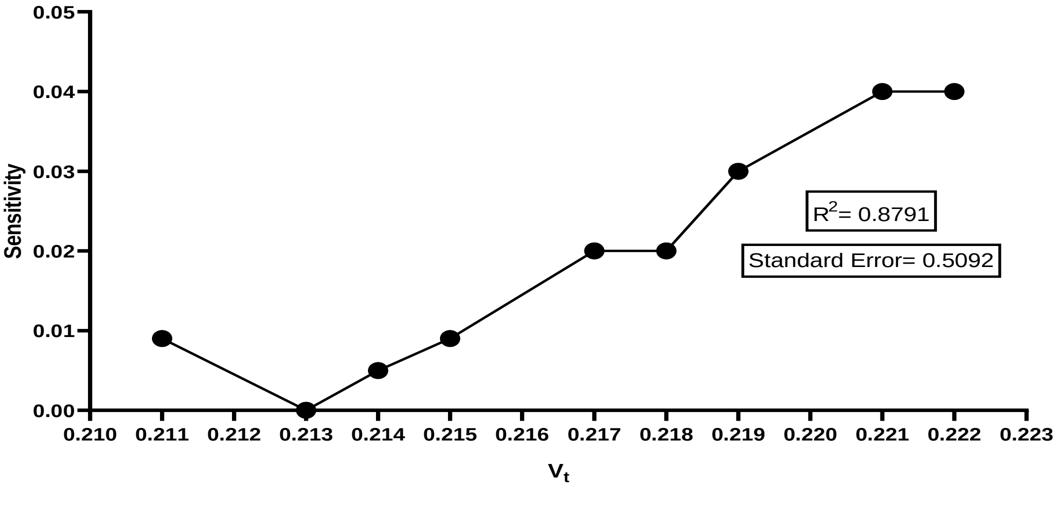


**Fig 3**: - Sensitivity of different polymers as a sensor.

Fig 3 shows sensitivity of different polymer to sense boron ions in the given mixture. The sensitivity of the device is calculated with respect to threshold voltage when biopolymer mixture is filled in the underlap cavity. The sensitivity of device linearly increases when the dielectric constant of underlap region increases. This will detect the small change in dielectric and show large change in threshold voltage.

## 4.6 **Conductance**

Conductance is defined as the degree to which any sample conducts electricity, in terms of the ratio of current flowing to the potential difference of the sample.

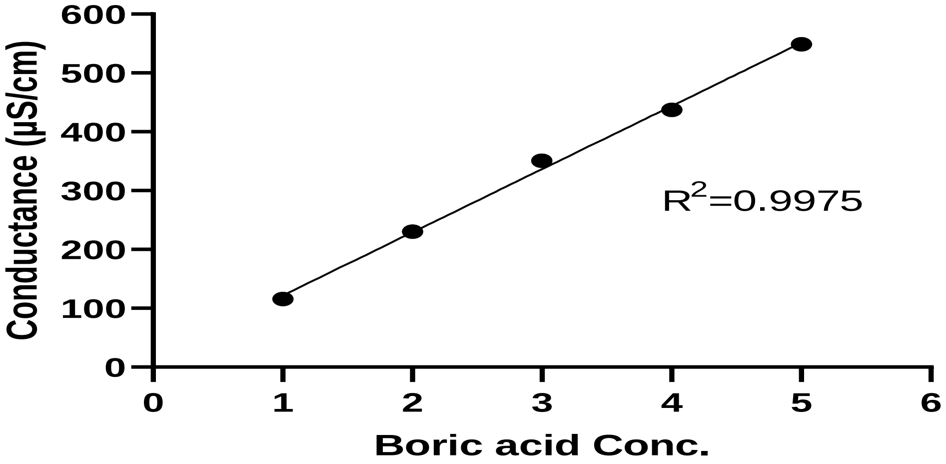


**Fig 3.1**: - Conductance of Boric acid (µS/cm).

The Conductance increases with increase in Boric acid concentration in Distilled water. The increase in conductivity is due to the presence of electrolytes as the mobility of the ions increases as the dielectric constant of the solvent decreases. There is a decrease in conductance at higher temperatures as boric acid becomes weak, or gets strongly associated, as do all acids and bases in aqueous solution.

# Chapter 5

## Salient Findings

- Boron is an essential micronutrient which is required by living beings in trace amounts.
- Due to emerging industries of glass, ceramic, cosmetics and several other factors, like combustion of coal etc. boron emission into the environment has increased.
- To determine the concentration of boron in various sample solution spectrophotometric methods have been implemented. These methods have several limitations such as low sensitivity, not very precise, time consuming, expensive, sophisticated instrument, larger sample volume.
- To overcome this limitation, a sensor is proposed. This sensor is designed in SILVACO TCAD tool.
- Different polymers were tested for their ability to remove boron from the sample solution based upon their dielectric properties.
- Different dielectric constant of the polymers were then used in TCAD tool and observe the change in drain current and threshold voltage of the MOSFET device.
- At last, sensitivity of the device having different dielectric constant is observed in the TCAD tool.

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# Appendix-I

ATLAS

Provides general capabilities for physically-based two (2D) and three-dimensional (3D) simulation of semiconductor devices.

It is designed to be used in conjunction with the VWF (VIRTUAL WAFER FAB) INTERACTIVE TOOLS. The VWF INTERACTIVE TOOLS, which include DECKBUILD, TONYPLOT, DEVEDIT, MASKVIEWS, and OPTIMIZER, are documented in the VWF INTERACTIVE TOOLS USER MANUALS.

It is supplied with numerous examples that can be accessed through DECKBUILD.

ATLAS: -

- Runs in the DECKBUILD interactive run-time environment.
- Is interfaced to TONYPLOT, the interactive graphics and analysis package.
- Accepts input from the ATHENA and SSUPREM3 process simulators.
- Is interfaced to UTMOST parameter extraction and device modelling software.
- Can be used in experiments with the VWF AUTOMATION TOOLS.
- DECKBUILD provides an interactive run time environment.
- TONYPLOT supplies scientific visualization capabilities.
- DEVEDIT is an interactive tool for structure and mesh specification and refinement.
- MASKVIEWS is an IC Layout Editor.
- The OPTIMIZER supports black box optimization across multiple simulators.
- It is often used in conjunction with the ATHENA process simulator. ATHENA predicts the physical structures that result from processing steps. The resulting physical structures are used as input by ATLAS, which then predicts the electrical characteristics associated with specified bias conditions. The combination of ATHENA and ATLAS makes it possible to determine the impact of process parameters on device characteristics.

ATLAS is a physically-based device simulator that predicts the electrical characteristics which are associated with specified physical structures and bias conditions. This is achieved by approximating the operation of a device onto a two or three dimensional grid, consisting of a number of grid points called nodes. By applying a set of differential equations, derived from Maxwell's laws, onto this grid you can simulate the transport of carriers through a structure. This means that the electrical performance of a device can now be modelled in DC, AC or transient modes of operation.

There are three physically-based simulations. These are:

- It is predictive.
- It provides insight.
- It conveniently captures and visualizes theoretical knowledge.

Physically-based simulation has become very important for two reasons. One, it is almost always much quicker and cheaper than performing experiments. Two, it provides information that is difficult or impossible to measure. The drawbacks of physically-based simulation are that all the relevant physics must be incorporated into a simulator, and numerical procedures must be implemented to solve the associated equations. These tasks have been taken care of for users of ATLAS.

Most ATLAS simulations use two input files: -

- The first input file is a text file that contains commands for ATLAS to execute.
- The second input file is a structure file that defines the structure that will be simulated.

ATLAS produces three types of output files: -

- The first type of output file is the run-time output, which gives you the progress and the error and warning messages as the simulation proceeds.
- The second type of output file is the log file, which stores all terminal voltages and currents from the device analysis.

- The third type of output file is the solution file, which stores 2D and 3D data relating to the values of solution variables within the device at a given bias point.

ATLAS is normally used in conjunction with the DECKBUILD run-time environment, which supports both interactive and batch mode operation.

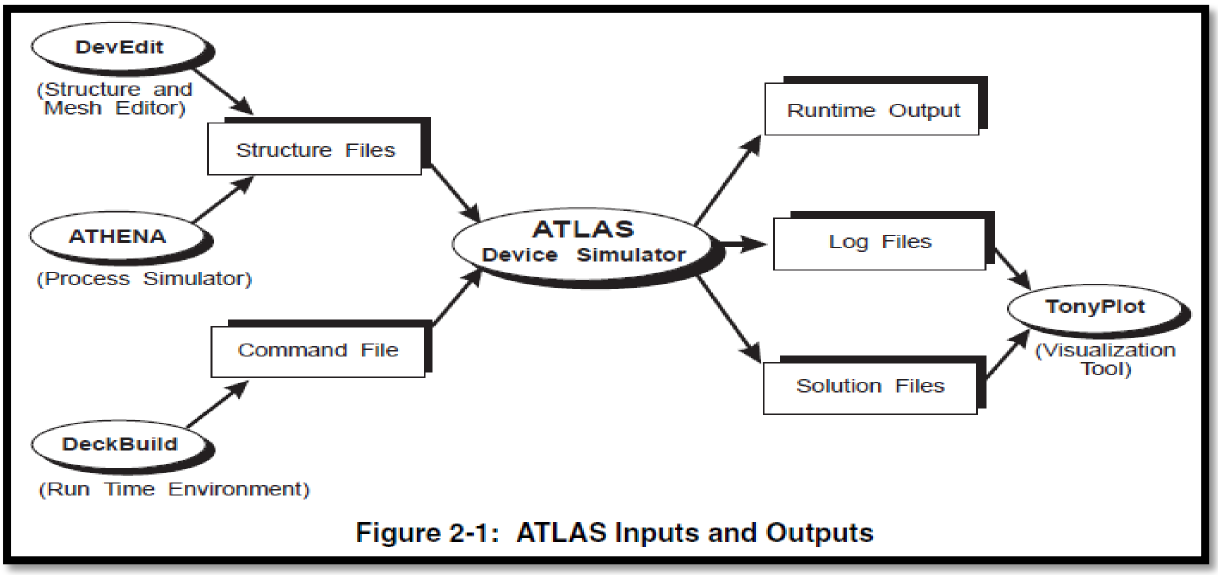
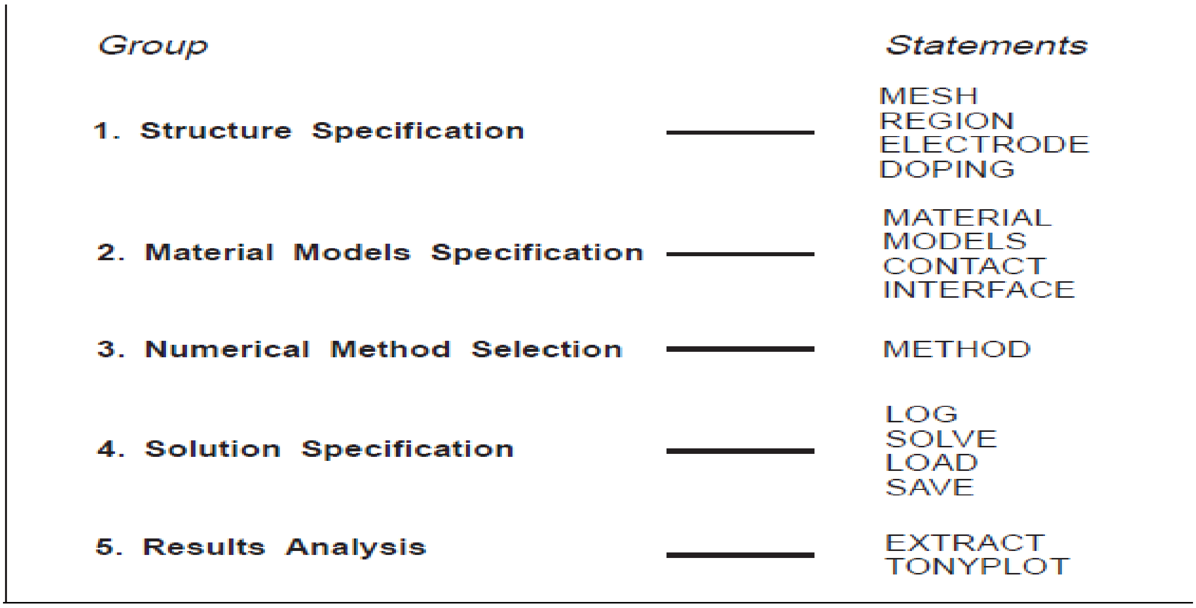


**Fig 3.2**: - Types of information that flows in and out of ATLAS.



| *Group* | *Statements* |
|---|---|
| **1. Structure Specification** | MESH<br>REGION<br>ELECTRODE<br>DOPING |
| **2. Material Models Specification** | MATERIAL<br>MODELS<br>CONTACT<br>INTERFACE |
| **3. Numerical Method Selection** | METHOD |
| **4. Solution Specification** | LOG<br>SOLVE<br>LOAD<br>SAVE |
| **5. Results Analysis** | EXTRACT<br>TONYPLOT |

**Fig 3.3**: - ATLAS Command Groups with the Primary Statements in each Group.

# Appendix-II

## CHEMICALS

### 1. Boric Acid Solution

400mg of Boric Acid (AR Grade) was dissolved in 20ml Distilled Water for stock solution. Further, dilution was made from the stock solution to have different concentration of Boric Acid ranging from 1ml to 5ml and volume was made up to 10ml by adding Distilled Water.

### 2. Polymer Solution

Different polymers were weighed and dissolved in distilled water.