

(12) United States Patent Kan et al.

(54) CHEMORECEPTIVE SEMICONDUCTOR

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STRUCTURE

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- **U.S. Cl.** **257/315**; 257/239; 257/414
- (58) Field of Classification Search 257/239, 257/261, 315, 321, 414 See application file for complete search history.

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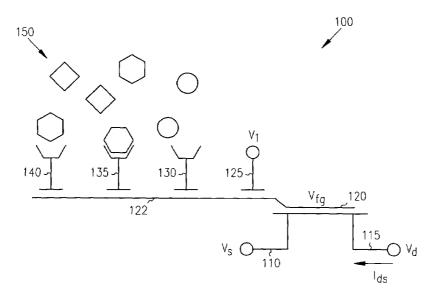
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(57)ABSTRACT

A field effect transistor has a floating gate with an extended portion. A selectively chemoreceptive finger or layer is electrostatically coupled to the extended portion of the floating gate, and induces a voltage on the gate in response to selected chemicals or other conditions affecting the finger. The voltage on the gate modulates current flowing between a source and a drain of the transistor, effectively sensing the presence of the selected chemicals or conditions. In one embodiment, multiple chemoreceptive fingers are electrostatically coupled to the extended portion of the floating gate. In a further embodiment, an array of such field effect transistors provide a sensor for multiple conditions.

13 Claims, 5 Drawing Sheets



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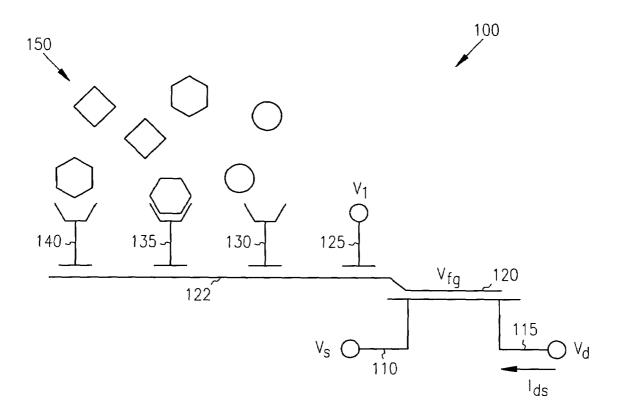


FIG. 1

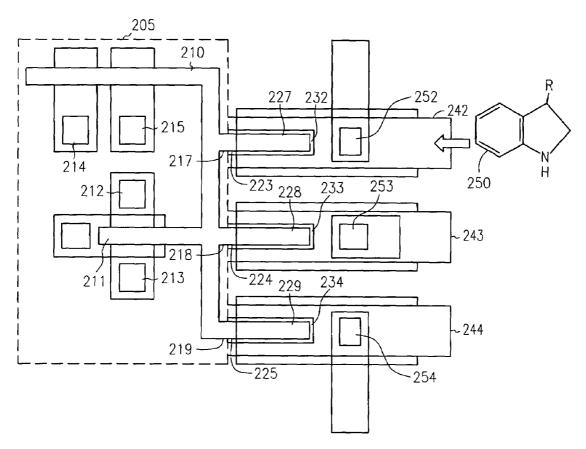


FIG. 2

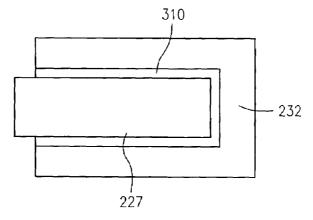


FIG. 3

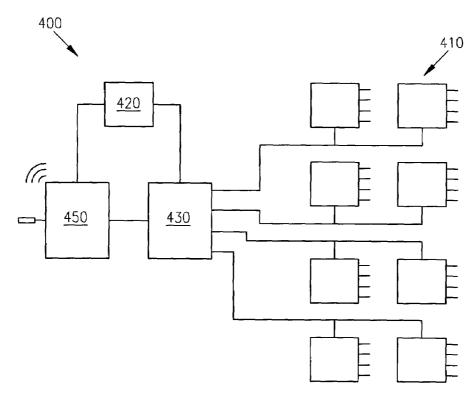


FIG. 4

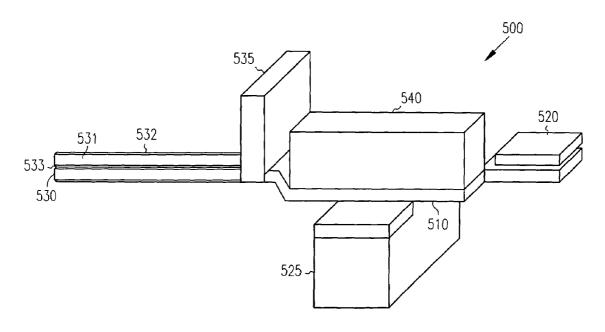


FIG. 5

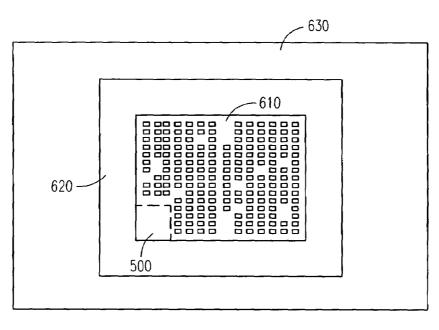
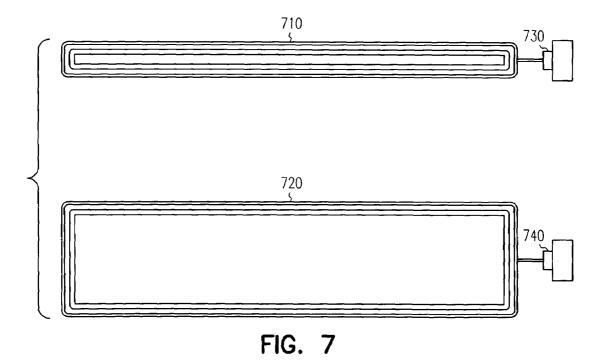


FIG. 6



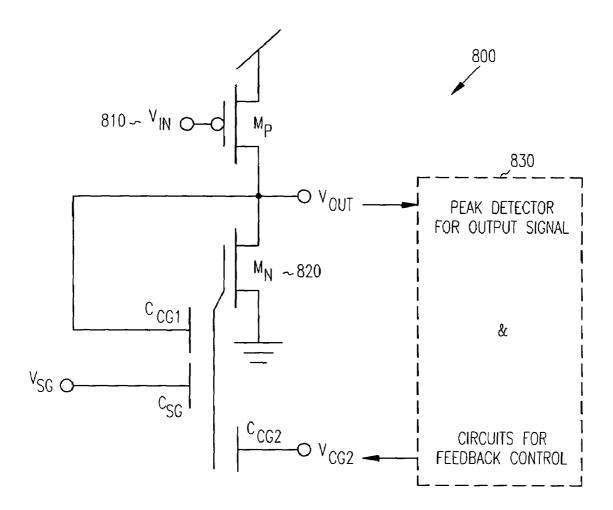


FIG. 8

CHEMORECEPTIVE SEMICONDUCTOR **STRUCTURE**

RELATED APPLICATIONS

This application claims priority from U.S. Provisional Application No. 60/422,014; filed on Oct. 29, 2002; which is incorporated herein by reference.

GOVERNMENT FUNDING

The invention described herein was made with U.S. Government support under Grant Number ECS-0210743 awarded by Nanoscale Exploratory Research (NER) and Grant Number R830902 awarded by the National Center for 15 ing subthreshold-slope variation. Environmental Research (NCER). The United States Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates to sensors, and in particular to a chemoreceptive semiconductor structure.

BACKGROUND OF THE INVENTION

Chemical and molecular sensing with solid-state devices have involved various approaches including microelectrode, microcalorimeter, acoustic wave devices, chemiresistors, chemicapacitors, chemomechanical sensors, and field effect transistor (FET) based sensors. Many attempts of forming 30 sensors with complementary metal-oxide-silicon (MOS) devices have also been made. Although sensitivity is high in a controlled environment, the devices are limited by sensing selectivity, contamination induced long-term drift in MOS characteristics, and system integration.

SUMMARY OF THE INVENTION

A field effect transistor has a floating gate with an extended portion. A selectively receptive finger is electro- 40 statically coupled to the extended portion of the floating gate, and induces a voltage on the gate in response to selected chemicals or other conditions affecting the finger. The voltage on the gate modulates current flowing between a source and a drain of the transistor, effectively sensing the 45 presence of the selected chemicals.

In one embodiment, multiple chemoreceptive fingers are electrostatically coupled to the extended portion of the floating gate. Each chemoreceptive finger is electrically isolated from the extended portion of the floating gate such 50 as by a nitride plug. In one embodiment, the fingers are referred to as control gates. The floating gate voltage is established through charge sharing or capacitive voltage division, as a weighted sum of the voltages applied to the control gates. The weight on each control gate is propor- 55 tional to the capacitance of the gate, and is normalized by the total capacitance of the floating gate.

In a further embodiment, and array of such field effect transistors forms a sensor for detecting one or more conditions. An optional independent power source and transmitter 60 provide for remote location of such arrays.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block schematic diagram representing a 65 floating gate transistor having a plurality of control gates, some of which are chemoreceptive.

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FIG. 2 is a plan view of a the transistor of FIG. 1 coupled to microfluidic fluid channels.

FIG. 3 is a plan view of a chemoreceptive control gate for the transistor of FIG. 1.

FIG. 4 is a block diagram view of an array of chemoreceptive control gate transistors.

FIG. 5 is a block schematic diagram representing a further exemplary floating gate transistor having a chemoreceptive layer.

FIG. 6 is a perspective view of a CMOS chip incorpo-10 rating a chemoreceptive transistor with a channel.

FIG. 7 is a block schematic diagram representing different width sensing gates.

FIG. 8 is a circuit diagram showing circuitry for indicat-

DETAILED DESCRIPTION

In the following description, reference is made to the 20 accompanying drawings that form a part hereof, and in which is shown by way of illustration specific embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that other embodiments may be utilized and that structural, logical and electrical changes may be made without departing from the scope of the present invention. The following description is, therefore, not to be taken in a limited sense, and the scope of the present invention is defined by the appended claims.

A four-input neuron metal oxide semiconductor (MOS) (vMOS) transistor is shown in block schematic form at 100 in FIG. 1. Transistor 100 comprises a source 110 and drain 115, and a gate 120 that modulates current flowing between 35 the source and drain. Gate 120 is extended as indicated at 122. Several control gates 125, 130, 135, and 140 are coupled to the extended area 122 of gate 120. The control gates are capacitively coupled in one embodiment to the extended area 122 of gate 120.

In one embodiment, the control gates 130, 135 and 140 comprise fingers that are coated with a chemoreceptive material, while control gate 125 is a normal vMOS control gate. The chemoreceptive material is selective in one embodiment, such that one targeted chemicals as shown generally at 150 bond with the material, creating a charge on the control gate that is capacitively coupled to the floating gate 120.

A floating gate voltage is established through charge sharing or capacitive voltage division, as a weighted sum of the voltages applied to the control gates. The weight on each control gate is directly proportional to that control gate's capacitance and is normalized by the total capacitance of the floating gate.

In one embodiment fewer, or more control gates are provided, and the extended area of the floating gate is formed sufficient to capacitively couple to such number of control gates. Not all the control gates need have chemoreceptive fingers, and the chemicals 150 such fingers are receptive to may be varied on the same transistor 100.

Transconductance gains of each control gate are selected via the control gate capacitances. Because the control gates perform their voltage summation by capacitive voltage division, operation of the transistor may be performed with very little power consumption. Since only the control gate capacitances are charged, there is little or no static power consumption as there is in prior resistive voltage division based devices.

In one embodiment, a normal MOS transistor is constructed. Instead of placing a second-level polysilicon electrode above an area of the floating gate, an opening in the oxide over the gate is constructed, extending through a passivation later all the way down to the floating gate. A thin layer of insulator is formed over the opening. On top of the insulator, a variety of thin films may be deposited to form a chemoreceptive control gate. The properties of the thin films determine a molecular/chemoreceptive property for the chemoreceptive control gate. Any CMOS technology may be used, as the chemoreceptive control gates are added using postprocessing steps following fabrication of the CMOS circuitry.

Each transistor can have any number of normal control gates and chemoreceptive control gates, and the molecular/ 15 chemoreceptive properties of each such gate is separately tailorable. In operation, the chemoreceptive control gates are exposed to a fluid, such as a liquid or gas. The molecules present in such fluid adhere to the various chemoreceptive control gates, and charged groups on the molecules capacitively induce a charge on the floating gate. In further embodiments, the chemoreceptive control gates are replaced with photoreceptive control gates, or other sensor control gates having sensors with the capability of modifying capacitance in response to a sensed condition.

FIG. 2 is a plan view of a CvMOS transistor used in a sensor configuration for detecting molecules/chemicals. A broken line 205 is used to identify a floating gate MOS transistor having an extended gate structure 210. The transistor comprise a standard gate 211, source, 212, drain 213, 30 and embedded floating gate structures 214, 215 for vMOS operations. Broken line 205 also represents a MOS window encapsulated from physical contamination. In one embodiment, the MOS transistor area has identical fabrication requirements with commercial Flash EEPROM.

The extended gate structure 210 is formed with three further extensions 217, 218, and 219 extending beyond broken line 205. An isolation area is formed at the end of each of the further extensions as indicated at 223, 224, and 225. In one embodiment, the isolation areas comprise nitride plugs. The nitride plugs serve as a dielectric between the further extensions, and corresponding fingers 227, 228 and 229. Each of the fingers is coated with a chemoreceptive layer 232, 233, and 234. The further extensions and corresponding fingers form electrodes of respective capacitors.

The fingers 227, 228, 229 are coupled to fluid by means of microfluidic channels 242, 243, and 244 to provide molecular and chemical samples in liquid or gas phase. The liquid phase involves the use of a buffer solution. The microfluidic channels deliver controlled sample molecules 50 250 with or without a buffer to the floating gate fingers with dielectric isolation and chemoreceptive coating that forms compact double layers (Helmholtz planes) with fluids. The channels may be independent for each finger, or may be coupled to form a chamber in one embodiment, such that 55 multiple fingers are coupled to the same chamber. The areas and wall characteristics of the floating gate fingers determines the response signature for sensing selectivity. In one embodiment, different subthreshold slopes are used for different chemoreceptive coatings.

Si diffused resistors **252**, **253**, and **254** are provided with contacts in the channels for providing a reference potential to the microfluidic channels. The resistors can be coupled to further circuitry for processing. The sensor can perform selectivity analysis at the chip level without resorting to A/D conversion and further digital processing, and hence can have low power operations.

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Further detail of finger 227 is shown in FIG. 3. The chemoreceptive layer 232 forms Helmholtz planes with the fluidic phase. Typical layers are receptive to polar gas, and liquids such as water and acetone. Many other types of layers are available and may be invented to be highly specific to other molecules/chemicals. Also more readily perceived in FIG. 3 is a thin dielectric isolation layer 310 disposed between the chemoreceptive layer 232 and the extended floating gate portion of finger 227. In one embodiment, this layer is approximately 2–6 nm thick, but may vary with different size sensors.

FIG. 4 shows an array 400 of sensors 410 used for detecting multiple different chemicals/molecules. In one embodiment, each sensor comprises multiple fingers coated with the same receptive layer. Different sensors are used to detect different chemicals/molecules or other physical manifestations, and some sensors may be redundant. The array includes a power supply 420, such as a solar cell(s), battery, or transformer for coupling to an independent power source. A controller 430 is formed to implement functions of receiving signals from the multiple sensors and processing them to identify what is sensed. The array further includes a transponder 450 coupled to the controller for communicating results to other devices for further analysis. In one 25 embodiment, the transponder comprises a RF or other electromagnetic based transponder. In further embodiments, the transponder comprises a modem, optical, or other electronic interface for communicating with other devices.

FIG. 5 shows an alternative chemoreceptive transistor 500. Transistor 500 comprises a source 510 and drain 515, and a gate 520 that modulates current flowing between the source and drain. Drain 515 is supported by a substrate 525. An extended floating gate 530 extends away from the drain 525.

In one embodiment, the extended floating gate **530** is formed of highly doped poly. A second highly doped poly layer **531** is separated from the first poly layer **530** by an inter-poly dielectric, such as an oxide **533**. Oxide **533** is formed by chemical vapor deposition (CVD) of SiO₂ in one embodiment to a thickness of approximately between 10 and 40 nm. Other thicknesses may also be used.

In one embodiment, second poly layer 531 is referred to as a sensing gate. It may be covered with an oxide, and selected portions of the sensing gate are then exposed through an oxide etch. The exposed areas are then coated with a chemoreceptive material 532, while control gate 520 is a normal vMOS control gate. They chemoreceptive material 532 may be formed as a layer by dipping the floating gate in a poly solution. The chemoreceptive material is selective in one embodiment, such that a targeted chemical will bond with the material, creating a charge on the material that is capacitively coupled to the extended floating gate 530, thus affecting current flow through the transistor 500.

channels may be independent for each finger, or may be coupled to form a chamber in one embodiment, such that multiple fingers are coupled to the same chamber. The areas and wall characteristics of the floating gate fingers determines the response signature for sensing selectivity. In one embodiment, different subthreshold slopes are used for different chemoreceptive coatings.

Si diffused resistors 252, 253, and 254 are provided with

In a further embodiment, a further poly coating is applied over the chemoreceptive material and is pattered with microfluidic channels. Such channels are patterned as desired to provide fluid to the chemoreceptive material. Examples of such channels are shown in FIGS. 2 and 6. The channels in one embodiment are about 400 um thick.

FIG. 6 illustrates channels around a CMOS chip 610 with transistor 500 formed thereon. A microfluidic channel 620 for controlled fluid delivery to transistor 500 is formed by bonding a patterned silicone elastomer layer 630 on top of CMOS chip **610**. The elastomer layer **630** obtains its pattern ⁵ from curing on a master silicon die with features made by DRIE (Dry Reactive Ion Etching) or other suitable technique. In one embodiment, the height of fluidic channels is about 150 μm. The MOS chip may use fabrication processes similar to those used for commercial Flash memories, and therefore the chemoreceptive transistor is readily compatible with the conventional CMOS integrated circuitry. The modular structure of the extended sensing area with elastomer encapsulation confines the sample fluid delivery in the $_{15}$ channel. It effectively eliminates possible contamination caused by the fluid to the gate oxide of the MOSFET.

Upon exposure of the extended floating gate polysilicon surface after the oxide etch on the sensing gates, four types of polymers are respectively used for the sensing-gate 20 coating, as listed in Table 1, to enhance selective responses and provide versatile comparisons with the uncoated polysilicon surface.

TABLE 1

A list of polymers and the corresponding molecular weight for sensing-gate surface coatings:			
Polymer Coating	Molecular Weight		
poly(vinyl acetate)	90,000		
poly(vinyl butyral)	100,000150,000		
poly(ethylene -co- vinyl acetate)	72:28 (wt.)		
poly(vinyl chloride)	110,000		

Coating solutions may be prepared at the room temperature. For poly(ethylene-co-vinyl acetate), 100 mg of the co-polymer is dissolved in 10 mL of benzene. For poly(vinyl acetate), poly(vinyl butyral), and poly(vinyl chloride), 20 mg of the polymer is dissolved in 10 mL of tetrahydrofuran (THF). After 10 to 15 minutes of mild agitation, the solution is visually inspected to ensure a proper mixture quality. The sensing area is then dipped into the solution to form a coating layer. After the solvent evaporates, a thin polymer layer is deposited on the sensing area. Other methods of applying the chemoreceptive layers may be utilized.

Two different sensing gates are used in one embodiment to facilitate comparison, as illustrated in FIG. 7. A first sensing gate, gate 1 at 710 is narrow, and has a sensing area of 4.8×356.8 µm and a second sensing gate 2 at 720 is wide, and has a sensing area of 76.8×356.8 µm in one embodiment. The polysilicon of the sensing gate is electrically isolated from the polysilicon of the extended floating gate by an inter-poly oxide of about 58 nm as illustrated at 535 in FIG. 5 to create a parallel-plate capacitance. A gate oxide of the n-channel MOSFET is about 30 nm. In one embodiment, EEPROMs indicated at 730 and 740 are fabricated with the MOSFETs to record channel responses for later reading.

The individual thickness and roughness of example polymer coatings may be measured with a stylus-based surface profiler and are listed in Table 2. The arithmetical-mean roughness (Ra) and root-mean-square roughness (Rq) are 65 calculated over about $100 \, \mu m$ on the wide sensing gate. Both Ra and Rq for the bare polysilicon surface are about 1 nm.

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TABLE 2

The data of thickness and arithmetical mean roughness (Ra)

Polymer Coating		Roughness	
	Thickness (nm)	Ra (nm)	Rq (nm)
poly(vinyl acetate)	50	64	88
poly(vinyl butyral)	25	20	27
poly(ethylene -co- vinyl	30	2	2
acetate) poly(vinyl chloride)	30	8	13

Fluid provided by the channels interacts with the chemoreceptive surface through the formation of the electrical double layer at the solid-liquid interface. The capacitive load and static charges introduced onto the floating gate cause specific changes in both subthreshold slopes (S) and threshold voltages (V_t). Normalization may be used to eliminate parasitic deviations between devices. Measurements taken by measuring responses in deionized water or other desired fluids may be used to obtain information used to normalize the responses.

To rapidly extract the information encoded in the form of subthreshold-slope variations on the sensing gates of the chemically receptive MOS (CvMOS) transistor, a simple circuit 800 of common-source amplification is used in one embodiment as shown in FIG. 8. An input signal V_m 810 feeds into a gate 815 of a PMOS transistor 820, and is composed of a DC bias and an AC signal. The load of this common-source amplifier is the CvMOS transistor. Block 830 comprises a peak detector for the output signal, and circuits for feedback control.

The extended floating-gate structure capacitively monitors solid-liquid interaction at the sensing area, and also enables EEPROM electron tunneling operations, which provide additional degrees of freedom for the sensing mechanism. Comparisons of subthreshold-slope responses between the bare polysilicon surface and four different types of polymer coatings on the sensing gates indicate the selectivity of such devices can be significantly enhanced through a sensory array with versatile surface coatings, along with the charge control in the floating gate through electrontunneling operations. Through the high transconductance gain of the MOS transistors, a high sensitivity can be derived, and the extraction of measured data can be realized by straightforward common-source amplifier circuitry.

I–V characteristics of the structure allow further utilization of specific adsorption to collect digitized information from multiple sensing gates. The multiple-input sensing structure may substantially reduce the need for digital-to-analog conversion (DAC) and digital signal-processing circuitry, and hence reduce the power consumption normally required for such sensor applications. Many different chemoreceptive materials may be used for specific-adsorption purposes. The thickness of such materials may be varied to provide different characteristics.

The invention claimed is:

- 1. A sensor comprising:
- a field effect transistor having a source, drain and floating gate, wherein the floating gate has an extended portion; a finger electrostatically coupled to the floating gate; 5 and
- a chemoreceptive layer coupled to the finger.
- 2. A sensor comprising:
- a field effect transistor having a source, drain and floating gate, wherein the floating gate has an extended portion; 10 and
- multiple chemoreceptive layers electrostatically coupled to the extended portion of the floating gate.
- 3. The sensor of claim 1 wherein the chemoreceptive layer is electrically isolated from the extended portion of the 15 floating gate.
- **4**. The sensor of claim **3** wherein the electrical isolation is provided by a nitride plug.
 - 5. A sensor comprising:
 - a field effect transistor having a source, drain and floating 20 gate, wherein the floating gate has an extended portion; and
 - multiple fingers capacitively coupled to the extended portion of the floating gate.
- **6.** The sensor of claim **5** wherein some of the fingers 25 comprise chemoreceptive layers capacitively coupled to the floating gate.
- 7. The sensor of claim 6 wherein a floating gate voltage is a weighted sum of voltages on the fingers.
- **8**. The sensor of claim **7** wherein the weight on each 30 control gate is directly proportional to the finger's capacitance, and is normalized by the total capacitance of the floating gate.

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- **9**. The sensor of claim **6** wherein the chemoreceptive fingers comprise a conductor and a film having chemoreceptive properties.
- 10. The sensor of claim 9 wherein the chemoreceptive fingers further comprises a dielectric isolator between the conductor and the chemoreceptive film.
 - 11. A method of sensing comprising:
 - providing a sample to multiple selectively receptive fingers to create a charge on the fingers;
 - inducing a voltage on a floating gate capacitively coupled to the fingers as a function of the charge on the fingers; and
 - modulating current through a source and drain based on the induced voltage on the floating gate.
 - 12. A sensor comprising:
 - a field effect transistor having a source, drain and floating gate, wherein the floating gate has an extended portion;
 - a finger supported by the extended portion of the floating gate;
 - a dielectric layer disposed between the extended portion of the floating gate and the finger; and
 - a chemoreceptive layer supported by the finger.
- 13. The sensor of claim 12 and further comprising a microfluidic channel formed proximate the chemoreceptive layer that selectively provides fluid to the chemoreceptive layer.

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