Robust pH-responsive group IV metal oxide functionalized porous silicon platforms

Joel F. Destino,^a Nadine D. Kraut,^b Lara E. Hargrave,^a and Frank V. Bright^{a*}

a. Department of Chemistry, Natural Sciences Complex, University at Buffalo, The State University of New York, Buffalo, NY 14260-3000, United States

b. PPG Industries Inc., 440 College Park Dr., Monroeville, PA 15146, United States

Abstract

We report a high stability pH-responsive sensor based on group IV metal oxide (ZrO_2 and HfO_2) functionalized porous silicon (pSi). These hybrid metal oxide-pSi (MOx-pSi) materials were tested during repeated pH 2-12 cycling and during continuous UV illumination. The photoluminescence (PL) response proved to be fully reversible unlike uncoated pSi. The MOx-pSi sensor platform was also stable for at least three years.

Keywords

Hafnia; Luminescence; pH Sensor; Porous silicon; Sol-gel processing; Zirconia

1. Introduction

As prepared, H-passivated pSi (ap-pSi) undergoes rapid oxidation in air [1] or water [2] in the absence/presence of photons [3, 4] to form oxidized pSi (ox-pSi). ox-pSi PL is dramatically different in comparison to ap-pSi [1, 5-7] and it undergoes rapid dissolution under acidic/basic conditions [8-11]. Given this, researchers have aimed at modify pSi by using hydrosilylation [12-16], silanization [17-21], and physisorbed coatings [12, 22] to minimize and ideally eliminate the aforementioned problems. Unfortunately, there are few reports on pSi passivation that demonstrate improved stability across wide pH ranges and constant illumination as one would encounter in chemical sensing applications [23].

Group IV metal oxides (e.g., TiO_2 , ZrO_2 and HfO_2) are unique materials with wide applicability (e.g., free-standing [24] and supported [25] catalysts, semiconductor gate dielectrics [26, 27], field-effect transistors [28, 29], and chromatographic stationary phases [30, 31]). ZrO_2 - and HfO_2 -based materials are attractive because they are known to exhibit improved pH and thermal stability [32-34] in comparison to SiO_2 . Further, Zr- and HfO_2 can be easily prepared by sol-gel processing [11], they cross-link to SiOH residues [35, 36], and ox-pSi has surface SiOH residues [37].

Herein we report ZrO₂ and HfO₂ functionalized ox-pSi for optically-based pH sensing. These materials were studied by using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and Fourier transform infrared (FTIR) spectroscopy. pH-dependent response and photostability experiments were conducted by using steady state PL emission measurements.

2. Materials and methods

2.1. Materials. The following were used: p-type B-doped <100> CZ processed 8-12 Ω·cm Si wafers (Alsil Supply Division, Y Mart Int.); HF (48-51%) (Acros); 200 proof ethanol (Decon Laboratories); pentanes (99.7%) (Fisher Scientific); Ga/In eutectic (99.99%), HfCl₄ (99.95%) and ZrCl₄ (99.95%) (Sigma Aldrich); NaOH pellets (Mallinckrodt); and 37% HCl (EMD). Deionized H₂O (≥18 MΩ cm) was produced by a 50k light Silex deionizer (AmeriWater).

2.2. MOx-pSi Fabrication. The MOx-pSi fabrication scheme is presented in **Fig. 1**. Briefly, ap-pSi and ox-pSi were prepared as described elsewhere [16, 37]. MOx sols were prepared from their chloride salts (30 mM ZrCl₄ or HfCl₄ in 1:9 (vol:vol) H₂O:EtOH). The ox-pSi surface was functionalized with Zr- or HfO₂ by spin coating two consecutive 100 μL sol aliquots at 150 RPM followed by 30 s at 1000 RPM. The reaction was completed by heating for 30 min at 300 °C and natural cooling to room temperature. (Note: Temperatures up to 700 °C were explored; 300 °C was selected because it yielded good PL while bonding MOx to the ox-pSi.)

2.3. Characterization. SEM micrographs were recorded by using a Hitachi model SU-70 equipped with EDS. Reflectance FTIR spectra were measured by using a Bruker Vertex 70 with Hyperion 3000 microscope attachment (4 cm⁻¹ resolution, 200 scans, 15x, ox-pSi blank). PL emission spectra were acquired by using an SLM-AMINCO 8100 spectrofluorometer (λ_{ex} = 325 ± 4 nm). Photostability was determined while monitoring the total PL (500-800 nm).

2.4. pH-dependent experiments. Aqueous pH solutions (10 mM) were prepared from HCl and NaOH. Solution pH values were determined by using a calibrated pH electrode/meter. The MOx-pSi samples were mounted in a custom flow cell with a quartz viewing window. A peristaltic pump served to flow solutions over the samples. The pH responses were determined by measuring the MOx-pSi PL-dependent signal during a rapid change in solution pH. The response time (*t*₉₀) is reported as the time to reach 90 % of the full response.

2.5. Statistical analysis. Results are reported as the mean and measurement standard deviation. Statistical significance is assessed by using analysis of variance (ANOVA) (95% confidence level) with *p* be ≤ 0.05 being statistically significant.

3. Results and discussion

Fig. 1 shows that the MOx-pSi hybrid materials exhibit strong PL in comparison to ox-pSi after pH cycling (compare PL images in **Fig. 1a** and **Fig. 1b**); ox-pSi undergoes complete dissolution (**Fig. 1b**) during our experiments and it is unsuitable for pH sensing. **Fig. 2** presents typical SEM, EDS, and FTIR data for our MOx-pSi platforms. **Figs. 2a** and **2d** show that the MOx-pSi platform is characterized by a ~200 nm thick ox-pSi layer atop a crystalline Si (c-Si) base. **Figs. 2b** and **2e** present ZrO₂- and HfO₂-pSi EDS spectra, confirming the presence of Zr and Hf, respectively. **Figs. 2c** and **2f** present ZrO₂- and HfO₂-pSi FTIR spectra, respectively [38]. The ZrO₂- and HfO₂-pSi IR spectra are characterized by a Zr-O-Si stretching band at 947 cm⁻¹ (highlighted, **Fig. 2c**) and a Hf-O-Si stretching band at 962 cm⁻¹ (highlighted, **Fig. 2f**) [39, 40]; confirming Zr-/HfO₂ is covalently bonded to the ox-pSi. The lower frequency IR bands are commonly observed in mixed Zr/HfO₂-SiO₂ materials and are associated with various M-O-Si geometries [35, 41].

Figs. 3 and **4** present typical pH-dependent PL emission spectra (**a**) and average PL and emission maximum ($\lambda_{em,max}$) response profiles (**b** and **c**) for ZrO₂- and HfO₂-pSi, respectively. Inspection of these results reveals several key points. First, the ZrO₂- and HfO₂-based materials behave similarly. Second, as the pH increases the MOx-pSi PL intensity decreases and the $\lambda_{em,max}$ blue shifts systematically. These changes are consistent with the pSi PL emission arising from Si nanocrystallites composed of Si, SiO_x, and SiO₂ (red, green, and blue emission bands, respectively) [42-44] coupled with pH-dependent dangling bond formation following proton extraction [8, 45].

Third, the MOx-pSi pH-dependent PL responses are linear over the entire pH range studied. HfO₂-pSi shows slightly improved sensitivity over ZrO₂-pSi based on PL intensity (-0.18 ± 0.02 vs. -0.12 ± 0.01 PL/pH unit, $p = 0.01$) and $\lambda_{em,max}$ (-3.9 ± 0.4 vs. -3.3 ± 0.3 nm/pH unit, $p = 0.11$) responses. The observed linear response is consistent with the complex MOx surface chemistry revealed by our IR measurements (**Figs. 2c** and **2f**) and hydroxyl groups with pK_a values ranging from 4 to 13 [34]. This scenario likely creates a pH buffer layer at the pSi surface [34], attenuating the impact on the pSi PL across large pH changes. Fourth, the MOx-pSi pH-dependent PL intensity response is only quasi-reversible; the response sensitivity systematically increases by ~ 2-fold with increasing cycle number ($p < 0.001$). Finally, the pH-dependent $\lambda_{em,max}$ response profiles are independent of cycle number ($p = 0.09-0.13$) showing a completely reversible response. Taken together these results show that the MOx-pSi-based materials, in a $\lambda_{em,max}$ -based measurement format, provide an analytically useful response between pH 2 and 12.

The MOx-pSi t_{90} values were typically 380 ± 10 s. However, t_{90} was also etching time (t_E , porosity) [16] and MCl_4 concentration dependent. Longer t_E yielded significant longer t_{90} (e.g., $t_E = 60$ and 150 s: $t_{90} = 610 \pm 30$ s and 880 ± 30 s, respectively ($p < 0.001$)). Increased MCl_4 also led to longer response times (300 mM, $t_E = 150$ s: $t_{90} = 1220 \pm 70$ s, respectively ($p < 0.001$)).

In an optical pH sensor stability is also very important. **Fig. 5** assesses the ap- and ox-pSi, ZrO_2 - and HfO_2 -pSi photostability in air under continuous UV illumination. These results show that no platform offers complete photostability during 90 min of continuous illumination. The ap-pSi, ZrO_2 - and HfO_2 -pSi platforms undergo a decrease in PL intensity over time. The ox-pSi sample undergoes a continuous PL intensity increase over time. Of the systems studied here, the ZrO_2 -pSi platform exhibits the best intensity-based photostability, being 4-fold better in comparison to ap-pSi and ~ 2 -fold better compared to ox-pSi ($p = 0.001$). Fortunately, the $\lambda_{em,max}$ response was unaffected by these intensity changes ($p > 0.52$), making it a more robust pH-response measurement.

Finally, long-term stability studies carried out over a three year time period for MOx-pSi samples stored under ambient conditions showed that they are exceedingly stable; 3 year old MOx-pSi samples exhibited statistically equivalent PL spectra and responses in comparison to freshly prepared samples ($n = 35$, $p = 0.59$).

4. Conclusions

ZrO_2 - and HfO_2 -pSi hybrid materials are easily prepared and their pH-dependent $\lambda_{em,max}$ response is fully reversible and analytically useful between pH 2 and 12 (0.1 pH resolution). By comparison, at pH > 8 , ap-/ox-pSi undergo complete dissolution in a few minutes. The ZrO_2 -pSi platform also exhibits significantly improved photostability, and is stable under ambient storage for at least three years.

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Figure Captions

Figure 1. MOx-pSi fabrication and visual characterization. (a) Overall fabrication protocol. Chemistries at the pSi surface are shown. (b) ap-pSi after exposure to pH 12 (contrast adjusted).

Figure 2. MOx-pSi SEM, EDS and IR characterization. ZrO₂-pSi: (a) cross-sectional SEM; (b) EDS spectrum; (c) IR spectrum. HfO₂-pSi: (d) cross-sectional SEM; (e) EDS spectrum; (f) IR spectrum.

Figure 3. Typical pH-dependent ZrO₂-pSi PL results. (a) PL emission spectra (top), normalized PL emission spectra (bottom). (b) pH-dependent intensity response (top), pH-dependent $\lambda_{em,max}$ response (bottom). (c) Consecutive pH-dependent intensity and $\lambda_{em,max}$ response cycles (dashed lines are drawn as a visual guide).

Figure 4. Typical pH-dependent HfO₂-pSi PL results. (a) PL emission spectra (top), normalized PL emission spectra (bottom). (b) pH-dependent intensity response (top), pH-dependent $\lambda_{em,max}$ response (bottom). (c) Consecutive pH-dependent intensity and $\lambda_{em,max}$ response cycles (dashed lines are drawn as a visual guide).

Figure 5. Typical photostability results.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

ZrO₂-pSi

HfO₂-pSi