Declaration

I, **Satyajit Das**, hereby declare that the present thesis, entitled **"Design and Development of Capacitive Sensor for Bitterness Assessment in Citrus Fruit Juices"**, is the record of work done by me under the supervision of Prof. Partha Pratim Sahu, Professor, Department of Electronics and Communication Engineering, Tezpur University, Tezpur. The contents of the thesis represent my original works that have not been previously submitted for any Degree/Diploma/Certificate in any other University or Institutions of Higher Education.

This thesis is being submitted to Tezpur University for the Degree of Doctor of Philosophy in Electronics and Communication Engineering.

Place: Tezpur University, Tezpur

Date:

(Satyajit Das)

TEZPURUNIVERSITY

(*A Central University Established by an Act of Parliament*)

Napaam, Tezpur-784028, Sonitpur, Assam, India

Certificate

This is to certify that the thesis entitled, "**Design and Development of Capacitive Sensor for Bitterness Assessment in Citrus Fruit Juices**", submitted to the School of Engineering, Tezpur University in partial fulfillment for the award of the degree of Doctor of Philosophy in Electronics and Communication Engineering is a record of research work carried out by **Mr. Satyajit Das** under my supervision and guidance.

All help received by him from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any other degree.

(*Supervisor*)

Partha Pratim Sahu
Professor, Department of
Electronics and Communication
Engineering
School of Engineering, Tezpur University

TEZPURUNIVERSITY

(*A Central University Established by an Act of Parliament*)

Napaam, Tezpur-784028, Sonitpur, Assam, India

Certificate of the External Examiner

This is to certify that the thesis entitled **"Design and Development of Capacitive Sensor for Bitterness Assessment in Citrus Fruit Juices"** submitted by **Mr. Satyajit Das,** Department of Electronics & Communication Engineering, School of Engineering, Tezpur University in partial fulfilment for the award of the degree of Doctor of Philosophy in Electronics & Communication Engineering has been examined by us on_____ and found to be satisfactory.

The committee recommends for the award of the degree of Doctor of Philosophy.

Supervisor **External Examiner**

(Prof. Partha Pratim Sahu) **( )**

Date:_____ **Date:_____**

Acknowledgement

At the very outset, I take it as an honour to express my profound gratitude and sincere thanks to my respected supervisor Partha Pratim Sahu, Professor, Department of Electronics and Communication Engineering, Tezpur University, for his invaluable supervision, guidance and constructive suggestions and particularly for his meticulous approach and gracious engagement at each and every stage of the course to make this project a reality and success.

I also express my gratitude to the Head of the Department, Electronics and Communication Engineering and all the faculty members and staff of the department for their untiring support and co-operation during the whole duration of my Ph.D. course. In addition I would also like to offer my sincere thanks to the institute authority for providing me the access to the laboratory and research facilities.

I wish to acknowledge Prof. P. Mishra, Professor, Department of FET, Tezpur University for her insightful suggestions. I offer my thanks to Dr. B. Mondal, Assistant Prof. Dept of ECE for his continuous help in my work. I would like to thank the Sophisticated Analytical Instrument Center (SAIC), Tezpur University, for providing facilities for characterization and express my gratitude to all staff members of SAIC. I offer my thanks to Dr. Arun Kumar Gupta and the research scholars of Food and Vegetable lab of FET dept. TU for their help in carry out my work. Also, I would like to express my gratitude to my lab mates and friends, Dr. Palash Phukan, Dr. Rewrewa Narzary, Dr. Jagat Das, Mr. Nithin Joseph Panicker, Dr. Mukut Senapati, Mr Geetartha Sarma, Mr. Mrigendra Yadav for their support and assistance. I am thankful to Ms. Honey Brahma for helping in the characterization process.

I am deeply gratefull to my father, mother, wife, my son, all my friends and family members for their unconditional support that have been my treasure and strength.

Last but not the least, heartiest thanks to the Almighty, who bestowed all his blessings on me.

Satyajit Das

Dedicated to my

Parents

List of Figures

Figure 2.1: The citrus fruits (a) Citrus Limetta (mosambi) (b) Citrus grandis (pomelo) (c) Citrus sinensis (orange)…….. 12

Figure 2.2: Chemical structure of (a) naringin and (b) limonin …….. 14

Figure 2.3: limonate- A-ring lactone (LARL) being converted to limonin in acidic medium and its reverse process……... 15

Figure 2.4: Degradation of limonin……...… 21

Figure 2.5: Working of an electro-chemical sensor with different components 25

Figure 2.6: Parallel plate capacitor……...…. 26

Figure 3.1 (a) the IDE structure (b) Gradual transformation of parallel to planar geometry……. 39

Figure 3.2: (a) Interdigitated Electrodes Structure (b) Side view of IDE showing capacitances formed (c) the unit cell of IDE with permittivities of different medium (d) showing fringing field and transverse filed penetrating the dielectric, air and substrate…….. 40

Figure 3.3: The capacitance model……..... 41

Figure 3.4: Design and optimization of IDE parameters to improve the performance of the sensor: (a) Interdigitated Electrodes Structure showing geometric parameters (b) Geometric view of comb structure designed in COMSOL Multiphysics (c) Mesh analysis of the comb structure (d) Electric field colormap of IDE (e) simulation concept/ steps..... 43

Figure 3.5: (a) IDEs capacitance vs metallization ratio for We = 1 mm, L = 5mm and and N=8 (b) capacitance vs width of the Electrodes for η=0.5, N=8 (c) Plots of Capacitance vs number of the Electrode fingers for η=0.5, N=8) (d) Change in capacitance with overlapping length of the fingers……..….. 44

Figure 3.6: (a) & (b) Capacitance vs permittivity of the material for different values of "a" keeping width of the of electrodes constant (c) & (d) capacitance vs permittivity of the material for different values of "w" keeping the gap between the electrode constant…….…….……. 47

Figure.4.1: steps for green synthesis of CeO_2 nanoparticles using D. indica petal aqueous extract ……..…….. 53

Figure 4.2: Reflux condenser……. 54

Figure 4.3: (a) FTIR spectroscopic images of samples C1, C2, C3 and C4 (b) UV- spectroscopic images of samples C1, C2, C3 and C4. ……... 55

Figure 4.4. Figure 4.4. EDS spectra of the, samples (a) as-synthesized (C1) b C2 (c) C3 (d) C4 (e) XRD pattern of the as-synthesized CeO2 NPs (C1) and annealed sample (C3) (f) Raman spectra of C1 and sample C3…… 56

Figure 4.5: (a) FESEM image of the CeO_2 nanoparticles sample (C1) (b) FESEM image of the sample (C3) annealed at 400°C (c) TEM image of the sample (C3) at 100nm scale (d) Particle size histogram of annealed CeO_2 NPs (C3)…… 58

Figure 4.6: (a) the process showing the synthesis of magnesium silicate and PVA composite (b) FTIR analysis of $MgSiO_3.xH_2O$ and $MgSiO_3.xH_2O$ + PVA (c) XRD pattern of Magnesium silicate ($MgSiO_3.xH_2O$) (d) EDX analysis showing weight and atomic percentage of the composite……..……. 59

Figure 4.7: SEM image of $MgSiO_3.xH_2O$ and PVA composite …….. 61

Figure 4.8: (a) Showing fabrication steps and (b) drop coating of CeO_2 +PVA over the IDE device (c) Fabrication flow chart of IDE sensor……... 62

Figure 4.9: Figure 4.9: a) The capacitance measuring set-using Aurduino UNO b) the PLX-DAQ data acquisition in PC…… 64

Figure 4.10: Sensing setup……... 64

Figure 4.11: (a) The equivalent circuit, showing charging and discharging of capacitor, Here, V- Supplied voltage, C=Cap. R= resistor through which the capacitor gets charged (b) the charging curve for capacitor …….…… 65

Figure 5.1: HPLC setup…….…… 76

Figure 5.2: Sensing Mechanism of Limonin and CeO_2…….…… 76

Figure 5.3: (a) time dependant analysis for the sensor at different concentrations of limonin standards (b) calibration curve with regression analysis……..…….. 77

Figure 5.4: (a) Time dependant selectivity study with interfering compounds tested independently (b) columns showing gradual increase in capacitance 80

response for limonin with insignificance change with respect to other interfering compounds…….…….

Figure 5.5: Response of sensor shows Bars representing sensor's response to DI water and limonin conc (90 ppb, 100 ppb. 1ppm) ……..…… 81

Figure 5.6: (a) time domain analysis of Citrus llimetta juice sample at different time interval after juice preparation at RT (b) limonin content in Citrus llimetta juice sample calculated at different time period (c) time domain analysis of Citrus grandis juice sample at different time interval after juice preparation at RT (d) limonin content in Citrus grandis juice sample calculated at different time period …… 82

Figure 5.7: HPLC analysis for (a) standard limonin (10 ppm) (b) Citrus grandis juice sample at different time (c) Citrus llimetta juice sample at different time…….. 83

Figure 5.8: Comparison of HPLC results with sensor's output…….....…….. 84

Figure 5.9: Response time calculation considering real juice sample at 0h 85

Figure 5.10: Reusability of sensors (a) sensor tested with 5 ppm limonin standard (b sensor tested with 5 ppm limonin standard……. 86

Figure 6.1: adsorption of limonin on the surface of magnesium silicate…….. 95

Figure 6.2: (a) Gallic acid standard curve (b) Standard regression analysis for Quercetin……. 100

Figure 6.3: (a) capacitive response of the sensor with 4mM $MgSiO_3.xH_2O$ for different concentration of limonin (b) calibration curves of the sensor for 1mM, 2mM, 4mM $MgSiO_3.xH_2O$-PVA composite…….. 102

Figure 6.4: (a) Selectivity study using interfering compounds usually present in juice (b) bar graph exhibiting a gradual increase in capacitance with respect to limonin concentration with insignificance change for other interfering compounds ……...……. 104

Figure 6.5: (a) Time-dependent capacitive response for model juices prepared (b) variation of sensors output with model juices……... 105

Figure 6.6: Detection limit of IDE sensor…...…….. 105

Figure 6.7: sensor's performance on the electrodes fabricated on paper with andwithout sensing materials……..…….. 106

Figure 6.8: (a) real time analysis of the citrus limetta juice sample at different time intervals after juice preparation (b) quantification of limonin content in real juice sample using HPLC…...…… 106

Figure 6.9: comparison of sensor's response with HPLC analysis in term of limonin quantification……..……. 107

Figure 6.10: (a) real time analysis of the citrus grandis juice sample at different time intervals after juice preparation (b) quantification of limonin content in real juice sample using HPLC…….. 107

Figure 6.11: bar showing decrease in limonin content of juice (held for 6 hrs of its preparation) with its percentage reduction when expose to the sensor for 60s and 120s (a) Citrus limetta at 0h(b) Citrus grandis at 0h (c) Citrus limetta at 6h (d) Citrus grandis at 6h…….…… 110

Figure 6.12: sensory evaluation of magnesium silicate treated and untreated juice……... 115

Figure 6.13: comparative study for fresh and debittered juice with respect to TPC, TFC and antioxidant activity for (a) citrus limetta (b) citrus grandis……...……. 116

Listof Tables

Table2.1: Few Limonin assessment methods / techniques reported……..... 19

Table 3.1: Comparison of different electrode materials……. 42

Table 3.2: Capacitance for IDE vs metallization ratio for W_e=1 mm and N=8.. 46

Table3.3: Capacitance for IDE vs Width of the Electrodes for η=0.5, N=8…… 46

Table 3.4: Capacitance for IDE vs number of the Electrode fingers for η=0.5, N=8…… 46

Table 3.5: Capacitance for IDE vs overlapping length of the Electrode fingers for η=0.5, N=8……... 47

Table 4.1: Calculation of average crystal size of CeO_2 Nanoparticles particles… 57

Table 4.2: Calculation of average crystal size of MgSiO3 particles…….. 60

Table 4.3: Accuracy measurement of the capacitance measuring set up ……. 65

Table 5.1: Calculation for the prediction interval..... 78

Table 5.2: Residual plot……. 78

Table 5.3: Real time domain analysis using sensor and HPLC analysis for accuracy measurement for *citrus limetta*……..... 83

Table 5.4: Real time domain analysis using sensor and HPLC analysis for accuracy measurement for *citrus grandis*…… 85

Table 5.5: Reusability of IDE sensor……..... 87

Table 5.6: Shelf life of the sensor …… 88

Table 5.7: Comparative study with previously reported devices…….. 89

Table 6.1: calculation for the prediction interval……. 103

Table 6.2 Residual plot……..……. 103

Table 6.3: Sensor based and HPLC analysis results for Citrus grandis fruit juice 108

Table 6.4: Reusability of IDE sensor ……... 109

Table 6.5: Reproducibility of IDE sensor……. 109

Table 6.6: concentration of limonin, and its percentage removal in citrus limetta and citrus grandis juices treated with the fabricated device/sensor based on magnesium silicate hydrate……… 111

Table 6.7: Toxicity study of Magnesium Silicate……. 112

Table 6.8: Toxicity study for PVA……... 113

Table 6.9: Comparison of some of the reported sensors/devices for limonin quantification and debittering ……. 116

Table 6.10: Cost and complexity comparison of some of the reported sensors/devices for limonin quantification/debittering…… 118

Table 6.11: Cost estimation (approximate) of the fabricated sensor……..... 119

Nomenclature

Symbols:

a	Gap between two consecutive electrodes
β	Line broadening at half the maximum intensity
C_{total}	Total capacitance
C_{I}	Internal capacitance
C_{e}	Edge capacitance
K(k)	first-order elliptic integral,
k	elliptical modulus Fringe capacitances along the length L
C_f	Fringe capacitances along the width W
C_{stray}	Stray capacitance
C_{test}	Capacitance under test (unknown capacitance)
C_{s}	Capacitance due to ε_s
C_{t}	Capacitance due to ε_m
C_{f}	Capacitance due to ε_o
t	Thickness of the electrode
D	Average Crystallite size
e^-	Electrons
ε_0	Permittivity in vacuum
ε_{m}	Relative permittivity of sensing layer
ε_{s}	Relative permittivity of substrate
G	Gap between Electrode fingers
h	Hours
h	Height of the sensing layer
K	Dimensionless shape vector, constant
k	Modulas of elliptical integral
L_{f}	Overlapping Length of the electrode

L_e	Length of the electrode
ns	Nano seconds
N	Number of electrodes
$OH^{\cdot}$	Hydroxyl radical
O^{-}	Oxygen ionic species
$O_2^{-\cdot}$	Anionic superoxide radicals
R^2	Regression coefficient
R	Sensor response
s	second
V_{Out}	Output Voltage
V_{in}	Input voltage
W	Width of the electrode fingers
q	Charge
R	Resistance
σ	standard deviation
θ	Diffraction angle
λ	X-ray wavelength

Abbreviations:

Ag	Silver
Au	Gold
CeO_2	Cerium oxide
CAM	(cytoplasmatic acetate mevalonate).
CNP	Ceria Nanoparticles
DPPH	1,1-Diphenyl-2-picryl-hydrazyl
2DMs	Two-dimensional materials

DO	Dissolved oxygen
DI	De-ionized
EIA	Enzyme-linked-immuno adsorbent assay
EDX	Energy Dispersion
FTIR	Fourier transform infrared
FESEM	Fourier Enhanced Scanning Electron Microscopy
FWHM	Full Width Half Median
GC	Gas chromatography
GAC	Gallic Acid Content
GLC	Gas Liquid chromatography
HPLC	High performance Liquid chromatography
HLB	Huanglongbing
IDEs	Interdigitated electrodes
LCD	Liquid crystal display
LOD	Limit of detection
LARL	Limonite A-ring lactone
MRF	Magnetic Resonance Finger Printing
MUT	Material under test
MIPs	Molecularly imprinted polymers
MgO	Magnesium Oxide
nm	Nano metre
NDT	Nondestructive testing
NPs	Nanoparticles
OFS	Optical fiber sensor

OECT	Organic Electrochemical Transistor
ppm	Parts per million
ppb	Parts per billion
PVA	Poly Vinyl Alcohol
POF	plastic optical fiber
PTFE	Polytetrafluoro ethylene
RT	Room temperature
RSD	Relative standard deviation
Rpm	Rotation per minute
RIA	Radioimmunoassay
SiO_2	Silicon Di oxide
SD	Standard Deviation
SNR	signal to noise ratio
SEM	Scanning Electron Microscopy
TLC	Thin Layer Chromatography
TPC	Total Phenolic Content
TEM	Transmission Electron Microscopy
TFC	Total Flavonoid Content
UV	Ultra –violate
UV-Vis	Ulta violet vissible
XRD	R- ray Diffraction