

## Formation of Molecular Templates for Fabricating On-Chip Biosensing Devices

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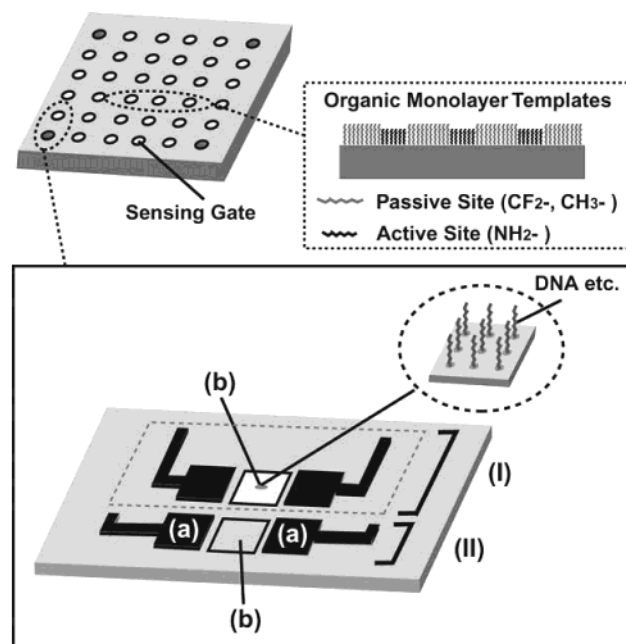
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Formation of organosilane monolayers having various functional groups on silicon oxide surfaces for fabricating on-chip biosensing devices was investigated. Alkyl and perfluoro-alkyl functionalized monolayers were prepared by a chemical vapor deposition, and amino functionalized monolayers were formed by a liquid phase reaction. Each monolayer was confirmed to be closely packed and composed of single moiety species. A molecular patterning process using these organic monolayers was performed. The monolayer patterns were uniformly formed on the substrate by using ultraviolet light patterning and oxygen plasma ashing processes. The pH responsibility at the liquid/modified electrode interface was examined by using capacitor profiles of the structure of monolayer/silicon oxide/silicon. The amino modified surface showed good pH sensitivity of  $-44$  mV/pH. This value was similar to that of the silicon nitride surface. On the other hand, the potential was not changed in any pH solutions in the case of the alkyl and perfluoro-alkyl monolayer-modified surface. It was demonstrated that the pH response of these surfaces was greatly affected by the variation of the functional group. Furthermore, by using the patterned monolayers, fabrication of a multichannel electrode for multiple detection of pH response was achieved.

## 1. Introduction

Biosensing systems, such as enzyme, immuno sensors, and DNA micro arrays, are widely used in the field of medical care and medicine manufacturing.<sup>1–3</sup> In particular, recent progress in genome engineering requires a high performance integrated micro-multi biosensing system, which can be utilized for the recognition of a individual biomolecule and the analysis of bioreactions at the single molecular level. To realize a highly sensitive biosensing system, precise fabrication of the electrode parts for molecular recognition is a significant issue. For this, the development of new detection devices with high sensitivity is strongly demanded. Especially, it is desired that the electrode surfaces have the supermolecular structure that mimics cell systems. To fabricate such an electrode, application of the template for the ordered-arrangement of the molecules is effective. Organic monolayers have self-assemble ability onto the surfaces;<sup>4,5</sup> the monolayer-modified electrode is suitable as the template for orderly immobilization of biomolecules. On the other hand, it is preferable that the detection system can detect the signal immediately and with a high sensitivity. A field-effect transistor type electrode can directly detect surface reactions as an electric signal, with the capability for the on-chip integration. In the present work, we have studied the formation of a functionalized organic monolayer modified electrode on silicon wafer surfaces and the development of the detection system utilizing semiconductor device such as a field effect transistor.

Figure 1 shows the basic design of the on-chip integrated biosensing devices including reference devices. To fabricate these devices, it is required that the organic monolayer having a different functional group is position selectively formed on



**Figure 1.** Schematic design of on-chip integrated micro-multi biosensing device. (a) source and drain electrode, (b) gate electrode. (I) shows sensing FET that have amino-monolayer modified gate electrode as a recognition and detection site. (II) shows reference FET that have alkyl- or perfluoroalkyl-monolayer modified gate electrode.

each gate electrode. At the sensing electrode, the amino functionalized monolayer is suitable for immobilization of DNA, enzyme, etc. For the reference electrode, an alkyl or perfluoro-alkyl functionalized monolayer is effective. Hence, the formation of various functionalized monolayers and their patterning are one of the key processes for fabrication on-chip biosensing

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devices. It is assumed that such an on-chip sensing device has the ability that the single molecule can be accurately detected.

Especially, formation of very thin monolayers onto the electrode enables immediate detection of the signal that originates in the bioreaction. Moreover, it seems that effective arrangements of molecules to the bioreaction onto the electrodes is acquired by using the monolayer templates. The multidetection of the molecule is expected to be achieved, for this device is easy to miniaturize and to integrate.

Organosilane self-assembled monolayers (SAMs) have been widely applied to control physical and chemical properties of the surfaces of glass, quartz, SiO<sub>2</sub>/Si wafers, and silica particles.<sup>4</sup> Many researchers have studied the formation process of the organosilane monolayers and synthesis of the silanization reaction in hydrocarbon solvents such as toluene, bicyclohexyl, hexadecane, etc.<sup>4</sup> In some cases of the liquid phase modification, microdefects often exist at the modified surface because the SAM formation is thought to involve self-assembly of monomer or small oligomer units on the surface in a noncovalent manner to give well-ordered monolayer domains or islands on the surface surrounded by bare substrate.<sup>6–9</sup> Such silane formation on the silica surface shows that island formation occurs leading to a multilayer.<sup>10</sup> Hence, to achieve complete modification, precise control of the modification procedure is required. On the other hand, more recently, the monolayer modification process by a quite simple method using a gas-phase silanization reaction, that is a chemical vapor deposition (CVD) method, was proposed by Sugimura et al. for application to ultrahigh-resolution patterning resists and patterned monolayer templates.<sup>11–17</sup> This method has proved to have the capability of forming a homogeneous, defect free monolayer coating onto the surfaces,<sup>11–14</sup> which is believed to be suitable for our objectives.

In the present work, we investigate the formation of organosilane monolayers having various functional groups on silicon oxide surfaces using this process and the development of a molecular patterning process using an organic monolayer. In addition, the pH response at the liquid/electrode interface was investigated in order to confirm the characteristics of these surfaces in each solution. Moreover, by applying the molecular patterned substrate, we attempted to fabricate the multichannel electrode for multiple detection of the pH response.

## 2. Experimental Section

**Monolayer Preparation.** N-type Si(100) wafers (8–12  $\Omega$  cm) covered with thermally grown silicon oxide (ca. 30 nm) were used for the present work. The silicon oxide film was formed at 950 °C in an N<sub>2</sub> atmosphere. The backside of the wafers was selectively coated with Ti (20 nm)/Pt (80 nm) to form an electric contact. Metal coating was performed by using an electron-beam evaporator at a pressure of under  $8 \times 10^{-6}$  Pa. The wafers were treated with SPM (96% H<sub>2</sub>SO<sub>4</sub>: 30% H<sub>2</sub>O<sub>2</sub> = 4:1) at 120 °C followed by rinsing with 18 M $\Omega$  cm deionized (DI) water. In this experiment, three types of organosilanes, that is, octadecyltrimethoxysilane (ODMS, 97%, Gelest Inc.), (heptadeca-fluoro-1,1,2,2-tetrahydro-decyl)trimethoxysilane (FAS, 97%, Gelest Inc.), and 3-aminopropyltriethoxysilane (APS, 97%, Aldrich Inc.), were used as precursors. The wafers were placed together with a glass cup filled with 0.2 cm<sup>3</sup> of organosilane (ODMS or FAS) liquid into a 20 cm<sup>3</sup> Teflon vial. The vial was sealed with a cap and then heated for 5 h in an oven at a constant temperature of 110 °C<sup>11–14</sup> for 8 h. In the case of APS, the wafers were immersed in dehydrated toluene solvent including 1 vol % APS liquid at 60 °C for 7

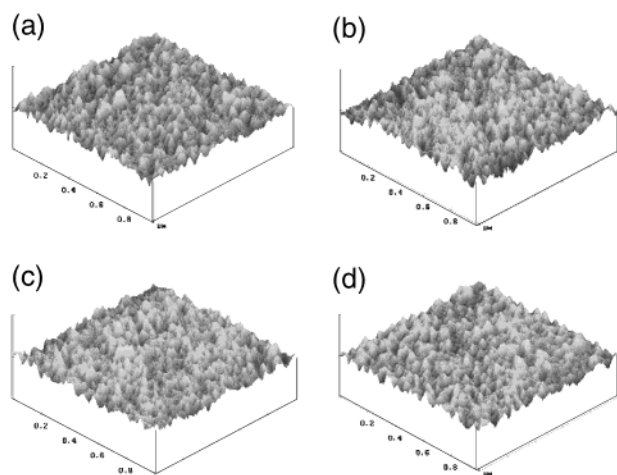
min<sup>18</sup> since the formation of the APS monolayer was found to proceed easily in the liquid phase, rather than the gas phase. It has been reported that the complete monolayers using these modification procedures.<sup>11–14,18</sup> All of the monolayer preparations were performed in the dry room of –80 °C in dew point.

**Molecular Patterning Processes.** A position selective formation of monolayers having different functional group onto the substrate at microscale was performed by using the photolithography process. The alkyl or perfluoro-alkyl monolayer modified substrate was covered with conventional photoresist (Tokyo Ohka Kogyo Ltd., OFPR-800 500 cP), and then patterning was carried out with a 350 nm UV lamp (Mikasa Ltd., MA-10). This patterned substrate is exposed with oxygen plasma (Technics Ltd., GIGA-ERCH 100-H) at the condition of the input power of 200 W and the oxygen flow rate of 80 sccm for removal of monolayer. The resist pattern is used for the mask for plasma ashing. After the plasma ashing process, the photoresist was removed by acetone and treated with a trichloroethylene–toluene mixture solution, and then, the amino silane monolayer was formed on the exposed clean oxide layer.

**Characterization.** Ellipsometric measurements were performed with a Gardner variable angle ellipsometer (Gardner Ltd., LB125B) using a helium–neon laser at an incident angle of 70°. The monolayer thickness was calculated using an index of refraction of 1.46 for the silicon oxide. Atomic force microscope (AFM) images were obtained under a near-contact condition at low tip pressure using the Digital Instruments Nanoscope IIIa AFM in contact mode with a silicon nitride cantilever. X-ray photoelectron spectra were obtained on a XPS spectrometer (JEOL Ltd., JPS-9000 MX) equipped with an Al K $\alpha$  source, a monochromator, a concentric hemispherical analyzer, and a multichannel detector. A takeoff angle of 15° from the surface was used. Spectra of C(1s) (280–296 eV binding energy), Si(2p) (95–110 eV binding energy) were recorded. The potential–current profiles were measured using a light addressable potentiometric sensor (LAPS; Huso Ltd., HECS-9058 LAPS Meter). Electrochemical measurements were made in a cell in which a bored cone of Teflon was pressed down against the sample. Ohmic contacts were made between the back of the silicon coated by Ti/Pt and a steel plate, which was connected to the working electrode connection of a potentiostat. Platinum counter and Ag/AgCl reference electrodes were used for the measurement. Linear sweep voltammetry was performed under irradiation with 644 nm pulsed LED at 12.5 kHz from the backside of silicon in the dark condition at 25 °C. The output shows capacitor profiles, that is potential–photocurrent profiles, depending on the structure of monolayer/silicon oxide/silicon. The solutions were used for conventional standard pH buffer solutions (pH 4.01, 6.86, and 9.18), and a (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + (H<sub>2</sub>SO<sub>4</sub> or NH<sub>3</sub>) buffer solution (pH 5.50 and 8.00) was used for these measurements.

## 3. Results and Discussion

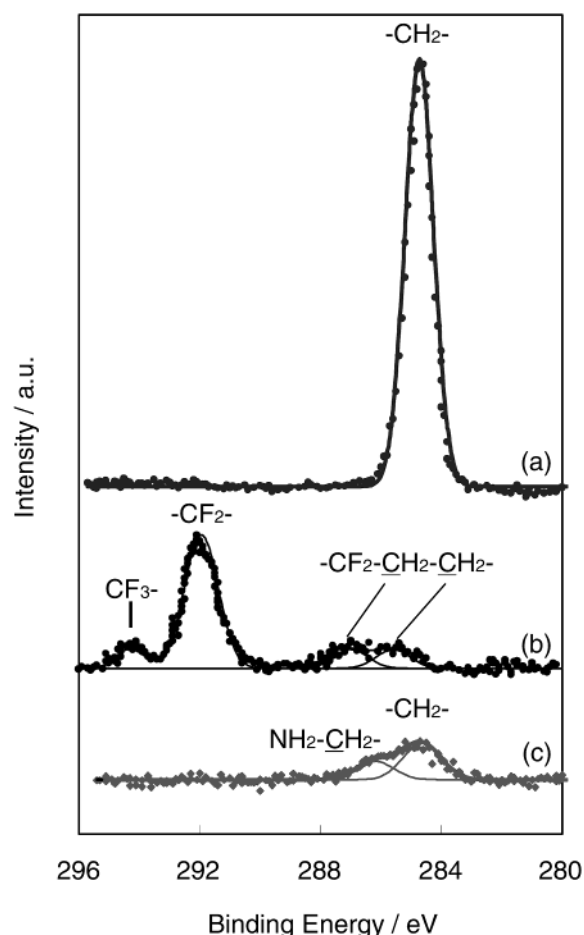
**A. Modification of Organosilane Monolayer on SiO<sub>2</sub>/Si Substrate.** The thickness of each organosilane monolayer was estimated to be 20 (ODMS), 13 (FAS), and 6 Å (APS), respectively. The water-contact angles of these monolayer covered SiO<sub>2</sub>/Si substrates were 105° (ODMS), 120° (FAS), and 60° (APS), respectively. These values correspond to those in previous reports.<sup>11–13,18,19</sup> Figure 2 shows contact mode AFM images of the modified surfaces measured under a near-contact condition at low tip pressure. The RMS and Ra values for each modified surface are indicated to be similar to those of the bare silicon oxide surface. Also we have checked these modified



**Figure 2.** Contact mode AFM images of organosilane modified  $\text{SiO}_2$  surfaces. (a)  $\text{SiO}_2$ , (b) APS modified surface, (c) FAS modified surface, (d) ODMS modified surface. Scan area  $1 \mu\text{m} \times 1 \mu\text{m}$ , z scale from 0 to 2 nm. RMS and Ra values for the surfaces were (a) 0.138, 0.112; (b) 0.141, 0.112; (c) 0.145, 0.116; and (d) 0.130 nm, 0.103 nm, respectively.

surfaces by using a lateral force microscope (LFM). It was confirmed that the LFM images for the monolayer surfaces were flat and homogeneous, without detecting any local deviation in the friction force even on the nanometer scale. If any micro-defects, which indicated the exposed silicon oxide regions, existed at the monolayer surface, the change in contrast must be observed due to the change in the frictional force between chip surfaces caused by the difference of the hydrophobicity of silicon oxide and the modified surface. This result was similar to that reported by Sugimura et al.<sup>11–13</sup> Therefore, it is suggested that the modified surfaces are flat and uniformly formed at the monolayer level.

Chemical properties of the modified surface were characterized by XPS. Figure 3 shows the carbon (1s) narrow spectra of the modified surfaces. For the spectrum of the ODMS modified surface, a single peak at 284.7 eV originating in  $\text{CH}_2$  bonds is observed. For the FAS modified surface, the spectrum can be deconvoluted into four components; 285.5 (10%), 287.0 (10%), 291.8 (70%), and 294.1 eV (9.8%), which were assigned as  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CF}_2-$ ,  $-\text{CF}_2\text{CF}_2-$ , and  $-\text{CF}_2\text{CF}_3$ , respectively. For the APS modified surface, the spectrum can be deconvoluted into two components, 284.7 eV (68%) and 286.1 eV (32%), which were assigned as  $-\text{CH}_2\text{CH}_2-$ , and  $-\text{CH}_2\text{NH}_2$ , respectively. These ratios of carbon (1s) peaks in the modified surface show reasonable correlation to those of each fragment of the moiety. On the other hand, to quantitatively compare the amount of carbon, fluoride, and nitrogen, we used the integrated peak areas of the carbon (1s), fluoride (1s), and nitrogen (1s) XPS narrow scans and accounted for the differences in atomic sensitivity. Since it was assumed that the FAS modified surface was composed of perfluoro-alkyl chain moieties, the 17 fluoride atoms and 10 carbon atoms were included in a single moiety. Similarly, for the APS modified surface, the numbers of nitrogen and carbon atoms were 3 and 1, respectively. The ratio of the integrated peak areas of the fluoride (1s) and carbon (1s) XPS narrow scans for the FAS modified surface was estimated to be 1.71, and the ratio of nitrogen (1s) and carbon for the APS modified surface was 2.91. These data indicate that the surfaces were composed of single moiety species, either FAS or APS, respectively. Hence, it is considered that each silane molecule is attached onto the surface without accompanying the co-reaction, and no impurities exist on the surface.



**Figure 3.** X-ray photoelectron spectra in the C1s region of organosilane modified  $\text{SiO}_2$  surface. (a) ODMS modified surface, (b) FAS modified surface, and (c) APS modified surface.

**TABLE 1: Coverage for Each Monolayer and Molecular Length of Each Moiety**

	C/Si	adsorbate areal density/ $\text{SiO}_2$	adsorbate areal density/ maximum	molecular length/ $\text{\AA}$	
		areal density	areal density	expt	calc
ODMS	1.10	0.85	1.02	26.0	25.5
FAS	0.39	0.58	1.02	15.9	15.6
APS	0.22	0.81	1.01	6.8	6.7

The coverage of the modified surface is calculated by using the integrated peak areas of the carbon (1s) and silicon (2p) XPS narrow scans. Table 1 lists the ratio of organic adsorbates per all reaction sites of the ideal quartz surface and the areal density of the adsorbate to maximum areal density.<sup>20,21</sup> The maximum areal densities were adapted to the value of the cross-sectional area of each molecule, which are 18.0 (ODMS), 27.5 (FAS), and 20.0  $\text{\AA}^2$  (APS), respectively. The areal density of the ideal quartz surface is  $(15.7 \text{\AA}^2)^{-1}$ . The areal density of the adsorbate to the maximum areal density became the effective coverage. The areal density of each modified surface indicates nearly 1.0. Moreover, we estimate the molecular length of each moiety from the integrated peak areas of the carbon and silicon. These experimental data show expected values compared with the calculated one (Table 1). Based on these XPS characterizations, it is considered that each modified surface is closely packed and is composed of a single moiety species. In addition, as described above, the modified surfaces were indicated to be

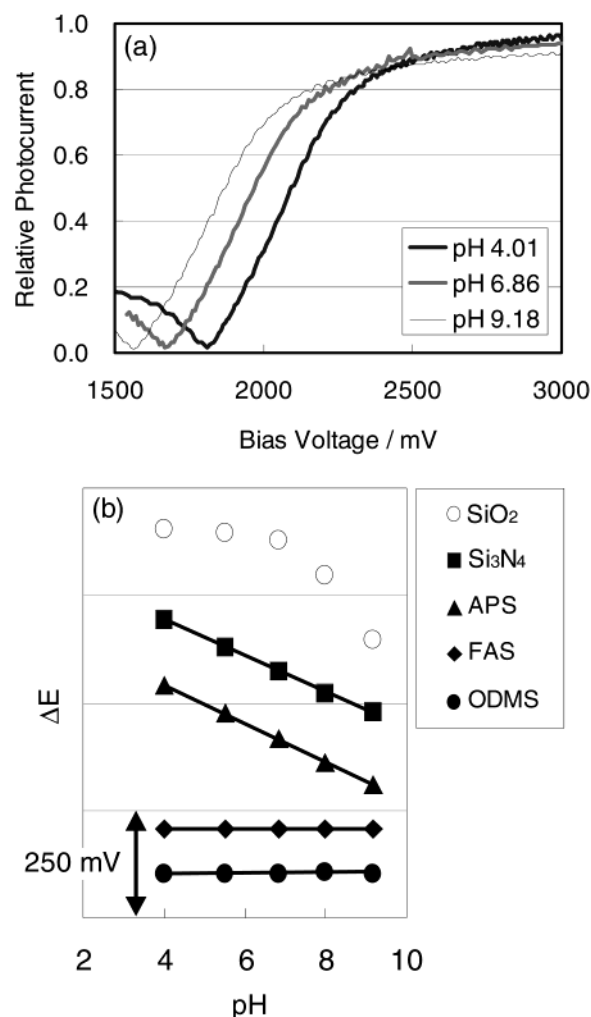


flat and homogeneous from the AFM investigation. Therefore, each modified surface was expected to be formed as a monolayer.

**B. pH Responsibility at the Liquid/Monolayer Modified Electrode Surface.** To apply these monolayer-modified surfaces having different functional groups to the on chip biosensing devices, it is significant to understand their behavior in each solution. We investigate the pH responsibility at the liquid/modified electrode interface to characterize the electrode in solution.

The pH responsibility is estimated from capacitance profiles of the substrates. Linear sweep voltammetry was performed using the substrate consisting of the monolayer/silicon oxide/silicon structure under the irradiation of an infrared pulsed diode. This measurement was based on the photoeffect in silicon; when a pulsed infrared light was irradiated to the silicon substrate having field-effect structures such as metal/insulator/semiconductor structures or electrolyte/insulator/semiconductor structures, the space charge region in the semiconductor was inversed depending on the degree of the modulation frequency. As a consequence, a modulation of the light intensity would lead to an ac current of the modulation frequency. The dependence of this photocurrent on the external voltage was shown as a capacitor profile.<sup>22–26</sup> As the operation check of this light addressable potentiometric measurement, the bias voltage–photocurrent profiles are measured using test substrates that have a silicon nitride/silicon oxide/silicon structure. Since it is well-known that the silicon nitride surface shows good pH response in solution, this film was deposited onto the silicon oxide/silicon substrate by plasma enhanced chemical vapor deposition (PECVD) at the thickness of 200 nm. The I–V profiles of the silicon nitride/silicon oxide/silicon substrate indicate the typical capacitor-like profiles. Moreover, the threshold voltage is shifted in each pH solution (Figure 4a). When these values are plotted versus pH, it is confirmed that the potential is linearly changed toward pH at the sensitivity of  $-44$  mV/pH (Figure 4b). The shift of threshold voltage depends on the changes of the surface potential at the liquid/silicon nitride interface. The silicon nitride surface was immersed in aqueous solution; hydrolysis produces both amphoteric Si–OH sites and basic Si–NH<sub>2</sub> sites. These sites directly interacted with the solution to either bind or release hydrogen ions, which created a charge on the nitride surface that was opposed by an ionic charge in the solution. This formed a double layer capacitance across which the potential drop occurs. Therefore, the threshold voltage is shifted accompanied with the pH change in solution.

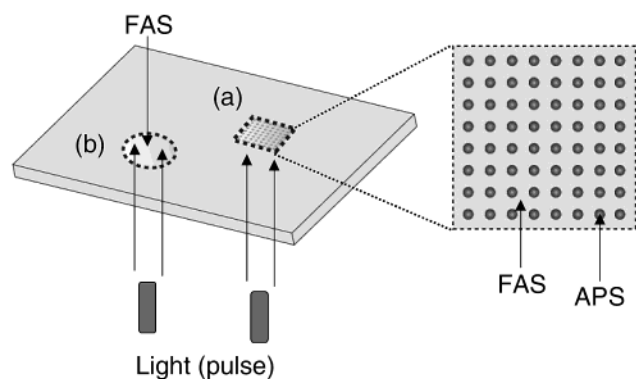
Then, the capacitance profiles of each monolayer-modified substrate are also analyzed by the LAPS system. Figure 4b shows the pH-potential profiles of each monolayer-modified surface. The APS modified surface shows a good pH sensitivity of  $-44$  mV/pH, which is quite similar to that of the silicon nitride coated surface. On the other hand, for the ODMS and FAS modified surface, the potential is not changed in each pH solutions. Such a difference in pH response at each modified surface can be considered below; for the APS modified surface, unreacted Si–OH and modified O–Si–(CH<sub>2</sub>)<sub>3</sub>–NH<sub>2</sub> sites exist at the surface in the ratio of 0.19:0.81 as was shown in Table 1. At the surface, a hydrophobic interaction between each moiety is weak, because the aminopropyl moieties are short chain. The structure of the modified surface becomes slightly disordered. Therefore, the Si–OH and Si–(CH<sub>2</sub>)<sub>3</sub>–NH<sub>2</sub> sites at the modified surface are expected to directly interact with the solution to either bind or release hydrogen ions. Thus, it was considered that the APS modified surface shows pH response in solution.



**Figure 4.** (a) Capacitor profiles of silicon nitride/silicon oxide/silicon electrode in each pH solutions. (b) pH-potential profiles of each monolayer modified electrode.

For the ODMS or FAS modified surface, the unreacted Si–OH sites also exist at the surface; however, each moiety (Si–(CH<sub>2</sub>)<sub>17</sub>–CH<sub>3</sub>, Si–(CH<sub>2</sub>)<sub>2</sub>–(CF<sub>2</sub>)<sub>7</sub>–CF<sub>3</sub>) is long chain and hydrophobic, resulting in a well ordered and highly hydrophobic surface. Hozumi et al. have demonstrated that the  $\zeta$ -potentials of ODMS– and FAS–SAMs formed on the SiO<sub>2</sub>/Si substrate by the CVD method, that is our modification method, were as good as those of polyethylene and poly(tetrafluoroethylene) plates.<sup>15</sup> The result indicates that both the ODMS– and FAS–SAMs are concluded to have covered their substrate almost completely.<sup>15</sup> These surfaces are likely to inhibit the reaction of the unreacted Si–OH sites with ionic species in the solution. Since the closely packed long chain alkyl monolayer modified surface blocks the solution, it is expected that the pH response mainly depends on the end functional group of the moiety and the length of alkyl chains. CH<sub>3</sub>– and a CF<sub>3</sub>– functional groups are known to be inactive with ionic species; therefore, these surfaces do not show the pH response in the solution.

As described, it is demonstrated that the pH response of these surfaces greatly changes by a variation in functional group. The APS modified surface has the capability of being used as an electrode for ion sensitive FET, whereas ODMS and FAS surfaces are applicable to an electrode for reference FET. It is expected that the fabrication of such a molecular template is effective for fabricating an on-chip device including reference electrodes.



**Figure 5.** Schematic design of experimental setup for multiple detection of pH response using multichannel electrode composed of patterned monolayer with different functional groups. (a) APS pattern site; array of the dots with 30  $\mu\text{m}$  in diameter. (b) FAS site.

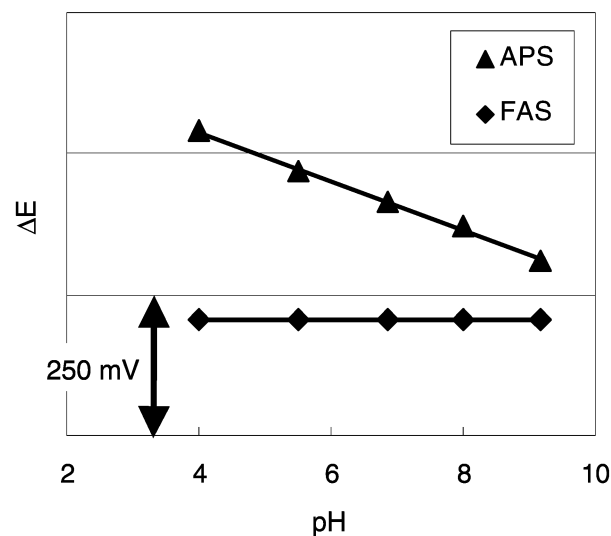
**C. Multiple Detection of pH Response Using the Molecular Patterned Substrate.** The multiple detection of pH response by the multichannel electrode was attempted using the organic monolayer modified substrate. We perform a position selective formation of monolayers having different functional groups onto the substrate in the microscopic scale.

In this experiment, the following molecular patterned substrate was fabricated, as is schematically seen in Figure 5. A FAS monolayer is formed onto the whole surface, and then the APS monolayer position is selectively formed at only the (a) site. The APS pattern was the array of dots with 30  $\mu\text{m}$  in diameter. As mentioned in section B, the pH response could be controlled by a variation of the functional group of the monolayer. It is expected that different pH responses can be measured at the same time by position selective formation of the active and passive sites for pH response on the same substrate. In other words, it is considered that on-chip multiple pH detection becomes possible by using the monolayer patterned substrate including the reference site which shows inactive for pH response. For example, APS was an active monolayer that shows good pH responsibility, and FAS was an inactive monolayer that shows an always-constant potential in each pH solutions. Then, by applying a substrate selectively patterned with a monolayer with different functional groups, the multiple detection of pH response is performed. The measurement was carried out using two diodes that were arranged on the backside of the (a) and (b) site.

As is seen in Figure 6, it is observed that the threshold voltage is shifted depend on pH at the APS patterned site, whereas the voltage is not changed regardless of the change in pH at the FAS site. This result is expected from that for the bare surface shown in Figure 4b. Therefore, on-chip multiple pH detection is achieved using the monolayer patterned substrate. It is indicated that this monolayer-patterned substrate is applicable to the template for the molecular recognition site on the integrated biosensing devices.

#### 4. Conclusion

Various functionalized organosilane monolayers were formed on a  $\text{SiO}_2/\text{Si}$  substrate by a quite simple method, which were proved to be composed of closely packed single moiety. Then, the pH response of these monolayer-modified electrodes was measured. It was clarified that the difference in the response was due to the variation in functional group of monolayer. Based on these results, on-chip multiple detection of the pH response by applying a molecular patterned substrate was performed, successfully achieving the multiple detections. From these



**Figure 6.** pH-potential profiles of pH response multichannel electrode. APS plots show the response of patterned APS site.

results, it is expected that the APS modified surface has the capability of being used as an electrode for ion sensitive FET, whereas ODMS and FAS surfaces are applicable to an electrode for reference FET. Furthermore, by using these organic layer modified electrodes, novel-sensing devices that are highly sensitive and precisely controllable could be developed.

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