

Improved sensitivity of pH sensors based on hydrothermally grown nickel oxide nanosheets on Si surface with pyramidal cones

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Abstract:

In this work, the use of Si (100) substrate with pyramidal cones is proposed for the hydrothermal growth of nickel oxide (NiO) nanosheets (NSs) to improve the pH sensing performance for the first time. With an optimized KOH based etching process at 90 °C for 40 min, a surface area gain of around 91% can be obtained from the etched Si substrate. NiO NSs hydrothermally grown on the proposed Si substrate were used as pH sensing electrodes. The pH sensors based on NiO NSs synthesized at 90 °C for 7.5 h shows a near Nernstian response of 56.5 mV/pH in a pH range 2-12 buffer solutions and a near perfect linearity of 0.999. It is attributed to the dual surface roughening scheme considerably increases the sensing area and, in turn, increases the amount of surface sites for H⁺ sensing to promote the sensing performance.

1. Introduction

Recently, the use of high surface-to-volume ratio materials such as carbon nanotube (CNT) and metal oxide nanostructures such as zinc oxide (ZnO) based materials, tin oxide (SnO₂), vanadium pentoxide (V₂O₅), etc., to enhance the detection sensitivity of pH sensors were demonstrated. [1-6] It shows that the increase in the amount of ion adsorption sites through increasing the surface area of metal oxides nanostructures, in addition to material itself, should be very beneficial for H⁺ sensing. Among metal oxides, NiO is a p-type wide bandgap semiconductor with excellent electro-chemical performance and thermal/chemical stability. [7] With the features of cheap and facile to produce nanostructures, it has attracted a growing attention in the fields of sensing and photo catalyst applications.

In this work, Si (100) substrate with pyramidal cones prepared by a simple KOH/IPA chemical etching is proposed to serve as a platform for hydrothermal growth (HTG) of NiO nanosheets (NSs) for pH sensing, as a result, surface area and the amount of ion adsorption sites can be maximized and improved pH sensing performance can be expected. The etching condition for Si substrates which could maximize surface area gain (SAG) is investigated. In addition, the HTG of NiO NSs with different surface morphologies through different HTG times and their effects on pH sensitivity in pH 2-12 buffer solutions are examined and discussed.

2. Experimental

Fig. 1(a) depicts the schematics of sensing electrodes based on NiO NSs synthesized on Si (100) substrates with pyramidal cones (called sample A). To clarify the effectiveness of pyramidal cones in enhancing pH sensing performance, NiO NSs sensing electrodes based on plane Si substrates (Fig. 1(b), called sample B) are also prepared for comparison. In experiments, p-type Si (100) wafers were used. To prepare pyramidal cones with different sizes on Si surface, a wet chemical etching using a mixed solution of 5%wt KOH and 7%wt IPA at different temperatures (85, 90, and 95 °C) for 40 min was made. Prior to HTG processes, to serve as a seed layer for the HTG of NiO NSs, Au/Ti layers with a thickness of 150/150 nm were deposited on roughened and plane Si substrates using e-beam evaporation. For the synthesis of NiO NSs, these samples were immersed in a chemical solution mixed with 70 mM Ni(NO₃)₂·6H₂O and 70 mM C₆H₁₂N₄ at 90 °C for 4.5, 6, 7.5, 9, and 10.5 h, respectively, followed by a thermal annealing in air at 400 °C for 40 min to fully convert the as-grown Ni(OH)₂ NSs to NiO NSs. The morphology and structure of the NiO NSs were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), and selected-area electron diffraction (SAED). For pH sensing, the samples were sealed with epoxy resin except for the defined area of sensing window with a size of 0.5 cm×0.5cm (Fig. 1(c)). Finally, a metal wire was bonded with silver paste on the Au/Ti layer followed by curing at 120°C for 30 min (Fig. 1(d)). For pH sensitivity measurements, an EGFET configuration (Fig. 1(e)) was used and buffer solutions with pH value ranging from 2 to 12 were employed.

The potential difference between the sensing electrode and the reference electrode $\Delta V (= V_G - V_R)$, indicating the amount of charges adsorbed on the sensing electrode, was recorded for each buffer solution and the sensitivity and linearity of the pH sensor were evaluated from the experimental $\Delta V - \text{pH}$ curve.

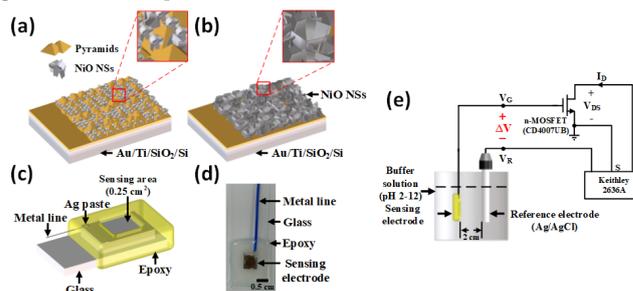


Fig. 1 Schematics of the prepared sensing electrodes, package, and pH sensing measurement. (a) Sample A, (b) sample B, (c) packaged sensing electrode, (d) OM image of the sensing electrode, and (e) schematic of the EGFET configuration used for pH measurement.

3. Results and Discussion

Fig. 2 show the SEM images of the pyramidal cones formed on Si substrate after an etching process at 85, 90, and 95 °C for 40 min, respectively. The temperature of the etching solution strongly affects both the size and density of the pyramidal cones. The size and density of pyramidal cones are low and with a poor uniformity are found on samples etched at 85°C (Fig. 2(a)). In contrast, the sample etched at 95°C has pyramidal cones with enlarged size and reduced density (Fig. 2(c)). With the SAG is defined as $(SA_1 - SA_2)/SA_2 \times 100\%$, which SA_1 and SA_2 are the surface area of Si with and without pyramidal cones, respectively, the SAG of the Si with pyramidal cones obtained from 85, 90, and 95 °C etching are about 22%, 91%, and 41%, respectively. Note that the sample etched at 90°C has the highest SAG, which might be due to both the size and density of pyramidal cones are optimized, is used for the preparation of sample A in this study.

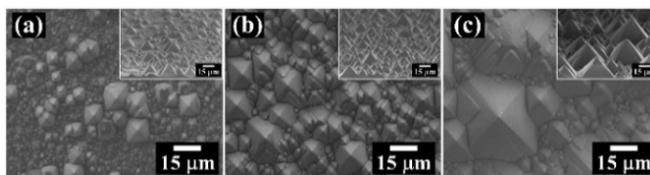


Fig. 2 Top-view SEM images of pyramidal cones formed on Si substrates subjected to chemical etching at different temperatures. (a) 85 °C, (b) 90 °C, and (c) 95 °C. Insets show the corresponding cross-section-view SEM images.

Fig. 3 shows SEM images of the NiO NSs synthesized on Si wafer with and without pyramidal cones at 90 °C for different HTG times. The average surface area (SA) and density of NiO NSs estimated within an area of 25×25 μm² are summarized in Table I. The NiO NSs show a highly hierarchical porous structure perpendicular to the substrate surface, which might be due to nuclei aggregation to a lamellar structure. [8] Both the height and width of NiO NSs increase with increasing the HTG time in the range of 4.5 to 10.5 h (Figs. 3(a)-(e)). It shows that there is no noticeable change in NSs density for the HTG time ranging from 4.5 to 7.5 h. Nevertheless, the density of NSs drastically decreases with increasing the HTG time in the range of 7.5-10.5 h. It suggests that extending the growth time might accelerate the agglomeration of NSs, resulting in a reduced

density and SA. Note that, the NiO NSs on pyramidal-type Si for 7.5 h exhibited the largest SA of about $1,638 \mu\text{m}^2$. The SEM image of NiO NSs grown on plane Si wafer for 9 h (namely sample B (9 h)) is shown in Fig. 3(f), it has a relatively smaller SA of about $1,176 \mu\text{m}^2$. This result might confirm the effectiveness of using the platform of Si with pyramidal cones.

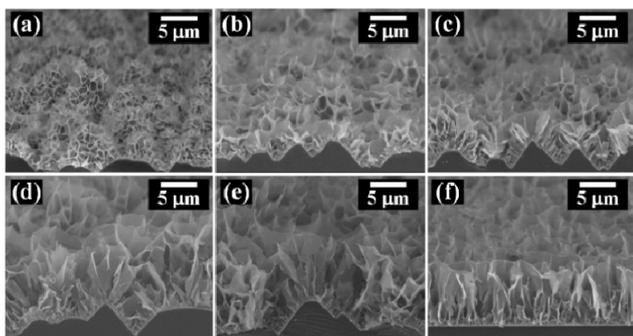


Fig. 3 SEM images of the NiO NSs synthesized on Si wafer with and without pyramidal cones at 90 °C for different HTG times. (a) 4.5 h, (b) 6 h, (c) 7.5 h, (d) 9 h, and (e) 10.5 h, respectively, and (f) on plane Si wafer for 9 h.

Table I The average SA and density of NiO NSs on pyramidal and planar Si

Items	Sample A					Sample B (9 h)
	4.5 h	6 h	7.5 h	9 h	10.5 h	
SA of a single NS (μm^2)	2.48	7.57	11.7	17.5	19.1	21
Density of NS (no./ $25 \times 25 \mu\text{m}^2$)	144	124	140	62	47	56
Total SA (μm^2)	357	939	1,638	1,085	898	1,176

Fig. 4(a) shows XRD pattern of the NiO NSs on roughened Si at 90 °C for 7.5 h (namely sample A (7.5 h)). The diffraction peaks at 37.28° , 43.28° , 67.88° , and 75.28° were indexed as (111), (200), (220), and (311) planes, respectively, showing the presence of a cubic NiO structure, which matched the JCPDS card no. 4-0835. Fig. 4(b) shows the HRTEM image took from the peripheral region of a NiO NS (the right upper inset in Fig. 4(b)). The gaps between lattice fringes are about 2.41 Å and 2.08 Å, which corresponding to (111) and (220) planes, respectively. The corresponding SAED pattern (the right lower inset in Fig. 4(b)) reveals the NiO NS is polycrystalline structure.

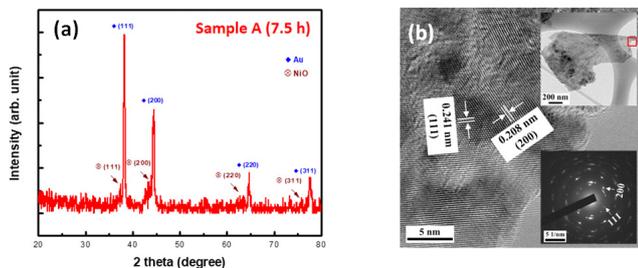


Fig. 4 (a) XRD pattern, (b) TEM, HRTEM, and SAED pattern of the HTG NiO NSs on Au/Ti/pyramidal Si at 90 °C for 7.5 h.

Fig. 5(a) and 5(b) show the I_D - V_R curves obtained from sample A (7.5 h) and sample B (9 h), respectively. The transfer curves shift toward the positive V_R axis direction with increasing the pH value, it is attributed to the decrease in the amount of H^+ (or increase in OH^-) adsorbed on the sensing electrode lowers the electrical potential of therein. The ΔV as a function pH of samples A (7.5 h) and B (9 h) is plotted in Fig. 5(c). It reveals that the sensitivity (linearity) of sample A (7.5 h) and sample B (9 h) are of 56.50 mV/pH (0.999) and 53.64 mV/pH (0.998), respectively. Note that sample A (7.5 h) shows a near-Nernstian response among all the prepared samples for having the largest SA for the adsorption sites of H^+/OH^- ions. It suggests the use of appropriately roughened Si wafers could be beneficial to the sensing performance of pH sensors based on NiO NSs.

The dependence of sensitivity and linearity of the two types of samples on the HTG times for the synthesis of NiO NSs is shown in Fig. 5(d) and the corresponding quantized values are listed in Table II. It reveals that the trend of the influence of HTG time on pH sensitivity in a good agreement with the SA listed in Table I. It is noted that the extension of HTG time over 7.5 h for sample A and 9 h for sample B, respectively, not only decreases pH sensitivity but also eliminates the effectiveness of the

platform of Si with pyramidal cones.

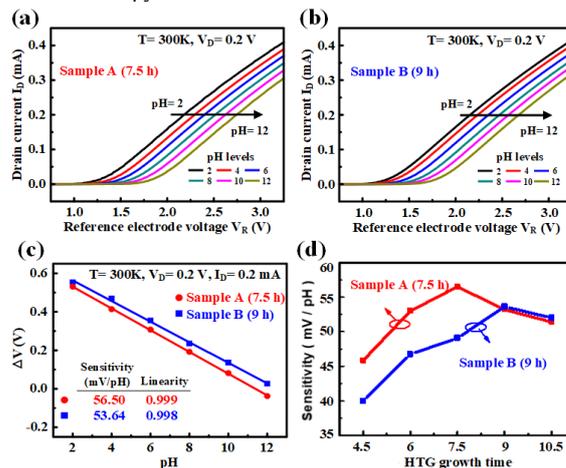


Fig. 5 Measured I_D - V_R of the prepared pH sensor with sensing electrode based on (a) sample A and (b) sample B. (c) Comparison of the ΔV -pH characteristics. (d) Sensitivity as a function of HTG time.

Table II Sensing performance of pH sensor based on NiO NSs

	HTG times	4.5 h	6 h	7.5 h	9 h	10.5 h
		Sample A	Sensitivity (mV/pH)	45.84	53.00	56.5
	Linearity	0.993	0.996	0.999	0.996	0.998
Sample B	Sensitivity (mV/pH)	39.97	46.73	49.08	53.64	52
	Linearity	0.990	0.999	0.996	0.998	0.993

Fig. 6 shows the hysteresis characteristics of sample A (7.5 h). The stability tests were carried out under a loop circle of $\text{pH } 7 \rightarrow 4 \rightarrow 7 \rightarrow 10 \rightarrow 7$ for 1 min in each pH buffer solution with the n-MOSFET operated at $V_D = 0.2 \text{ V}$ and $I = 0.2 \text{ mA}$. A hysteresis voltage as low as 5.88 mV is realized, suggesting the proposed sample A (7.5 h) has a good stability for pH sensing.

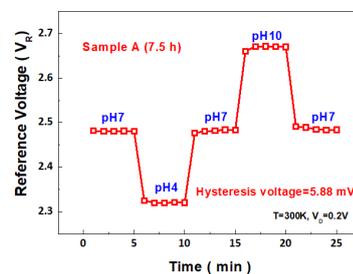


Fig. 6 Hysteresis characteristic of the sample A (7.5 h).

4. Conclusions

The pH sensors based on NiO NSs synthesized on Si substrate with pyramidal cones showing a near-Nernstian response (56.5 mV/pH) and superior linearity of 0.999 have been demonstrated. Experimental results confirms that the surface area enlargement through the proposed dual surface roughening scheme is very crucial in improving the sensing performance of pH sensors. With pyramidal cones obtained from a suitable KOH/IPA etching process to Si (100) substrate, it leads to an SAG of around 91%, which is very beneficial to enhance the pH sensitivity of sensors based on NiO NSs. It is expected such a dual surface roughening scheme could be a potential mean for other sensors based on metal oxides nanostructures.

Acknowledgements

This work was supported by the Ministry of Science and Technology (MOST), Taiwan, under contract No. MOST 105-2221-E-006-196-MY3.

References

- [1] Y.-S. Chien et al., *IEEE Electron Device Lett.* **33** (11), 1622 (2012).
- [2] J.-L. Wang et al., *J. Nano. Mat.* **2013**, 1 (2013).
- [3] N. M. Abd-Alghafour et al., *J. Mater. Sci.* **28**, 1364 (2017).
- [4] C.-C. Yang et al., *Coating* **9**, 251 (2019).
- [5] K. Nguyen et al., *RSC Adv.* **8**, 19449 (2018).
- [6] T. Yu et al., *J. Mater. Chem. A* **3**, 11991 (2015).
- [7] F. Motahari et al., *RSC Adv.* **4**, 27654 (2014).
- [8] D. E. Yates et al., *J. Chem. Soc. Faraday Trans.* **1** (70), 1807 (1974).