Analytica Chimica Acta xxx (2018) 1–7

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Gallium indium eutectic masking prior to porous silicon formation creates unique spatially-dependent chemistries

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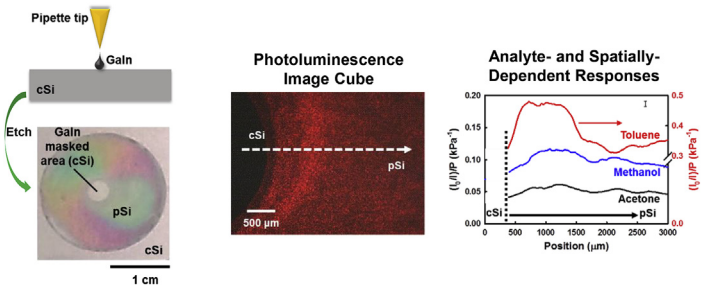
HIGHLIGHTS

- Unique porous silicon (pSi) micro-arrays can be created by using GaIn masks.
- Array elements show analyte- and spatially-dependent responses.
- The relative O_2Si-H to Si-H band amplitude ratio is spatially dependent.
- Responses arise from competition between analytes and different pSi surface sites.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 December 2017
Received in revised form
14 May 2018
Accepted 18 May 2018
Available online xxx

Keywords:
Gallium indium eutectic
Gaseous analyte response
Porous silicon
Spatially-dependent chemistries
Spatially-dependent response

ABSTRACT

We demonstrate that gallium indium (GaIn) eutectic can be used to create interesting crystalline Si/porous silicon (cSi/pSi) platforms that exhibit unique analyte- and spatially-dependent photoluminescence (PL) responses. Here we characterize these cSi/pSi regions by using profilometry, scanning electron microscopy (SEM), wide-field PL microscopy, and Fourier transform infrared (FTIR) microscopy. As we move along a vector from the cSi/pSi interface out into "bulk" pSi, the: (i) analyte-dependent, PL-based response initially increases and then decreases; (ii) total PL emission intensity, in the absence of analyte, increases; (iii) pSi thickness increases; and (iv) relative O_2Si-H to Si-H band amplitude ratio decreases. Thus, the analyte-dependent PL response magnitude is correlated to the extent of pSi oxidation; which can be easily controlled by using GaIn eutectic as a mask during the pSi fabrication process.

1. Introduction

Porous silicon (pSi) can be created by using several methods [1–3], including by anodic bias of crystalline silicon (cSi) in an HF/EtOH solution [4]. The final pSi properties, such as Si nanocrystallite size, pore structure, and thickness, depend on many variables (e.g., HF concentration, etching current density, etching time, illumination conditions, cSi resistivity, and dopant type and density within the cSi) [5–7]. The Si nanocrystallites that form within pSi exhibit quantum confinement effects [8], leading to bright red-orange photoluminescence (PL) at room temperature under blue or green excitation [9]. As prepared, H-passivated pSi (ap-pSi) is

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https://doi.org/10.1016/j.aca.2018.05.052
0003-2670/

readily oxidized in air or water to form oxidized pSi (ox-pSi) and pSi is rapidly dissolved under acidic or basic conditions, rendering nearly all pSi-based platforms chemically unstable [10–12]. However, the ability to adjust the pSi nanocrystallite size and surface chemistry has motivated researchers to investigate strategies to stabilize the pSi surface chemistry by, for example, hydrosilylation [13], metal oxide coatings [11], physisorbed coatings [14], and silanization [15]. With improvements to the pSi chemical stability and the ability to tailor the nanocrystallite surface chemistry, applications in biochemical and chemical sensors, electronics, and medical implants have emerged [16–22].

Researchers have exploited the pSi intrinsic PL for optosensing applications and analyte-dependent responses have been reported [18,19,23]. For example, although gaseous, linear aliphatic alcohols (i.e., methanol, hexanol) cause the pSi PL to be quenched, the response sensitivity was reported to depend on the alcohol dielectric constant (ε) [23]. Given this, pSi is seen by many as a platform for multi-analyte detection strategies. In this context, we have previously reported contact pin-printing as a method to produce microarrays for simultaneous, multi-analyte detection [24–28]. In our original reports each spot within the array was thought to be homogeneous and designed to respond uniquely to each analyte. A variation on this strategy is to create sensing spots in a microarray format wherein each spot exhibits spatially-dependent chemistries (i.e., inhomogeneous) that in turn will yield analyte- *and* spatially-dependent responses, increasing platform diversity dramatically.

Our goal was to fabricate a pSi platform which yields the aforementioned analyte- and spatially-dependent responses. In this paper, gallium indium (GaIn) eutectic was physically deposited onto cSi prior to creating pSi by electrochemical etching. The result is pSi with a core cSi region where the GaIn eutectic was initially deposited. The PL from the region of interest (ROI) near the cSi/pSi interface exhibits spatially-dependent analyte responses. We establish a relationship between the observed responses and the ROI chemistry by using profilometry, scanning electron microscopy (SEM), wide field PL microscopy, and Fourier transform infrared (FTIR) microscopy.

2. Materials and methods

2.1. Materials and reagents

The following were used: p-type B-doped ⟨100⟩ CZ processed 8–12 Ω cm Si wafers (Alsil Supply Division, Y Mart Int.); hydrofluoric acid (48–51%) (Acros); 200 proof ethanol (Decon Laboratories); acetone (99.7%), methanol (99.8%), pentanes (99.7%), potassium hydroxide pellets, and toluene (99.9%) (Fisher Scientific); GaIn eutectic (99.99%) and polydimethysiloxane (PDMS, 17,000 MW) (Sigma-Aldrich); copper sheet (McMaster Carr); 1200 grit silicon carbide sandpaper (model CH-8500) (Sia Abrasives Industries); colloidal graphite (isopropanol base) (PELCO); and double coated carbon conductive tape and carbon rod (Ted Pella). Deionized water (>18 MΩ cm) was produced by using a 50 k light Silex deionizer (AmeriWater).

2.2. Fabricating GaIn eutectic masked pSi

The basic fabrication protocol is shown in Fig. 1. Initially, we tried to contact pin print (CPP) [24–28] the GaIn eutectic onto the cSi surface; however, the eutectic adhered very strongly to our metal and ceramic pins and the print quality proved poor. Previous authors reported that GaIn eutectic does not adhere well to PDMS [29]. Given this, we dip coated a standard 20 μL micropipette tip with PDMS (Fig. 1A). The coated pipette tip was then allowed to dry

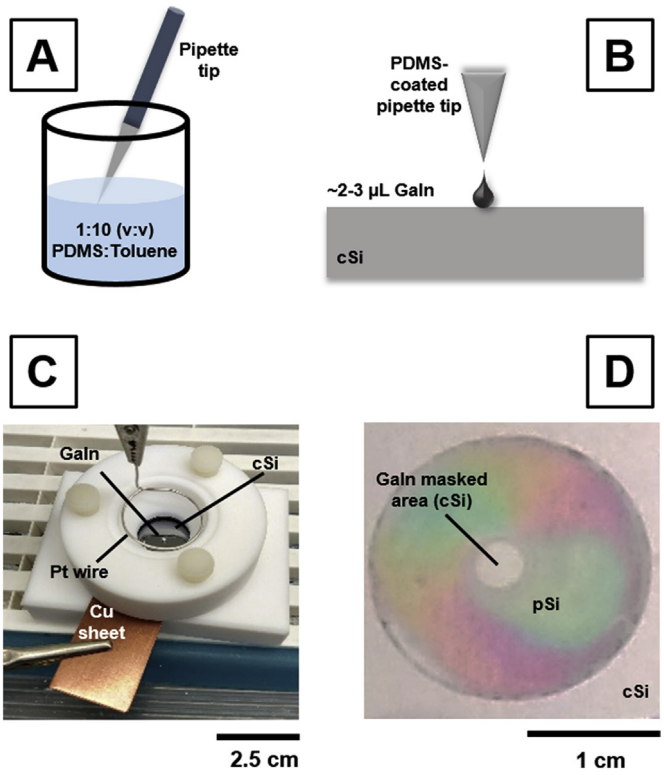

Fig. 1. Simplified protocol for creating pSi surrounding a GaIn eutectic masked area. (A) Coat pipette tip with PDMS. (B) Deliver GaIn eutectic to the clean cSi surface. (C) Digital image of electrochemical etching cell with GaIn eutectic delivered onto a cleaned cSi surface. (D) Typical white light optical image from a formerly GaIn eutectic masked area surrounded by pSi.

in air for 0.5 h.

An as-received cSi wafer was cut into 2.5 cm × 2.5 cm squares by using a glass slide cutter (OM Laboratory, Chigasaki). The wafer matte surface was then cleaned with 1200 grit silicon carbide sandpaper to improve contact to the anode collector (a 5.1 cm × 2.5 cm x 650 μm thick piece of copper sheet). To further facilitate collector-to-anode (Si wafer) contact, a thin GaIn eutectic layer was applied to the wafer matte side by using a cotton swab. The wafer was then placed within a custom-made Teflon etching cell [24,25,30]. The PDMS-coated pipette tip and a Rainin pipette were then used to transfer ~2–3 μL of GaIn eutectic directly onto the clean, polished cSi wafer surface (Fig. 1B and C). To avoid disturbing the GaIn eutectic spot, we slowly filled the cell with the etching solution (1:2 (v:v) HF:ethanol). A platinum wire loop cathode was then inserted into the etching solution and a 21 mA/cm^2 current density was maintained throughout the etching process by using a DC power supply (Keithley, model 2400-LV).

After etching for 60 s, the power supply was turned off and the etching solution was carefully removed from the cell. The pSi sample was then removed from the cell and soaked for 2.5 min in the following solutions (20 mL): 1:2 (v:v) H_2O:ethanol, ethanol, and pentanes. The pSi specimen was then placed in an evacuated desiccator (<150 torr) for at least 15 min to remove residual solvent. For long-term storage the pSi specimen was kept in an evacuated desiccator. Fig. 1D presents a typical optical image from a cSi/pSi specimen formed by using a GaIn eutectic mask. The specimen consists of a cSi core region where the GaIn eutectic was deposited surrounded by pSi. [Note: We have formed features where the cSi core ranges from 2 to 5 mm in diameter. However, cSi cores that are <2 mm in diameter proved difficult to reproduce and locate by

Please cite this article in press as: C.M. Collado, et al., Gallium indium eutectic masking prior to porous silicon formation creates unique spatially-dependent chemistries, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.05.052