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Gas Release

An *X–Y* Addressable Matrix Odor-Releasing System Using an On–Off Switchable Device**

Hyunsu Kim, Jongjin Park, Kunbae Noh, Calvin J. Gardner, Seong Deok Kong, Jongmin Kim, and Sungho Jin**

In recent decades, much research has been dedicated to the development of virtual reality for entertainment,[1] engineering,[2] and medical application.[3] Virtual reality can be made more realistic with an artificial three-dimensional visual or other sensory environment using the experience of moving seats,[4] odors of explosives or flowers,[5] sprinkling water, laser lights, and wind blowing. Odor-releasing devices that allow repeatable, remote, and reliable switching of odor flux, in particular, could have a significant impact on the effectiveness of virtual reality. However, although various devices for the added sense experience have been developed recently, very few odor-generating devices with practical and useful control of induced sense of smell have been reported.

The development of an odor-releasing system that can provide specific odor selectively began in the early days as a crude device. The oldest system is “Sensorama”,[6] a game machine, wherein odor is presented according to the scene on the display and the chair or steering wheel vibrates. After Sensorama, there were discussions about which movie needs odor presentation, referring to some experiments on providing odors synchronously as the movie scenes evolve. In the AMLUX theatre, there was an attempt to add odor information to visual media. Also, there have been some tests to induce the relaxation effect through odor presentation in art objects. Furthermore, there were some approaches to utilize odor information for the fire-fighter training system,[7] and the soldier training system by using a scent collar.[8] These systems present odor information by evaporating bulk smelly material or by spraying it using propellant gas or inkjet technology.

However, these well-known technologies are coarse and crude in nature, and it is hard to apply them to delicate home electronics or personal devices owing to their bulkiness, their lack of reproducible release over multiple cycles, their slow response times to stimuli, as well as their inability to dynamically adjust the amount/intensity of odor according to the recipient’s needs. Therefore, the development of odor-releasing or transferring systems for the electronic device virtual reality has been difficult. Moreover, televisions, home-theatre, or video-game devices are getting thinner and smaller, requiring faster and more accurate control.

Indeed, no existing device could overcome all of these limitations at the moment. For example, an automatic aerosol dispenser containing odor-filled reservoirs can achieve rapid on-demand odor delivery but the odor-storing cans are filled with compressed gas or flammable solvents used as propellants and require a complicated valve system which is difficult to scale down. The desirable odor-generating systems should not depend on a mechanical switching system and should be thin enough to insert into small devices. For these reasons, innovative technologies are needed. The primary requirement to the development of a gas-release device for odor generation is an accurate control capability. From this perspective, an ideal device for odor generation should safely contain a suitable quantity of odor-releasable solution, can release little or no odor in the “off” state, and be repeatedly switched to the “on” state without mechanically disrupting the device.

In recent years, many researchers have been trying to develop on–off switchable devices for drug release using polymers,[9–11] because some polymers have good reversible switching properties. We have employed in our new odor-generating system, a stable polymer, polydimethylsiloxane (PDMS), a representative silicone elastomer. PDMS is optically clear and, in general, is considered to be inert, non-toxic, and non-flammable. One of the primary fields of applications for PDMS is the embedding or encapsulation of electronic components by casting, which prolongs the lifespan of the circuit chips. A silicone elastomer such as PDMS, exhibits mechanical elasticity, acts as a dielectric isolator, and protects the components from environmental factors and mechanical shock over a relatively large temperature span (e.g., 50–200 °C).[12] In addition, the inertness and stability of PDMS has been traditionally utilized as a biomaterial in implants, catheters, drainage tubing, and membrane oxygenators.[13] We have therefore utilized the desirable properties of PDMS for the development of our on–off switchable odor releasing system. Cross-linked (cured) PDMS elastomer does not allow aqueous solvents to infiltrate and swell the polymer,[14] so that it can be used as a container which can store a water-based liquid. Although elastomers are not

[*] H. Kim,[+] K. Noh, C. J. Gardner, Dr. S. D. Kong, Prof. Dr. S. Jin
Materials Science and Engineering
University of California, San Diego
9500 Gilman Drive, La Jolla, CA 92093-0411 (USA)
Fax: (+1) 858-534-5698
E-mail: jin@ucsd.edu
Homepage: http://maeweb.ucsd.edu/~jin/
Dr. J. Park,[+] Dr. J. Kim
Samsung Advanced Institute of Technology, Frontier Research Lab
Samsung Electronics Co., Ltd.
Suwon, Gyeonggi-Do 443-742 (Korea)
Fax: (+82) 31-280-9349
E-mail: jongkim@samsung.com
[+] These authors contributed equally.

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usually completely impermeable to most gases, the gas permeability decreases with increasing cross-linking.[15,16] As will be discussed below, we utilized *X–Y* matrix addressable localized heating from an *x–y* grid electrical resistance heating wires, which induces a local reversible shrinkage/expansion of PDMS and this thermally induced volume change can open a tiny exit hole on the top of the specific odor-container element to release gas as described in Figure 1 a.

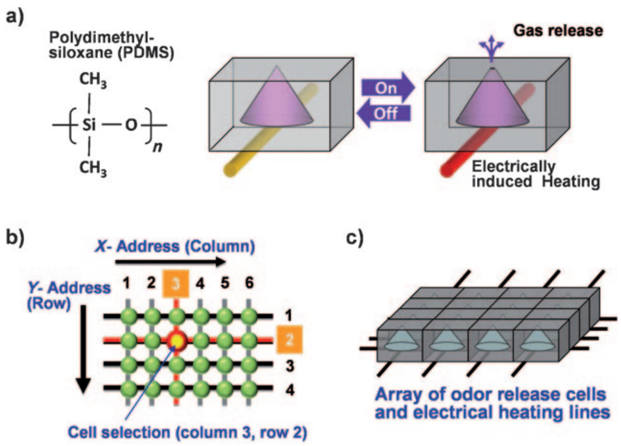

Figure 1. a) Proposed action of a gas/odor-release device based on an elastic chamber material. b) a diagram illustrating the *x–y* coordinate cell-selection method, and c) a *X–Y* matrix structured odor-releasing system with 4x4 cells.

Herein, we report a gas/odor release system based on a gated PDMS chamber array which is employed as a rapid, repeatable, and reliable gas/odor release upon electrical actuation. A novel two-dimensional (2D) cell-chamber array capable of selective odor generation is proposed as described in Figure 1 b,c. The proposed *X–Y* matrix structured odor-release system has an array of gas/odor containers with rows and columns of electrical heating lines, in which only the intersecting cell (and no other cells) from many arrayed cells is allowed to pass beyond the threshold accumulation of gas/odor pressure to force-open the cell gate for gas/odor release. (see Supporting Information for operating strategy of *X–Y* matrix array odor/gas chambers.).

We have demonstrated the single-cell operation of a PDMS gas/odor-release device. The fabrication process for the device and the configuration of the measurement apparatus for this experimental setup are illustrated in the Supporting Information Figures S1 and S2. The size (volume) of a cone-shaped cell is 0.077 mL. Each of the PDMS cells has a gate at the top made of a puncture hole (but without actually removing any of the PDMS material), which elastically keeps the hole tightly closed if unactivated, but opens allowing the gas/odor release when activated by electrical heater lines. Ammonia was injected into the cell cavity through the puncture hole. The system was designed in such a way that a certain threshold pressure is required to overcome the elastic closure force of the gate. This threshold pressure is made to occur only when the specific targeted chamber is heated simultaneously by two crossing lines (both *x*-line and *y*-line), thus providing *X–Y* matrix selectivity for any one chamber cell. The detector setup has the capability to monitor real-time data change as a gas detector. This provides a better control for the assessment of the amount of gas released during operation because traditional gas measurement techniques using gas chromatography and photo-acoustic spectroscopy suffer from the major drawbacks of being slow, being operationally impractical, and do not allow for real-time measurements.[17]

One of the compounds that we have chosen as the source of an odor is aqueous ammonia. The aqueous ammonia can easily be filled into the chamber cell regardless of container shape and easily generates odor from the solution on electrical actuation in the form of ammonia gas. It is believed that the primary mechanism for gas/odor release is the pressure-buildup beyond the threshold to open the elastic gate, but a contribution from the thermal expansion mechanism that geometrically alters the pore dimension may also play a role. Further research is needed to elucidate the exact mechanism of gas/odor release in our device system. The electric current for heating the Nichrome electrical heating wires positioned underneath the chamber cell array was kept at 1.5 A for the sample. The Nichrome alloy is a well known commercially available electrical heating element made of 80% Ni and 20% Cr in weight, having a high electrical resistivity of approximately 150 μΩ-cm.

Liquid NH_4OH was injected with a hypodermal syringe to the chamber. Figure 2 shows the detected ammonia gas during the "on" state. Continuous release of odor was performed by continuous passage of electrical current to the heating wire. Real-time monitoring has been conducted instantaneously in percentage by volume for the sampled gas in the air. The maximum volume concentration of ammonia gas was approximately 0.6 vol% of all gases involved (ammonia + oxygen + nitrogen). The area under the gas concentration curve was integrated and used to

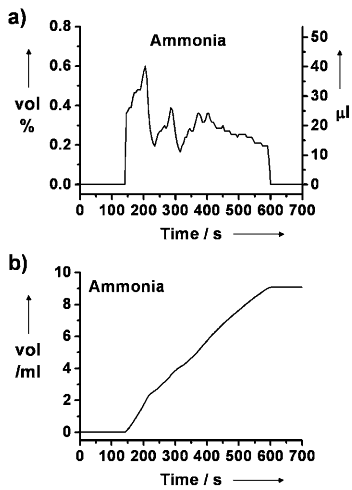

Figure 2. a) The concentration of gas (ammonia) release detected versus actuation time (vol% on the left axis, released volume in μL on the right axis), and b) total accumulated amount of released ammonia as a function of actuation time.

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calculate the total amount of released gas. Since the gas flow rate in the gas monitor is $6.7\,mL\,s^{-1}$, the concentration can easily be converted into volume. Figure 2b shows the accumulated amount of ammonia. Total amount of ammonia gas released is estimated to be 9 mL.

Another PDMS device was constructed and used for a leakage test. When the device filled with ammonia was kept in the "off" state (without applied current) for 24 h, no noticeable signal of ammonia was detected. This implies that the elastically closed "gate" is very tight and can hold the gas in place without leakage. As gas molecules can escape through even extremely small nanopores, this leakage test data is quite encouraging. Thus, the PDMS container with electrical actuation system could be used as a reversible/repeatable gas/odor-releasing device.

Shown in Figure 3 are the results of the on–off switching of the PDMS gas/odor-release system. When the system is in the "on" state, that is, an electrical current of 1.5 A is applied to the heating wires, the maximum concentration of measured ammonia is about 0.4 vol% (of the total gas detected) for

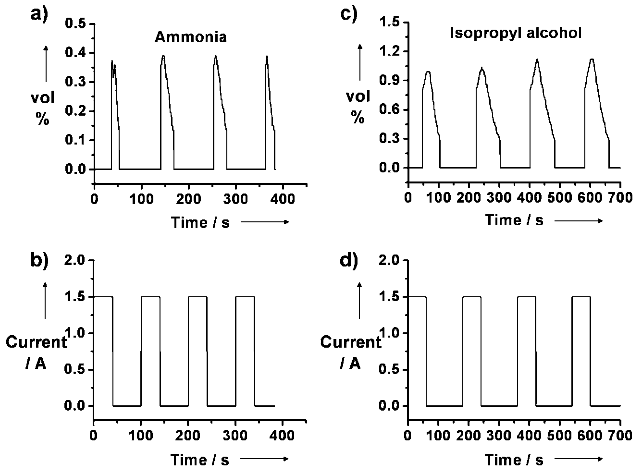

Figure 3. On–off switchable gas release (a,c) and applied current intensity (b,d) for ammonia (a,b), and isopropyl alcohol (c,d).

each cycle. The abrupt increase of concentration in the "on" state could allow the gas/odor to be detected by a human nose (see below).

During the "off" state (no electrical current), the temperature of the PDMS decreased and the gate shut so that no ammonia flux was detected (Figure 3). The ammonia flux could be switched on and off over multiple thermal cycles with high reproducibility, suggesting that the system is fully reversible. It is conceivable that the thermal expansion near the base of the PDMS container causes the PDMS container near the puncture hole to shrink and reduce the compressive stress on the elastomer gate thus assisting in the release of gas. The gas/odor release device was turned "on" with approximately 40 second time lag after the current was applied and turned "off" with approximately 40–50 second lag (Figure 3), which is presumably due to some delay in heat propagation and the time it takes to clear the previously released gas from the chamber. We have observed a very similar on–off switching behavior when the model gas was switched to other gases, such as isopropyl alcohol, a typical anhydrous volatile liquid unlike aqueous ammonia (Figure 3b,d).

We have shown reproducibility over four thermally induced cycles (Figure 3), although many more cycles can be performed with essentially a similar fidelity. For industrial application, a similar amount of gas flux should be switched on and off over many cycles. Therefore, the engineering performance of the odor generating device on multiple cycles will be investigated with the focus on duration in more detail in the future. While the on–off switchable release of ammonia gas over multiple thermal cycles has been successfully demonstrated using PDMS-based devices without leakage in the "off" state, an important aspect to consider in using the odor-releasing device in virtual-reality applications is how to control the odor releasing system containing multiple odors. Although all the individual cells can be separately actuated by individual actuation/control system, this would require too many actuation control devices: N^2 for a X–Y matrix array of odor/gas chambers (where N is the number of the rows or columns in a square matrix). Therefore, we have created an X–Y coordinate system (Figure 1b,c) and attempted to operate the PDMS gas-releasing system with crossed heating wires on the bottom of the release chambers, so that we need only $2N$ controllers instead of N^2 controllers (see the Supporting Information). For 10000 odor chambers, 200 controllers instead of 10000 controllers would be sufficient.

We chose isopropyl alcohol as a gas to test the odor-release function and controllability for the X–Y matrix system (Figure 4a,b) When 1.6 A current was applied to the row wires, no gas release was detected. However When 1.6 A was applied to the row wires and 1 A was applied to the column wires together, the cell at the intersection was activated for gas release. (The column electrical wires were placed/attached closer to the chambers, they require less current than for the row wires to reach the same temperature). The measured maximum concentration of isopropyl alcohol was about 1 vol% for each on–off release cycle (Figure 4a). When the electric current of the column wires was off, the

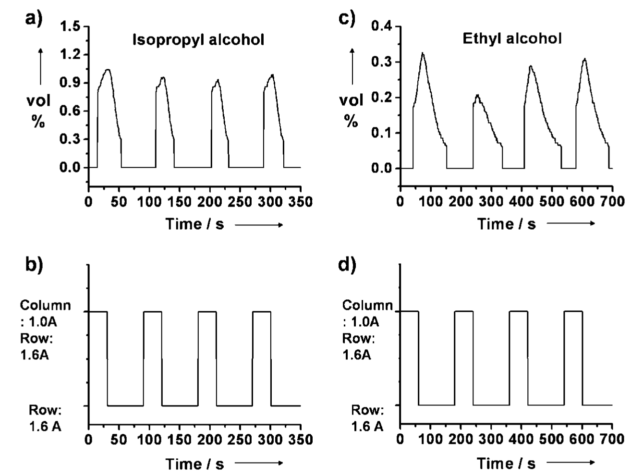

Figure 4. Gas concentration released and applied current for a),b) isopropyl alcohol, and c),d) ethyl alcohol during the on–off control of the PDMS gas-release device with crossed heating wires.

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concentration of isopropyl alcohol released decreased down to the "off" state even though the row wires remained activated. We have found a similar on–off switchable release performance using ethyl alcohol (Figure 4 c,d). When we tested gas release from a cell adjacent to the selected cell, no interference was observed between the two cells (Supporting Information, Figure S3). Since the 2D cell array was designed to allow individual cells to maintain a set distance apart, the continuous "on" state of one cell should not affect the operation of adjacent cells. However, if the neighboring cells were too close to each other, leakage heat to cause the neighboring cell to reach the operating temperature for gas release.

Sometimes, visualization using various colorimetric methods including gas-sensor arrays[18–21] can be utilized, instead of gas-detection electronic systems, to indicate the release of gas/odor in a simple manner. These colorimetric gas tubes are conveniently connectable to the Tygon tubing in the gas-measurement apparatus without changing the configuration and the gas enters through one end of gas detection tube. Figure 5, shows two released gases being detected by using gas detection tubes. The color of the gas detector tube is changed by a reaction of the reagent in the tube and the incoming gas [Eq. (1), Eq. (2)]. Gas detector tubes were successfully used for the quick measurement of present gases.

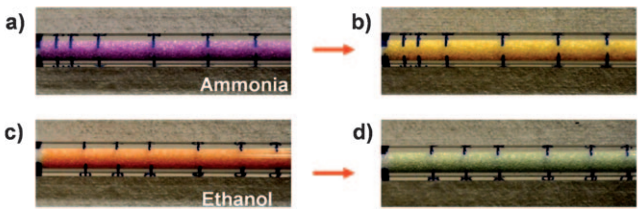

Figure 5. Color visualization photographs from ammonia and ethyl alcohol gas detection tubes. a),b) for ammonia gas before and after gas sampling, respectively. c),d) for ethyl alcohol gas before and after sampling, respectively.

$$3\,NH_3 + H_3PO_4 \rightarrow (NH_4)_3PO_4 \quad (1)$$

$$C_2H_5OH + Cr^{IV} + H_2SO_4 \rightarrow Cr^{III} + \text{oxidation products} \quad (2)$$

The results show that the *X–Y* matrix gas-release system offers controllable gas release.

Since the final potential applications would be aimed at odor sensing by the human nose, we utilized human olfaction as a detector for two types of distinctively different perfumes as model odors (see the Supporting Information). Traditional sensing systems have insufficient sensitivity towards perfumes which consist of a mixture of various ingredients and additives. We used the "Live by Jennifer Lopez" and the "Passion by Elizabeth Taylor" as perfume odor materials instead of isopropyl alcohol and ethyl alcohol. Figure 6 shows the experimental data for the on–off switchable release of these two different perfumes. Similar to isopropyl alcohol and ethyl alcohol, two perfumes were detected in turn by on–off switching processes for each cell. (See supporting Information for more details.)

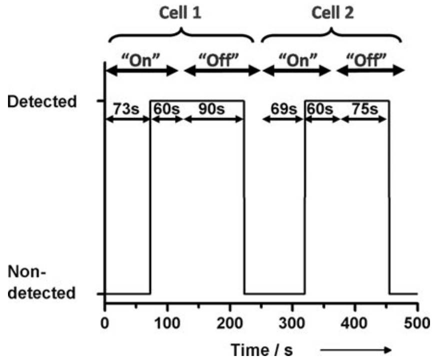

Figure 6. Real-time responses of human olfaction measured for the smell of two perfumes, "Live by Jennifer Lopez" (Cell 1) and "Passion by Elizabeth Taylor" (Cell 2).

The type of *X–Y* matrix vapor/odor-releasing system reported herein has the potential to improve the quality of virtual reality system for 3D TVs, cell phones, and other portable devices, and could also be useful for various entertainment, chemical engineering, and medical applications, such as combinatorial studies of multiple gas reactions and vapor-based drug development.

In conclusion, we have demonstrated a novel *X–Y* matrix structured odor-releasing system with an elastomer-based device. Relatively low cost and compact design of the system may be achieved through the proposed switchable gas-release method. In addition, odor-release measurements with real-time data-logging were also developed for model liquid/gas samples, such as ammonia, ethyl alcohol, and isopropyl alcohol, as well as two perfumes.

The electrical actuation system enabled on–off switching of gas release. The main advantage of the proposed system is that the individual cells can be filled with different odorants which can be released on demand without interference. Thus, this *X–Y* matrix odor-releasing system has the potential to greatly improve the quality of virtual reality systems.

Further improvements in fabrication, the use of advanced materials, and device structures for storing a large amount of odor, for example, in high-aspect-ratio chambers, or in solid form rather than liquid form, would make the capacity and duration of odor release much larger. Enhanced odor release kinetics may also be explored using nanostructured, large-surface-area materials and distributed 3D networked actuators. These advances are being investigated to develop a more robust and reproducible odor generating system, which will be reported in future publications.

Experimental Section

The gas/odor releasing device was made using PDMS elastomer. PDMS was processed according to the instructions for a commercial elastomer (Dow Corning, Sylgard-184). The mixing ratio A-(monomer):B(hardener) was 10:1. After being weighed, the compound was thoroughly mixed for 5 min and then left for 10 min to let air bubbles diffuse out of the liquid. The mass was then poured into

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the mold and degassed, in order to prevent micro-bubbles at the bottom of the mold. A plastic Petri dish (Falcon, 35 mm in diameter) was used as a mold. The filled dish was carefully sealed with a plastic lid which had a cone-shaped polytetrafluoroethylene (PTFE) template to produce a cone-shaped cavity in the PDMS, and then hardened in the oven (Thermolyne, OV12900) for 30 min at 80 °C. After the hardening process, the PTFE was removed from the PDMS and the shaped PDMS was placed on the mixed PDMS liquid for the second hardening process. The fabrication process for the gas/odor release device and the configuration of the measurement apparatus for this experimental setup are illustrated in Supporting Information, Figure S1 and S2.

Nichrome resistance wires (Jelliff Corporation, 0.01 inch in diameter) for the internal heating system were attached to the bottom of the PDMS container with a third PDMS liquid hardening, after removing the plastic Petri dish, used to seal the cavity. Aqueous Ammonium hydroxide (Fisher, 14.8N), isopropyl alcohol (Fisher), and ethyl alcohol (Rossville Gold Shield) were used as solutions for gas generation. Ammonium hydroxide solution was injected into the PDMS container by using the syringe (BD, 10 mL in volume) and the syringe needle (BD, 0.31 mm in diameter). A sealed Petri dish (Fisherbrand, 60 mm in diameter) was used for the measurement of the generated gas.

For heating the PDMS container, constant current was applied to the Nichrome wires by a DC power supply (BK precision, 1627A). The generated gas was measured by a gas monitor (RAE systems, VRAE) with data logging. The sealed Petri dish and the gas monitor were connected by the flexible tubing (Tygon, 0.125 inch in diameter). One of the PDMS samples was prepared for leakage measurement. A simple-to-use color changing tubes (RAE systems, Gas Detection Tube) were used for visualization of gas release.

The perfumes, “Live by Jennifer Lopez” and “Passion by Elizabeth Taylor”, were used as solutions for odor generation. The distance between the odor generation system and the detecting human nose was fixed at 30 cm.

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