

Ion-sensitive field-effect transistor based pH sensors using nano self-assembled polyelectrolyte/nanoparticle multilayer films

Yi Liu, Tianhong Cui*

Department of Mechanical Engineering, University of Minnesota, 111 Church ST SE, Minneapolis, MN 55455, United States

Received 22 June 2006; received in revised form 7 August 2006; accepted 8 August 2006

Available online 18 September 2006

Abstract

This paper demonstrates the fabrication and characterization of a pH sensor based on a layer-by-layer (LBL) self-assembly technique. This pH sensor is based on an ion-sensitive field-effect transistor (ISFET). Two types of self-assembled polyelectrolyte/nanoparticle multilayer films work as the critical components for the transistor. One multilayer film embedded with nanoparticles is PSS/In₂O₃ which operates as the channel, and the other multilayer film is PDDA/SiO₂ which serves as the gate dielectric. The mobility of the ISFET is 35.68 cm²/V s at room temperature. The drain current decreases distinctly with increasing pH values in a solution. The temperature effect on the mobility of the ISFET is also investigated in this research. Results show increasing temperature can greatly enhance the carrier mobility. The results introduce a new approach employing a low-cost layer-by-layer nano self-assembly technique to fabricate pH sensors with a high sensitivity and a good reproducibility. © 2006 Elsevier B.V. All rights reserved.

Keywords: pH sensor; Transistor; Layer-by-layer self-assembly; Polyelectrolyte/nanoparticle multilayers

1. Introduction

Since the pioneer work by Decher [1], there has been growing interest in polyelectrolyte multilayer films based on layer-by-layer (LBL) nano self-assembly. This technique involves fabrication of multilayer films through physical adsorption of oppositely charged layers. The process is very inexpensive and environmental friendly using only wet benches. It is easy to control surface properties of existing objects and devices through surface functionality of the built-up films. Initially, the LBL technique was used for the assembly of oppositely charged polyelectrolyte and proteins [2]. Later, it has been extended to a wide variety of other interesting materials such as light emitting polymers [3], enzymes [4], nanotubes [5], nanoparticles [6], etc.

Nanoparticles represent an interesting class of materials that bridge the gap between individual molecules and bulk materials. They have been intensely studied recently due to the recognition that nanoparticles exhibit electronic, catalytic and optical properties that differ from the bulk material. Nanoparticle can also

improve the mechanical properties of bulk or composite materials. For example, the presence of silica-sol nanoparticles in the polymer matrix can lead to an increase of both Young modulus and impact strength [7]. Nanoparticles have large surface-area-to-volume ratio, which is very important and makes them very interesting as catalysts and biolabels [8]. Layer-by-layer self-assembled polyelectrolyte/nanoparticle multilayer thin films are nanoparticle-polymer hybrids. These hybrids combine the unique mechanical properties of nanoparticles and polymers including flexibility and tensile strength. Many applications have been found for these polyelectrolyte/nanoparticle multilayer thin films. For example, Kotov and coworkers reported light emitting from films of self-assembled luminescent CdTe nanoparticles [9]. Recently, our group has demonstrated a fully operational field-effect transistor fabricated from semiconducting and dielectric nanoparticles thin films [10]. Layer-by-layer electrostatic assembly of electrically charged materials is proving to be an increasingly useful and versatile technique for the formation of multilayered thin films with a wide range of electrical, magnetic, optical properties, etc.

Monitoring the concentration of hydrogen ions in solutions is very important in many industrial processes. Precise monitoring of pH values is necessary in order to reduce costs and improve yields. For example, in many chemical processes some materi-

* Corresponding author.

E-mail address: tcui@me.umn.edu (T. Cui).

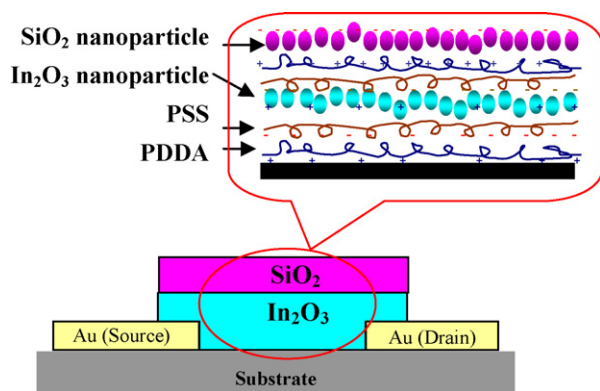


Fig. 1. The schematic diagram of the nanoparticle thin film based ISFET.

als have to be immersed in acids or strong caustic solutions at a specific pH for a specified period of time. In pharmaceutical and food processing, measurement systems have to meet specific hygienic designs, and must withstand many sterility cycles while providing traceability for validation purposes. Compared to the pH strips, the pH sensor is one of the most useful tools to monitor the pH value in these applications. Depending on the principle of operation, a pH sensor could be based on optical fibers [11], microcantilevers [12], ion-sensitive field-effect transistors (ISFET) [13], etc.

In this paper, the fabrication and characterization of a pH sensor based on ISFET using LBL self-assembled polyelectrolyte/nanoparticles as building blocks is presented. The general site-bending model is used to explain the pH sensitive behavior. The effect of temperature on the characteristics of the transistor is also investigated and discussed in detail.

2. Experiment

A cross section of the polyelectrolyte/nanoparticle based ISFET is shown as Fig. 1. The fabrication of the ISFET began with a standard 4 in. silicon wafer. A layer of wet thermal SiO₂ 300 nm thick was grown on the surface. Chromium (Cr) 100 nm thick and gold 200 nm thick were deposited on the oxidized wafer using e-beam evaporation. Gold (Au) is

used as the source/drain electrodes of the ISFET. Chromium served as the adhesive material between the gold and the insulating substrate. Following metal deposition, a layer of photoresist (type 1813 from Shipley Corporation) was spin-coated on the wafer and patterned by optical UV lithography. Next, the Cr/Au electrodes were formed by etching the unprotected metals. The channel width and channel length between the source/drain electrodes were 1000 μm and 10 μm, respectively. After the dry etching, the second lithography was performed to pattern another layer of spin-coated photoresist. This was to protect the testing pads as well as to open a window above the channel region for the self-assembly of nanoparticle thin films. The wafer was then alternately immersed in aqueous poly(dimethyldiallyl)- ammonium chloride) (PDDA) (MW 200 K and 300 K, from Sigma–Aldrich Corp.) and poly(styrenesulfonate) (PSS) (MW 70 K, from Sigma–Aldrich Corp.) solutions, in a sequence of [PDDA (10 min) + PSS (10 min)]₃. The three bi-layers of PDDA/PSS served as the precursor layers to enhance the subsequent adsorption of nanoparticle layers. PDDA and PSS also functioned as the sandwich layer between two neighboring nanoparticle layers, forming the polyelectrolyte/nanoparticle multilayers. Between the immersions in polyelectrolyte or nanoparticle solutions, there was intermediate rinsing using deionized water for 1 min to remove the residues from the deposition of previous layers. Following the deposition of precursor layers, the In₂O₃ and SiO₂ nanoparticle dispersions were coated on the entire surface of the wafer in a sequence of [In₂O₃ (14 min) + PSS (10 min)]₅ + [PDDA (10 min) + SiO₂ (4 min)]₆ to produce an organized “sandwich” of the semiconducting In₂O₃ thin film and the insulating SiO₂ thin film. The SiO₂ nanoparticle dispersion was obtained through Nissan Chemical Corporation, and In₂O₃ nanoparticles came from Sigma Corp. All chemicals used in the fabrication process were at the reagent grade, and were used without further purification. Following the layer-by-layer nano self-assembly process, the wafer was cut into small pieces using a dicing saw for the measurement. Scanning electron microscopy (SEM) was used to investigate the self-assembled nanoparticle thin films. Fig. 2a and b shows images of self-assembled In₂O₃ nanoparticles and SiO₂ nanoparticles.

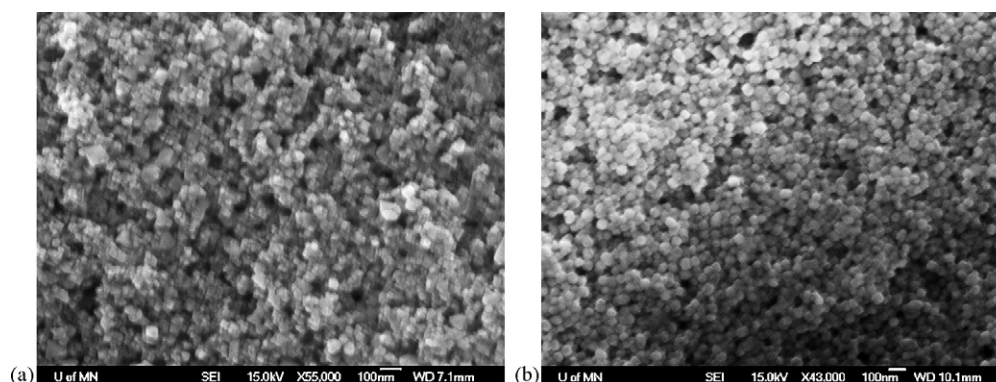


Fig. 2. The SEM image of the self-assembled nanoparticle thin films: (a) In₂O₃ nanoparticle thin film; (b) SiO₂ nanoparticle thin film.

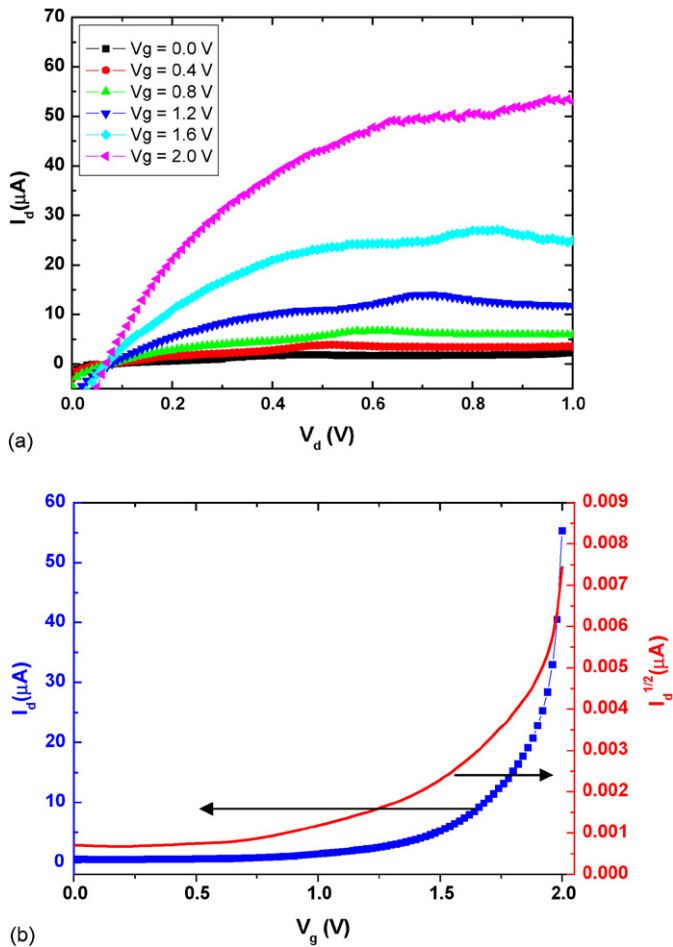


Fig. 3. (a) The output characteristic of the ISFET; (b) the transfer characteristic of the ISFET.

3. Results and discussion

The self-assembled polyelectrolyte/nanoparticle ISFET was characterized using a HP 4156B semiconductor parameter analyzer. Fig. 3a and b shows the output and transfer characteristics of the ISFET immersed in a buffer solution (KH_2PO_4 : K_2HPO_4) with a pH value of 5 at room temperature. An Ag/AgCl reference electrode serves as the gate electrode. From Fig. 3a, it is apparent that the ISFET behaves very similarly to a traditional metal-oxide-semiconductor field-effect transistor (MOSFET). With an increase of the drain voltage, the drain current increases linearly first until saturation is reached. At higher positive gate voltages, the drain current is higher, indicating that the In_2O_3 nanoparticle thin film is an n-type semiconductor.

The operating principles of the ISFET within the pH solution can be explained based on the site binding theory [14]. The surface of the SiO_2 nanoparticle thin film contains hydroxyl groups in the form of SiOH . These groups may donate or accept a proton from the solution, leaving a negatively charged or a positively charged surface group, respectively. The oxide surface charge can be described by the following equilibrium reactions between amphoteric SiOH surface sites and the H^+ ions in the

solution [15]:



The potential difference Ψ between the surface of the SiO_2 nanoparticle surface and the bulk electrolyte solution can be expressed as [16]:

$$\Psi = \frac{Q_0 + Q_S}{C_H} + \frac{2kT}{q} \sinh^{-1} \left(\frac{Q_0 + Q_S}{\sqrt{8\epsilon k T c}} \right) \quad (3)$$

where C_H is the Helmholtz capacitance, c the solution concentration, ϵ the dielectric constant, T the temperature, and Q_0 and Q_S are the charge densities of the insulator and the semiconductor surface, respectively. The I - V characteristic of a typical ISFET can be described based on the general MOSFET theory as in the following expressions [17]:

In the saturation region,

$$I_d = \frac{\mu C_{in} W}{2L} (V_g - V_T)^2 \quad (4)$$

In the linear region,

$$I_d = \frac{\mu C_{in} W}{L} \left(V_g - V_T - \frac{1}{2} V_d \right) V_d \quad (5)$$

In these expressions, I_d is the drain current, V_g is the gate voltage, V_d is the drain voltage, μ is the carrier mobility, W is the channel width and L is the channel length, respectively. From Eqs. (3)–(5), we can see the drain current of the ISFET is dependent on both the pH value and temperature of the solution.

For the ISFET under investigation, the saturation mobility at room temperature based on Eq. (4) is $35.68 \text{ cm}^2/\text{V s}$. This mobility is very close to that of undoped In_2O_3 thin films prepared by reactive evaporation [18]. We have also measured the gate current–voltage characteristic of the ISFET, and found that the gate current is also dependent on the gate voltage. Fig. 4 shows the gate current with respect to the gate voltage at a drain voltage of 1 V. It is observed that the gate current is relatively high (about 1/9 of the drain current) when gate voltage is 2.0 V, but decrease

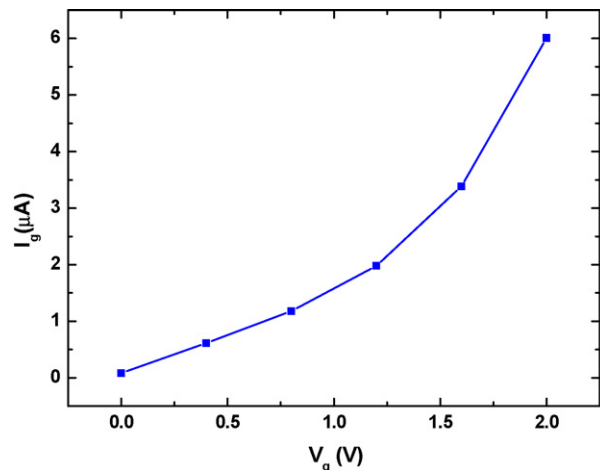


Fig. 4. The gate current with respect to the gate voltage when drain voltage is fixed.

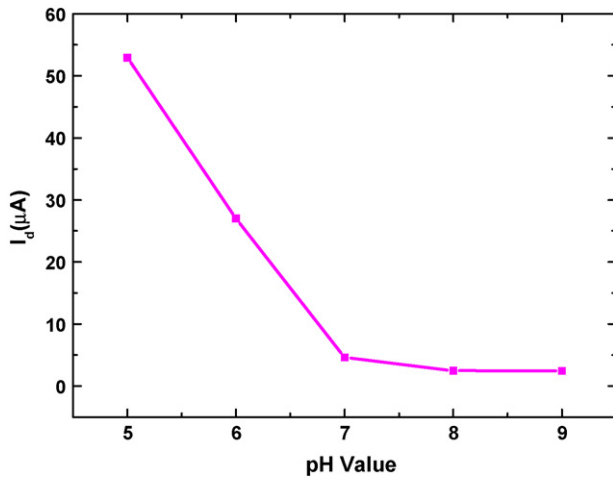


Fig. 5. The pH response of the ISFET.

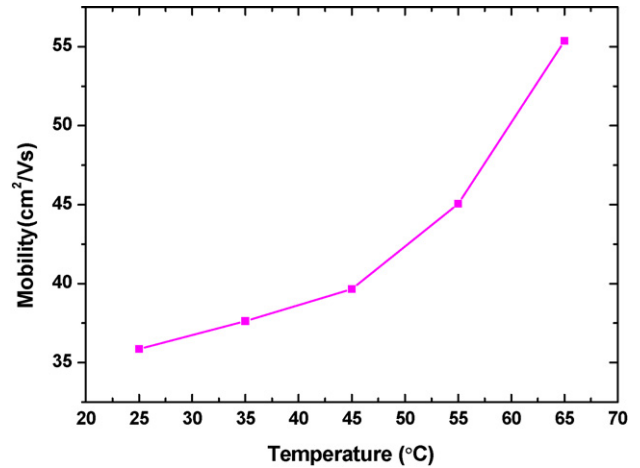


Fig. 6. The effect of temperature on the mobility of the ISFET.

rapidly when the gate voltage reaches zero. This implies that there are hydrogen ions passing through the gate dielectric layers and participating in the charge transport at a positive gate bias. Since the diameter of the hydrogen ion is less than 0.3 nm, it may easily penetrate the small spaces among the SiO_2 nanoparticles (diameters of 40–60 nm). Since polyions (PDDA and PSS) within the multilayer films are also conductive in solution, the total charge carriers in the channel should include hydrogen ions, electrons from the gate-affected In_2O_3 semiconductor thin film and the polyions between the nanoparticle thin films. These carriers greatly increase the channel's conductivity as well as the charge transport ability. Therefore, the calculated mobility based on Eq. (4) should be an "equivalent mobility" that considered all the charge carriers. This mobility of the ISFET in liquid is much larger than our previous field-effect transistor in atmosphere using layer-by-layer self-assembled In_2O_3 nanoparticle thin films as the channel [10]. Similar behavior is also observed by Henrik et al. in an all-polymer field-effect transistor, which also has an abnormal high mobility in a humid environment [19].

Fig. 5 shows the relationship between the drain current of the ISFET and the pH value of different buffer solutions at a gate voltage of 2 V and a drain voltage of 1 V. When the pH value of the solution is less than 7, the concentration of hydrogen ions is larger than that of hydroxide ions. The drain current decreases linearly with respect to the pH value. When the pH value of the solution is higher than 7, more hydroxide ions exist in the solution than hydrogen ions. The drain current decreases further, but with a very flat slope. This phenomenon indicates that many hydrogen ions have participated in the charge transport within the channel region, and played a key role in the relative high charge carrier mobility.

The effect of the buffer solution temperature on the ISFET characteristic, especially on the carrier mobility, has also been investigated. Fig. 6 shows the carrier mobility of the ISFET at temperatures ranging from 25 $^{\circ}\text{C}$ to 65 $^{\circ}\text{C}$. It is evident that the carrier mobility increases rapidly with the increasing temperature. This is due to the stronger Brownian motion of the

ions (both hydrogen ions and the polyions) at higher temperatures. The increased movement of the ions at higher temperature increases the total equivalent mobility of the device. Eq. (3) also indicates the effect of the temperature on the output characteristic of the ISFET. At higher temperature, the surface potential difference Ψ will also be elevated. This surface potential difference will add to the gate voltage, and hence promote more charge carriers to the charge transport process.

In order to reduce the gate leakage current, we have spin-coated a thin layer of insulating polymer, polymethyl methacrylate (PMMA), on top of SiO_2 nanoparticle thin film of the ISFET. Measurement of the gate leakage current of this ISFET shows that the gate leakage current is reduced by three orders. Fig. 7 shows the pH response of the ISFET to the drain current. It is observed that the drain current also tends to linearly decrease when the pH value increases from 5 to 7, but decreases smaller when the pH value further increases to 9. This indicates that the self-assembled ISFETs have a linear sensitivity to pH values at an acid environment with a good reproducibility, compared to the previous results.

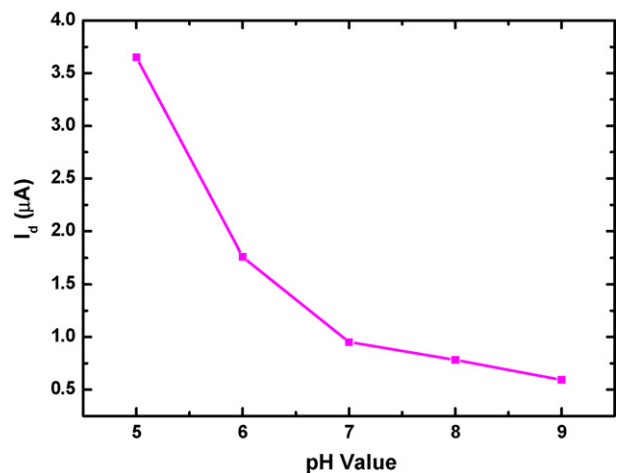


Fig. 7. The pH response of the ISFET with a thin layer of PMMA on the surface.

4. Conclusion

The fabrication and characterization of a pH sensitive ISFET using self-assembled polyelectrolyte/nanoparticles as building blocks has been demonstrated. Multilayers of polyelectrolyte/nanoparticles, PSS/ In_2O_3 and PDDA/ SiO_2 , serve as the channel and gate dielectric, respectively. The drain current of the ISFET is more sensitive in an acid solution ($\text{pH} < 7$) than in the base solution ($\text{pH} > 7$). The temperature effect on the characteristic of the ISFET was also investigated and discussed. A site binding model could be used to explain the pH sensitivity and the temperature dependence. The results introduce a new approach employing a low-cost layer-by-layer nano self-assembly technique to fabricate pH sensors with a high sensitivity and a good reproducibility. This may open a new way for biosensing applications based on this promising nano self-assembly technique with further research in the future.

References

- [1] G. Decher, Fuzzy nanoassemblies: toward layered polymeric multicomposites, *Science* 277 (1997) 1232–1237.
- [2] Y. Lvov, K. Ariga, T. Kunitake, Layer-by-layer assembly of alternate protein/polyion ultrathin films, *Chem. Lett.* 6 (1994) 2323–2326.
- [3] A. Wu, D. Yoo, J.-K. Lee, M.F. Rubner, Solid-state light-emitting devices based on the tris-chelated ruthenium(II) complex: 3. High efficiency devices via a layer-by-layer molecular-level blending approach, *J. Am. Chem. Soc.* 121 (1999) 4883–4891.
- [4] W. Kong, X. Zhang, M.L. Gao, H. Zhou, W. Li, J.C. Shen, A new kind of immobilized enzyme multilayer based on cationic and anionic interaction, *Macromol. Rapid Commun.* 15 (1994) 405–409.
- [5] M. Zhang, Y. Yan, K. Gong, L. Mao, Z. Guo, Y. Chen, Electrostatic layer-by-layer assembled carbon nanotube multilayer film and its electrocatalytic activity for O_2 reduction, *Langmuir* 20 (2004) 8781–8785.
- [6] N.A. Kotov, I. Dekany, J.H. Fendler, Layer-by-layer self-assembly of polyelectrolyte-semiconductor nanoparticles composite films, *J. Phys. Chem.* 99 (1995) 13065–13069.
- [7] M. Garcia, G. van Vliet, S. Jain, B.A.G. Schrauwen, A. Sarkissov, W.E. van Zyl, B. Boukamp, Polypropylene/ SiO_2 nanocomposites with improved mechanical properties, *Rev. Adv. Mater. Sci.* 6 (2004) 169–175.
- [8] P. He, N. Hu, Electrocatalytic properties of heme proteins in layer-by-layer films assembled with SiO_2 nanoparticles, *Electroanalysis* 16 (2004) 1122–1131.
- [9] A. Mamedov, A. Belov, M. Giersig, Nataliya, N. Mamedova, N.A. Kotov, Nanorainbows: graded semiconductor films from quantum dots, *J. Am. Chem. Soc.* 123 (2001) 7738–7739.
- [10] T. Cui, Y. Liu, M. Zhu, Field-effect transistors with layer-by-layer self-assembled nanoparticle thin films as channel and gate dielectric, *Appl. Phys. Lett.* 87 (2005) 183105.
- [11] D. Cui, Q. Cao, J. Han, J. Cai, Y. Li, Z. Zhu, Optical-fibre pH sensor, *Sens. Actuators B* 12 (1993) 29–32.
- [12] Y. Zhang, H. Ji, D. Snow, R. Sterling, G.M. Brown, A pH sensor based on a microcantilever coated with intelligent hydrogel, *Instrum. Sci. Technol.* 32 (2004) 361–369.
- [13] R. Kuhnhold, H. Ryssel, Modeling the pH response of silicon nitride ISFET devices, *Sens. Actuators B* 68 (2000) 307–312.
- [14] C.D. Fung, P.W. Cheung, W.H. Ko, A generalized theory of an electrolyte-insulator-semiconductor field effect transistor, *IEEE Trans. Electron Devices* 33 (1986) 8–18.
- [15] P. Bergveld, Proceedings of the IEEE Sensor Conference on Theory and Practice ISFET, Toronto, Canada, 2003, pp. 1–26.
- [16] R. Kuhnhold, H. Ryssel, Modeling the pH response of silicon nitride ISFET devices, *Sens. Actuators B* 68 (2000) 307–312.
- [17] S. Martinoia, G. Massobrio, L. Lorenzelli, Modeling ISFET microsensor and ISFET-based microsystems: a review, *Sens. Actuators B* 105 (2005) 14–27.
- [18] S. Noguchi, H. Sakata, Electrical properties of undoped In_2O_3 films prepared by reactive evaporation, *J. Phys. D: Appl. Phys.* 13 (1980) 1129–1133.
- [19] H.G.O. Sandberg, T.G. Backlund, R. Osterbacka, H. Stubb, High-performance all-polymer transistor utilizing a hygroscopic insulator, *Adv. Mater.* 16 (2004) 1112–1115.

Biographies

Yi Liu received his BS degree in telecommunication engineering from Beijing University of Posts and Telecommunications (Beijing, China) in July 1998, and his PhD degree in mechanical engineering from University of Minnesota at twin cities (Minnesota, US) in May 2006. Since then, he joined the vacuum process department at Seagate Technology Inc. His research interests include micro/nanofabrication, microelectromechanical systems (MEMS), nanotechnology, biosensor, polymer microelectronics, etc.

Tianhong Cui received his BS degree from Nanjing University of Aeronautics and Astronautics in 1991, and his PhD degree from the Chinese Academy of Sciences in 1995. He is currently the Nelson Associate Professor in mechanical engineering at the University of Minnesota. From 1999 to 2003, he was an Assistant Professor of electrical engineering at Louisiana Technical University. Prior to that, he was a STA fellow at National Laboratory of Metrology, and served as a Postdoctoral Research Associate at the University of Minnesota and Tsinghua University. His current research interests include MEMS/NEMS, nanotechnology, and polymer electronics.