Surface Conductivity in Methyl-monolayer/Si Heterojunction Structure in the Presence of Water

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The heterojunction between Si(111) semiconductor and the well-ordered methyl monolayer was formed to investigate the channel conduction at the surface in the heterojunction structure. With the presence of water, the methyl monolayer/Si heterojunction structure showed switching action with a high tranceconductance of 2.8×10^{-3} A/V under the application of bias voltage, while without the presence of water, such a switching behavior was not observed. The methyl monolayer/Si heterojunction structure worked as a p-type mode with the presence of water at the modified surface.

Molecular devices are very promising for various future applications. One of the components of molecular device is organic monolayers. While there are many reports on surface modification of SiO_2 or metal with monolayers,[1,2] more interesting approach on direct modification on Si has been highly required for the formation of semiconductive layers that enable a molecular transistor action. We focus on short-chain alkyl reagents to form a well-ordered alkylated Si surface to create a possibility of molecular transistor.[3,4] In our previous study,[4] a well-defined and closely-packed methyl-modified Si(111) surface was successfully produced. The stability of the modified surface was also evaluated,[4] and moreover, the methyl modified Si showed a higher conductivity than that of the bare H-terminated surface in an aqueous solution. Since the methyl adlayer-attached Si surface can be expected to behave as a conductive layer under the applied bias voltage, the high surface conductivity in the methyl monolayer/Si heterojunction structure is a very unique phenomenon, especially in the presence of water. Based on our previous results, in the present work, we investigate the channel conduction in the methyl monolayer/Si heterojunction structure, which is a promising candidate for fabricating the future molecular transistor.

H-terminated n-type Si(111) wafer (3–8 Ω cm, 625-μm thick) was used as a starting substrate. The methyl monolayer on Si was formed through the reaction between Grignard reagent and Cl-terminated surface.[3–5] Al (200-nm thick) was evaporated on the methyl monolayer modified Si(111) and on the back side of the substrate to make electrical contacts. The evaporation was performed under the pressure of 2.0×10^{-5} Pa and the rate of 0.16 nm/s to avoid a damage of the methyl monolayer. A photoresist as a passive layer to make an insulation between electrodes and water layer was covered the entire surface. Then a specific area (2.0×2.0 mm square) of the photoresist was removed by successive steps for the irradiation of ultraviolet light ($\lambda = 365$ nm) and for the development using tetramethylammonium hydroxide solution. The length of the passive layer between the patterned pore and each of the source and the drain electrodes was 0.50 mm. The channel length and width were 3.0 and 2.0 mm, respectively.

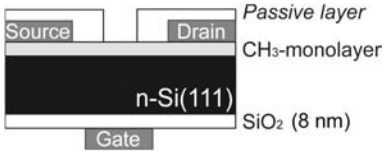

Figure 1. Schematic illustration of the structure of the transistor-like device with the methyl monolayer/silicon heterojunction structure.

In order to clarify the channel conductivity in the methyl monolayer/Si heterojunction structure in the presence of water at the surface, we fabricated a transistor-like structure illustrated in Figure 1. A droplet of ultra-pure water was placed on a patterned region of the methyl monolayer, prior to the electrical measurement. The measurements were started after 5 min from time when water was dropped on the device. As shown in Figures 2a and 2b, the current (I)–voltage (V) characteristics of the device demonstrate a switching action controlled by the gate voltage (V_g). The threshold voltage is approximately 0.05 V. It should be emphasized that the channel modulation characteristics is very steep within the range of V_g from 0 to 0.4 V. The transconductance (g_m) of the device is estimated to be 2.8×10^{-3} A/V. In addition, the drain current is saturated by the application of V_g higher than 0.4 V. Note that these characteristics were quite reproducible even after the measurements were repeated over 10 times. For a typical transistor, the drain current generally increases with the applied gate bias, since a channel region is induced into the *n*-Si substrate by the application of V_g. In the present case, the channel region is not expanded by the applied gate bias during the device operation; therefore, only the methyl monolayer modified surface is assumed to behave similarly to an effective channel layer, and high transconductance is assumed to be caused by the extreme thickness of the methyl monolayer.

To confirm whether the monolayer/Si heterojunction structure contributes well to such a switching action, we investigated the electric characteristics of the device without methyl monolayer that had direct contact between Al and Si. The I–V characteristics of the device indicate that I_d increase linearly with an increase in V_d (Figure 2c). In addition, no channeling is observed. From these results, the switching action was proved to be induced from the heterojunction structure formed between a semiconductor and a monolayer of methyl molecule with the presence of water.

The characteristics of the device were also investigated under humid air (humidity: 50%), as well as under dry ambient (Ar

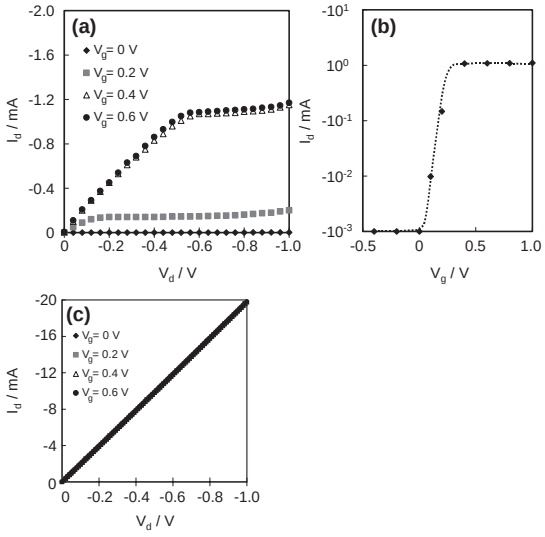

Figure 2. (a) I_d–V_d characteristics of the device with methyl monolayer/silicon heterojunction structure. (b) I_d–V_g characteristics. [I_d at $V_d = -0.6$ V plotted as a function of V_g] (c) I_d–V_d characteristics of the device without methyl monolayer.

atmosphere) by using the device shown in Figure 1. When the device was operated under the humid air, I–V characteristics with effective transistor responses were obtained (Figure 3a). In this case, the threshold voltage and the g_m were approximately 0.05 V and 3.0×10^{-4} A/V, respectively. On the other hand, the I–V characteristics of the device, measured under dry condition are shown in Figure 3b, showing different results with those for humid condition. Under those conditions there was no channel modulation due to the application of the gate bias. In this case, the g_m of the device shows a low value of 4.0×10^{-8} A/V.

From these results, the effective channeling in the methyl monolayer/Si heterojunction structure is considered to be induced by water or moisture on the surface. The surface conduction properties of the heterojunction structure seems to behave similarly to those of H-terminated diamond.[6–8] It is known that H-terminated diamond acts as a thin p-type conductive layer in moist air or in water, and also behaves as an insulating layer in dry condition. For the conductivity of the diamond, it has been suggested that adsorption of both hydrogen and atmospheric adsorbates at the surface are necessary, because a [$H_3O^+/(H_2O + H_2)$] redox reaction in an adsorbed water layer on H-terminated diamond provides the electron sink for the subsurface hole accumulation layer.[6,7]

Based on the knowledge for the diamond surfaces, we discuss on the conduction mode of channeling layer induced by the heterojunction structure. The characteristics of the device in the present work could be regarded as that of a junction field effect transistor. The bottom of Si substrate is polarized negatively, that is, electrons tend to concentrate to the bottom region, by charging the Si dioxide layer with applying the positive V_g. At the same time, electrons tend to lack slightly at the top of Si surface. If the channeling takes place, the conduction mode can be expected to be p-type. However, it is expected that channel modulation is difficult to achieve only by such a degree of the dielectric. Indeed, the device without methyl monolayer does not show switching behavior. It is assumed that the switching behavior of the device having the heterojunction structure is induced

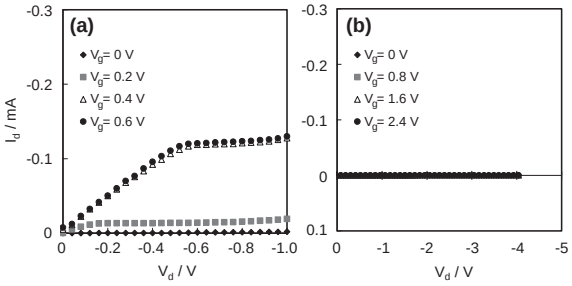

Figure 3. I_d–V_d characteristics of the device with the heterojunction structure (a) in humid air (at 25 °C, 50%), (b) in dry condition.

by electron donation from the methyl modified Si surface to water layer, and the carrier modulation seems to be caused by hole generation. The methyl modified surface has durable to water with better reactivity to redox reaction than the H–Si in an aqueous solution containing redox species.[4] Moreover, the carrier mobility of the device was estimated to be 440 $cm^2\ V^{-1}\ s^{-1}$. This value was similar to hole mobility of single crystalline Si.[9] Therefore, it is indicated that the surface conductivity is p-type mode, and that appears by hole generation from Si atoms by the redox reaction between methylated surface and water layer.

In conclusion, the device with the methyl monolayer/Si heterojunction structure showed switching behavior in the presence of water, whose conduction mode was regarded as p-type. Our finding of the p-type surface channel conduction in the methyl monolayer/Si heterojunction structure could be useful for fabricating new molecular devices that worked in the system of aqueous solution.

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