MONOLITHICALLY INTEGRATED μPID ON μCOLUMNS FOR ULTRACOMPACT MICRO-GAS CHROMATOGRAPHY

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ABSTRACT

This report describes a monolithically integrated microfluidic photoionization detector (μPID) on a microfabricated gas chromatography (μGC) column via wafer-level batch processing based on a silicon-on-insulator (SOI) architecture. The integrated chip enables an ultracompact (0.9 liters and 0.9 kg), fully automated, and battery-operated μGC system. Rapid separation of seven volatile organic compounds (VOCs) in ~2 min at room temperature is demonstrated.

KEYWORDS

Microfabricated gas chromatography, monolithic integration, photoionization detector

INTRODUCTION

Microfabricated gas chromatography (μGC) has enabled portable, low-power, and rapid analysis across a diverse fields, such as industrial, biomedical, and environmental applications [1]. Most μGC devices currently employ hybrid integration, connecting components through off-chip interconnects (e.g., capillary guard columns). Monolithic integration offers key advantages, including enhanced system robustness, reduced human error, lower labor, minimized cold spots and dead volumes, and cost savings through batch fabrication. This work focuses on the integration of a separation micro-columns (μcolumns) and a detector onto a single chip.

Among sensor types, integrated photoionization detector (PID) has proven superior due to its rapid response and high sensitivity [2, 3]. However, state-of-the-art integrated PIDs suffer from drawbacks, such as reliance on bulky helium cartridges, co-planar collection electrodes, and single-die microfabrication processes [2, 3]. In contrast, advanced standalone microfluidic PIDs (μPIDs) feature parallel-plate electrodes, operate without auxiliary gases, and achieve parts-per-trillion (ppt) sensitivity with a six-order linear dynamic range [4, 5].

This paper presents a microfabrication process for monolithic integration of such a μPID with a μcolumn batched-processed on a wafer scale. A new integrated device architecture of μPID on μcolumn (*i.e.*, integrated column-PID (iCPID)) is introduced based on silicon-on-insulator (SOI) structure. The buried oxide (BOX) provides electrical insulation between the μPID and μcolumn, and its etch-through part serves as vertical microfluidic vias for fluidic connections between two components. This enables monolithic integration of a vacuum-UV lamp-based parallel-plate μPID on a μcolumn with embedded on-chip heater, all achieved through wafer-scale batch process. We also demonstrate an ultracompact μGC system design based on iCPID.

DESIGN AND WORKING PRINCIPLE

As illustrated in Figure 1, the iCPID is based on an SOI platform with a vertical stacking architecture, where the μPID resides on top of the μcolumn. There are two etched-through vertical holes (*i.e.*, microfluidic via) at the inlet and outlet of the μPID. They fluidically connect the μPID and μcolumn, while the BOX electrically isolating them on SOI. A glass layer is anodically bonded to the SOI to seal the μcolumn. The heater of μcolumn is patterned on the same layer as the μPID with an additional layer of SiO_2 for electrical isolation. A VUV lamp (Krypton for 10.6 eV) is hermetically mounted on the μPID by epoxy and for photoionization.

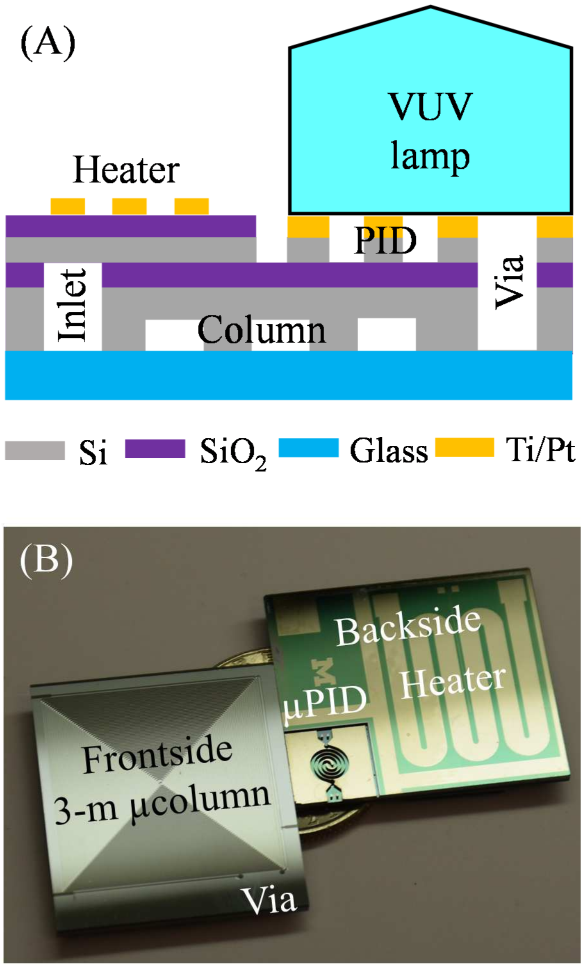

Figure 1: (A) Device architecture of iCPID. The iCPID is constructed on a silicon-on-insulator (SOI) structure. Device layer (backside) is designated for heater and μPID. Handle layer (frontside) is designated for μcolumn where a glass substrate is capped on the SOI. A vacuum-UV

(VUV) lamp is hermetically sealed by UV epoxy on µPID and microfluidic vias. (B) Photograph of iCPID dies (left: 3-m µcolumn side up; right: µPID and heater side up).

FABRICATION

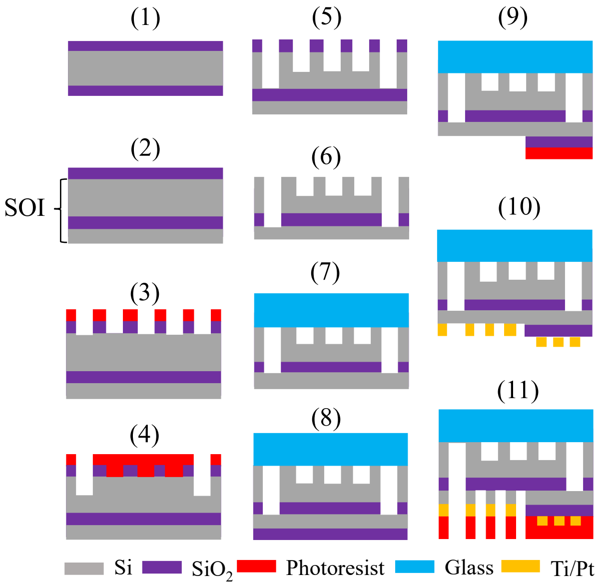

Figure 2: Microfabrication processes of iCPID. (1) Thermal oxidation; (2) Fusion bonding; (3) SiO_2 RIE (reactive ion etching); (4) Si DRIE (deep-RIE); (5) Si DRIE (hard mask); (6) HF (hydrofluoric acid) strip; (7) Anodic bonding; (8) PECVD (plasma enhanced chemical vapor deposition) SiO_2; (9) SiO_2 RIE; (10) Evaporation and lift-off; (11) Si DRIE.

The monolithic microfabrication process for the iCPID is outlined in Figure 2. The handle wafer was thermalized with 2 µm thermal oxide first. Both wafers first underwent RCA clean. After a dielectric barrier discharge (DBD) of atmospheric N_2 plasma treatment on the bonding side of both wafers, a 400 µm thick, double-side polished Si wafer (<100>, p-type, 0.001-0.005 Ω*cm) was fusion bonded to a 400 µm thick, double-side polished Si wafer (<100>, p-type, 1-10 Ω*cm) with 2 µm thick thermal oxide under vacuum at 400°C and 20 MPa for 4 hours to generate the SOI wafer where the conductive wafer serves as the device layer and the insulating wafer serves as the handle wafer. The oxide on the handle layer was then patterned to create a hard mask for the µcolumn, inlets and pass-through microfluidic vias. Next, photolithography was used to selectively expose the inlets and pass-through vias for a deep reactive-ion etching (DRIE) etch of ~150 µm in depth. The photoresist was then stripped and DRIE continued with the hard mask to simultaneously etch the µcolumn to a final depth of 250 µm while the inlets and pass-through vias were etched to the buried oxide layer (BOX) with the final depth of 400 µm. After stripping the thermal oxide and BOX on the pass-through vias with HF, the handle layer was anodically bonded to a 550 µm thick borofloat glass wafer to seal the µcolumn. Next, 1 µm of SiO_2 was deposited on the device layer by plasma-enhanced chemical vapor deposition (PECVD) and the area where the µPID resides was etched away by RIE. A layer of Ti/Pt (30/360 nm) was patterned on the device layer using lithography, evaporation, and liftoff to define the µPID electrodes and µcolumn heater simultaneously. Finally, DRIE was used for generating the µPID. The µPID was etched down to the BOX.

EXPERIMENTAL RESULTS

Figure 3 showcases the ICPID architecture. During operation, the gas mixture enters the inlet of the iCPID, and is subsequently separated by the µcolumn whose temperature is ramped by the integrated heater. At the end of the µcolumn, the separated molecules take path through the microfluidic via entering the µPID where they are detected non-destructively. This top-down architecture of the iCPID minimizes the overall footprint by allowing the µPID to be stacked directly on the µcolumn while avoiding any off-chip interconnection in between.

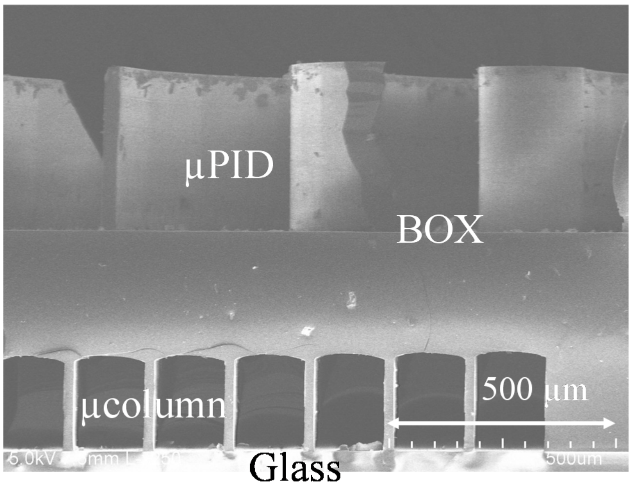

Figure 3: Scanning electron microscopy (SEM) of a cross-section of the iCPID featuring monolithically integrated µPID on µcolumn.

The iCPID was coated with Polydimethylsiloxane (PDMS) non-polar stationary phase and packaged into an ultracompact µGC system, dubbed integrated cube (*i.e.*, iCube). The system consisted mainly of a stainless steel preconcentrator, an iCPID, a pump, an air filter, two microfabricated Y-connectors, two 3-port valves, a set of four 5500 mAh rechargeable batteries and an in-house control circuit board. Components were fluidically interconnected using flexible Polytetrafluoroethylene (PTFE) tubes and guard columns. The components and fluidic diagram for the iCube along with its operation are depicted in Figure 4(A). For iCube operation, the analytes were sampled from a gas storage bag into the preconcentrator before backflush injection into the iCPID. Ambient air, which was filtered through an inline filter to remove moisture and hydrocarbons, was used as the carrier gas at a flow rate of ~0.9 mL/min. Separation was conducted isothermally at room temperature (~22 ºC). A representative chromatogram of a standard sample containing seven VOCs is shown in Figure 4(B), showing that separation can be completed within 100 s.

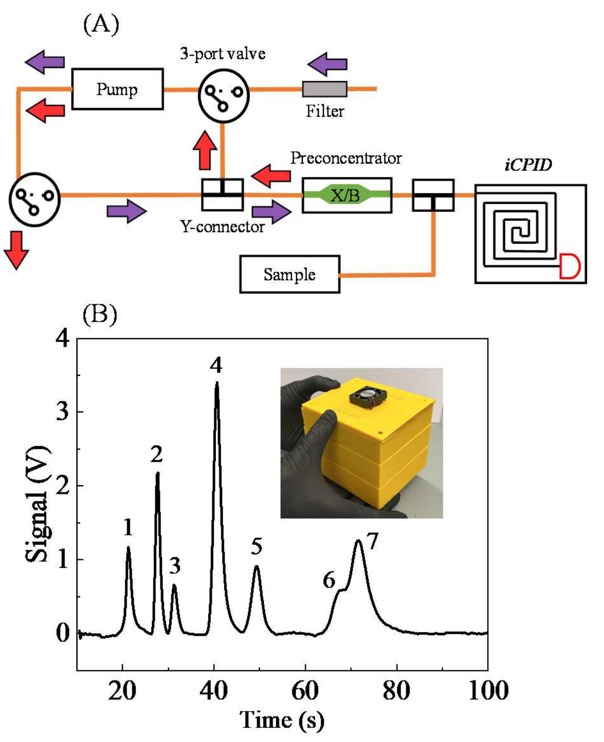

Figure 4: (A) System schematic of the ultracompact μGC device, named integrated Cube (i.e., iCube). The sampling and analyzing path are indicated with red and purple arrows respectively. (B) Chromatogram of (1) acetone, (2) benzene, (3) heptane, (4) toluene, (5) octane, (6) ethylbenzene, and (7) xylene generated by the iCube. Filtered air was used as the carrier gas with a flow rate of 0.9 mL/min. Inset shows the photograph of the iCube that occupies 0.9 liters and weighs 0.9 kg.

DISCUSSION AND CONCLUSION

In summary, this work reports a monolithically integrated microfluidic photoionization detector (μPID) on a microfabricated gas chromatography (μGC) column via wafer-level batch processing on an SOI platform. Such device architecture provides a smaller chip footprint, more robust fluidic connection by eliminating off-chip interconnects, and potential reduced cost for future mass production on the wafer scale. The iCPID enables an ultracompact (0.9 liters and 0.9 kg), fully automated, and battery-operated μGC system. Rapid separation of seven volatile organic compounds (VOCs) in ~2 min at room temperature is demonstrated.

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