Bi_2O_3/Nb_2O_5 thick film capacitive pH sensor using AD5933 impedance converter

Prof. Khalil Arshak,

O. Korostynska, E. Gill, A. Arshak, K. Kaneswaran

Microelectronics and Semiconductors Research Centre

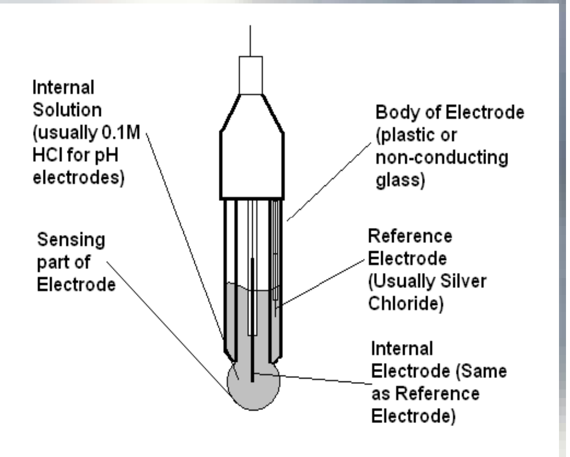
University of Limerick, Limerick, Ireland, e-mail: khalil.arshak@ul.ie

Basis for Research

The pH of a solution is the activity of hydronium ions H_3O^+ in the solution:

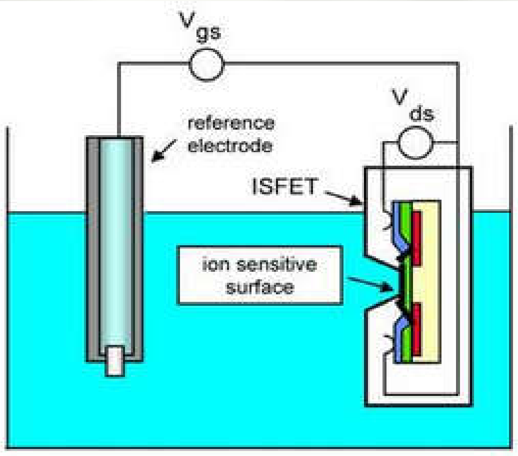
$$pH = -\log[H_3O^+]$$

- pH sensors are required in many medical and industrial applications. Some common areas of use are:
  - Monitoring water pollution
  - Blood and other body fluid measurements
  - Use in labs to identify a chemicals level of "acidity"



Schematic Diagram of Simple Glass Electrode

- The most popular potentiometric approach utilise glass electrode because of its high selectivity for hydrogen ions in a solution, reliability and straight forward operation.
- Other examples include:
- Ion selective membranes
- Ion-selective field effect transistors
- Two terminal microsensors
- Fibre optic
- Fluorescent sensor
- Polymer and metal oxides based pH-sensors.



Schematic representation of an ISFET pH measuring system

Basis for Research

- This work presents the novel system that utilises change in the resonant frequency and impedance as an indicator of the pH level of the solution, brought in contact with a sensor.

- Mixed metal oxides of Bi_2O_3 and Nb_2O_5 formed the basis for thick film capacitive sensors investigated in this research work.

- AD5933 impedance converter was used to monitor real-time changes in the electrical properties of tested capacitors.

- The system showed superior sensitivity to the pH level, with instant response being recorded.

- Heating the sensors restored their initial properties, and they were repeatedly used for pH sensing.

- It is envisaged that findings of this work would form the basis for compact system employed for real-time pH monitoring.

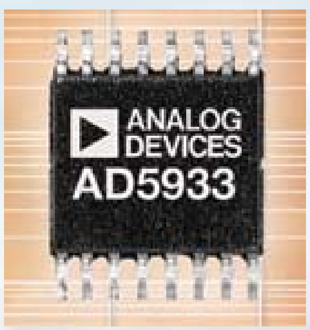
AD5933 Impedance Converter

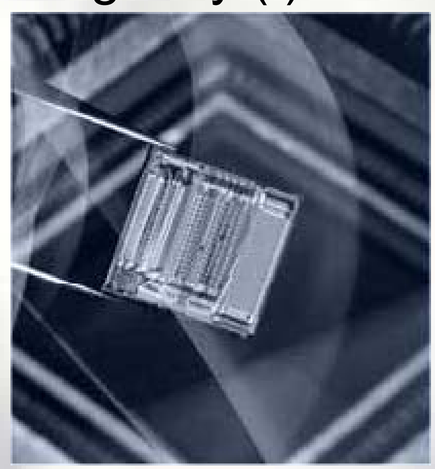
- The AD5933 is a high precision impedance converter system solution which combines an on-board frequency generator with a 12-bit, 1 MSPS, analog-to-digital converter (ADC).

- The frequency generator allows an external complex impedance to be excited with a known frequency.

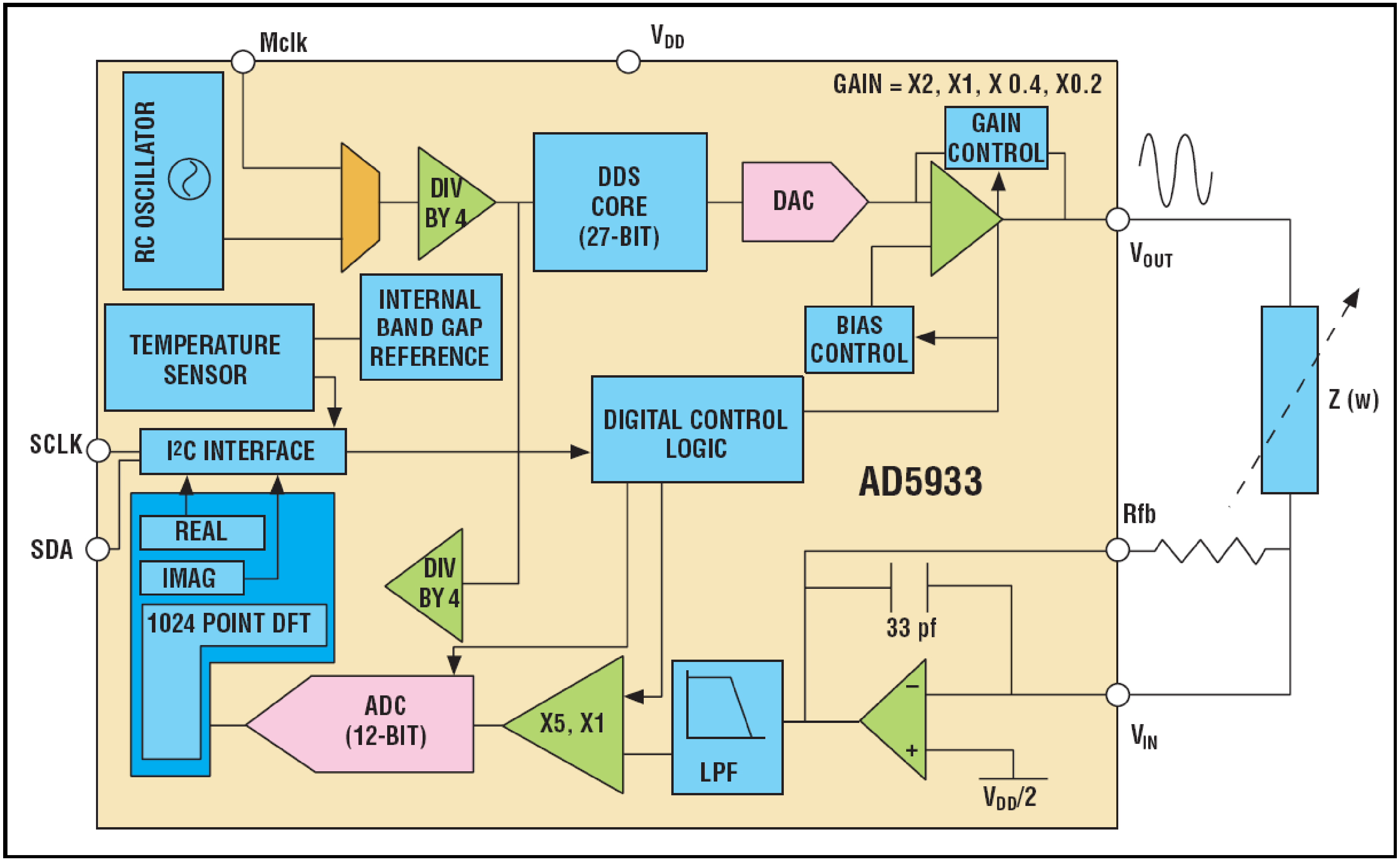
- The response signal from the impedance is sampled by the on-board ADC and a discrete Fourier transform (DFT) is processed by an on-board DSP engine.

- The DFT algorithm returns a real (R) and imaginary (I) data-word at each output frequency.





AD5933 Impedance Converter



AD5933 Impedance Converter

- The excitation signal for the transmit stage is provided on-chip using DDS techniques which permit sub-hertz resolution.

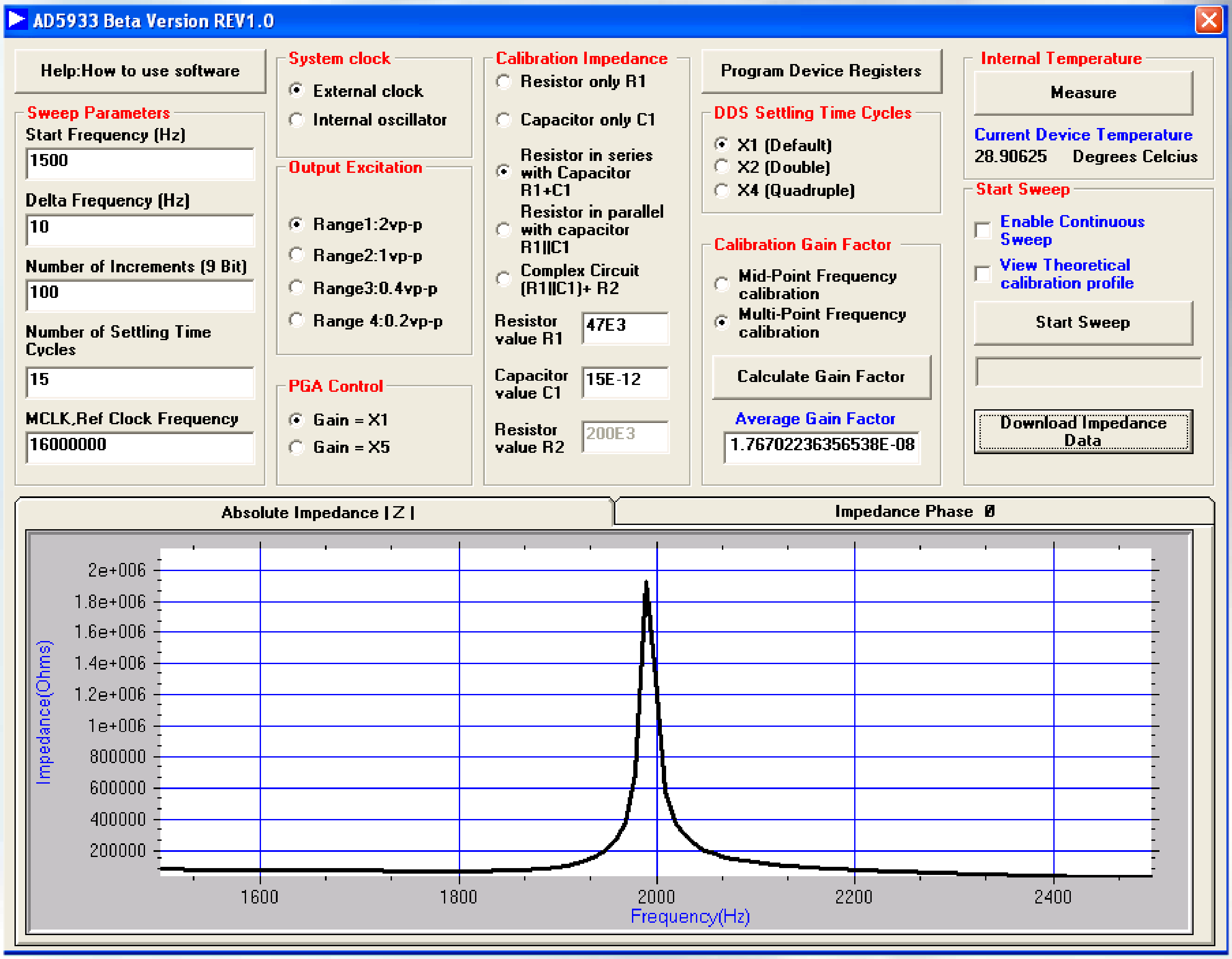
- The receive stage receives the input signal current from the unknown impedance, performs signal processing, and digitizes the result.

- The evaluation board for the AD5933 on-board components include an ADR423 3.0 V reference that acts as a stable supply voltage for the separate analog and digital sections of the device and an ADP3303 ultrahigh precision regulator that acts as a supply to the on-board universal serial bus controller, which interfaces to the AD5933.

- The user can power the entire circuitry from the USB port of a computer.

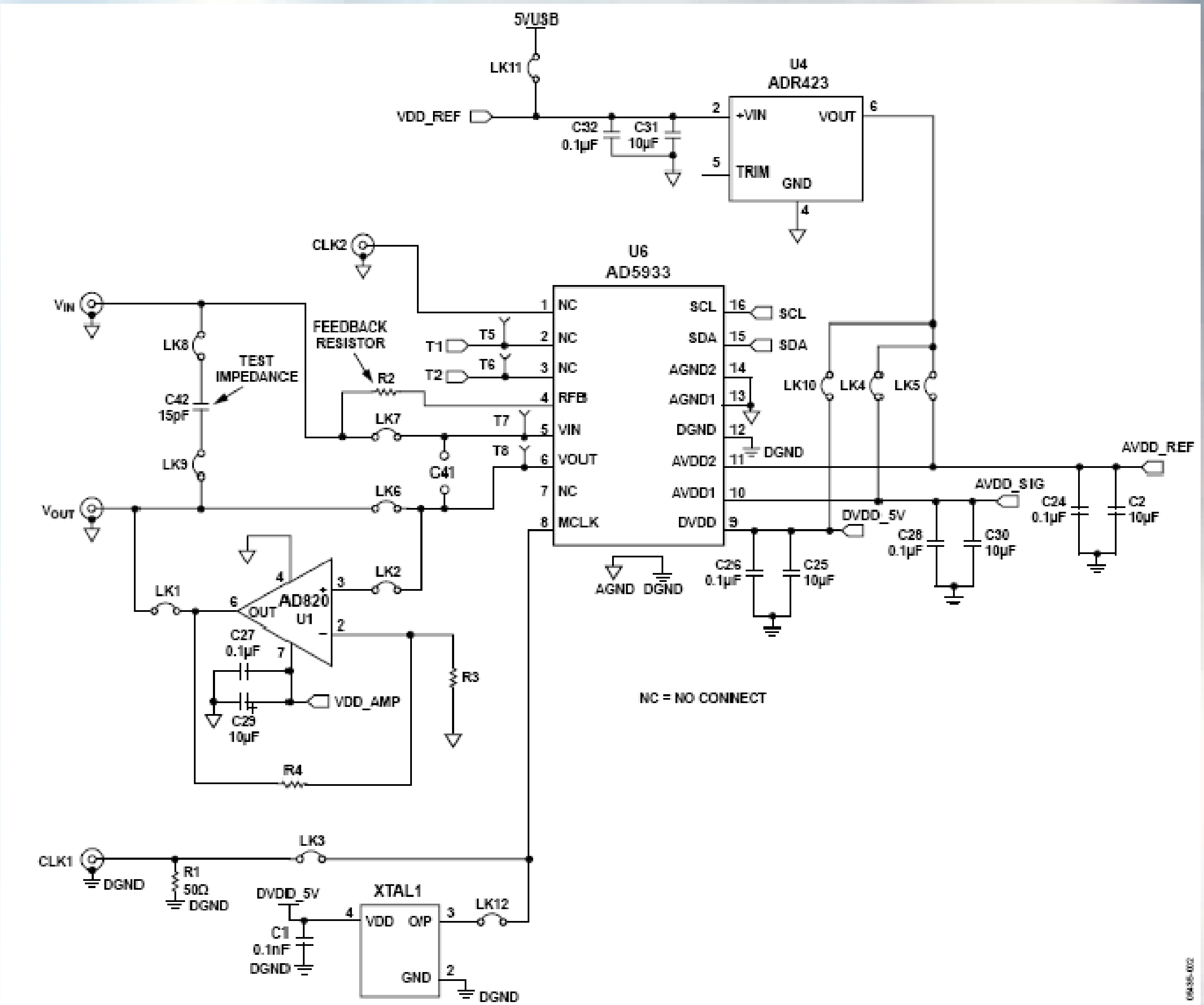
- The user interfaces to the USB microcontroller through a Visual Basic® graphic user interface located on and run from the user PC.

AD5933 Impedance Converter



Graphical representation of AD5933 impedance converter software interface

AD5933 Impedance Converter



The evaluation board schematic EVAL-AD5933EB. © Analog Devices.

Thick film sensors preparation

- Four various compositions were prepared for this work: 100 wt.% Bi_2O_3; 25 wt.% Bi_2O_3 and 75 wt.% Nb_2O_5; 75% Bi_2O_3 and 25 wt.% Nb_2O_5; and 100% Nb_2O_5.

- Initially, powders in corresponding weight proportions were mixed with isopropanol to form slurry, which was then wet ball milled in alcohol for 24 h.

- The alcohol was evaporated from the mixtures by drying them at 120 °C.

- The powder was then fired at 800 °C (at a rate 5 °C per min) for 5 h, followed by cooling (at a rate of 3 °C per min).

- After firing the pellets were crushed with a mortar and pestle, suspended in isopropanol and shear mixed at 11,000 rpm for 4 min and 13,000 rpm for 1 min in order to break up any aggregates.

- The alcohol was then evaporated from each mixture to obtain the final powder.

Thick film sensors preparation

- To form thick film pastes, each powder was mixed with 7 wt.% of binder (polyvinyl butyral) and a suitable amount of solvent.
- Capacitors were then screen-printed using a DEK 2102 automatic screen-printer. Commercial silver paste was used for the conducting layers and the active area of the device measured around 2 mm × 3 mm.
- The operation principle of this approach is based on the change of their capacitance as a result of pH effect, which in turn leads to changes in the resonant frequency being measured.
- To monitor the response of the thick film sensors to various pH values, a controlled amount of a solution with known pH level (pH 2, pH 5, pH 8 and pH 10) was dispensed onto the device sensing area.
- The changes in electrical parameters, in this case the resonant frequency shift and impedance variation, were instantly recorded using AD5933 impedance converter.
- This novel approach to pH measurement allows real-time monitoring, and accounts for both remote control and data management.
- The system is compact and could be further considered into commercial handheld pH monitoring system.

Results and Discussions

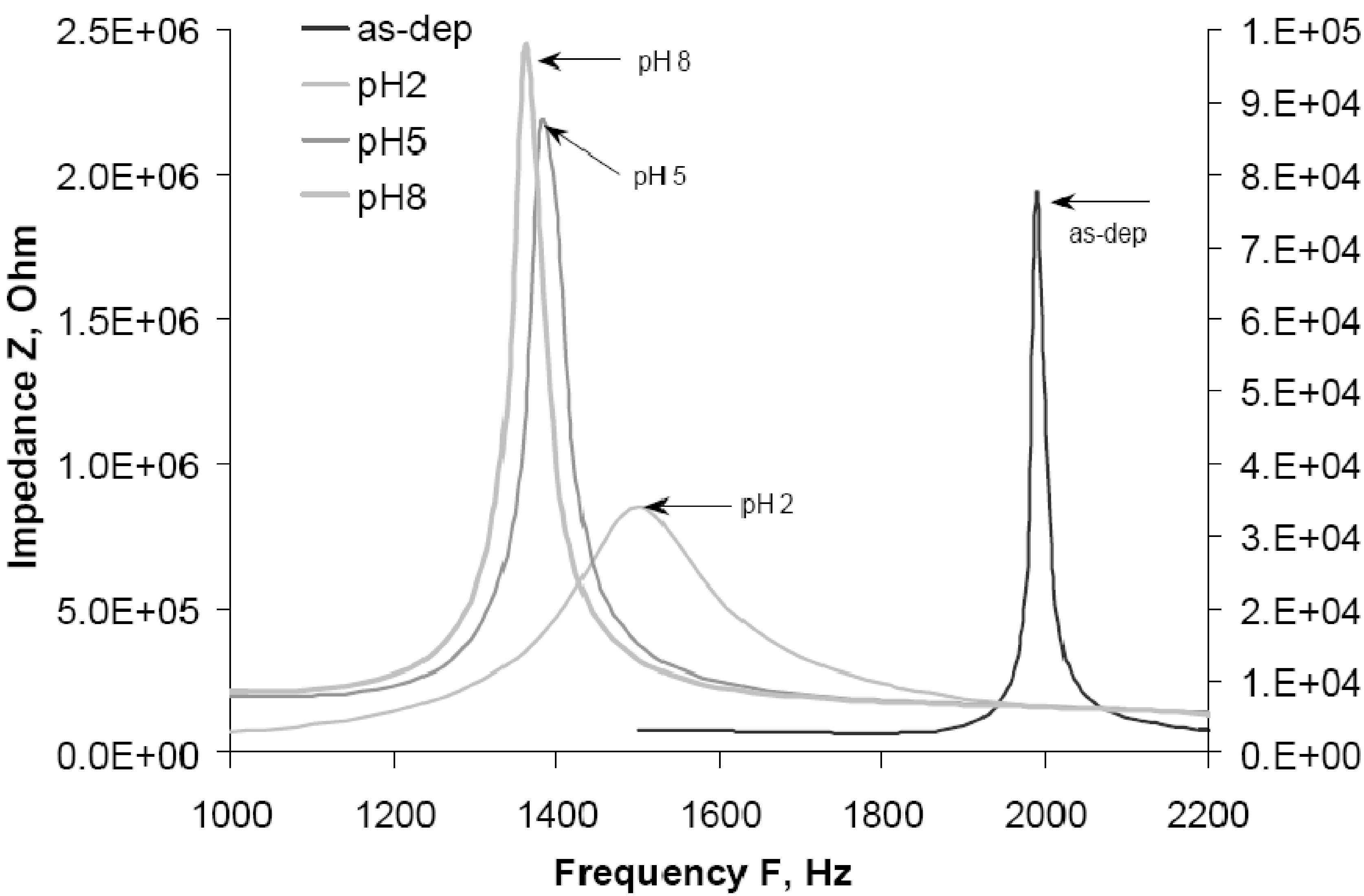
- A set of commercially available resistors and capacitors were used to tune up the system, comprising Bi_2O_3 metal oxide based thick film pH sensor for the resonant frequency of ~2 kHz.

- Real-time continuous monitoring offered via AD5933 allows tracing complex response of the sensor, which is brought into contact with the solution of known pH.

- It is thought that the excess ions in the test solutions (hydronium (H_3O^+) and hydroxide (OH^-)) react with the metal oxide layer and cause changes in its fundamental electrical characteristics.

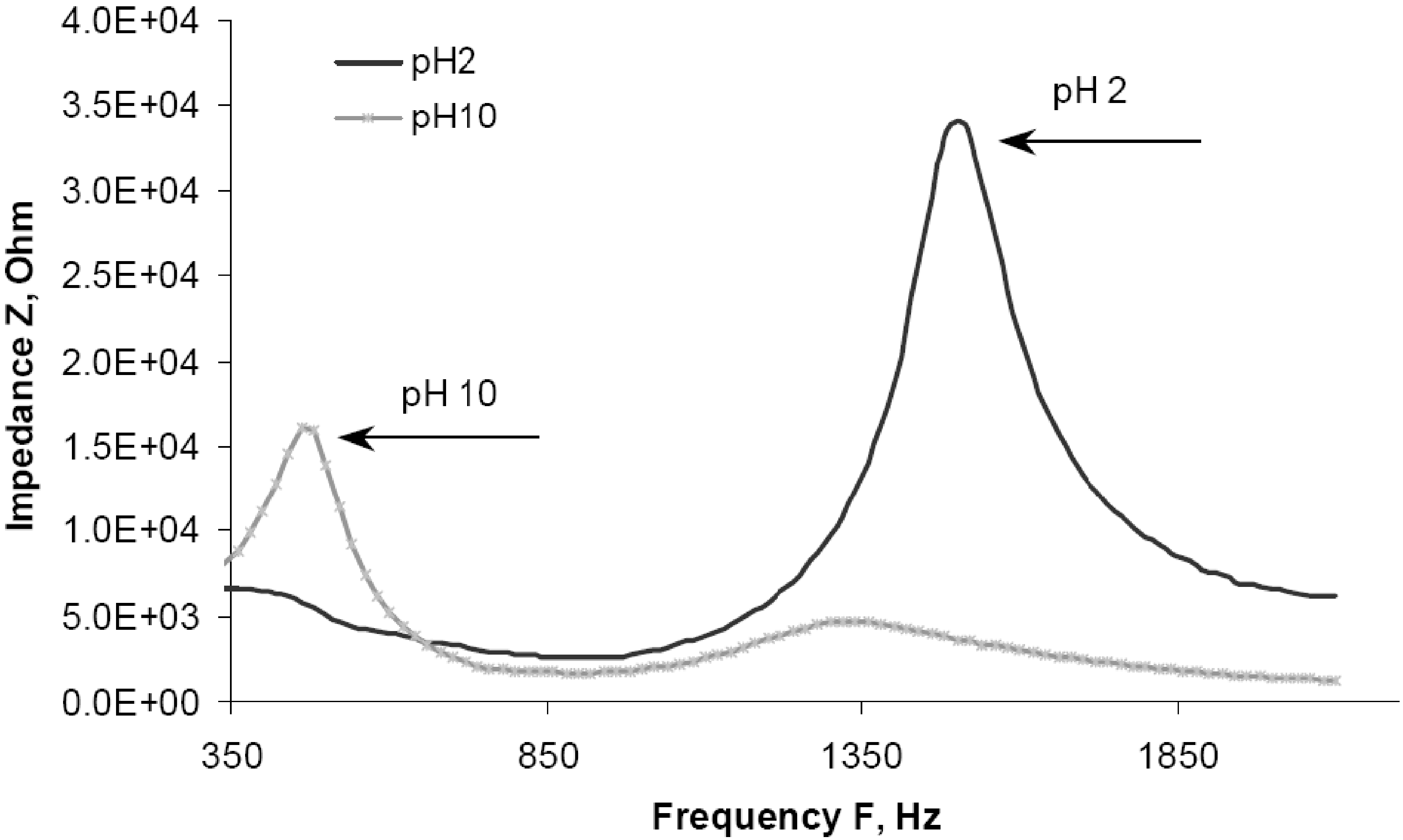
- Although the chemistry of the process is complex and multi-staged, the change in the resonant frequency alone is considered as attractive alternative for pH monitoring.

Results and Discussions



Change in the resonant frequency and impedance values of the Bi_2O_3 thick film pH sensor.

Results and Discussions



Change in the resonant frequency and impedance values of the Bi_2O_3 thick film sensor as a result of pH 2 and pH 10.

Results and Discussions

- For consistency, the response of Bi_2O_3 sensor to various pH levels was recorded after 1 min to allow signal settling and time to react.

- However, usually not more than few seconds were required for both the resonant frequency and the value of the impedance to change.

- A contact with the solution of pH 2 caused the resonant frequency to decrease from initial 2 kHz to about 1500 Hz.

- It is interesting to point out that as the solution was naturally drying/evaporating, the sensor has recovered its initial properties within 5 min.

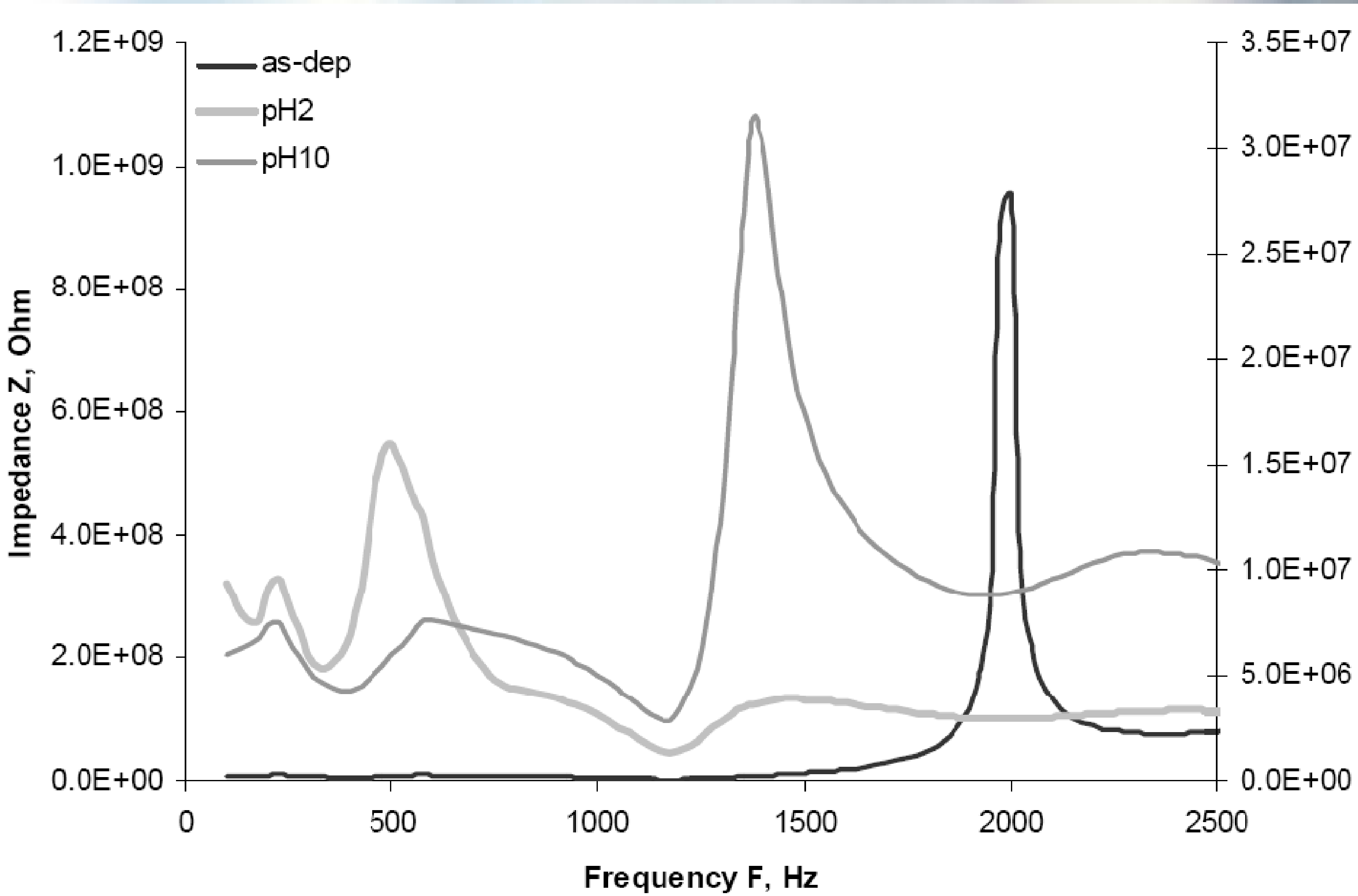
- Subsequent measurement of pH provided identical result and once again the sensor properties were restored.

- This observation is vital for the development of reusable sensors.

Results and Discussions

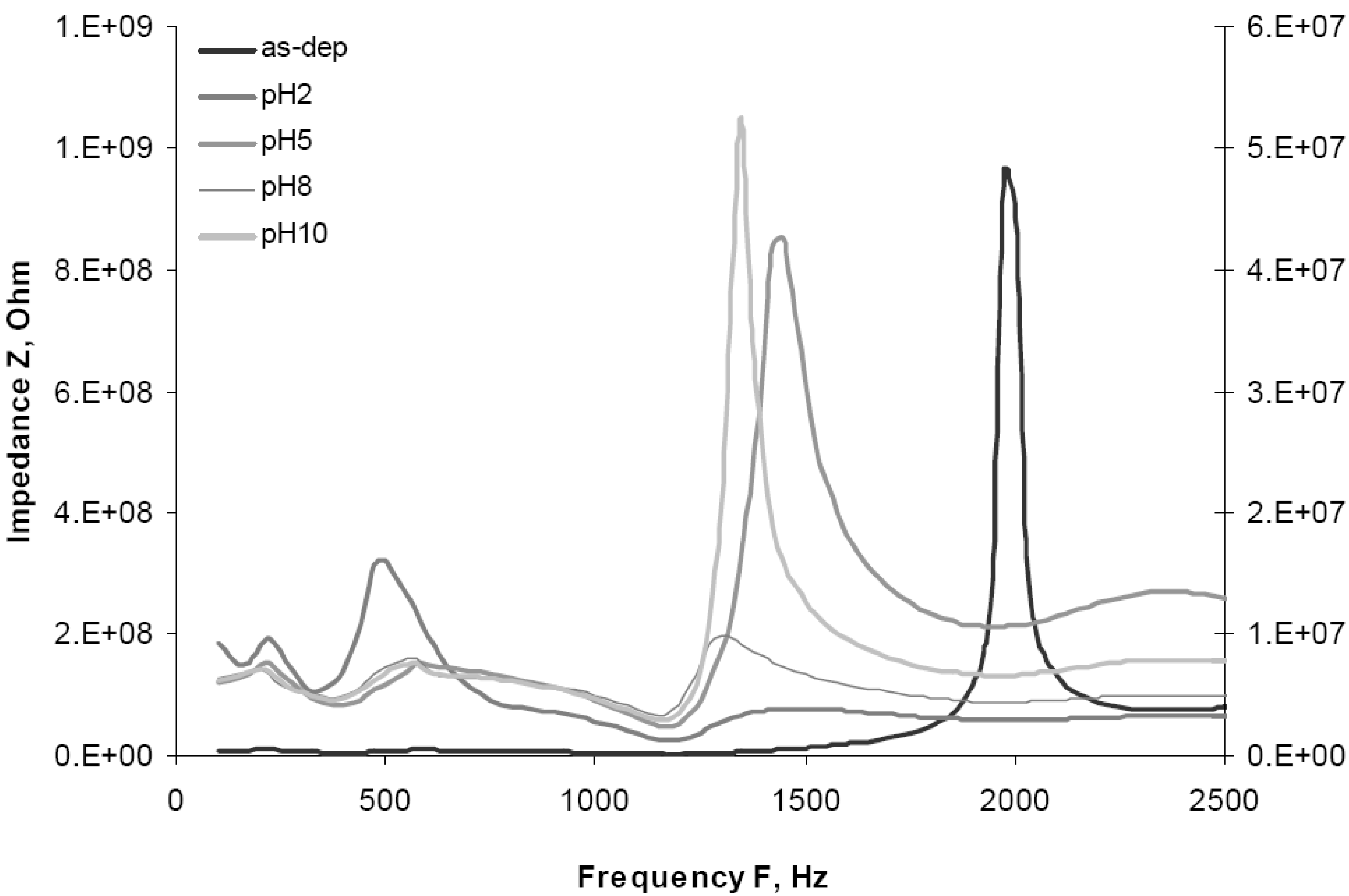
- A contact with the solution of pH 5 and pH 8 resulted further changes in the electrical properties of the sensor, which manifested a decrease in the resonant frequency to 1380 Hz and 1360 Hz respectively.
- This time the sensor required longer recovery periods for the resonant frequency to shift back to 2 kHz. These were 10 min for pH 5 and ~20 min for pH 8.
- The sensor showed tremendous change in its properties after being brought into contact with solution of pH 10.
- A resonant frequency shifted towards 500 Hz and the value of the impedance decreased by order of 2.
- Thermal heating is known to restore the properties of thick film devices. To speed up the sensor recovery time, exposure to elevated temperature of 60 °C for 10 minutes was applied. This allowed the remaining of the solution to dry out and these sensors were ready for further use.
- One may conclude that no irreversible chemical reaction took place between the solution and mixed oxide sensing layer.

Results and Discussions



Change in the resonant frequency and impedance values of 25 wt.% Bi_2O_3 and 75 wt.% Nb_2O_5 mixed sensor as a result of pH 2 and pH 10.

Results and Discussions



Change in the resonant frequency and impedance values of the Nb_2O_5 thick film pH sensor.

Results and Discussions

- Significant changes were recorded in the resonant frequency and impedance values of 25 wt.% Bi_2O_3 and 75 wt.% Nb_2O_5 and pure Nb_2O_5 pH sensors respectively.

- Unfortunately, they were less consistent that exhibited by counterpart Bi_2O_3 thick film sensor.

- Further investigation into material composition is underway.

- It is expected that the particle size of the metal oxide, forming the basis of the sensitive layer, would affect its sensitivity and response / recovery times, with nanoprecursor -based materials being the most favourable option.

- Moreover, various sensor configurations would be examined to reveal the most sensitive device layout and the electrodes structure.

Conclusion

- A novel real time pH monitoring system based on AD5933 impedance converter is presented, with its schematic given in details.

- The change in the resonant frequency and impedance serves as an indicator of the pH level of the solution, brought in contact with a sensor, forming a part of the EVAL-AD5933EB evaluation board.

- Screen-printed metal oxide thick films were used as prototype pH sensors, with Bi_2O_3 demonstrating the utmost level of sensitivity and fastest recovery time.

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