A device platform with nanochannels, fabricated by either top-down or bottom-up nanofabrication technologies, has been attracting notable attention in various fields and applications. As a representative case of such nanochannel device platform, a nanogap-embedded field-effect-transistor (FET) has shown a great potential as a fast and label-free detection tool for a specific target material by monitoring the changes in electrical characteristics such as the threshold voltage or conductivity.[1-2]

In a recent publication, for example, we reported that the nanogap-embedded FET can detect biomolecules in a very sensitive way by confining them within the nanogap and by monitoring the induced change in the effective dielectric constant of gate dielectrics, which is directly tied to the threshold voltage of the FET under study.[3] Alternatively, a conductivity change that was induced upon bridging the gap with a conductive nanomedium was used as an unlabeled biosensor.[3,4] In those devices, it is often difficult to confirm in a direct way whether the nanogap or channel is really filled with a target material due to its vulnerability under the common spectroscopic methods used for such study. [5] That is, other than the indirect evidence provided by its own electrical signal, there is hardly any physical observation method that can give information on how far the fluids can infiltrate into the gap or channel.

Given these facts, it would be beneficial to have molecules or nanostructures that are soluble and small enough to infiltrate nanometric gaps or channels and yet are robust and chemically stable enough to not be damaged during electron microscopy or other spectroscopic techniques. It would be even better if electrical changes can be induced by filling the gap with those types of molecules or nanostructures. In that respect, fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) is regarded as highly promising due to its high solubility,[5,6] thermal stability,[7] and molecular dimension comparable to that of the fullerene C_{60} (7.10 Å in diameter).[8,9] PCBM is also known to have a relatively good electron transporting/accepting property, and thus has been a popular choice for electron acceptors in solution-processed organic solar cells[5] and for the n-type active layer in organic thin-film transistors.[6]

In this study, PCBM was explored as an indicator to analyze, in a combinatorial manner, the behavior of nanofluids that infiltrated into a lateral nanogap by using electron microscopy or spectroscopy and by providing a new protocol of charge-based detection that is enabled by the electron accepting properties of PCBM in the PCBM-embedded field-effect transistor (PeFET), in which the lateral nanogaps on both sides are filled with PCBM. These embedded PCBM-driven by the nanofluidics can serve as discrete charge storage nodes for memory application, which are very similar to the trap sites in the silicon-oxide-nitride-oxide-silicon (SONOS) device.[10] It should be noted that the proposed approach can thereby link electronics and nanofluidic phenomena. Furthermore, the PeFET is investigated as a potential solution to overcome the limitation of multibit operable nonvolatile memory in a single cell. The PeFETs can offer mass-producibility and a relatively low cost because the process used to produce them requires only one more facile etch process and dipping process than the conventional complementary metal oxide semiconductor (CMOS) processes. For more specifics on the 2-bit operation scheme and its limiting factors, see Experimental Section and Supporting Information (SI), Figure S1 and S2.

A lateral nanogap device was fabricated from a conventional metal-oxide-semiconductor FET (MOSFET) underneath the polycrystalline silicon gate on both the source and drain sides by using the wet-etching and the oxidation process, as shown in Figure 1a; for more specific process details, see Experimental Section and Figure S3 (SI). The length and height of the gap were controlled by the etching and oxidation time. In order to examine the fluidics in the nanogap, the nanogap device was immersed in a prepared PCBM solution in chlorobenzene (5 mg mL^{-1}) for a day. The device was then dried at 150 °C on a hot plate for an hour under a nitrogen environment in order to remove any residual solvent.

The cross-sectional transmission electron microscopy (TEM) images of the PeFET with a nanogap that has the height of 26 nm and the length of 513 nm are shown in Figure 1b. Despite the relative indistinctiveness of individual PCBM particles in the TEM images, the energy dispersive
spectroscopy (EDS) mapping clearly shows the high intensity signal for carbon within the nanogap, which supports the presence of the PCBM molecules that are fully embedded in the nanogap by capillary force (Figure 2). In addition, an ultimately scaled nanogap device (minimum height: 4.1 nm, gap length: 200 nm) was fabricated for investigating the presence of nanofluidics through a procedure that is summarized in Figure S3 (SI; also see Figure S4-(a) for TEM images of 4.1-nm gap PeFETs). However, EDS analysis was not applicable for such a fine dimension, due to the interference of background signals. Thus, a high-resolution electron energy loss spectroscopy (EELS) was performed. As one can see in Figure S4-(b) (SI), a peak at 284 eV is easily observed, which is identified as the carbon K-edge that is associated with π* excitation. This indicates the existence of sp² bonds in the target material, which are a signature of fullerenes, carbon nanotubes, and graphite. The simple fluidic modeling also supports the belief that PCBM molecules can be driven by capillary force in order to be infiltrated deep into the far end of the gaps. For the 10-μm width device, the unfilled range in its width direction is estimated to 4 μm based on the modeling when the position of the advanced solution in its depth direction, “x”, is 200 nm, the deepest location which PCBM-solution can reach. For more details on the fluidic modeling, see the Experimental Section and Figure S5 (SI).

By filling the charge storing media in the gap, a new protocol of charge-based detection can be developed by mimicking the flash memory operation scheme. For example, fullerene-embedded flash memory, in which fullerene C₆₀ molecules are embedded within the gate dielectric layer by thermal evaporation in vacuum, was recently introduced. In this work, a gate voltage (V₉) of 12 V and a drain voltage (V_D) of 6 V were applied as a pulse that has a duration of 80 μs. Under this condition, electrons travelled through the channel, thereby acquiring high energy from the lateral electric field by drain bias and colliding with silicon atoms. This process, known as the impact ionization mechanism, can generate highly energetic electron-hole pairs, as illustrated in the inset of Figure 3. The generated hot electrons, near the drain region, gain a sufficient energy that helps them tunnel through the energy barrier (∼3.1 eV) of the bottom oxide, i.e., the tunneling oxide of 3.1 nm thickness.

In order to ascertain that the memory effect originated from the presence of PCBM molecules, two other control devices were also fabricated: one with the nanogap filled by poly(4-vinylphenol) (PVP) and the other processed only with chlorobenzene without PCBM (Figure S6 (SI)). Compared to the curve obtained after filling with PCBM, the curve obtained after filling with PVP was shifted to left side due to the high dielectric constant of PVP. Among these three cases, only the PeFET showed a conspicuous shift (1.45 V) of threshold voltage (V_T). This shift was due to the high electron receptivity of the PCBM molecules that stemmed from the unique icosahedral symmetry of their parent molecule C₆₀ and its lowest unoccupied molecular orbital (LUMO) level (∼-4.3 eV) that is lower than the conduction band edge of Si. Such a shift is significant enough to function as an indicator of the gap-filling. On the other hand, PVP, which is often used for polymer dielectric materials, may modify the dielectric constant in the lateral gap region from those cases where the gap is void. However, PVP does not exhibit gate-induced change in V_T because PVPs do not serve as charge storage nodes.

The value of the V_T shift in the PeFET and the relationship between the charge density and the V_T shift is simply given by:

\[
qN_Q = C_{ox}\Delta V_T
\]

where \(q\) is the electronic charge (C), \(N_Q\) is the stored electron density (\(\# \text{cm}^{-2}\)), and \(C_{ox}\) is the normalized oxide capacitance (8.6 × 10⁻⁹ F cm⁻²). \(N_Q\) is estimated to be 7.8 × 10¹² cm⁻². For 30 nm gap height, assuming 24 PCBM layers which has
ArgusLab software,[14] it is predicted that approximately one
the length of the methyl ester side group that was estimated by

Figure 3. Feasibility of the PCBM as an indicator for stored-charge
detection in the nanogap. After applying a pulse, the shift of the drain
current–gate voltage ($V_D - V_G$) curve appeared only for the PCBM-filled
device, based on its unique structure. The inset represents the charge
storing mechanism.

4.4 \times 10^{13} \text{ cm}^{-2} \) of areal density from the size of an individual
PCBM particle (1.23 nm in the longest axis; estimated by adding
the diameter of a C_{60} molecule taken from the literature[8,9] and
the length of the methyl ester side group that was estimated by
ArgusLab software.[14] It is predicted that approximately one
electron can reside in every 120 PCBM molecules.

In addition to the detection of nanogap-filling, the PeFET
has a great potential for use in nonvolatile memory devices
because PCBM can function as discrete charge storage nodes.
Due to the simplicity of the processes used to employ PCBM as
charge storage nodes for nonvolatile flash memory applications
the PeFET may offer an ideal solution that can provide reliable
and high-density nonvolatile features, with little addition of
total cost, because this technology combines the well-proven
reliability and performance of Si-based nanotechnology and
the easy solution-processability of PCBM.

Moreover, the primary virtue of the PeFET stems from the physically
separated charge storage nodes that are confined in the
nanogaps on both sides of the gate in PeFET. Until now,
conventional nonvolatile flash memories have undergone
aggressive miniaturization. Now, major flash memory
industries are making an attempt to develop a multibit-per-cell
device as well as other alternatives so that it alleviates the
pressure of scaling-down for high memory density. The NROM
and MirrorBit concepts are intended to be used for spatially
localized charge storing through the channel hot electron
injection mechanism in the SONOS structure as a charge trap
flash memory.[15–17] Using this concept, as illustrated in Figure
S1a (SI), four possible states for 2 bits are possible. In this case, a
double read scheme is required to distinguish those four states.
For example, in the “10” state, in which the charges are stored in
the oxide/nitride/oxide (O/N/O) near the drain junction, the
forward can be read by applying the positive gate and drain bias
with a grounded source terminal. This shows an off-state
current that is four orders higher than the reverse read when a
positive gate and a source bias with a grounded drain terminal
are applied, as shown in Figure S1b (SI), which was simulated by
Atlas-Silvaco.[18] The current difference occurs because the
forward drain bias lowers the potential barrier effectively ($\Phi_{BL,B}$), but the reverse source bias does not affect the potential
reduction ($\Phi_{RS,S}$), as can be seen in Figure S1c (SI) showing the
simulation results obtained using Atlas-Silvaco[19]. If, on the contrary, we apply high source voltage and grounded drain
voltage instead of high drain voltage, charges can be stored at
the source side and thereby source/drain-side read can be
detected separately.

As conventional SONOS Flash memory shrinks to 40 nm,
however, lateral charge spreading imposes a technical barrier to
the implementation of a 2-bit-per-cell architecture due to the
narrowed sensing margin caused by the second bit effect.[19]
In order to overcome this drawback, the physically separated
O/N/O quantum well structure was introduced for further
scaling-down with the expense of complicated processing.[20]
Also, PeFET can be free from the interference of lateral charge
spreading without too much addition of complex process or
structure due to the spatial isolation provided by the remaining
gate oxide region which was not etched by oxide etchant
(Figure S2 (SI)). After storing charges in the drain side through
a programming operation, the off-state current ($I_{OFF}$) difference
between the drain-side-sensing and source-side-sensing
directions reveals the possibility of a 2-bit-per-cell operation,
as shown in Figure 4; for a more specific explanation of the
2-bit-per-cell scheme, see the Experimental Section and
Figure S1 (SI).

Figure S7a (SI) represents the data retention characteristics
that were measured for 1 week. Cyclic durability (endurance)
was also tested. It did not show a sign of device aging, even after
10^4 cycles (Figure S7b (SI)). From the results of the retention
and endurance tests, the feasibility of PCBM as an effective
charge storage node for nonvolatile memory can be verified.
Together with the aforementioned advantage of the proposed
structure with lateral nanogaps, one may regard the PeFET
configuration as a promising candidate for next-generation
multibit nonvolatile memory that can potentially extend the

Figure 4. Drain current–gate voltage ($I_D - V_G$) and source current–gate
voltage ($I_S - V_G$) curves for the different scanning directions after storing
charges in the drain side. The off-state current for the drain-side scanning
is 3 orders of magnitude larger than that for the source-side scanning. The
simulated results are in agreement with the measured results.
lifetime of conventional flash memory by eliminating the problems that can be induced by the charge spreading.

In summary, the existence of PCBM molecules inside the 4.1 nm thick nanogap was confirmed by high-energy spectroscopy analysis with TEM, EDS, and EELS thanks to the high thermal stability of PCBM, proving the infiltration of the PCBM solution into the nanogaps by capillary force. It is noted that such infiltration still works, even for a dimension that is only a few times larger than the size of the molecules. These results strongly support the feasibility of the devices with nanogaps to accommodate a small number of molecules by capillary force. In addition, the results shown here demonstrate that the PCBM-embedded FET can open up a pathway towards developing a multibit-per-cell flash memory that is free from the problems associated with the charge-spreading effect with a good mass-productibility.

Experimental Section

**PCBM characterization:** PCBM-embedded nanogap devices were characterized by field emission transmission electron microscopy (FEI, Tecnai G2 F30). High-resolution TEM (HRTEM) images were obtained at 300 kV and EDS elemental mapping was conducted. High-resolution EELS was performed by field-emission-TEM (JEOL, JEM-2100F) and EELS spectrum was obtained at 200 kV.

**Electrical characterization:** Electrical measurements were performed with a semiconductor parameter analyzer, HP 4156C. The drain current was measured while the gate voltage was performed with a semiconductor parameter analyzer, HP 4156C. To evaluate the memory performance, threshold voltage was measured while the gate voltage was performed in the shielded probe station. To support and verify the electrical characteristics, electrical potential profile was extracted as in Figure S1-c (SI).

The drain current of 10 mV was obtained while the gate voltage was performed with a semiconductor parameter analyzer, HP 4156C. To evaluate the memory performance, threshold voltage was measured while the gate voltage was performed in the shielded probe station. To support and verify the electrical characteristics, electrical potential profile was extracted as in Figure S1-c (SI).

**Device fabrication:** In order to fabricate the MOSFET device, 800 nm thermal oxide was grown on a (100) oriented p-type silicon wafer by using the conventional local oxidation of silicon (LOCOS) process (Figure S3a, SI). The gate oxide thickness was then etched by using a chlorine-based plasma with a masking photosist that was defined by optical lithography. Then, the gate oxide was etched by hydrofluoric (HF) acid, as shown in Figure 5A (SI). Then, phosphorus (31P+) with 20 keV energy was implanted for source–drain formation (Figure 5D, SI). The gate oxide was carved, in part by etching, with the aid of a buffered oxide etchant (BOE) in order to form the lateral nanogap. For the 513 nm long and 26 nm thick gate oxide, the etching time was 8 min 20 s, and for the 200 nm long and 3 nm thick gate oxide, the etching time was 19 min 40 s through the BOE (Figure S3e, SI). The oxide was thermally grown again at 700 °C for 30 min for the bottom tunneling oxide that has 3 nm thickness and the top control oxide that has 4.5 nm thickness, simultaneously (Figure 5F, SI).

Meanwhile, PCBM 60 (Nanowire-C) was dissolved in chlorobenzene (5 mg mL−1). Finally, the nanogap MOSFET was immersed into the PCBM 60 solution for a day, and then dried at 150 °C on a hot plate for an hour under a nitrogen environment in order to remove any remaining solvent (Figure S3g, SI).

**Fluidic modeling:** The fluidic behavior in the nanofluidic channel can be modeled with the aid of spheric model geometry of the nanochannel (Figure S5a, SI). The advancing meniscus by surface tension of the PCBM solution in a Poiseuille flow had a constant Young-Laplace pressure drop (ΔP∞) in a width-directional flow that had thermodynamic equilibrium, as follows:

\[ \Delta P_{\infty} = \frac{2 \gamma \cos \theta}{h} + \frac{1}{d-x} \gamma \cos \theta \]  

where \( \gamma \) is gap height (4.1 nm), \( d \) is gap depth (= 200 nm), \( x \) is the depth-directional position of solution, \( y \) is the surface tension per unit area of the solution, and \( \theta \) is the contact angle between the surface material of the gap and solution. As the solution flows into the nanogap, the inner air-pressure (\( P_{\infty} \)) in the closed nanogap increases in proportion to the solution-advancement position (\( x \)) in which is the width-directional distance of the advanced solution. Thus, the pressure increment (\( \Delta P_{\infty} = P_{\infty} - P_0 \) in the inner gap is derived as

\[ \Delta P_{\infty} = P_0 \left( \frac{dW}{(d-x)(W-2y)} - 1 \right) \]  

where \( P_0 \) is the initial pressure in the inner gap, \( W \) is the width (= 10 μm). The maximum advanced distance (\( y_{max} \)) was obtained when this capillary pumping system reached the equilibrium state, \( \Delta P_{\infty} = \Delta P_{\infty} \). In order to extend the descriptions of the microfluidics to those of the nanofluidics, the effect of electro-osmosis by charge convection currents, which is one of the predominantly influential factors in nanofluidics, was neglected due to the nonionic charges in the used solution. In this simple model, \( \gamma \) and \( \theta \) of chlorobenzene were known to be 33 mN m\(^{-1}\) and less than 10\(^{-1}\) respectively.

As shown in Figure 5B (SI), \( y_{max} \) was obtained as a function of \( x \) and for the various \( \gamma \) (15 to 33 mN m\(^{-1}\)) in order to reflect the variation by unknown factors for nanofluidics with fixed \( \theta = 10^\circ \). When \( x \) is 200 nm and \( \gamma \) is varied from 15 to 33 mN m\(^{-1}\), \( y_{max} \) ranged from 500 nm to 3 μm for \( h = 4.1 \) nm.

**Keywords:** capillary filling · nanofluidics · nanogap field-effect transistor · nonvolatile memory · PCBM

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