

# Polycrystalline Nb<sub>2</sub>O<sub>5</sub> Compared on Constant-Capacitance Structures and on Ion-Sensitive Field-Effect Transistors for pH-Sensing

Christopher Beale,\* Matthias Wambold, Patrick Bott, Laurence Kühne, Falah Al-Falahi, Eberhard Kurth, Olaf Hild  
Fraunhofer Institute for Photonic Microsystems (IPMS), Maria-Reiche-Str. 2, 01109 Dresden, Germany

\*Corresponding author's e-mail address: christopher.dyer.beale@ipms.fraunhofer.de

## Abstract

Investigating the suitability of a pH-sensing layer for ion-sensitive field-effect transistors can be costly and time consuming. Ways to develop sensing layers with cheaper and faster methods, such as the use of electrolyte-insulator-semiconductor structures measured at constant-capacitance, may aid enormously in investigating less understood materials such as Nb<sub>2</sub>O<sub>5</sub>. This work shows that constant-capacitance measurements, using 2 different samples having polycrystalline Nb<sub>2</sub>O<sub>5</sub> at 2 different annealing temperatures of 800 °C and 950 °C, can predict successful integration of Nb<sub>2</sub>O<sub>5</sub> into ISFETs that approach Nernstian sensitivity and exhibit low hysteresis from pH 1 to pH 13.

## 1 Introduction

Applications in electrochemical sensing require sensors which are robust and perform stable measurements in a variety of environments. Such environments include agriculture, food and drink processing, and biomedical applications [1–3]. In the measurement of pH, ion-sensitive field-effect transistors (ISFETs) offer several advantages over the traditional glass electrode, such as the ability of ISFETs to be miniaturized on silicon chips and the resistance of ISFETs to breakage. ISFETs rely on a metal oxide insulator to act as a sensing dielectric that drives an analog transistor, where an optimal choice has been Ta<sub>2</sub>O<sub>5</sub> due to its stability and corrosion resistance [1, 2, 4]. Although Ta<sub>2</sub>O<sub>5</sub> has excellent properties for pH-sensing, the status of Ta as a conflict metal and the lower abundance of Ta in comparison to other options calls for the investigation of other metal oxide insulators for pH-sensing with ISFETs [5, 6].

One candidate for replacing Ta<sub>2</sub>O<sub>5</sub> is Nb<sub>2</sub>O<sub>5</sub>, where both metal oxide insulators have been used in the creation of electrolytic capacitors [7]. Even though Nb<sub>2</sub>O<sub>5</sub> capacitors have a higher direct current (DC) leakage than Ta<sub>2</sub>O<sub>5</sub> capacitors, if implemented correctly the higher dielectric constant of Nb<sub>2</sub>O<sub>5</sub> may allow for higher capacitive coupling at the same thickness on an ISFET. Alternatively, thicker layers with Nb<sub>2</sub>O<sub>5</sub> may yield a similar capacitive coupling while possibly giving a longer lifetime to the ISFET due to more metal oxide that would need to be corroded away by the environment. Moreover, Nb is not a conflict metal and has a 10x higher abundance than Ta, thus making Nb a cheaper and more sustainable choice in the production of ISFETs [5].

Previous research from our group with Nb<sub>2</sub>O<sub>5</sub> has been performed with electrolyte-insulator-semiconductor (EIS) structures, where the surface potential of the sensing dielectric versus pH is measured with capacitance-voltage (C-V) measurements and alternating current (AC) [8]. The use of EIS structures, where for our group the sensing dielectric is deposited directly onto Si wafer with a thin SiO<sub>2</sub> layer on its surface, allows for quick and low-cost investigations of a sensing dielectric before its integration with ISFETs. Measured pH-sensitivities of EIS samples prepared by our group which are covered with Nb<sub>2</sub>O<sub>5</sub>, however, have been shown to be lower than the theoretical

Nernstian slope which is 58.17 mV/pH at 20 °C [8]. Thus, one of the challenges in developing sensing dielectrics for ISFETs is understanding how experiments with EIS translate over to producing ISFETs. This work therefore compares the sensing properties of EIS samples with ISFETs to see if ISFETs can be successfully produced by learning from the results of EIS measurements. The comparison is then used to determine if polycrystalline Nb<sub>2</sub>O<sub>5</sub> is suitable as a sensing dielectric for ISFETs used in pH-sensing.

## 2 Materials and methods

The fabrication and pH-measurements of the EIS samples preceded those of the ISFETs, where the details of which are described below.

### 2.1 Sample and device fabrication

For the EIS samples, different n-type (1-5 Ωcm) 200 mm (100) Si-wafers were prepared with 65 nm dry SiO<sub>2</sub> gate oxide. Thin films of Nb<sub>2</sub>O<sub>5</sub> of about 120 nm were then deposited by radio frequency sputtering from a ceramic target in an O<sub>2</sub>/Ar atmosphere. 2 different wafers were then annealed by rapid thermal annealing (RTA), one at 800 °C and the other at 950 °C. The annealing was carried out at both temperatures for the same duration: 20 minutes in O<sub>2</sub> and 10 minutes in Ar [8]. A forming gas anneal at 440 °C for 30 minutes in 10 % H<sub>2</sub> / 90 % He and subsequently for 10 minutes in 100 % He was then performed. The wafers were then diced into EIS samples, with samples having an area of 15 mm × 15 mm. A sample contacts the measurement solution with a circular opening which is sealed with an O-ring that has an approximate diameter of 10.3 mm.

For the ISFETs, the same Nb<sub>2</sub>O<sub>5</sub> layers on a 65 nm dry SiO<sub>2</sub> gate oxide were integrated with p-channel field-effect transistors (FETs) to create ISFETs. The ISFETs were manufactured at the 200 mm wafer production line at Fraunhofer IPMS.

### 2.2 pH-measurements with EIS samples

The pH-sensitivity and hysteresis were characterized for the EIS samples with the constant-capacitance (ConCap) method [2, 8]. First, the C-V curve was measured at pH 7

to find the ConCap parameters for the sample. This was performed by sweeping a DC gate voltage from inversion to accumulation of the semiconductor chip (e.g., -5 V to 5 V) with an alternating current (AC) voltage of 20 mV<sub>p</sub> and a frequency of 100 Hz between the Si backside and the Ag/AgCl reference electrode in solution. The device used was a HP 4284A LCR meter, and the measurement cell was set in a dark Faraday cage.

A fixed potential was then chosen from the C-V curve in the depletion region where the  $\Delta C/\Delta V$  was the highest. The EIS-sample then underwent a conditioning step in ConCap mode with pH 7 buffer solution and an applied electrical potential for 16.5 h. After 16.5 h, the sample was exposed to pH 7 buffer for 5 minutes, then pH 1 buffer for 50 min, then pH 7 buffer for 5 minutes, then pH 13 buffer for 50 min, and finally pH 7 buffer for 5 minutes.

Conditioning was followed by a pH-sensitivity and hysteresis measurement in 1 pH unit steps, with each step lasting 5 min, from pH 7 to pH 1, then from pH 1 to pH 13, and finally from pH 13 to pH 7 at room temperature (approximately 22.5 °C). All pH buffers were Merck 20 °C Titrisol®, except for pH 7 which was Merck 20 °C Certipur®. A stepped curve like the ones shown in **Figure 1a** and **1c** was recorded, and the measured potential was taken as the average of the last minute of measurement. Since the measurement cell is not temperature-controlled, the pH-sensitivity and hysteresis were calculated by averaging the certified pH values of the buffer at 20 °C and 25 °C to take an approximate pH value at 22.5 °C.

### 2.3 pH-measurements with ISFETs

Measurements with ISFETs were performed in a temperature-controlled measurement cell, where up to 10 ISFETs were measured simultaneously versus a glass Ag/AgCl reference electrode. The reference electrode was maintained at 22 °C and in 3 M KCl outside of the measurement cell, and the measurement cell makes contact to the electrode through a tube connected to a diaphragm. The pH buffers for all measurements used were as described for the EIS samples, and the measurement cell was shielded from light.

9 ISFETs from wafer 1 with an RTA treatment of 800 °C and 10 ISFETs from wafer 2 with an RTA treatment of 950 °C were selected to form 2 measurement groups, where chips from a group were measured simultaneously. Group 1 were ISFETs exposed to 800 °C RTA (ISFETs 1-01 to 1-09), and Group 2 were ISFETs exposed to 950 °C RTA (ISFETs 2-01 to 2-10). Before measuring in constant charge mode, an approximate isothermal operating point at pH 7 was determined at  $V_{BS} = 0$  V and  $V_{DS} = -0.5$  V by sweeping  $I_{DS}$ , where the temperature was varied from 20 °C to 80 °C in 10 °C steps in pH 7 buffer. The approximate isothermal operating  $I_{DS}$  was found to be -190  $\mu$ A for Group 1 (800 °C RTA) and -170  $\mu$ A for Group 2 (950 °C RTA).

The pH-sensitivity and hysteresis measurements were then performed at 20 °C to minimize temperature deviations in buffer behaviour. The  $V_{GS}$  values versus pH were recorded in constant-charge mode for each ISFET, where the other FET values were fixed at the values stated above.

A separate measurement was performed for each group, where the buffer was changed in 1 pH unit steps with each step lasting 20 minutes. The pH was first decreased from pH 7 to pH 1, then increased from pH 1 to pH 13, and finally decreased from pH 13 to pH 7. The  $V_{GS}$  values over the last 3 min of a measurement step were averaged and then taken as the measured  $V_{GS}$  for each step, which was then used to calculate the pH-sensitivity via a linear fit. This linear fit for each ISFET was then subtracted from the measured  $V_{GS}$  points for the respective ISFET to calculate its hysteresis, which here is shown as the mV-deviation from the fit line. The pH-deviation scale on the plot is then set by using the fitted slope for the respective EIS samples and the average slope for the respective ISFET groups.

## 3 Results and discussion

The pH-sensitivity of the EIS samples is first compared here with that of the ISFETs. This is followed by a comparison of the hysteresis. This comparison is then used to determine whether EIS can serve as a suitable aid in developing ISFETs with Nb<sub>2</sub>O<sub>5</sub> pH-sensing layers. As a point of reference, the Nernstian slope at 20 °C is 58.17 mV/pH, and the slope at 22.5 °C is 58.66 mV/pH.

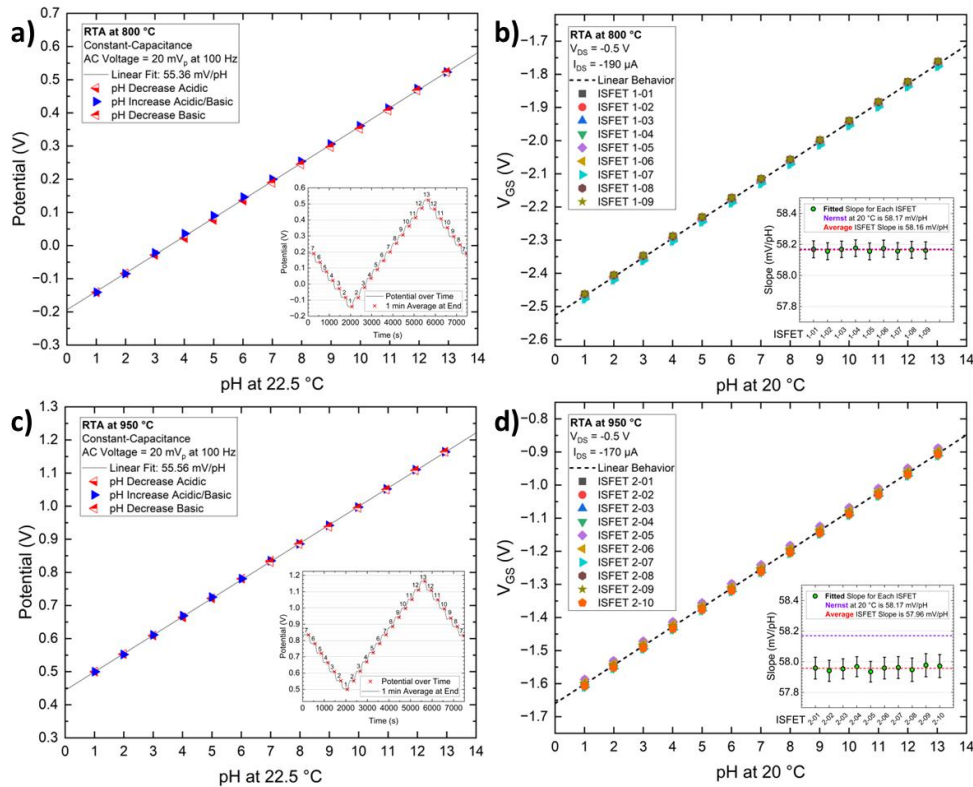
### 3.1 pH-sensitivity: EIS versus ISFET

The pH-measurement curves for the RTA treatment at 800 °C are shown in **Figure 1a** for the EIS sample and **Figure 1b** for the Group 1 ISFETs. The fitted slope of 55.36 mV/pH for the EIS sample is about 3 mV less than the Nernstian slope at 22.5 °C, while the average slope of 58.16 mV/pH at 20 °C for the 9 ISFETs approaches the Nernstian value within error. Additionally, both the EIS sample and the ISFETs maintain linear behavior from pH 1 to pH 13.

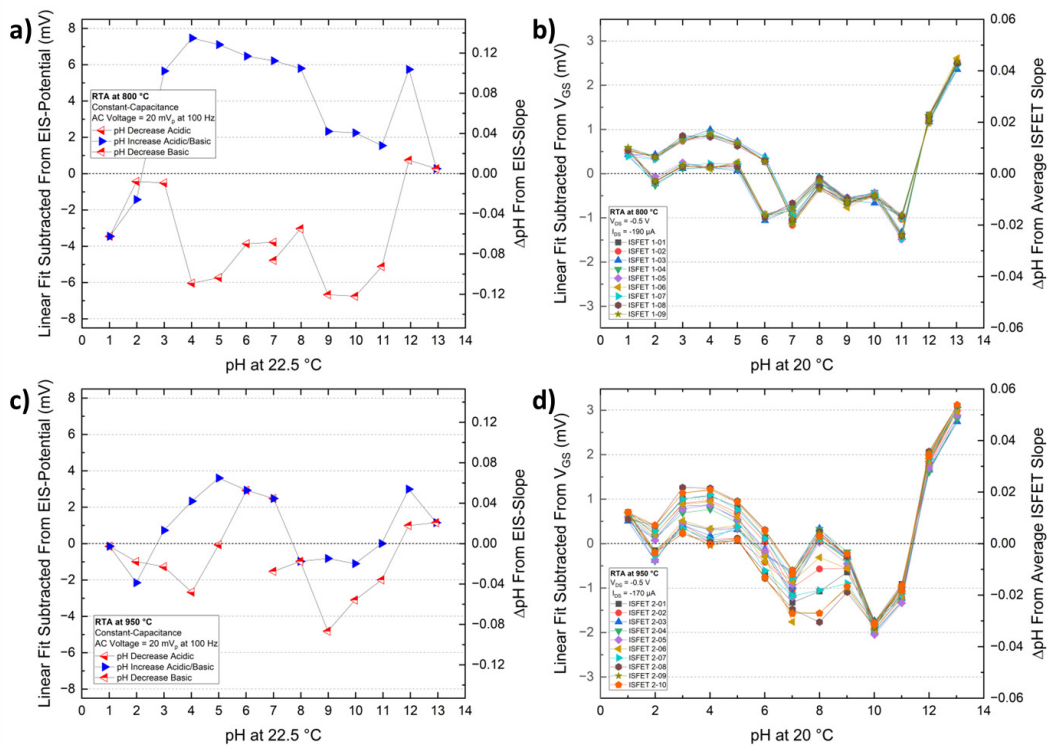
The curves for the RTA treatment at 950 °C are shown in **Figure 1c** for the EIS sample and **Figure 1d** for the Group 2 ISFETs. The fitted slope of 55.56 mV/pH for the EIS sample is also about 3 mV less than the Nernstian slope at 22.5 °C and is close to the slope for the EIS sample with RTA at 800 °C. However, unlike the Group 1 ISFETs, the 10 ISFETs in Group 2 do not reach Nernst within error, exhibiting an average slope of 57.96 mV/pH at 20 °C. Nonetheless, this small deviation of about 0.2 mV from Nernst demonstrates that both RTA treatments can be used to make ISFETs with high pH-sensitivities. Furthermore, both the EIS sample and the ISFETs treated with the 950 °C RTA treatment maintain linear behavior from pH 1 to pH 13.

### 3.2 pH-hysteresis: EIS versus ISFET

Hysteresis curves for the RTA treatment at 800 °C are shown in **Figure 2a** for the EIS sample and **Figure 2b** for the Group 1 ISFETs. The deviation from the fit line for the EIS sample from pH 1 to pH 13 extends to about  $\pm 8$  mV or roughly  $\pm 0.15$  pH units. Over the same pH range, the ISFETs show a much lower deviation from fit, with a maximum at pH 13 of +2.5 mV and just under +0.05 pH units.



**Figure 1** pH-measurement from pH 1 to pH 13 with an RTA treatment at 800 °C for an EIS sample shown in **a)** and for the Group 1 ISFETs shown in **b)**, while an RTA treatment at 950 °C of an EIS sample is shown in **c)** and the Group 2 ISFETs are shown in **d)**. The pH-sensitivity increases by about 3 mV/pH from the ConCap to the ISFET measurements.



**Figure 2** Hysteresis, calculated as the mV-deviation from the fit line from pH 1 to pH 13, is shown here with an RTA treatment at 800 °C for an EIS sample in **a)** and for the Group 1 ISFETs in **b)**, while an RTA treatment at 950 °C of an EIS sample is shown in **c)** and the Group 2 ISFETs are shown in **d)**. The ISFETs exhibit less hysteresis than the EIS samples in ConCap mode, where the 800 °C EIS sample shows different behaviour from the Group 1 ISFETs.

In **Figure 2c**, the EIS sample for the RTA treatment at 950 °C shows smaller deviations than the 800 °C sample, being down to about -5 mV or -0.10 pH units. The hysteresis with the Group 2 ISFETs in **Figure 2d**, however, is quite similar to the Group 1 ISFETs, with Group 2 showing a deviation of approximately +3 mV and reaching +0.05 pH units at pH 13.

### 3.3 Nb<sub>2</sub>O<sub>5</sub> EIS and ISFET measurements

Although the fitted slopes to the EIS data are further away from Nernst than the fitted slopes for the ISFETs, the almost equal slopes for the EIS curves with both RTA treatments appears to predict that the ISFETs will also be similar with both RTA treatments. Reasons why the EIS samples exhibit lower sensitivity may be due to the use of AC rather than DC as used with the ISFETs, where the use of AC means that EIS measurements are more dependent on the solution conductivity and the ionic strength.

The difference in hysteresis behaviour between the EIS samples with different RTA treatments, where the 800 °C shows a larger deviation at more pH steps, may indicate that EIS is not a good predictor of hysteresis with ISFETs. The similarity in behaviour with Group 1 and Group 2 ISFETs seems to indicate that hysteresis may be more affected by other variables, which may include temperature variations that need to be managed. The lack of temperature-control with the EIS measurements shown here thus sheds light on the main flaw of the comparison between the EIS measurements and the ISFET measurements. Nonetheless, the hysteresis data from the EIS measurement may prove useful for future investigations when combined with the fitted pH-sensitivity.

In taking the Nb<sub>2</sub>O<sub>5</sub> measurement results from the EIS and ISFET curves, the usefulness of creating relatively cheap and fast EIS samples with Nb<sub>2</sub>O<sub>5</sub> is sufficient for screening whether the layer is suitable for integration with ISFETs. Thus, this indicates that different preparation treatments for Nb<sub>2</sub>O<sub>5</sub> can first be examined with EIS, and if found to have a high pH-sensitivity and low hysteresis, that the layer can be integrated with an ISFET. This of course does not consider the variation among ISFET constructions; however, if the properties of the ISFET are largely known and controlled by the manufacturer, then preparing EIS samples of Nb<sub>2</sub>O<sub>5</sub> beforehand is a great way to make research and development of Nb<sub>2</sub>O<sub>5</sub> ISFETs faster and cheaper.

## 4 Conclusion

EIS samples in ConCap mode and ISFETs in constant-charge mode were compared for pH-sensitivity and hysteresis, where polycrystalline Nb<sub>2</sub>O<sub>5</sub> served as the sensing layer. 2 separate RTA treatments, one at 800 °C and the other at 950 °C, were also compared. The results showed that pH-sensitivities with EIS samples predicted good performance with ISFETs and with both RTA treatments. The predictive power of the hysteresis measurement with EIS samples was, however, less promising. Nonetheless, the

hysteresis calculated with EIS measurements may serve as valuable information when supported with pH-sensitivity measurements for Nb<sub>2</sub>O<sub>5</sub> sensing layers.

## 5 Acknowledgments

Parts of the results have been obtained with resources provided by the project "REISen", which is co-financed with tax money on the basis of the budget passed by the Saxon State Parliament.

We would like to thank Nils Funke, Hans-Georg Dallman, Henry Niemann, and Götz Ringmann for helping with the ISFET measurements.

## 6 References

- [1] P. Bergveld, "Thirty years of ISFETOLOGY," *Sensors and Actuators B: Chemical*, vol. 88, no. 1, pp. 1–20, 2003, doi: 10.1016/S0925-4005(02)00301-5.
- [2] M. J. Schöning, D. Brinkmann, D. Rolka, C. Demuth, and A. Poghossian, "CIP (cleaning-in-place) suitable "non-glass" pH sensor based on a Ta<sub>2</sub>O<sub>5</sub>-gate EIS structure," *Sensors and Actuators B: Chemical*, 111-112, pp. 423–429, 2005, doi: 10.1016/j.snb.2005.03.053.
- [3] E. Najdenko, F. Lorenz, H.-W. Olf, and K. Dittert, "Development of an express method for measuring soil nitrate, phosphate, potassium, and pH for future in-field application," *J. Plant Nutr. Soil Sci.*, 2023, doi: 10.1002/jpln.202300166.
- [4] Y. G. Vlasov, Y. A. Tarantov, and P. V. Bobrov, "Analytical characteristics and sensitivity mechanisms of electrolyte-insulator-semiconductor system-based chemical sensors—a critical review," *Analytical and bioanalytical chemistry*, vol. 376, no. 6, pp. 788–796, 2003, doi: 10.1007/s00216-003-1957-3.
- [5] G. J.-P. Deblonde, A. Chagnes, V. Weigel, and G. Cote, "Direct precipitation of niobium and tantalum from alkaline solutions using calcium-bearing reagents," *Hydrometallurgy*, vol. 165, pp. 345–350, 2016, doi: 10.1016/j.hydromet.2015.12.009.
- [6] Oluwale Ojewale, "Mining and illicit trading of coltan in the Democratic Republic of Congo," Institute for Security Studies, INTERPOL, and the Global Initiative Against Transnational Organized Crime, Online 29, Mar. 2022. Accessed: January 2024. [Online]. Available: <https://enactafrica.org/research/research-papers/mining-and-illicit-trading-of-coltan-in-the-democratic-republic-of-congo>
- [7] Y. Freeman, *Chapter 2. Basic Technology. In: Tantalum and Niobium-Based Capacitors.*: Springer International Publishing, 2018.
- [8] F. Al-Falahi, C. Beale, E. Kurth, P. Reinig, and O. Hild, "Thermal annealing of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> thin films for CMOS based chemical sensors," in *MikroSystemTechnik Kongress 2023*, Dresden, 2023.