Electrochemistry Communications 13 (2011) 488–490

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

pH measurements with ZnO based surface acoustic wave resonator

Xiaotun Qiu [a], Rui Tang [a], Shih Jui Chen [b], Hao Zhang [c], Wei Pang [c], Hongyu Yu [a,d,*]

[a] School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, AZ 85287, United States
[b] Department of Electrical Engineering–Electrophysics, University of Southern California, Los Angeles, CA 90089, United States
[c] College of Precision Instrument and Opto-Electronics Engineering, Tianjin University, Tianjin, 300072, People's Republic of China
[d] School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, United States

ARTICLE INFO

Article history:
Received 4 February 2011
Received in revised form 18 February 2011
Accepted 24 February 2011
Available online 3 March 2011

Keywords:
pH
Surface acoustic wave resonator
ZnO
Acoustoelectric effect

ABSTRACT

This paper investigated pH measurements using ZnO based surface acoustic wave resonator (SAW). The resonant frequency of the SAW decreased as pH value changed from 7 to 2 (acid region) or from 7 to 12 (alkaline region). The detection limits were 0.03 and 0.02 pH change, respectively, which were comparable to commercial pH meters. The interaction between hydronium (H_3O^+) or hydroxide (OH^-) and ZnO was proposed to be responsible for the frequency drop. Both hydronium and hydroxide can increase the conductivity of the ZnO film, resulting in the resonant frequency decrease due to the acoustoelectric effect.

1. Introduction

The measurement of pH is very important in chemistry, biology, and environmental science. A number of different pH sensors are available nowadays. The classical method to determine pH values employed glass electrodes. They possessed good sensitivity, selectivity and long lifetime. However, the limitations, such as high impedance, high temperature instability and mechanical fragility restricted further applications in certain circumstances [1]. As a result, non-glass pH electrodes, especially solid-state pH sensors using metal oxides, began to draw considerable attention, because they are mechanically robust, and less sensitive to cation interference [2]. Metal oxides, such as RuO_2 [3], TiO_2 [4] and ZnO [5], have been used to fabricate pH value monitors. However, most of them require a reference electrode to operate, which leads to a bulky structure.

Surface acoustic wave travels along the surface of a material exhibiting elasticity, with amplitude that typically decays exponentially with depth into the substrate. Therefore in a surface acoustic wave resonator (SAW), the acoustic energy is confined in the near-surface region of a solid, resulting in high acoustic wave sensitivity to surface perturbations. Many sensing applications have been realized with SAW, such as UV, gas and bio-sensing [6–8]. In this study, a novel pH sensor using ZnO based SAW was developed. No reference electrodes were employed. Meanwhile, the response signal of the sensor was in the frequency domain, which provided great potential for incorporating the sensor into a wireless sensing network [9].

In the following sections, the design and fabrication of the SAW pH sensor were described. The pH response of the sensor was presented and the sensing mechanism based on the interaction between hydronium (H_3O^+) or hydroxide (OH^-) and ZnO was investigated.

2. Experimental

The schematic structure of the SAW pH sensor is shown in Fig. 1. The SAW was fabricated on top of a silicon substrate. A sputtered ZnO film (3.9 μm) was used both as the pH sensitive layer and the piezoelectric actuation layer for the SAW sensor. The top electrode was made of Au (0.2 μm). The fabrication process of the SAW was as follows. First, ZnO was radio-frequency (RF) sputtered and etched (wet chemical etching) to form the desired pattern. Then the top Au electrode was deposited by electron-beam (e-beam) evaporation and patterned by lift-off. The electrodes consisted of 5 pairs of fingers, with an aperture of 480 μm and a spatial periodicity of 40 μm.

The ZnO film was characterized by X-ray diffraction (XRD) using Cu K_α radiation. Solutions of various pH values were introduced to the active region of the SAW sensor using a mechanical pipette (Biohit, Helsinki, Finland). The pH values were calibrated by a commercial pH meter Exstik II (Extech Instruments, Waltham, MA). The SAW sensor was tested on a probe station with Ground-Signal-Ground 150 μm pitch probes from Cascade Microtech Inc (Beaverton, OR). The calibration was carried out with an impedance standard substrate using a short-open-load (SOL) method. The resonant frequency of the SAW was monitored with an Agilent E5071C network analyzer (Agilent, Santa Clara, CA) and recorded by a LabVIEW program (National Instruments, Austin, TX).

* Corresponding author at: School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, AZ 85287, United States. Tel.: +1 4807277454; fax: +1 4809650616.
E-mail address: hongyuyu@asu.edu (H. Yu).

1388-2481/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2011.02.028

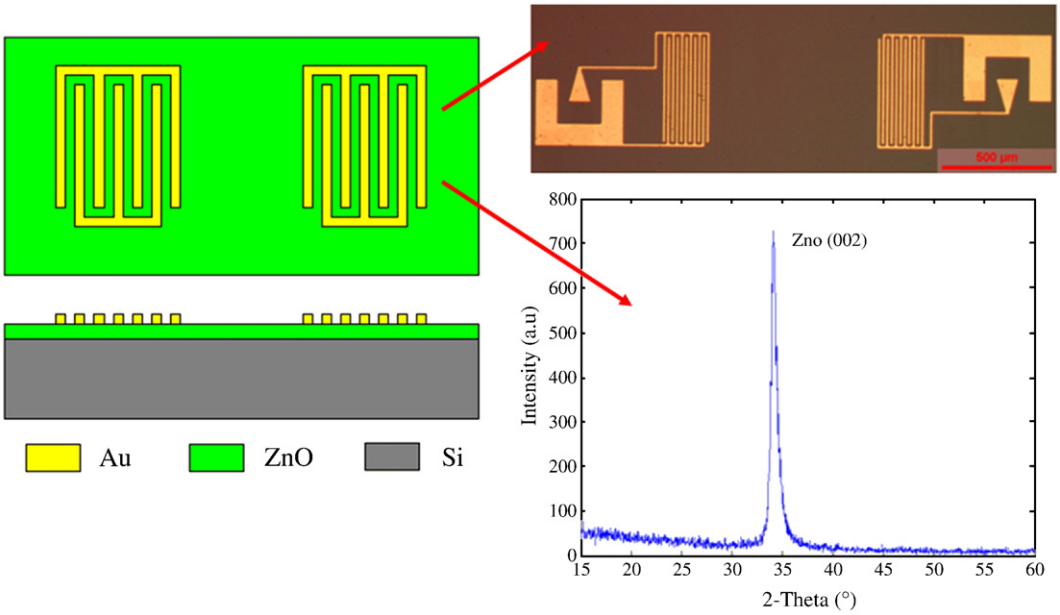

Fig. 1. Schematic structure of the SAW *p*H sensor with a photograph of the top view of a fabricated device and an XRD trace of the ZnO film illustrating that it has <002> crystal orientation.

Sodium chloride (NaCl) solutions with different concentrations were prepared as comparison samples. Their role was to demonstrate that the response of the SAW sensor was induced by the *p*H values not the conductivity of the solution.

3. Results and discussion

From the ZnO XRD trace, only the Bragg reflection corresponding to (002) planes was observed, indicating that the film had a preferred growth orientation along the wurtzite C axis, which was normal to the silicon substrate (Fig. 1).

The resonant frequency of the SAW sensor was 177 MHz, which was suitable for integration with a wireless sensor network. The noise floor of the sensor was around 20 kHz. Previous study showed that, for SAW with different thickness of ZnO films, the acoustic velocity was determined by the product of hk (h, ZnO thickness; $k=2\pi/\lambda$, wave factor; λ, acoustic wave length) [10]. At a certain wavelength, if hk is smaller than 0.3, no acoustic wave mode can be detected due to the low electromechanical coupling for a very thin ZnO film [11]. As the thickness increases, the Rayleigh (R) mode resonant peak starts to appear. Theoretical analysis shows that the acoustic velocity is close to that of the substrate at $hk \sim 0$, and varies monotonically until it approaches the acoustic velocity of the surface material at $hk \gg 1$. The SAW *p*H sensor had an hk value of 0.61. Thus, the acoustic velocity of the sensor was between that of the ZnO film and the silicon substrate. The Rayleigh velocities of the SAW propagating in the ZnO and silicon are 2700 m/s and 4680 m/s, respectively [10]. Therefore, the resonant frequency of the R mode wave should be between 67.5 MHz and 117 MHz. In this case, the resonant peak observed in the *p*H sensor was not R mode. In layered structures, where the substrate has a higher acoustic velocity than the overlaying film, Sezawa (S) mode wave can be generated [11]. The S wave exhibits a higher phase velocity (higher resonant frequency) compared with the R wave for a certain thickness of the ZnO film. Therefore, S wave was detected in the SAW sensor and used to monitor *p*H variations. The observation of S wave resonant frequency in the SAW *p*H sensor was in agreement with the results of the previous study conducted by Du *et al.*, which obtained S mode resonance in their ZnO based SAW with an hk value of 0.6 [10]. The appearance of S wave in a resonator with $hk<1$ implied good crystallinity of the ZnO, because only films with high crystal quality and large electromechanical coupling coefficient can generate S wave under such circumstances.

The response of the SAW sensor to different *p*H values is shown in Fig. 2. In the acid region, the frequency decreased linearly as the *p*H

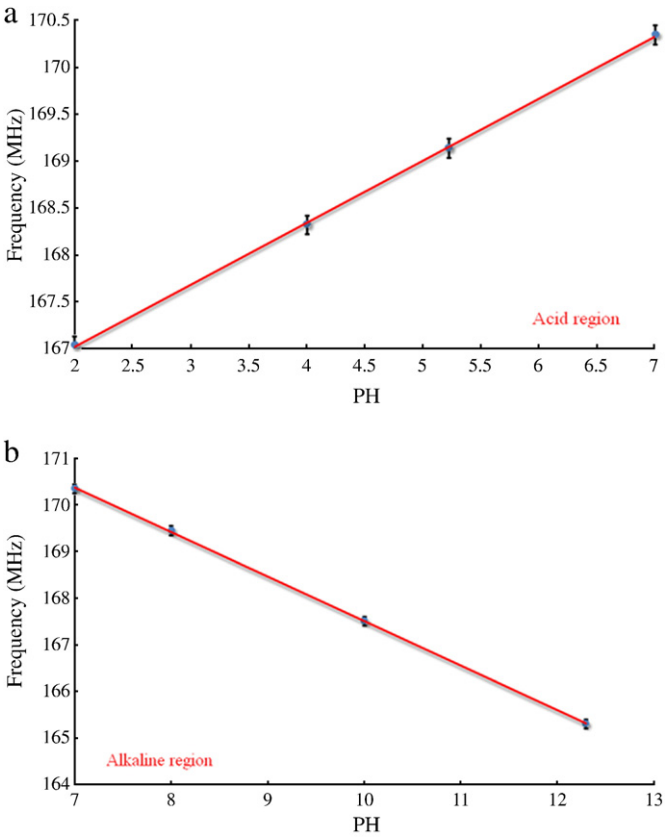

Fig. 2. The response of the SAW sensor to different *p*H values: (a) In the acid region, the frequency decreased linearly as the pH value decreased with a detection limit of 0.03 *p*H change; (b) In the alkaline region, a linear relationship between the frequency and the *p*H values can be identified with a detection limit of 0.02 *p*H change. The frequency decreased as the *p*H value increased.

value decreased with a detection limit of 0.03 *p*H change. In the atmosphere, oxygen is adsorbed on the surface of ZnO as negatively charged ions by capturing free electrons from the film, thereby creating a depletion layer with low conductivity near the surface. ZnO is an amphoteric oxide in which an electropositive metal atom gives the oxygen a sufficient negative charge to strip a proton from a neighboring hydronium [5]. In this way, surface oxygen ions were neutralized and the conductivity of the ZnO film increased due to the shrinking of the surface depletion layer. In the alkaline region, a linear relationship between the resonant frequency and *p*H values can be identified with a detection limit of 0.02 *p*H change. The frequency, however, decreased as the *p*H value increased. The metal ions in the ZnO film are electropositive enough to serve as an electron acceptor from a neighboring hydroxide [5]. Therefore, the conductivity of the ZnO film also increased in this case.

Surface acoustic waves in piezoelectric films are accompanied by a potential wave and electric fields originating from the polarization of the material under mechanical deformation. The electric fields interact with different carriers in a two-dimensional electron system (2DES) close to the surface. Consequently, the 2DES influences the propagation of the surface wave. It alters the wave velocity and produces an attenuation. The shift in the SAW phase velocity v is given by

$$\frac{v-v_o}{v_o} = \frac{K^2}{2}\frac{1}{1+(\sigma/\sigma_m)^2} \tag{1}$$

where K^2 is the effective electromechanical coupling coefficient, σ is the sheet conductivity, and σ_m is a material constant. The velocity v_o is the phase velocity on a free surface [12]. This velocity shift is accompanied by an attenuation of the wave intensity given by

$$\Gamma = \frac{\pi K^2}{\lambda}\frac{\sigma/\sigma_m}{1+(\sigma/\sigma_m)^2} \tag{2}$$

Since the SAW carries a flux of momentum equal to $1/v$ times the flux of energy, a loss of wave energy is accompanied by a loss of momentum. This loss of momentum appears as a force on the electron system. This phenomenon is generally known as the acoustoelectric effect [12]. In the acid region, as *p*H value decreased, the interaction between hydronium and ZnO was enhanced, resulting in an increase of the film conductivity. From Eq. (1), a larger σ means a smaller v. Therefore, the phase velocity decreased as the conductivity of the film increased. The resonant frequency of the SAW is proportional to the phase velocity at certain wavelengths. Thus, a drop of resonant frequency can be expected. Similar analysis holds true in the alkaline region, as the interaction between hydroxide and ZnO also enhances the film conductivity. In Eq. (1), a higher K^2 is desirable in order to yield a higher sensitivity to *p*H changes. Sezawa mode usually possesses a higher K^2 (4%) compared with that (K^2~0.49%) of the Rayleigh mode [10]. Thus, as mentioned above, S wave was used in the *p*H sensing applications in this study.

NaCl solutions with different concentrations were tested using the SAW sensor as comparison samples. No appreciable frequency changes were observed (Fig. 3), demonstrating that the response of the sensor was due to the interaction between hydronium or hydroxide and ZnO not the conductivity of the solution.

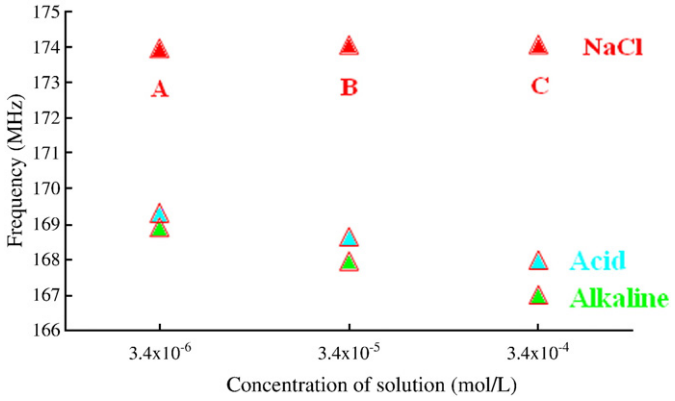

Fig. 3. The response of the SAW sensor to NaCl solutions with different concentrations (sample A: 3.4×10^{-6} mol/L, sample B: 3.4×10^{-5} mol/L, and sample C: 3.4×10^{-4} mol/L). The frequency shift between sample A and C was 0.11 MHz. However, for the acid and alkaline solutions with same ion concentrations, the frequency shifts were 1.33 MHz and 1.92 MHz, respectively. The results demonstrated that the response of the sensor was due to the interaction between hydronium or hydroxide and ZnO not the conductivity of the solution.

4. Conclusions

In this paper, we developed a ZnO based Surface Acoustic Wave Resonator as *p*H value monitors. The resonant frequency of the SAW decreased linearly as *p*H value decreased from 7 to 2 in the acid region. While in the alkaline region, the resonant frequency decreased linearly as *p*H value increased from 7 to 12. The detection limits were 0.03 and 0.02 *p*H change, respectively. The interaction between hydronium or hydroxide and ZnO was responsible for the frequency drop. Both of them can increase the conductivity of the ZnO film, resulting in the resonant frequency decrease due to the acousto-electric effect. NaCl solutions were used as comparison samples in the testing. The results demonstrated that the response of the sensor was due to the interaction between hydronium or hydroxide and ZnO not the conductivity of the solution.

Acknowledgments

We would like to thank Dr. Eun Sok Kim at University of Southern California for providing ZnO films. This work was supported by NASA Astrobiology Institute and ASU graduate dissertation fellowship.

References

[1] P. Shuk, K.V. Ramanujachary, Solid State Ionics 86–88 (1996) 1115.
[2] A. Fog, R.P. Buck, Sens. Actuators 5 (1984) 137.
[3] B. Xu, W. Zhang, Electrochim. Acta 55 (2010) 2859.
[4] R. Zhao, M. Xu, J. Wang, G. Chen, Electrochim. Acta 55 (2010) 5647.
[5] S.M. Al-Hilli, M. Willander, A. Öst, P. Strålfors, J. Appl. Phys. 102 (2007) 084304.
[6] P. Sharma, K. Sreenivas, Appl. Phys. Lett. 83 (2003) 3617.
[7] C. Wen, C. Zhu, Y. Ju, H. Xu, Y. Qiu, Sens. Actuators A 159 (2010) 168.
[8] S. Sankaranarayanan, R. Singh, V. Bhethanabotla, J. Appl. Phys. 108 (2010) 104507.
[9] Y. Huang, Y. Chen, T. Wu, Nanotechnology 21 (2010) 095503.
[10] X. Du, Y. Fu, S. Tan, J. Luo, A. Flewitt, W. Milne, D. Lee, N. Park, J. Park, Y. Choi, S. Kim, S. Maeng, Appl. Phys. Lett. 93 (2008) 094105.
[11] T. Wu, W. Wang, J. Appl. Phys. 96 (2004) 9.
[12] A. Wixforth, J. Kotthaus, G. Weimann, Phys. Rev. B 40 (1989) 7874.