HIGHLY SENSITIVE DETECTION OF VOC USING IMPACT IONIZATION INDUCED BY PHOTOELECTRON

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ABSTRACT

We have developed a highly sensitive volatile organic compounds (VOCs) sensor using impact ionization induced by photoelectron. A novel mechanism of VOC detection, the screening effect of VOC cations, was proposed and experimentally verified for the first time. The fabricated sensor could detect various concentrations of toluene ranging from 500 down to 10 ppm under long wavelength of UV light (254 nm) illumination. In addition, reliable and repeatable sensing characteristics were obtained at the exposure to ethylene with high ionization energy.

INTRODUCTION

Volatile organic compounds (VOCs), organic chemicals emitted as gas state from diverse solids or liquids, are found both in- and outdoors in daily life. Some VOCs such as toluene, ethylene, and acetaldehyde are known as hazardous gases that have a detrimental effect on both environment and human health [1]. In particular, VOCs emitted from various household products, including paints, wood preservatives, and dry-cleaned clothing, cause many chronic diseases such as sick building syndrome, skin complaint or cancers [2]. Accordingly, the detection of VOCs is an important issue to prevent health risk from them.

A number of different operation principles for VOC sensing have been developed to actualize the monitoring of VOCs [3-9]. One of the most common approaches is to use semiconducting metal oxides as sensing materials such as SnO_2 nanofibers [10], WO_3 thick-film [11], and metal-coated ZnO nanowires [12]. Despite high sensitivity with low detectable limit down to a few ppm, metal oxide-based VOC sensors have several drawbacks: poor selectivity and high operation temperature (300–400°C) [13]. As an alternative, photoionization detectors (PIDs) attract attention since they can selectively detect VOCs at room temperature [14]. However, UV light source of PID (wavelength of 117 nm) is bulky and expensive, making this way unsuitable for the integration to compact devices or the application to distributed environmental monitoring system. In addition, the photon energy for gas ionization in most of commercialized PIDs is limited (~10 eV) [15], thus the detection of gas species with higher ionization energy such as ethylene (10.51 eV) [16] and acetylene (11.41 eV) [17] with this approach is impossible. Although the detection of VOCs using impact ionization by accelerating photoelectrons was proposed to overcome the limitations of PIDs [18], the sensitivity was very low and the poor output signal was hardly discriminated from noise, making it difficult to detect various concentrations of VOCs.

In this work, we report the successful detection of VOCs at various concentrations using impact ionization induced by photoelectron and present the novel detection mechanism that is different from typical PID. Unlike the existing PIDs that require very short wavelength of UV light (117 nm) generated from expensive source, we could achieve comparable result using relatively long wavelength of UV light (254 nm) from low-cost source. We observed decrease in current of the tested sensor very sensitively at the exposure to toluene or ethylene.

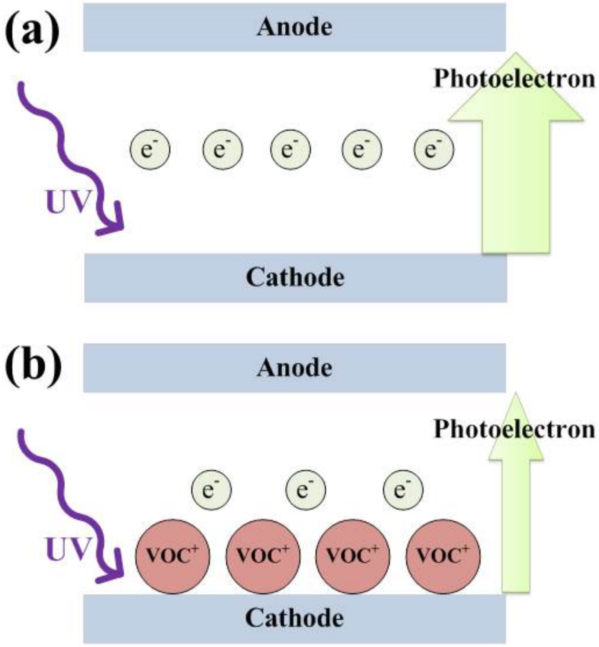

Figure 1: Illustration of proposed sensor transduction mechanism. (a) Under illumination with UV light onto cathode, photoelectrons are emitted by photoelectric effect. (b) Ionized VOC cations by impact of accelerated photoelectron are adhered onto the cathode, thereby reducing the open surface of cathode for photoelectron emission. Consequently, the emission of photoelectron is reduced by screening effect of VOC cations.

WORKING PRINCIPLE

Figure 1 depicts the mechanism for VOC detection based on impact ionization induced by accelerated photoelectrons. Under illumination with UV light, cathode emits electrons originated from photoelectric effect and the photoelectrons transfer to anode due to the electric field applied, generating a photocurrent (Figure 1a) [19]. When VOC is introduced between the cathode and anode, they collide with the accelerated photoelectrons and would be ionized. The ionized VOC cations are adhered onto the cathode, thereby reducing the open surface of cathode for photoelectron emission. Consequently, the emission of photoelectron, i.e. photocurrent is reduced by the screening effect of VOC cations as described in Figure 1b.

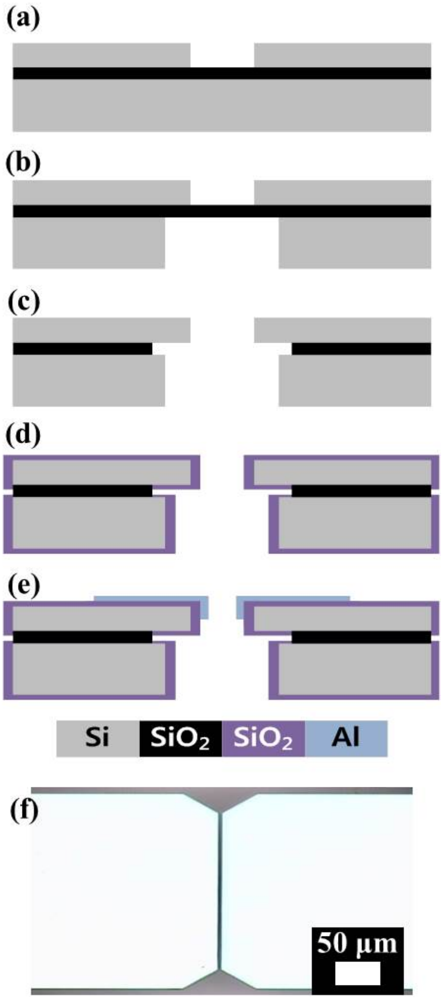

Figure 2: The fabrication process and optical microscope image of the tested sensor. (a) The positive photoresist is patterned on the front side of wafer and the device layer is etched by DRIE. (b) The substrate is etched by DRIE using sputtered aluminum as a hard mask (c) Buried oxide layer is wet-etched by buffered HF. (d) Silicon dioxide layer is formed by thermal oxidation. (e) Aluminum is sputtered through shadow mask to define the anode and cathode. (f) Optical microscope image of the fabricated device.

FABRICATION

The fabrication process of the tested sensor is schematically described in Figure 2. The sensor is batch-processed on a silicon-on-insulator (SOI) wafer through bulk micromachining. The device layer of the SOI wafer is n-doped silicon with a thickness of 20 µm, and the buried oxide layer and base substrate have a thickness of 2 and 400 µm, respectively. Firstly, the positive photoresist is patterned on the front side of wafer and then the device layer is etched by deep reactive ion etching (DRIE) (Figure 2a). For the substrate etching, aluminum is sputtered and patterned on the backside by lithography and wet etching to be used as a hard mask for deep etching. Subsequently, the DRIE is performed on the backside and the remaining aluminum layer is completely removed in piranha solution (Figure 2b). The buried oxide layer is wet-etched by buffered hydrofluoric acid to form the suspended structure (Figure 2c). Finally, thermal oxidation (Figure 2d) is followed by aluminum sputtering through shadow mask to define the anode and cathode (Figure 2e). The optical microscope image of the fabricated sensor is shown in Figure 2f.

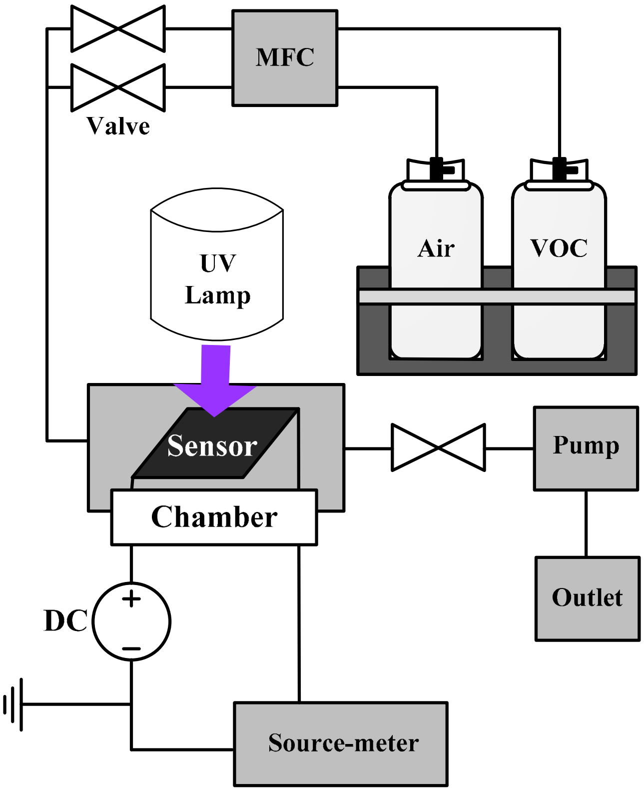

Figure 3: The schematic of the experimental setup to evaluate the performance of the tested sensor.

EXPERIMENTAL RESULTS

To evaluate the performance of the tested sensor, we explored the sensor output with respect to two different species of VOCs, toluene and ethylene. The schematic of the experimental setup is described in Figure 3. For UV light irradiation, a 254 nm UV lamp with the power of 15 W was used (LF 215MS, UVITEC). Of many electrode materials available for photoelectron emission, aluminum is chosen as photoemission material as well as the electrodes for its work function (4.06~4.26 eV) [20] lower than the photon energy of 254 nm UV light (4.88 eV). For VOCs detection, the tested sensor is first placed onto a chamber with UV on and then exposed to air that flows into the chamber for 5 min to stabilize the photocurrent. Subsequently, toluene or ethylene diluted in air is introduced for 5 min while the current is monitored. The flow rates of both air and VOCs are adjusted by mass flow controller unit and the pressure in the chamber is pumped down to about 10 Torr. To accelerate photoelectrons, high voltage (400 V) is applied to electrodes by DC power supply (B. 130, KSC) and the current is measured using sourcemeter (2400, Keithley Instruments).

The transient response of the sensor with- and without UV light illumination was investigated under different concentrations of toluene as shown in Figure 4. The initial current of the sensor with UV light illumination (22.4 nA) was higher than that in dark (9.2 nA), indicating the generation of photoelectron on the cathode. Under UV light illumination, the current decreased by 15.5% and

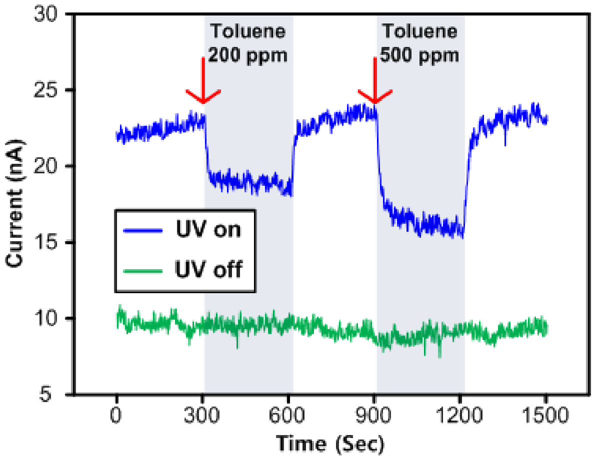

Figure 4: The transient response of the sensor with- and without UV light illumination at the exposure to 200 and 500 ppm toluene.

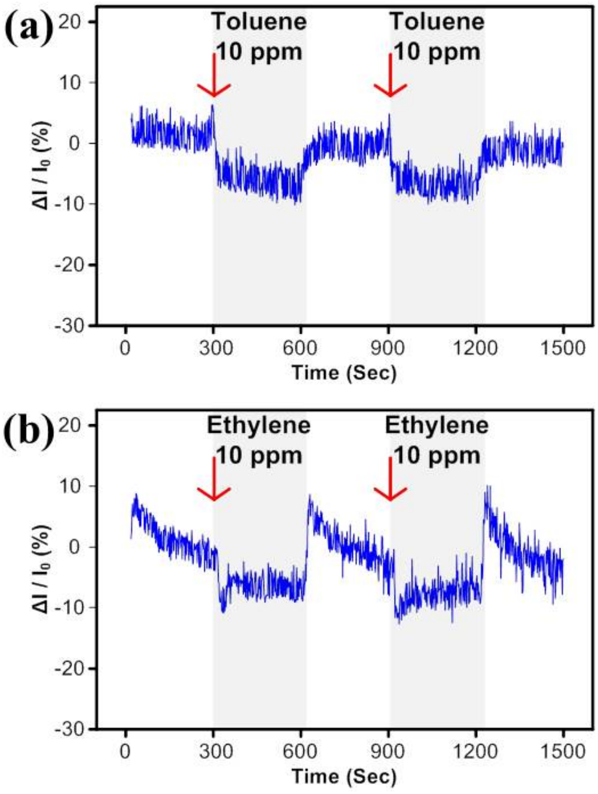

Figure 5: The relative change in current with respect to time at the periodic exposure to 10 ppm (a) toluene and (b) ethylene.

26.8% (blue line) at the exposure to 200 and 500 ppm toluene, respectively, which is consistent with the screening effect on the cathode due to the adherence of VOC cations as described above. On the other hand, the current in dark showed no considerable changes at the exposure to toluene. These experimental results elucidate the detection mechanism of our proposed sensor and highlight the role of the accelerated photoelectrons during the sensing process. Figure 5 plots the relative change in current with respect to time at the periodic exposure to low concentrations of toluene and ethylene (both 10 ppm). The measured relative change in current was 6.51 and 7.53% for toluene and ethylene, respectively. Notably, we achieved reliable and reproducible detection for ethylene with high ionization energy (10.51 eV) and this is a highly advantageous aspect of our approach compared to commercialized bulky PIDs which cannot produce reliable measurement data for VOCs with ionization energy above 10 eV.

CONCLUSION

In summary, we demonstrated a VOC sensor based on impact ionization of gas molecules induced by accelerated photoelectrons. The sensor was fabricated through standard microfabrication process on SOI wafer. When the sensor with UV light illumination was exposed to 200 and 500 ppm toluene, we observed the decrease in the current by 15.5% and 26.8%, respectively, whereas it showed no detectable change of current in dark. We infer this is originated from the screening effect of VOC cations under UV light illumination. The sensor also exhibited the reliable and reversible change in the current by 6.51% and 7.53% upon the exposure to 10 ppm toluene and ethylene, respectively. On the basis of the results, it is expected that our sensor could serve as a highly sensitive and VOC species-selective sensing solution.

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