HOKKAIDO UNIVERSITY

Title	Fundamental Study of InP-Based Open-Gate Field-Effect Transistors for Application to Liquid-Phase Chemical Sensors
Author(s)	Yoshizawa, Naoki; Sato, Taketomo; Hashizume, Tamotsu
Citation	Japanese Journal of Applied Physics, 48(9), 091102 https://doi.org/10.1143/JJAP.48.091102
Issue Date	2009-09
Doc URL	https://hdl.handle.net/2115/42586
Rights	© 2009 The Japan Society of Applied Physics
Type	journal article
File Information	JJAP48_091102.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Japanese Journal of Applied Physics, 48 (2009) 091102

Fundamental Study of InP-Based Open-Gate Field Effect Transistors for Application to Liquid-Phase Chemical Sensors

Naoki Yoshizawa, Taketomo Sato, and Tamotsu Hashizume

Research Center for Integrated Quantum Electronics, and Graduate School of Information Science and Technology, Hokkaido University, N-13, W-8, Kita-ku, Sapporo 060-8628, Japan

We prove with this paper that InP-based open-gate Field Effect Transistors (FETs) work well as liquid-phase chemical sensors. The open-gate FET clearly exhibited current saturation and a pinch-off behavior in the electrolyte, resulting in a rapid response to the gate bias applied via the electrolyte. A series of sensing measurements showed that the surface potential of the InP linearly changed with the pH values of the electrolytes in a pH range from 3.0 to 12.0. The pH sensitivity of the open-gate FETs depended on the ion species contained in the electrolyte. A Si_3N_4 layer was useful as an ion selective membrane for the InP open-gate FETs to improve the selectivity of H^+ ions.

1. Introduction

A liquid-phase chemical sensor that is based on an ion-sensitive field-effect transistor (ISFET) is one of the most promising instruments for biochemical sensing. Since ISFETs are electronic devices that detect potential changes in the gate area with a current signal, they are applied to various biochemical sensors by employing specific ion-selective membranes. ISFETs in pH and glucose sensors are common examples of their applications where they have many advantages over conventional amperometric sensors, such as short response times, miniaturization, and high-density integration.

Liquid-phase sensors based on ISFETs have been extensively studied for Si metal-oxide-semiconductor (MOS) structures[1,2]. Significant research efforts have been devoted on designing a device structure for improving the sensitivity and stability by changing the gate insulators[3-5]. Another approach for improving the device performance is to use compound semiconductors as substrate materials. In particular, for III-V compound semiconductors such as InP-, GaAs-, and GaN-related materials, drastic improvement in sensitivity is expected because of their superb electrical properties. Recently, ISFETs that are based on high electron mobility transistors (HEMTs) have demonstratively shown the capabilities of III-V compound materials for use in various liquid-phase sensors[6-8].

The purpose of this study is to investigate the feasibility of liquid-phase chemical sensors that are based on InP open-gate FETs. InP has been attracting attention as a sensor material due to its surface sensitive nature. Various gas sensors that form on n-type InP have been recently reported, such as H_2 gas sensors[9,10] and NO_2 gas sensors[11]. In this study, we show that InP-based open-gate FETs work well as pH sensors in various electrolytes.

2. Experimental Procedure

An n-type InP epitaxial layer with a thickness (a) of 200 nm was grown on a Fe-doped semi-insulating (001) InP substrate to fabricate an open-gate FET. Hall measurements showed that the carrier concentration (N_D) was $8x10^{16}$ cm^{-3} and the mobility (μ) was 2700 cm^2 V^{-1} s^{-1}. As shown in Fig. 1, source and drain ohmic contacts were formed on mesa-etched islands on the InP epitaxial layers by depositing the GeAuNi layers and annealing them at 400°C for 5 min. Then, a 100-nm-thick SiO_2 film was deposited on the surface using plasma-enhanced chemical vapor deposition (PECVD) at 300°C. Finally, the open-gate window that was 10 μm in length (L_G) and a 125 μm in width (W_G) was formed by using standard photolithography and etching processes, as shown in the inset photograph in Fig. 1.

Figure 2 shows the experimental setup used in this study for a series of electrochemical measurements. The open gate FETs were set on a Tefron holder, and the source and drain electrodes were connected to the outer circuit via the embedded wires. The top surface except for the open-gate area was covered by an epoxy or negative-type photoresist. The gate bias was applied with a semiconductor parameter analyzer to the electrolyte/InP interface at the open-gate area via a saturated calomel electrode (SCE). For a series of pH-sensing measurements, a 0.01-M KCl solution was added as a base electrolyte, and HCl, H_3PO_4, and NaOH solutions were used for the pH control. The pH values of the electrolytes were measured using a digital pH-meter after calibration with standard reference solutions.

3. Results and Discussion

3.1 Basic properties of open-gate FETs in an electrolyte

In order to clarify the basic properties of open-gate FETs, source drain current voltage (I_{ds}-V_{ds}) measurements were first carried out by changing the gate potential, V_{gs}. Figure 3 shows some typical I_{ds}-V_{ds} characteristics of an open-gate FET measured in a 0.1-M phosphate buffer solution (PBS) with a pH of 7.0 in the dark. The device clearly exhibited current saturation and pinch-off behaviors just like conventional Schottky-gate FETs. The result indicates that the depletion layer was formed underneath the open-gate and it suppresses the current flow from the source to the drain contacts.

In a similar fashion as that in conventional Schottky-gate FETs, the source-drain currents, I_{ds}, of open-gate FETs can be described by the gradual channel approximation using the following equation:

$$I_{ds} = I_P \left\{ \frac{3V_{ds}}{V_P} - 2\left[\frac{\left(V_{ds} + V_{bi} - V_{gs}\right)^{3/2} - \left(V_{bi} - V_{gs}\right)^{3/2}}{V_P^{3/2}} \right] \right\} , \quad (1)$$

where I_P and V_P are the pinch-off current and pinch-off potential, respectively, which can be expressed as

$$V_P = \frac{qN_D a^2}{2\varepsilon} , \quad (2a)$$

and

$$I_P = \frac{W_G \mu q^2 N_D{}^2 a^3}{6\varepsilon L_G} , \quad (2b)$$

where q is the electron charge and ε is the dielectric constant of InP. The built-in potential, V_{bi}, of open-gate FETs is determined by the difference in electrochemical potential between the semiconductor and the electrolyte. Therefore, V_{bi} changes with the surface condition in the open-gate area.

The solid lines in Fig. 3 show the theoretical I_{ds} -V_{ds} curves calculated by using eq. (1) when taking the series resistances of both the source and drain contacts into account. As shown in Fig. 3, the experimental data were well reproduced using the calculation with a V_{bi} of 0.57 eV. This indicates that the I_{ds} currents of open-gate FETs can be well controlled by changing the surface gate bias, V_{gs}.

3.2 Current response to acid and alkali solutions

The current response characteristics of InP-based open-gate FETs were investigated for pH-controlled electrolytes. Figures 4(a) and 4(b) show the transient behaviors of I_{ds} measured by successively adding HCl and NaOH solutions every minute, respectively. The gate bias (V_{gs}) was set at 0 V during both measurements, and the drain bias (V_{ds}) was set at 0.5 V to evaluate the transfer characteristics in the linear region. As shown in Fig. 4(a), as the pH value decreased from 5.5 to 2.5 with the addition of the acid solution, I_{ds} increased as if a positive gate bias was additionally applied to the surface. On the other hand, as the pH value increased from 5.6 to 11.7 with the addition of the alkali solution, I_{ds} decreased as if a negative gate bias was applied. The response time from both measurements was estimated to be about 300-400 ms, which seems to be limited by the pH exchange rate in the electrolyte but not by the intrinsic device response. This result is comparable to the ISFETs based on AlGaAs/GaAs[6] and AlGaN/GaN[7,8] hetero-structures.

In order to further clarify the relation between the I_{ds} and pH values, we plotted the I_{ds}

currents obtained here in Fig. 5 as a function of the pH of the electrolyte. The I_{ds} curves showed a discontinuous point at a pH of around 5.6 because the I_{ds} measurements were interrupted to switch the adding solution between HCl and NaOH. However, we found that the linear relation between the I_{ds} and pH values were obtained in both the acid and alkali regions. As reported by Marin et al.[12], the V_{bi} of n-type InP varies with the surface potential difference caused by the change in H^+ ion concentration in the electrolytes. In the present case, the surface potential in the open-gate area changed as a reflection of the pH values, leading to increases and decreases in the I_{ds} currents of the open-gate FETs. As shown in Fig. 5, the anomalous behavior of I_{ds} was observed in a pH range below 3.0, where the I_{ds} decreased with the pH values. This is probably because the InP surface in the open-gate area was dissolved into the acid electrolyte with a low pH value. We found from these results that InP open-gate FETs work as pH sensors in a wide range from 3.0 to 12.0. This covers the optimum pH range for various enzymatic reactions, such as lipase (pH= 4.0-5.0), amylase (pH= 6.7-7.0) and trypsin (pH= 7.8-8.7)[13], showing the possibility of the use of InP-based open-gate FETs for biochemical applications.

3.3 pH sensitivity and selectivity

In order to clarify the pH sensitivity of InP open-gate FETs, the relation between the surface potential and the H^+ concentration was investigated in pH-controlled electrolytes. Figure 6 shows the pH sensitivity curves obtained for the electrolytes containing HCl and H_3PO_4 solutions. The vertical axis indicates the surface potential difference measured from the reference values obtained at a pH of 7.0. We found that the surface potentials linearly related to the pH values for both electrolytes, but there were differences in the slopes of the curves. A pH sensitivity of 44.3 mV/pH was obtained for the HCl electrolyte, which was higher than the 37.6 mV/pH obtained for the H_3PO_4 electrolyte. This suggests that the surface potential was affected by not only the H^+ ions, but also other ions contained in the electrolytes such as the Cl^- and PO_4^{3-} ions.

In order to improve the selectivity for the H^+ ions, the thin silicon nitride (Si_3N_4) films were used in the gate area of present FETs. Si_3N_4 film has been commonly used as an ion selective membrane for pH sensing with Si-based ISFETs[5], but has not been used with InP-based ISFETs. Therefore, the gate controllability of Si_3N_4/InP FETs in the electrolyte was first investigated by changing the Si_3N_4 thickness. Figure 7 shows the I_{ds}-V_{gs} characteristics measured in a PBS electrolyte with a pH= 7.0. The thickness of the Si_3N_4 films was measured by using a standard ellipsometric technique. The I_{ds} currents for 12-nm-thick Si_3N_4 films only slightly changed with the gate bias. As the film thickness was decreased, however, the controllability of the I_{ds} currents recovered. For the 7 nm thickness, the I_{ds} currents changed by about 300 μA in a bias range from 0 to -2 V.

Figure 8 shows the potential sensitivity curves of an InP-based open-gate FET with a Si_3N_4 gate film thickness of 7 nm. We found that there was no significant difference in the sensitivity obtained for the two kinds of electrolytes, which is contrary to the results shown in Fig. 6. The curve slopes were 38.0 and 37.5 mV/pH for the HCl and H_3PO_4 electrolytes, respectively. These results suggest that the selectivity of H^+ ions was improved by using the Si_3N_4 films on the open-gate area. However, the pH sensitivity was smaller than the theoretical value of 58.9 mV/pH at 24˚C predicted by using the Nernst equation. One of the possible reasons for this is that high-density states were induced in the energy band gap near the Si_3N_4/InP interface. The electric field generated by the adsorbed ions in the open-gate area seems to be partly terminated by the charged interface states. In such a situation, the surface potential can only be slightly changed with the ion concentration in the electrolyte. Various approaches for reducing the interface states have been proposed for the InP, such as sulfur treatments[14-16], application of a Si interface layer[17], and electrochemical treatment[18,19]. For example, a large reduction in the interface states was achieved for the SiN_x/InP interfaces by using a gaseous H_2S treatment, which resulted in recovery of the potential controllability[15]. Surface passivation is a key issue for the InP-based open-gate FETs, and the optimization of the passivation process would help to further improve their sensitivity.

4. Conclusions

We investigated the feasibility of producing liquid-phase sensors that are based on InP open-gate FETs. The open-gate FET clearly exhibited current saturation and a pinch-off behavior in an electrolyte, resulting in a rapid response to the gate bias applied via the electrolyte. We found from a series of sensing measurements that the I_{ds} currents of open-gate FETs linearly change with the pH values of electrolytes containing HCl, H_3PO_4, and NaOH for a wide pH range from 3.0 to 12.0. The pH sensitivity was not the same between different electrolytes, showing that the surface potential in the open-gate area was affected by not only H^+ ions, but also other ions. The selectivity for H^+ ions was improved by forming Si_3N_4 films on the open-gate area. Further investigation and improvement of the surface passivation process seems to improve both the sensitivity and ion selectivity of liquid-phase chemical sensors based on InP open-gate FETs.

Acknowledgements

This study was financially supported by the Ozawa and Yoshikawa Memorial Electronics Research Foundation and by a Grant-in-Aid for Young Scientists B (19760208) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

References

1) P. Bergveld: IEEE Trans. Biomed. Eng. **17** (1970) 70.

2) P. Bergveld: IEEE Trans. Biomed. Eng. **19** (1972) 342.

3) M. Esashi, and T. Matsuo: IEEE Trans. Biomed. Eng. **25** (1978) 184.

4) L. Bousse, N. F. De Rooij, and P. Bergveld: IEEE Trans. Electron Devices **30** (1983) 1263.

5) M.-N. Niu, X.-F. Ding, and Q.-Y. Tong: Sens. Actuators B **37** (1996) 13.

6) S. M. Luber, K. Adlkofer, U. Rant, A. Ulman, A. Gölzhäuser, M. Grunze, D. Schuh, M. Tanaka, M. Tornow, and G. Abstreiter: Physica E **21** (2004) 1111.

7) G. Steinhoff, M. Hermann, W. J. Schaff, L. F. Eastman, M. Stutzmann, and M. Eickhoff: Appl. Phys. Lett. **83** (2003) 177.

8) T. Kokawa, T. Sato, H. Hasegawa, and T. Hashizume: J. Vac. Sci. Technol. B **24** (2006) 1972.

9) H. -I. Chen, Y.-I. Chou, and C.-Y. Chu: Sens. Actuators B **85** (2002) 10.

10) T. Kimura, H. Hasegawa, T. Sato, and T. Hashizume: Jpn. J. Appl. Phys. **45** (2006) 3414.

11) K. Wierzbowska, L. Bideux, B. Adamowicz, and A. Pauly: Sens. Actuators A **142** (2008) 237.

12) F. I.-Marin, C. D.-Chouvy, M. Herlem, J.-L. Sculfort, and A. Etcheberry: J. Electroanal. Chem. **365** (1994) 283.

13) B. Harrow and A. Mazur: *Textbook of Biochemistry* (Saunders, Philadelphia, PA, 1966) p. 104.

14) H. Oigawa, J. F. Fan, Y. Nannichi, H. Sugahara, and M. Oshima: Jpn. J. Appl. Phys. **30** (1991) L322.

15) A. Kapila, X. Si, and V. Malhotra: Appl. Phys. Lett. **62** (1993) 2259.

16) K. Vaccaro, H. M. Dauplaise, A. Davis, S. M. Spaziani, and J. P. Lorenzo: Appl. Phys. Lett. **67** (1995) 527.

17) H. Takahashi, T. Hashizume, and H. Hasegawa: Appl. Surf. Sci. **123** (1998) 615.

18) C. Kaneshiro, T. Sato, and H. Hasegawa: Jpn. J. Appl. Phys. **38** (1999) 1147.

19) N. Simon, N. C. Quach, A. M. Gonçalves, and A. Etcheberry: J. Electrochem. Soc. **154** (2007) H340.

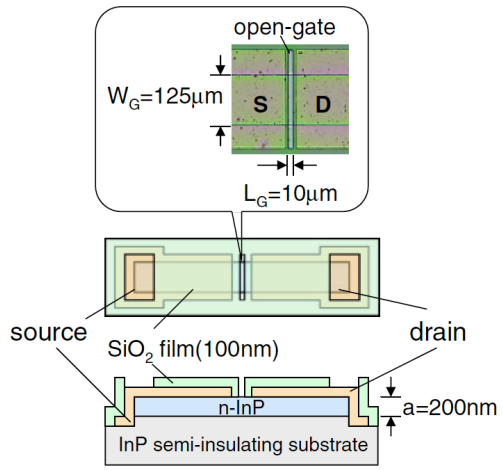


Fig.1 Schematic illustrations and micrograph of InP-based open-gate FET.

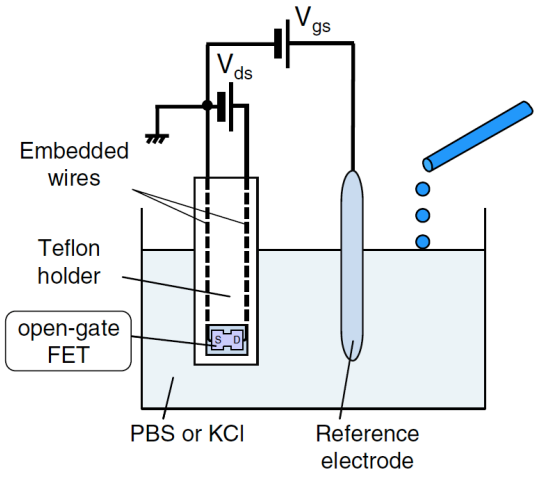


Fig. 2 Experimental setup for sensing measurements.

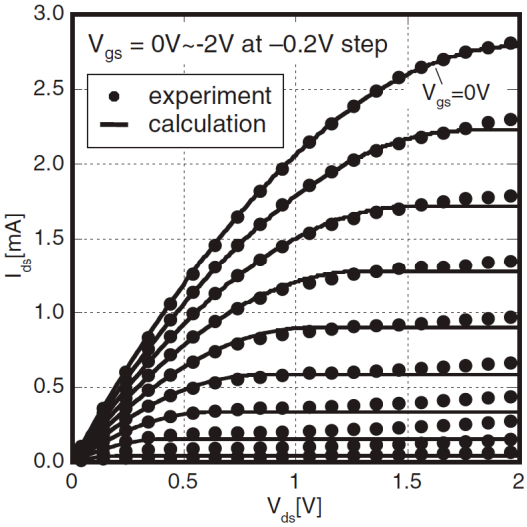
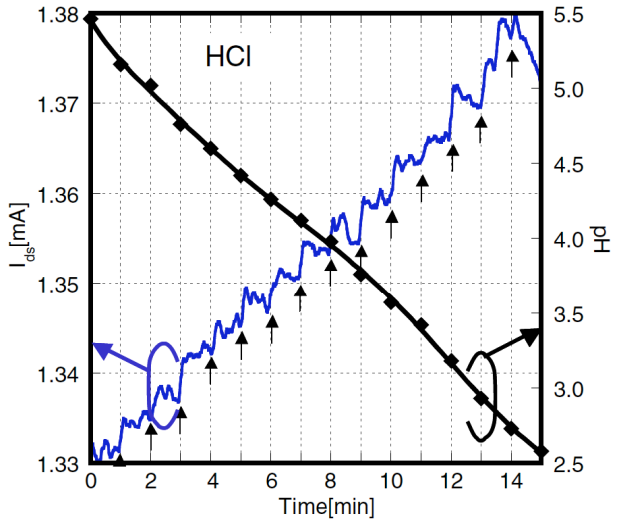
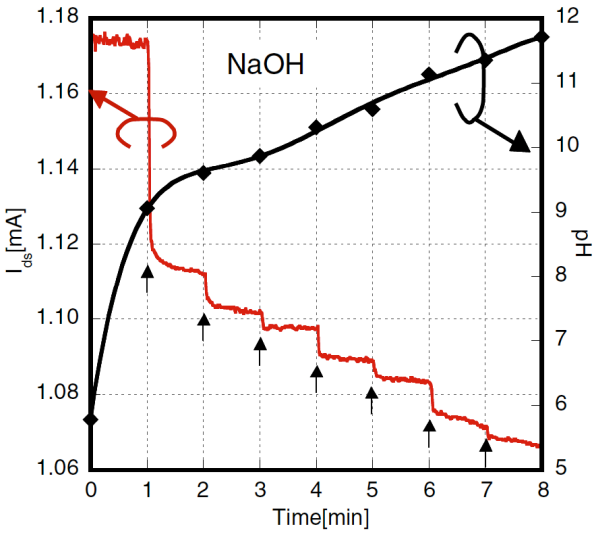


Fig.3 Typical I_{ds}-V_{ds} characteristics of open-gate FET measured in PBS electrolyte with pH=7.0.



(a)



(b)

Fig.4 Transient behaviors of I_{ds} currents as function of pH values of two kinds of electrolyte containing (a) HCl and (b) NaOH for pH control.

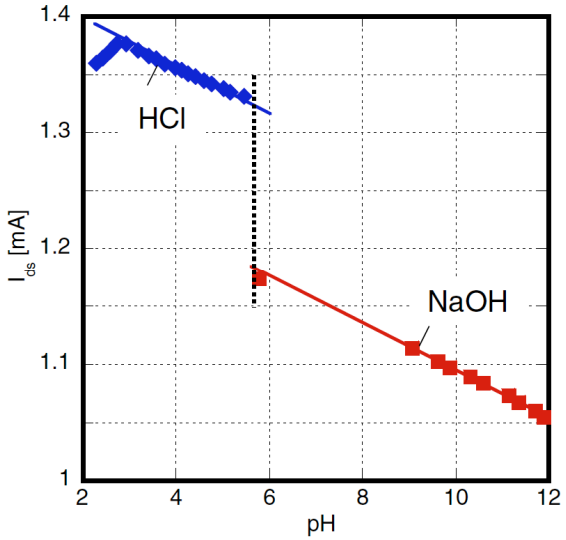


Fig.5 Relation between I_{ds} and pH values obtained by adding HCl and NaOH solutions.

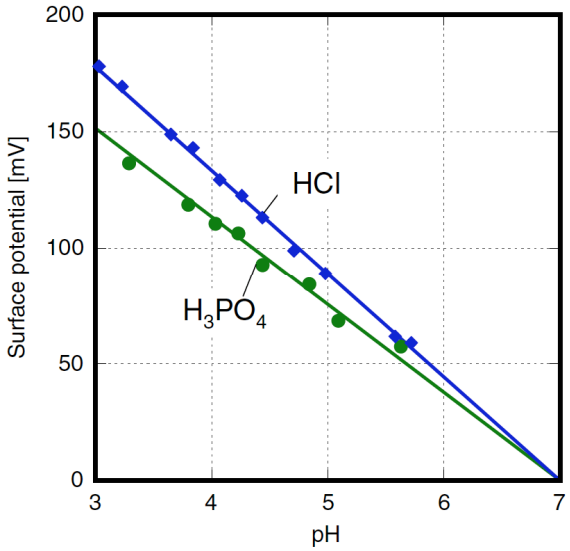


Fig.6 Relation between surface potential and pH values of electrolytes for InP-based open-gate FETs.

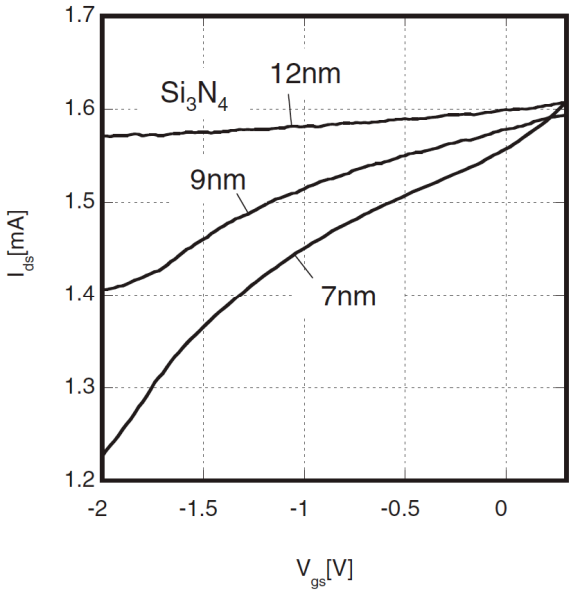


Fig. 7 I_{ds}-V_{gs} characteristics of open-gate FETs having Si_3N_4 films 7, 9, and 12 nm thick.

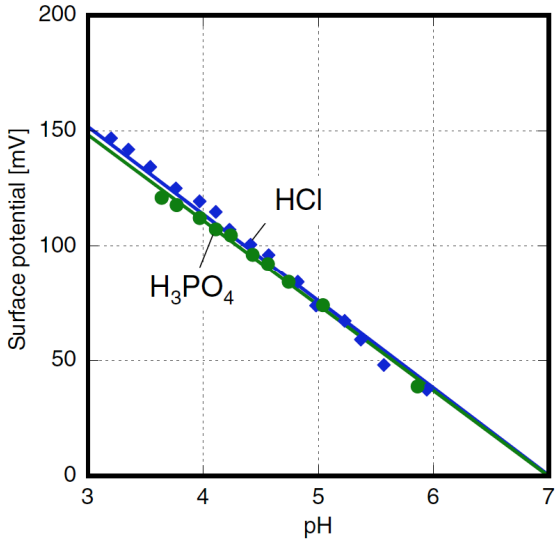


Fig.8 Relation between surface potential and pH values of electrolytes for InP-based open-gate FETs having Si_3N_4 films 7 nm thick.