GO/μ–IDEs/p-Si Based Real Time Sensors for F^- Detection in Natural Drinking Water

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***Abstract*—Molecular interaction between Graphene oxide (GO) synthesized using chemical oxidation of graphite and lithography patterned aluminum (Al) micro-interdigitated electrodes (μ–IDEs) on p–Si for aqueous fluoride ion (F^-) sensor is demonstrated. The strong hydrogen bonding and molecular adsorption of aqueous F^- onto the active hydrophilic sites (hydroxyl, carbonyl, carboxyl, epoxy) present in GO integrated with Al–μ–IDEs is examined using electrical characterization (current-voltage, capacitance-frequency). The current for GO-Al-μ-IDEs shows almost 2.3, 4.7 times increase for F^- solution of 0.1 and 1 ppm with respect to GO. Additionally, the integration of GO-Al-μ-IDEs shows almost three order increase in the current for F^- solution of 10 ppm. The adsorption of F^- onto the GO film results the increase in charge carriers and finally results the increase in the output current response. Owing to the saturation in the binding sites present onto GO for F^- solution of 100 ppm, the F^- penetrate the GO film and results the decrease in current of the sensor. Thus, the cost effective, easy processability and selectivity of proposed GO-integrated Al-μ-IDE based real time sensors have a great potential to be a forefront sensor for detection of aqueous F^- present in natural drinking water.**

***Index Terms*— F^-, Graphene oxide, Hydrogen bonding, Interdigitated electrodes, Lithography.**

I. INTRODUCTION

GRAPHENE OXIDE [1] a two dimensional nano-material has gained world-wide interest in electronics, biomedical, sensor, etc. owing to its remarkable properties including large surface to volume ratio, high carrier mobility, good water dispersibility, outstanding thermal and electrical conductivity [2]-[4]. GO is a promising material for fast and long-term chemical, bio-sensor applications owing to the existence of chemically reactive oxygen containing (hydrophilic) functional groups like hydroxyl, epoxy, carboxyl and carbonyl at the basal plane and edges [5].

On the other hand, the detection of inorganic/organic particulates in natural sources of drinking water from nuclear plants, drugs, cosmetics, industrial waste, etc. [6] have attracted an immense attention owing to its adverse effects on the human/animal life [7]. Among various inorganic constituents in water, the aqueous fluoride anion (F^-) has emerged as a severe health problem in many parts of the world [7] [8]. Although, F^- (smallest anion), is an important constituent and adds a significant role in the human/animal life, but the disproportionate intake results in adverse health effects like dental and skeletal fluorosis finally results into permanent bone deformation. The permissible range of fluoride in natural drinking water as per Indian and World Health Organization (WHO) standard is 1 and 1.5 ppm, respectively [8].

In order to meet the Indian and WHO measure, detection/removal of F^- is reported [8]-[10]. Although, the F^- detection/removal reported in literature is mainly based on optical techniques with the use of sophisticated instruments like UV-Vis, NMR, and colour change in the aqueous media. Hence, the above mentioned detection mechanism in aqueous medium suffers from detection in a precise wavelength, slow response and sensitivity [11], hold back these techniques to accept globally. Therefore, a highly sensitive, reliable, low power, cost effective, state of art F^- detection technique is highly desirable.

A GO nano-sheet, almost impermeable to liquid, vapour and gases (including helium), but excellent permeability to water molecules makes it a promising candidate for water treatment and detection. Recently, Borini *et al.* [12], reported ultra fast humidity sensing devices based on the interaction of GO nano sheets with water molecules.

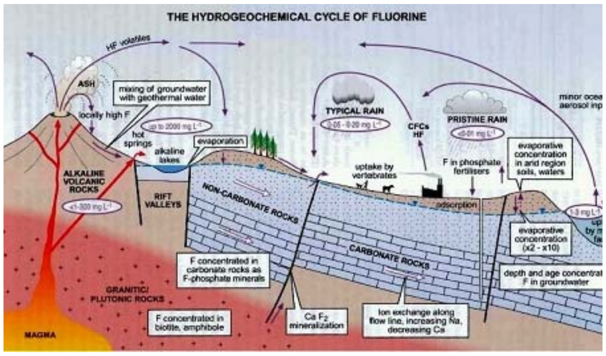

Fig. 1. Different sources of F^- contamination [6].

In the present study, an interaction between highly sensitive GO (as a sensing material) and aluminium (Al) micro-Interdigitated electrode (μ-IDEs) Micro-Electro-Mechanical-Sensor (MEMS) is fabricated for the detection of aqueous F^- in the range of 0.1-10 ppm. The interaction between F^- present in aqueous solution with GO and Al μ-IDEs is studied based on electrical characterization.

The paper is organized as follows: Section II presents the μ-IDEs working principle along with its advantages. A detailed experimental setup for the synthesis of GO, F^- stock solution, fabrication of sensor system based on the integration of GO and Al μ-IDEs over p–Si is presented in Section III. The electrical characterization of the sensor system for F^- detection in aqueous media ranging from 0.1-100 ppm is demonstrated in Section IV. Finally, we conclude in Section V.

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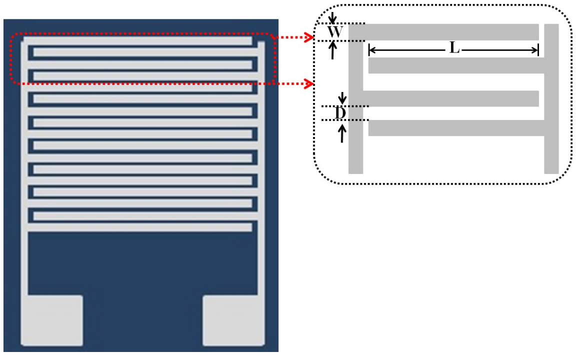

Fig. 2. Micro-Interdigitated electrode array along with its dimensiona parameters. From the figure it is clear that for present sensor system N=17.

II. IDE WORKING PRINCIPLE AND ADVANTAGES

IDEs based MEMS are potential candidate for surface acoustic wave (SAW), rapid biomedical and electrochemical sensors, owing to its several advantages [13, 14]. IDEs consist of two identical, parallel spaced array of electrode like a comb type structure to form an interdigitated system. IDEs have gained interest in sensing applications due to the cost effective, safe and simple mass fabrication steps involved.

The output characteristics of µ-IDEs are mainly dependent on the four dimensional parameters, number of electrodes (N), spacing (D) between the electrodes, length (L) and width (W), as shown in Fig. 2. On increasing the N, D and W for µ-IDEs it results in an increase in overall output signal due to increased surface area of µ-IDEs [15]. When a medium (GO, in present case) is placed between the µ-IDEs and potential is applied to the electrode, an electric field is set up in Al-µ-IDEs [14]. On addition of the sensing solution (aqueous F^-) to GO-Al-µ-IDEs, change in the dielectric constant, capacitance, conductance, impedance of µ-IDEs was observed.

The electrode material used plays a very important role to meet the enhanced sensitivity and reliability of the MEMS based chemical sensors. Presently, µ-IDEs were patterned over p–Si using aluminium (Al) as a metal electrode owing to its ease of patterning by lift-off (for thickness ≥ 150 nm), CMOS process compatible, high melting point, high adhesion with the substrate, capable of wire bonding for packaging, etc [16]. Even though, Al forms aluminium oxide (Al_2O_3) at low temperatures, and is highly sensitive for the removal of aqueous F^-, due to ion exchange formulation at the available hydrophilic sites on the surface [17].

Based on the above discussion, for the fabrication of highly reliable and sensitive GO integrated Al (µ-IDEs) senor for the detection of aqueous F^-, the dimensional parameters for the µ-IDEs array were chosen to be W= D = 300 µm, L=1 cm and N= 17.

III. EXPERIMENTAL

A. Synthesis of GO

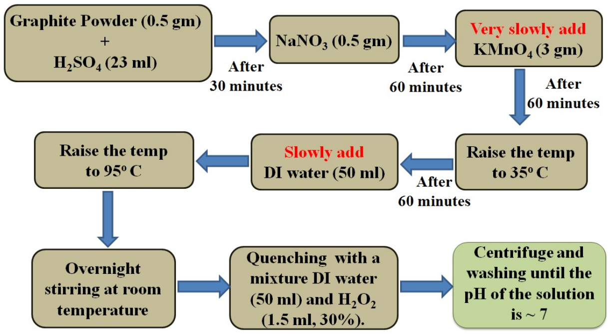

Fig. 3. Synthesis procedure of the graphene oxide (GO) based on chemical oxidation of graphite using Modified Hummers method.

Synthesis of Graphene oxide was carried out using modified Hummers method [5] through oxidation of extra fine graphite powder (particle size < 50 µm, 99.999% pure, Merck Make) with Sulphuric acid (H_2SO_4), Sodium Nitrate ($NaNO_3$) and Potassium permanganate ($KMnO_4$). De-ionized (DI) water with resistivity 18.2 MΩ/cm was used for preparation of F^- stock solution and wafer cleaning. The outline (as shown in Fig. 3) of the GO synthesis process is as discussed:

First, A glass beaker (500 ml) was kept in ice bath, graphite powder (0.5 gm) along with H_2SO_4 (23 ml) was added to the beaker and stirred for 30 minutes at 500 rpm.

Second, To the above solution add (0.5 gm) $NaNO_3$ with constant stirring for 60 minutes at 600 rpm.

Third, $KMnO_4$ (3 gm) was added very slowly (at a rate of ~ 0.5 gm/15 sec) to the previous solution. The slow addition of $KMnO_4$ was carried out to keep the temperature of the solution < 15 ^{o}C. Stir the resulting solution for 60 minutes at

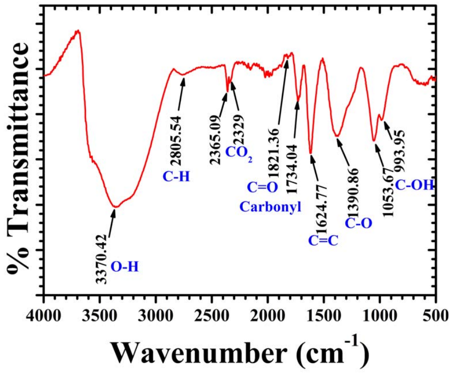

Fig. 4. FTIR transmittance spectrum of GO powder.

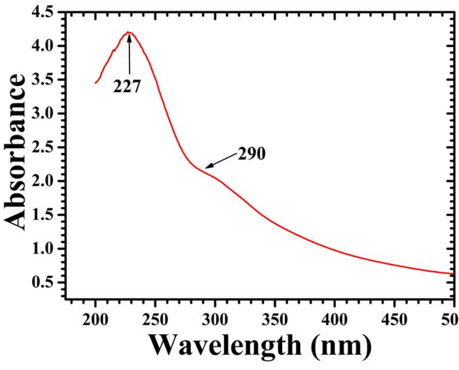

Fig. 5. UV-Vis spectra for GO (0.25mg/ml) dispersed in DI water.

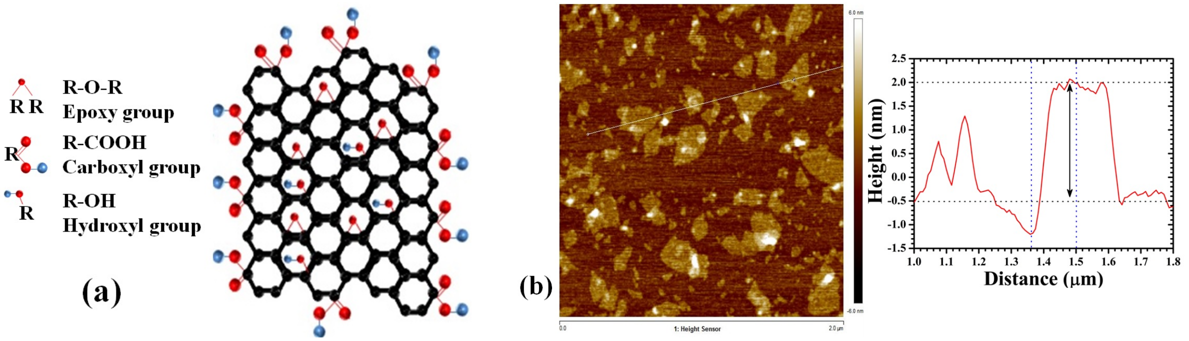

Fig. 6. Structure and Atomic Force Microscopy (AFM) of GO nano-sheets. (a) GO sheet along with the attached active oxygen containing functional groups. (b)AFM image and height analysis of GO nano sheets (~2.5 nm) deposited on p–Si substrates.

600 rpm.

Fourth, Remove the ice bath and slowly raise the temperature of the mixture to 35 ^{o}C along with continuous stirring for 60 minutes at 600 rpm.

Fifth, Slowly dilute the solution with the slow addition of DI water (50 ml) under continuous stirring at 600 rpm.

Sixth, Rapidly raise the temperature to 95 ^{o}C and stir the solution for 30 minutes followed by over-night stirring at room temperature for 600 rpm.

Seventh, The reaction was quenched with a mixture of DI water (50 ml) and H_2O_2 (1.5 ml, 30%).

Eight, The as prepared solution was centrifuged (at 3000 rpm for 5 min and 5000 rpm for 7 min) and washed with 4% wt HCl and DI water, to remove metal ions and acid residues. This step was repeated until the pH of the solution turns to 7.

GO dispersion of 0.25 mg/ml, filtered by 0.2 µm filter was used as a sensing precursor/material. FT-IR and UV-Vis characterization of GO powder was performed for the confirmation of available different oxygen containing hydrophilic functional groups attached to it. As shown in (Fig. 4) the FT-IR spectra of GO shows the characteristic hydroxyl (–OH), carbon–carbon (C=C), epoxy (C–O–C) carbonyl groups (CLO) of carboxylic derivatives stretching and absorption band peak at 3370.42, 1624.77, (1053.67 & 993.95), (1821.36 & 1734.04) cm^{-1}, respectively. As shown in Fig. 5, the UV-Vis, absorption spectra of GO exhibits a $\pi - \pi^*$, $n - \pi^*$ absorption band and shoulder at 227, 290 nm, respectively.

Fig. 6 shows the chemical structure and Atomic Force Microscopy (AFM) measurement for GO nano-sheets. Fig. 6 (a) shows the structure of GO sheet along with the active hydrophilic functional groups attached to its basal plane (epoxy, hydroxyl) and edges (carboxyl). Fig. 6 (b) shows the AFM tapping mode measurement for the GO nano-sheet over p–Si. The AFM image (2 x 2 µm) confirms the presence of bi or tri-layer GO (~ 2.5 nm) due to aggregation or self assembly of layers of GO during the drying process in the specimen preparation. However, in some areas monolayer of GO was also seen.

B. Preparation of fluoride ion stock solution

An aqueous F$^-$ stock solution of 100 ppm was prepared by the dissolution of 0.2210 gm of Sodium Fluoride (NaF) (Mw. 41.98871 g/Mol) in 1000 ml DI water. The further dilutions were made using the standard normality equation for the aqueous fluoride ion solution of 10, 1, and 0.1 ppm. In the present study, ~ 200 µl sensing solution of various concentrations was filled in the reservoir (with dimensions 2.5 x 2.5 x 0.8 cm) and utilized for sensing application.

C. Fabrication of µ-IDEs Arrays and Poly dimethyl siloxane (PDMS) based Integrated Reservoir for GO/ Al (µ-IDE)/Si Sensor

Standard RCA cleaned p–Si wafers with <100> orientation was used as a substrate for aqueous F$^-$ sensor. The p–Si substrates were dehydrated at 200 ^{o}C for 5 min. Thin film (~250 nm) of Al metal was deposited over the substrate using thermal evaporator under high vacuum (pressure of 9 x 10^{-7} m Bar). µ-IDEs structure was patterned over the Al/p–Si substrates with the help of Maskless Optical Lithography (Intelligent Micro Patterning) using Su-8(2002, Microchem) as a photo-resist material. Al etching was performed using standard etching procedure; the Su–8/Al/p–Si samples were kept in a mixture of acetic, nitric, ortho-phosphoric acid, DI water in the ratio 2:2:10:1 for 5 minutes at room temperature under stirring of 150 rpm. The unwanted Su-8 was washed out by placing the Su–8/Al/p–Si samples in N-Methyl-2-pyrrolidone (NMP), for 40-45 min at 70^{o}C under constant stirring of 200 rpm, followed by IPA, DI water rinse.

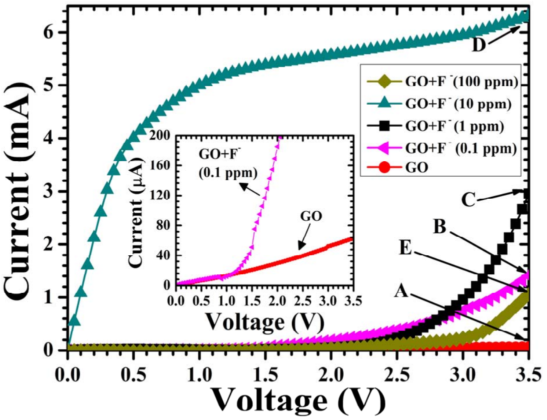

Fig. 7. Current -Voltage (I-V) Characteristics for GO-Al-µ- IDE with GO and GO+F$^-$ measured up to 3.5 V, with fluoride concentration ranging from 0.1-100 ppm. Satellite shows the enlarged I-V curves for GO and GO+F$^-$ (0.1 ppm)

Additionally, PDMS (Sylgard 184) base and curing agent based integrated reservoir for F^- sensing application was prepared. The base (10 gm) and the curing agent (1 gm) were taken in a beaker followed by mechanical stirring for 15 minutes. The degassing of the mixture was then performed using desiccator and vacuum pump. Pour the mixture over the mould to obtain the desired thickness and cure it on a hot plate at 150 ^{o}C for 30-35 minutes to form a solid. Carefully, remove the mould and the PDMS reservoir using a razor or dissection blade, and fix it over the Al based μ-IDE for the sensing of F^-.

IV. RESULTS AND DISCUSSION

The F^- present in the aqueous solution undergoes reversible reaction with the water molecules and result in HF, (a weak acid) and OH^-, (a strong base) which further decomposes into hydronium (H_3O^+) and F^-. The highly reactive F^- again under go reversible reaction with water and the process continues.

Fig. 7 shows the Current vs. Voltage (I-V) measurement (from 0 to 3.5 V) for the fabricated GO-Al (μ-IDEs) as a function of aqueous F^- ranging from 0.1-100 ppm. As shown in Fig. 7 inset, the I-V for reference GO (without F^-) varies from 0 to ~ 61.60 μA (point "A") at 3.5 V. With the addition of aqueous F^- solution of 0.1 ppm to GO-Al (μ-IDEs), the I-V curve starts to increase and finally attains maxima of ~ 1.4088 mA (point "B") at 3.5 V. On increasing the aqueous F^- solution to 1 and 10 ppm, the I-V curve shows a significant increase and finally saturates at ~ 2.91 (point "C"), ~ 6.29 mA (point "D"), respectively. On further increasing the F^- solution (100 ppm), the measured I-V curve for GO-Al-μ-IDEs decreases (with respect to 1 and 10 ppm) and saturates to 1.077 mA (point "E") at 3.5 V. There is almost 2.3, 4.7 fold increase in the current for 0.1, 1 ppm F^- solution with respect to GO reference. Additionally for 10 ppm F^- solution, there is almost three order increase in current with respect to GO reference. In contrast, for F^- solution of 100 ppm, the current value decreases by ~30.8% compared with 0.1 ppm F^- solution.

The significant increase in the current with the increase in aqueous F^- solution (0.1-10 ppm) attributes to the adsorption of the highly reactive F^- on the active hydrophilic binding sites such as –OH, C–O–C and CLO in GO integrated with μ-IDEs. It may also be considered that the active binding sites available in GO are more compared to the F^- present (up to 10 ppm). The F^- is adsorbed on the binding sites in GO surface owing to strong hydrogen bonding (by H_3O^+) and molecular interactions. As a result of this, the F^- don't generate stress (penetrate) in the GO film and thus the GO film is unaffected. The reduction in the output characteristics of GO-Al-μ-IDEs for F^- concentration of 100 ppm may be attributed to the saturation in the available binding sites in GO, hence the F^- penetrate the GO film. The penetration of F^- inside the GO film results the expansion of the film and leads to decrease in the conductivity and reduction in the current.

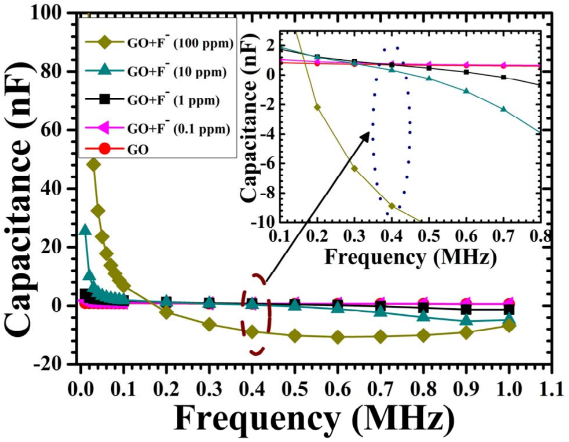

Fig. 8. Capacitance-frequency (C-F) Characteristics for GO-Al-μ- IDE with GO and GO+F^- measured up 1.1 MHz, with fluoride concentration ranging from 0.1-100 ppm. Inset shows the enlarged C-F curves for GO and GO+F^- with in frequency range (0.1-0.8 MHz)

Fig. 8 shows the Capacitance-Frequency (C-F) characteristics as a function of aqueous F^- solution of 0.1-100 ppm based on interaction of GO-Al-μ-IDEs. The measured capacitance for the reference GO (without F^-) is ~ 0.93 nF and decreases with the increase in frequency. The C-F characteristic shows a decrease in capacitance as a function of increasing F^- solution. The measured capacitance for GO-Al-μ-IDEs with addition of F^- solution of 0.1, 1, 10, 100 ppm is 0.78, 0.64, 0.26, -8.9 nF, respectively at 0.4 MHz. The decrease in capacitance value with the increase in F^- concentration confirms the adsorption of the F^- on the surface of GO, as the conductance increases. However, for 100 ppm F^- solution the capacitance approaches negative values, hence resulting in a strong inductive contribution.

IV. CONCLUSIONS

This work presents the strong interaction between the highly sensitive GO and Al-μ-IDEs for aqueous F^- detection in the range of 0.1-10 ppm. The aqueous F^- are adsorbed on the hydrophilic functional sites (–OH, C–O–C and CLO) available in GO and thus results the increase in sensitivity. Thus, the low cost, easy processability and selectivity of proposed GO-integrated Al-μ-IDE based real time sensors have a great potential to be a forefront sensor for detection of aqueous F^- present in natural drinking water.

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