



# A low-cost portable electrical sensor for hydroxyl ions based on amorphous InGaZnO<sub>4</sub> thin film at room temperature

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## ABSTRACT

The measurement and control of hydroxide ion (OH<sup>-</sup>) concentration in solution are essential in industrial processes. However, no portable sensing method directly targeting OH<sup>-</sup> ion with low-cost has been reported till date. Herein, we demonstrate an electrical detection method for OH<sup>-</sup> concentration in solution based on impedance spectroscopy of hydroxyl ions (OH<sup>-</sup>) attached to amorphous InGaZnO<sub>4</sub> (aIGZO) film surfaces. The systematic examination of impedance response reveals that the resistance component of impedance is sensitive to the OH<sup>-</sup> ions interaction with the film surface. Results of X-ray photoemission spectroscopy confirm that the change of the impedance property is directly attributed to the amount of hydroxyl radical on the film surface originated from OH<sup>-</sup> ions in the solution. The impedance behavior of the film upon interaction with OH<sup>-</sup> was reasonably described by the theoretical analysis of optical measurements based on a vacancy-dependent model. Developed by applying this mechanism as a reference application, an easy-to-use aIGZO thin film based resistance OH<sup>-</sup> sensor at room temperature shows superior sensitivity, reproducibility, and linearity in the alkali range. This study extends the understanding and usage of aIGZO thin film regarding surface-sensing for the detection of surface interaction and process involving chemical ions and species.

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## 1. Introduction

Quantitative assessment and control of hydroxide ion (OH<sup>-</sup>) concentration in solution are crucial in most chemical processes and reactions. To date, the detection of OH<sup>-</sup> ions has not received much attention since most applications have focused on hydrogen (H<sup>+</sup>) ions as the counterpart. The concentration of H<sup>+</sup> ions in solution can be evaluated by pH value [1,2], and has been applied to gross evaluations [2–5] and electrical pH sensing [1,6,7]. Nevertheless, these methods involving optical and electrical pH sensing suffer from the alkaline error, which limits their applications for OH<sup>-</sup> sensing [8]. Some reported optical pH sensing for high alkaline solution, but they were by no mean of portable [9,10]. Meanwhile, electrical pH meters commercially available for concentrated alkali

line solution requires costly electrode. A low-cost portable sensing scheme targeting at OH<sup>-</sup> become desirable specifically for alkalinity measurement at high concentration. Although several gas-phase sensing methods of hydroxyl ions have been reported [11,12], surface-sensing methods targeting at hydroxyl ions in solution have not been advanced.

Transparent oxide semiconductors (TOSs) have been applied for electrochemical and nano-optical surface-sensing [13,14]. Among amorphous transparent oxide semiconductors, amorphous InGaZnO (aIGZO), a typical inorganic metal oxide, has attracted considerable attention due to its superior electrical properties and its environmental/thermal stability [15,16]. In particular, aIGZO can be widely tunable in terms of controlling electron carriers following the incorporation of Ga ions to suppress excessive carrier generation via oxygen vacancies [17,18]. We reported in our previous studies, that aIGZO thin film has not only a superior but also tunable affinity for hydroxyl species on the surface [19,20]. K. Takechi et al. and other groups has employed aIGZO for pH sensing [21–24], nevertheless, the focus was drawn on the low pH range (≤8). Inspired by these studies and aforementioned physical and chemical prop-

*Abbreviations:* aIGZO, amorphous indium gallium zinc oxide; XPS, X-ray photoelectron spectroscopy.

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erties, in this work, aIGZO films were chosen as a host material for the electrical detection of hydroxyl ions.

Intensively employed in sensing research [25–28], impedance spectroscopy, a high sensitivity tool for surface reaction, was employed as an indicator of the electrical activity of aIGZO films in this work. The electrical activity on aIGZO films was examined before and after OH<sup>-</sup> treatments. The hydroxyl originated from the solution attached to the aIGZO film surface caused impedance changes. Above all, we demonstrate electrical detections of OH<sup>-</sup> ions based on the impedance and resistance behavior of OH<sup>-</sup> ions adsorbed onto aIGZO film surfaces. As an application reference, a ready-to-use electrical sensor for OH<sup>-</sup> in solution at room temperature was disclosed showing superior sensitivity, reproducibility, and linearity in the alkali range.

## 2. Experimental section

### 2.1. Film fabrication and surface-chemical pretreatment

The aIGZO films with a thickness of 70 nm were deposited on flat glass substrate by direct-current (DC) magnetron sputtering at room temperature (RT) [29]. A stoichiometric InGaZnO4 ceramic was chosen as the target material. Film growth was performed at room temperature (RT) with an Ar gas flow of 200 cc. Interdigitated array gold electrodes were deposited by the dc sputtering method for 5 min (45 nm). The films on glass substrates were sliced into small pieces (16 × 22 mm), and sonicated in deionized (DI) water for 15 min before drying by an air blower to clean the surface. Film samples were then treated chemically using NaOH solutions at different concentrations and varied treatment time. After rinsing three times with deionized (DI) water and air-dry, electrical measurements were conducted both before and after the OH<sup>-</sup> treatment. The oxygen-related species attached to the film surfaces was examined using O (1s) core-level spectra derived from X-ray photoelectron spectroscopy (XPS) on an instrument equipped with a monochromatized Al K $\alpha$  source in an ultra-high vacuum chamber above 10<sup>-10</sup> Torr (JEOL JPS-9010MC). XPS spectrum was calibrated by utilizing the Au 4f<sub>5/2</sub> peak at a photon energy of 87.5 eV. Samples treated with 50, 100, 150, and 200 mM NaOH solution for 30 min were mounted in line on the XPS stage with a standard gold film slice in the end for calibration. For each sample, high-resolution spectra were collected 10 times for averaging. XPS scan range was set to from 522 to 534 eV to target at the OH<sup>-</sup> (~529 eV) peak. XPS peak curve fitting (Multi-peaks Gaussian fitting) and area under peak calculations were carried out using Origin Lab 8.6 software.

Optical responses of the film samples were examined to investigate optical structures in the vicinity of band edges using a UV–vis spectrometer (JASCO V-670). The absorption spectra were recorded over a range from 200 to 1000 nm. The clean glass substrate was scanned first as the baseline for all samples. Film samples treated with 0, 100, 150, 200 and 250 mM NaOH solution for 30 min were then characterized sequentially for their absorption spectra.

Sodium hydroxide (NaOH, +96%), and other chemicals were obtained from Wako Pure Chemical (Tokyo, Japan). Nanopure water (>18.0M $\Omega$ ) purified by the Millipore Milli-Q was used in all experiments.

### 2.2. Electrical measurement

The impedance spectra in the frequency domains from 10<sup>4</sup> to 10<sup>6</sup> Hz were measured using an impedance analyzer under a zero bias with voltage oscillation amplitude of 50 mV (Solartron SI 1260) at room temperature. The electrodes comprised two-terminal configurations with interdigitated arrays. NaOH treatment: the samples were then treated with NaOH solutions at different con-

centrations (0, 50, 100, 120, 140, 160, 180, and 200 mM) for various durations (10, 20, 30, 40, 50, and 70 min), and then air dried for measurement after 3 times DI water washing. Impedance measurements were conducted before and after NaOH treatment. All impedance equal circuit models were fitted by ZView software (Scribner Associates Inc., USA), with a limited range from 10<sup>4</sup> Hz to 10<sup>6</sup> Hz.

Resistance measurements were conducted using a digital-electrical multi-meter (Sanwa DA32). Gold electrode patterned film samples were treated with NaOH solutions at 100, 120, 140, 160, 180, and 200 mM. The measurements were also conducted before and after NaOH treatment, and sensor responses were then calculated according to the equation defined.

## 3. Result and discussion

### 3.1. Impedance OH<sup>-</sup> sensor

Impedance signal shift was evaluated in this work to indicate the hydroxyl group attached to the surface, which is eventually related to the OH<sup>-</sup> concentration in the solution. The overall procedure of the sensing detection is schematically outlined in Fig. 1. Patterned with thin film gold electrode by dc sputtering, the aIGZO thin films were measured by impedance spectroscopy for the first time. The films were then dipped into the target OH<sup>-</sup> solutions for various durations. After the OH<sup>-</sup> interaction with the surface, impedance was measured again. The impedance variance before and after OH<sup>-</sup> interaction are closely related to the quantity of hydroxyl species on the film surface, and indicates OH<sup>-</sup> concentration in the solution.

Impedance obeys Ohm's law, which can be described as follows:

$$Z = Z' + jZ'' \quad (1)$$

where  $Z'$  and  $Z''$  indicate real and imaginary parts, corresponding to resistance and inductance, respectively. Both terms are referred in defining the magnitude of impedance:

$$|Z| = \sqrt{Z'^2 + Z''^2} \quad (2)$$

In an effort to elucidate the correlation between impedance shift and OH<sup>-</sup> interaction with the surface, we defined the change in impedance as follows:

$$\Delta Z = Z_{OH} - Z_0 = (Z'_{OH} - Z'_0) + j(Z''_{OH} - Z''_0) \quad (3)$$

where  $Z_0$  and  $Z_{OH}$  represent the impedance before and after OH<sup>-</sup> interaction with the surface, respectively. Fig. 2 exemplifies the processing of impedance response. The sample was treated by immersed into 0.2 M NaOH solution for 30 min with impedance measured before and after OH<sup>-</sup> treatment. Distinctive impedance shift upon OH<sup>-</sup> interaction can be observed in Fig. 2(a) and (b) in the form of bode plot showing that both  $Z'$  and  $|Z|$  components were subject to a clear shift from 70 to 150  $\Omega$  in the  $Z'$  component upon OH<sup>-</sup> treatment. A Nyquist plot is also depicted in Fig. 2(c) to clarify the origin of the calculated  $\Delta Z$  result shown in Fig. 2(d) according to Eq. (3). Following the same procedure, systematic examinations on the impedance changes of all samples were conducted under different OH<sup>-</sup> treatment conditions.

Fig. 3 summarizes the impedance shifts ( $\Delta Z$ ) at various OH<sup>-</sup> concentrations. The dipping time for all films was fixed for 30 min in order to evaluate the correlation between the impedance change and NaOH concentration of the solution. To illustrate frequency response of the impedance shift, Fig. 3(a) and (b) are presented in bode plot. Noticeable variance in the imaginary parts ( $\Delta Z''$ ) upon OH<sup>-</sup> treatment is only observed in high frequencies from 10<sup>5</sup> to 10<sup>6</sup> Hz while there is negligible or no change at lower frequencies. On the other hand, changes in the real parts ( $\Delta Z'$ ) following the treatments is observed in all frequency ranges. Changes in  $\Delta Z'$

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