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

Joel F. Destino [a], Nadine D. Kraut [b], Lara E. Hargrave [a], 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

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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.

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 ZrO_2 and HfO_2 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%), $HfCl_4$ (99.95%) and $ZrCl_4$ (99.95%) (Sigma Aldrich); NaOH pellets (Mallinckrodt); and 37% HCl (EMD). Deionized H_2O (≥ 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 $ZrCl_4$ or $HfCl_4$ in 1:9 (vol:vol) H_2O: EtOH). The ox-pSi surface was functionalized with Zr- or HfO_2 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

* Corresponding author.

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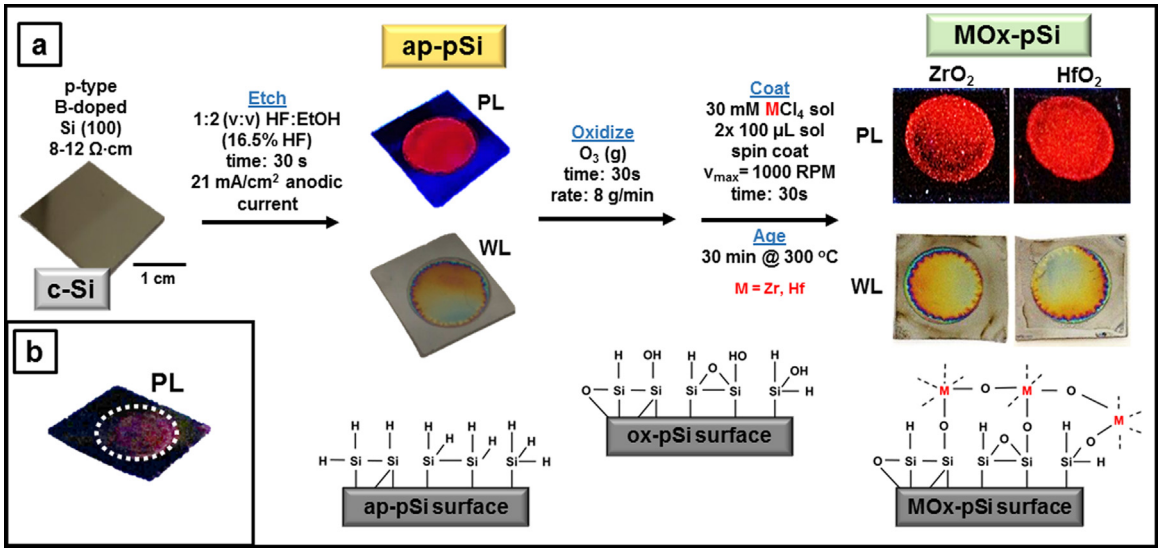

Fig. 1. MOx-pSi fabrication and visual characterization. (a) Overall fabrication protocol. Chemistries at the pSi surface areis shown. (b) ap-pSi after exposure to pH 12 (contrast adjusted).

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 ($\lambda_{ex}=325\pm4$ 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.

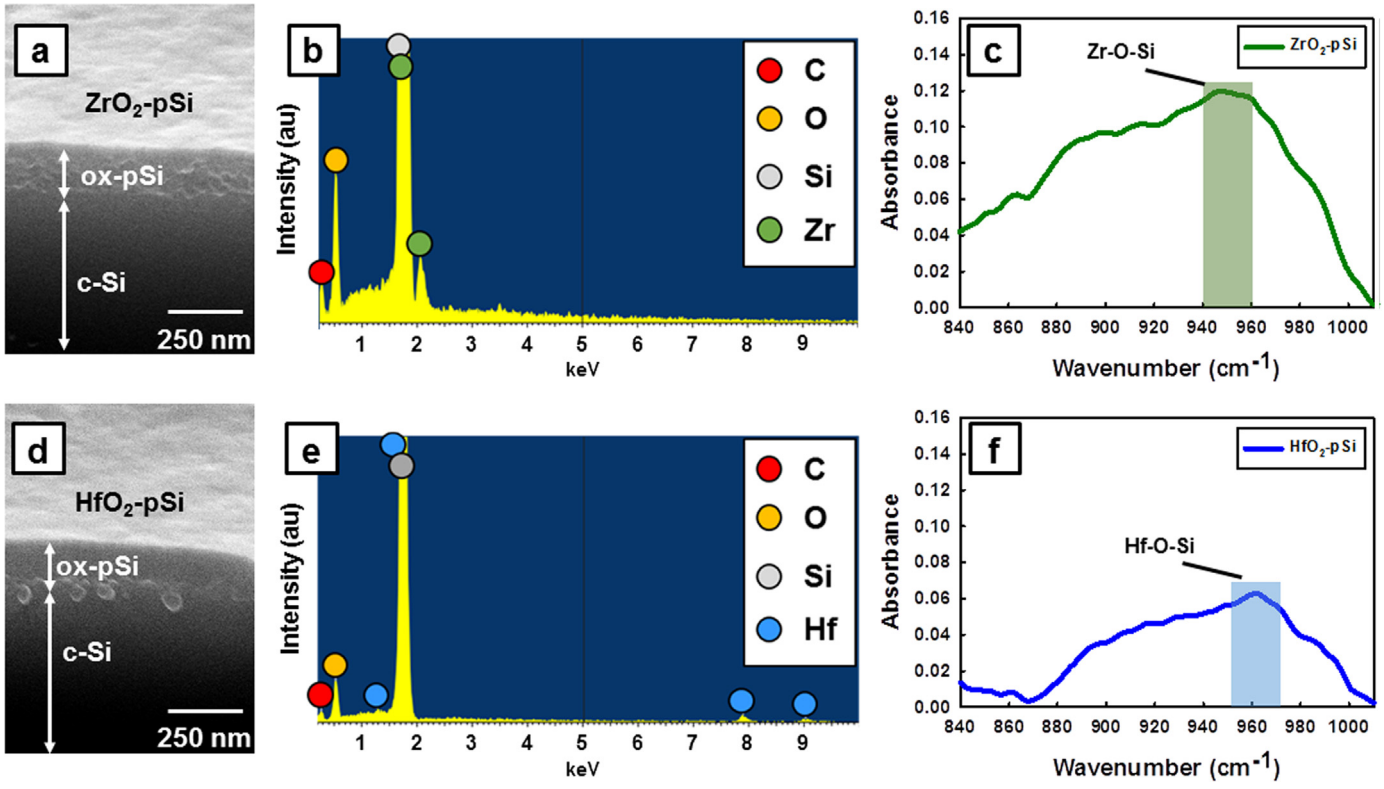

Fig. 2. MOx-pSi SEM, EDS and IR characterization. ZrO_2-pSi: (a) cross-sectional SEM; (b) EDS spectrum; (c) IR spectrum. HfO_2-pSi: (d) cross-sectional SEM; (e) EDS spectrum; (f) IR spectrum.