

Suppression of Drift in Ion-selective Field Effect Transistor by UV Light Irradiation

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Ion-selective field-effect transistors (ISFETs) are a type of potentiometric sensor with a wide range of potential applications. However, the application of ISFETs is hindered by the instability of the threshold voltage (V_T), known as the drift. In this study, we hypothesized that the charge trapping at the interface between the oxide layer and the Si substrate of ISFETs affects the drift, and we examined the effects of the irradiation of UV light on the drift. To investigate the drift more simply, we fabricated a Si wafer sample with a 30 nm Al_2O_3 layer, which is regarded as the sensing layer of an ISFET, and we measured the drift by capacitance–voltage measurements using an electrochemical cell. Results showed that the amount of drift after light irradiation decreased to 6.6% (37 mV/h) relative to the original drift (558 mV/h) in the best case. It was also suggested that the drift is caused by multiple charge trapping mechanisms. These results indicate that charge trapping is a cause of drift, and light irradiation can be used to suppress drift.

1. Introduction

Ion-selective field-effect transistors (ISFETs) are a type of potentiometric sensor that replaced the gate electrode of a metal-oxide-semiconductor field-effect transistor (MOSFET) with a sensing layer, an electrolyte, and a reference electrode.^(1,2) The concept of ISFETs was originally proposed by Bergveld in the early 1970s.⁽³⁾ Since the ISFETs have many advantages such as their amenability to miniaturization, quick response, compatibility with integrated circuits, and low output impedance, they have been intensively studied for various applications: the detection of biomolecules,⁽⁴⁾ the measurement of ion concentrations in the soil and water,⁽⁵⁾ the monitoring of cell activities,⁽⁶⁾ the observation of the Belousov–Zhabotinsky reaction,⁽⁷⁾ the fabrication of wearable ion-sensing devices,⁽⁸⁾ the observation of the activities of neural cells in the brain,⁽⁹⁾ and non-optical DNA sequencing.⁽¹⁰⁾

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However, the application of ISFETs is hindered by the problem of threshold voltage (V_T) instability, known as the drift.^(11–14) To explain the mechanism of the drift, several models have been proposed focusing on the interface between the sensing layer and the electrolyte. These models explain the cause of the drift from the viewpoints of the hydration of the surface of the sensing layer,⁽¹⁵⁾ the adsorption of molecules,⁽¹⁶⁾ and oxide etching.⁽¹⁷⁾ On the other hand, in the case of MOSFETs, it has been reported that the interface between the sensing layer and the Si substrate causes the instability of V_T since the interface traps and trap levels in the oxide layer near the interface (border traps) trap charges in the Si substrate.⁽¹⁸⁾

The studies of MOSFETs, which have Al_2O_3 as the oxide layer, indicated that the application of a positive bias voltage induces the trapping of electrons, resulting in the positive change of V_T .^(19–23) It was also reported that charge trapping and detrapping are promoted by light irradiation during the application of the bias voltage.^(24–28) These results suggest that the drift caused by charge trapping may not be negligible also in ISFETs and the drift may be affected by light irradiation as in the case of MOSFETs.

In this research, we examined the effects of light irradiation on the drift in an ISFET. We focused on the drift in an ISFET with the Al_2O_3 sensing layer directly deposited on a p-type Si substrate, and we fabricated a wafer sample with the same layer composition. We measured the drift of the wafer sample by capacitance–voltage (CV) measurements⁽²⁹⁾ and examined the effects of UV light irradiation on the drift.

2. Data, Materials, and Methods

In this research, we used a p-type Si (100) wafer with a thickness of 525 μm and a resistivity of 1–10 $\Omega\cdot\text{cm}$. To remove the native oxide layer, the wafer was rinsed in 1% HF solution for 1 min followed by deionized water, and the sample was dried by blowing nitrogen. On the Si substrate, a layer of Al_2O_3 with a thickness of 30 nm was formed by atomic layer deposition (ALD) at 200 $^\circ\text{C}$ using trimethylaluminum (TMA) as the precursor of Al and O_3 as the oxidant. ALD was performed using internally manufactured ALD equipment, and the thickness of the Al_2O_3 layer was confirmed by X-ray reflectometry. On the opposite side of the Si wafer, a 10-nm-thick Cr layer and a 100-nm-thick Al layer were deposited by physical vapor deposition using EBX-2000 (ULVAK, Inc., Japan) to form the working electrode.

Figure 1 shows the setup of the CV measurements. All experiments were performed in an electromagnetic shield covered by a black curtain. The samples used in the CV measurements were prepared by cutting the wafer into square pieces of approximately $1 \times 1 \text{ cm}^2$. For the CV measurements, a sample was placed on a Ni plate (The Nilaco Corp., Japan) with the working electrode side down, and the plate and the sample were then fixed to an electrochemical cell (VM2: EC Frontier Co., Ltd., Japan). The surface area of the sample was defined by a custom-made O-ring with an inner diameter of 6 mm; hence, the area was approximately 0.283 cm^2 . An Ag/AgCl reference electrode (RE-T8A), a Pt counter electrode (CE-100: EC Frontier Co., Ltd., Japan), and a LED light with a peak wavelength of 395 nm (OptoSupply Ltd., China) powered by R6244 (Advantest Corp., Japan) were attached to the cap. The intensity of the light at the sample surface was measured by an optical power meter (8250A) and an optical sensor (82311: ADC

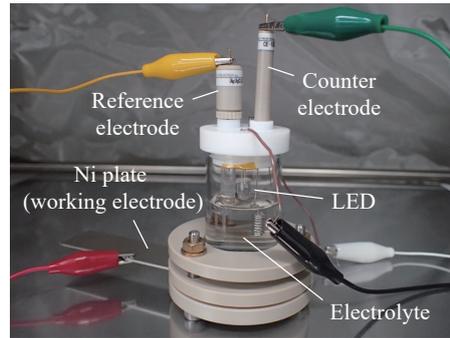


Fig. 1. (Color) Experimental setup of CV measurement and UV light irradiation.

Corp., Japan). The measurement wavelength of the power meter was set to 395 nm and the sensing part of the optical sensor was fixed to the cell. After putting on the cap, the intensity of the light without the electrolyte was adjusted to 1 mW. For the drift measurements, 14 mL of pH 6.86 phosphate buffer solution (FUJIFILM Wako Pure Chemical Corp., Japan) was used as the electrolyte.

CV measurements were started immediately after filling the cell with the electrolyte and covering the cell with the black curtain. The CV measurements were performed by using a frequency response analyzer (SI1260) and a potentiostat (SI1287: Solartron Analytical, UK). The frequency, the AC amplitude, and the sweep rate of the applied voltage were 1 kHz, 30 mV, and 50 mV/s, respectively. The sweep range of the voltage was from $V_{FB} - 3$ to $V_{FB} + 3$ V, where V_{FB} is the flatband voltage of the wafer sample. V_{FB} was determined by calculating the voltage at the flat band capacitance (C_{FB}), which is defined by the following equations:⁽²⁹⁾

$$C_{FB} = \frac{C_{OX} C_{FBS}}{C_{OX} + C_{FBS}}, \quad (1)$$

$$C_{FBS} = \frac{\varepsilon_0 \varepsilon_{Si}}{\lambda}, \quad (2)$$

$$\lambda = \sqrt{\frac{\varepsilon_0 \varepsilon_{Si} k_B T}{q^2 N_A}}, \quad (3)$$

where C_{OX} is the capacitance of the oxide layer per unit area, C_{FBS} is the silicon surface capacitance at the flat band voltage per unit area, ε_0 is the vacuum permittivity, ε_{Si} is the dielectric constant of Si, λ is the Debye length, k_B is the Boltzmann constant, T is the temperature, q is the elementary charge, and N_A is the acceptor density per unit area. In the drift measurements, the DC bias voltage was applied for 5 min after the CV measurements, and the CV measurements and bias voltage application were repeated until the total time of the bias voltage application reached 60 min. The voltage applied to the reference electrode was $V_T + 1.1$ V, which is the bias voltage applied in an ISFET.⁽³⁰⁾ V_T and V_{FB} are given by Eqs. (4) and (5), respectively as follows:⁽³¹⁾

$$V_T = V_{FB} + 2\phi_B - \frac{Q_B}{C_{OX}}, \quad (4)$$

$$V_{FB} = E_{ref} - \psi_0 + \chi_{sol} - \frac{\Phi_{Si}}{q} - \frac{Q_{ss} + Q_{OX}}{C_{OX}}, \quad (5)$$

where ϕ_B is the difference between the Fermi level and the intrinsic Fermi level, Q_B is the depletion charge, E_{ref} is the reference electrode potential relative to vacuum, ψ_0 is the surface potential caused by chemical reactions on the oxide surface, χ_{sol} is the surface dipole potential of the electrolyte, Φ_{Si} is the work function of Si, Q_{ss} is the surface state density at the silicon surface, and Q_{OX} is the fixed oxide charge. Since the pH of the electrolyte does not change during the measurements, these parameters are constant except for Q_{ss} and Q_{OX} . ϕ_B and Q_B are calculated using Eqs. (6) and (7), respectively, as follows:⁽²⁹⁾

$$Q_B = \sqrt{4\varepsilon_0\varepsilon_{Si}qN_A\phi_B}, \quad (6)$$

$$\phi_B = \frac{k_B T}{q} \ln\left(\frac{N_A}{n_i}\right), \quad (7)$$

where n_i is the intrinsic carrier concentration. In this research, T and ε_{Si} were 278 K and 11.7, respectively, and N_A was $1 \times 10^{-16} \text{ cm}^{-3}$ on average. The V_{FB} and V_T of the sample were calculated by analyzing the results of CV measurements with the sweep range from -6.0 to 3.0 V, and determined as 1.791 and 2.864 V, respectively. Therefore, the initial sweep range of the CV measurements was set to -1.209 to 4.791 V by referring to the value of V_{FB} . The sweep range and the bias voltage were kept constant in the drift measurements. Every drift measurement was performed without light irradiation (dark condition), and the drift was quantified by the difference in V_T from the initial value. To investigate the effect of light irradiation on V_T , UV light was irradiated during the application of the bias voltage, and the difference in V_T caused by light irradiation (ΔV_T) was calculated. The drifts after light irradiation were also analyzed to examine the effect of light irradiation on the drift.

3. Results

3.1 Measurement of drift without light irradiation

To estimate the drift without light irradiation, we first performed drift measurements under dark conditions. The bias voltage applied between CV measurements was $V_T + 1.1$ V (3.964 V), and the CV measurements were repeated until the total time of the bias voltage application reached 60 min. The results of the CV measurements are shown in Fig. 2(a). As indicated by the black arrow, a shoulder is observed in the CV curves, which is interpreted as representing the amount of Q_{ss} .⁽²⁹⁾ Figure 2(a) also shows that the CV curves shift toward the direction of the

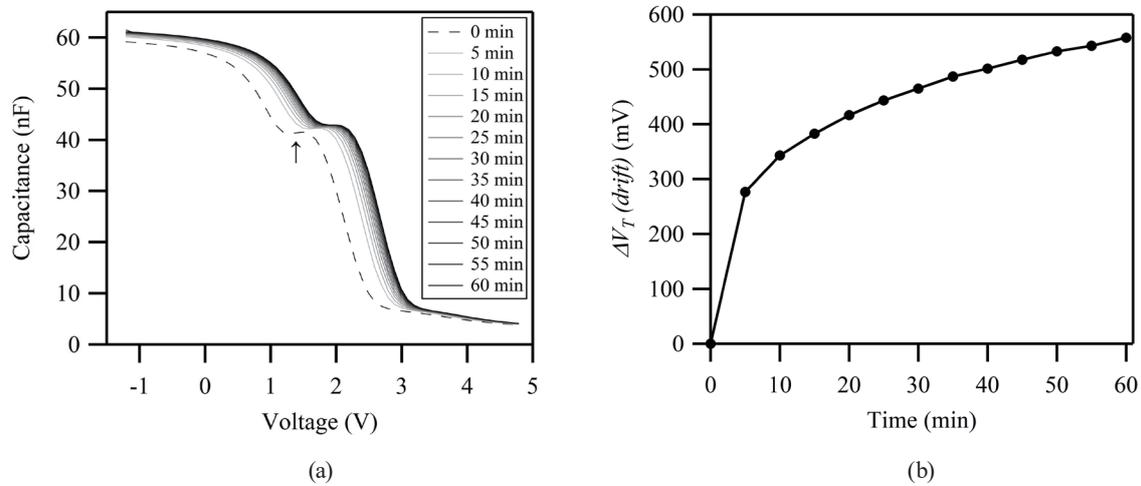


Fig. 2. Results of drift measurements under dark conditions. (a) Results of CV measurements. (b) ΔV_T caused by drift.

positive voltage over time and that the shift during 0–5 min is larger than the subsequent shifts. Figure 2(b) shows the drift of the sample. It shows that ΔV_T during 0–5 min (276 mV) is comparable to that during 5–60 min (281 mV) despite the difference in the duration of light irradiation, indicating that the mechanisms of drifts are different. Therefore, we divided the drift into two parts: the short-term (0–5 min) and long-term (5–60 min) drifts.

3.2 Effects of light irradiation on V_T

To examine the effect of light irradiation on ΔV_T , light irradiation and CV measurements were performed repeatedly using the same sample. The duration of each light irradiation was 5 min and the bias voltage during light irradiation was $V_T + 1.1$ V. CV measurements were performed before and after each light irradiation process to measure ΔV_T induced by light irradiation. The sweep range and bias voltage were updated from $V_{FB} - 3$ V to $V_{FB} + 3$ V and $V_T + 1.1$ V, respectively, by using V_T and V_{FB} immediately after light irradiation. The CV measurements and light irradiation were repeated until the total time of light irradiation reached 50 min.

The results are shown in Fig. 3(a). The dashed and solid lines are the results of the CV measurements before and after light irradiation, respectively. The results obtained after the same total light irradiation duration are shown in the same color. Figure 3(a) shows that light irradiation induces significant shifts of the CV curves toward the positive voltage direction. It also shows that the shoulder in the CV curves disappears as the duration of light irradiation increases, which was not observed in the case of CV measurements under dark conditions [Fig. 2(a)]. The disappearance of the shoulder suggests that electrons were trapped by the trap levels in the oxide layer and the density of the trap levels had changed. Figure 3(b) shows ΔV_T (circle) and the bias voltage relative to the initial V_T (triangle). It shows that both ΔV_T and bias voltage relative to the initial V_T increase significantly. ΔV_T after the first light irradiation for 5 min is 965 mV,

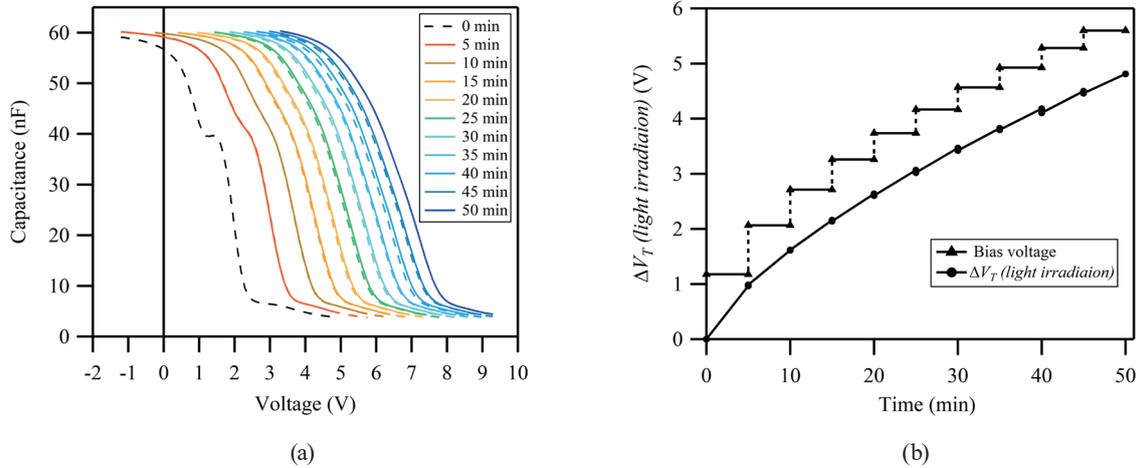


Fig. 3. (Color) Effects of UV light irradiation on V_T . (a) Results of CV measurements before and after light irradiation (dashed and solid lines, respectively). (b) ΔV_T induced by UV light irradiation.

which is greater than the drift in 60 min under dark conditions [558 mV, Fig. 2(b)]. These results suggest that light irradiation promotes the trapping of electrons and induces a large positive change in V_T .

3.3 Effects of bias voltage in light irradiation on drift

Since light irradiation had significant effects on V_T , we also examined the drifts after light irradiation. We performed light irradiation for 5 min before the drift measurements and analyzed the light-irradiation-induced ΔV_T and the drift measurement results. The sweep range and bias voltage of the drift measurements were updated using the results of CV measurements after light irradiation with the sweep range from $V_{FB} - 3$ V to $V_{FB} + 7$ V. Regarding ΔV_T after light irradiation for 50 min [5.599 V, Fig. 3(b)], the bias voltage during light irradiation was varied at V_T (2.864 V) + 2.1, 4.1, and 6.1 V. The drifts after the application of the bias voltage under dark conditions were also measured for comparison.

Figure 4(a) shows ΔV_T induced by light irradiation. It shows that ΔV_T after light irradiation is larger than those measured after bias voltage application under dark conditions. The drifts after bias voltage application with or without light irradiation are shown in Fig. 4(b). The figure shows that the total drifts after light irradiation were smaller than those measured after bias voltage application without light irradiation. Figure 4(c) presents the short-term (black) and long-term (gray) drifts of each sample. It shows that light irradiation is effective for suppressing the long-term drift, and the long-term drift is the smallest after the application of the bias voltage at $V_T + 6.1$ V. It also shows that the short-term drift is suppressed by bias voltage application and that the short-term drift is not necessarily suppressed by light irradiation. The amount of short-term drift increases with the applied bias voltage before the drift measurement. These results suggest that there may be an optimal condition of light irradiation to suppress the short-term drift.

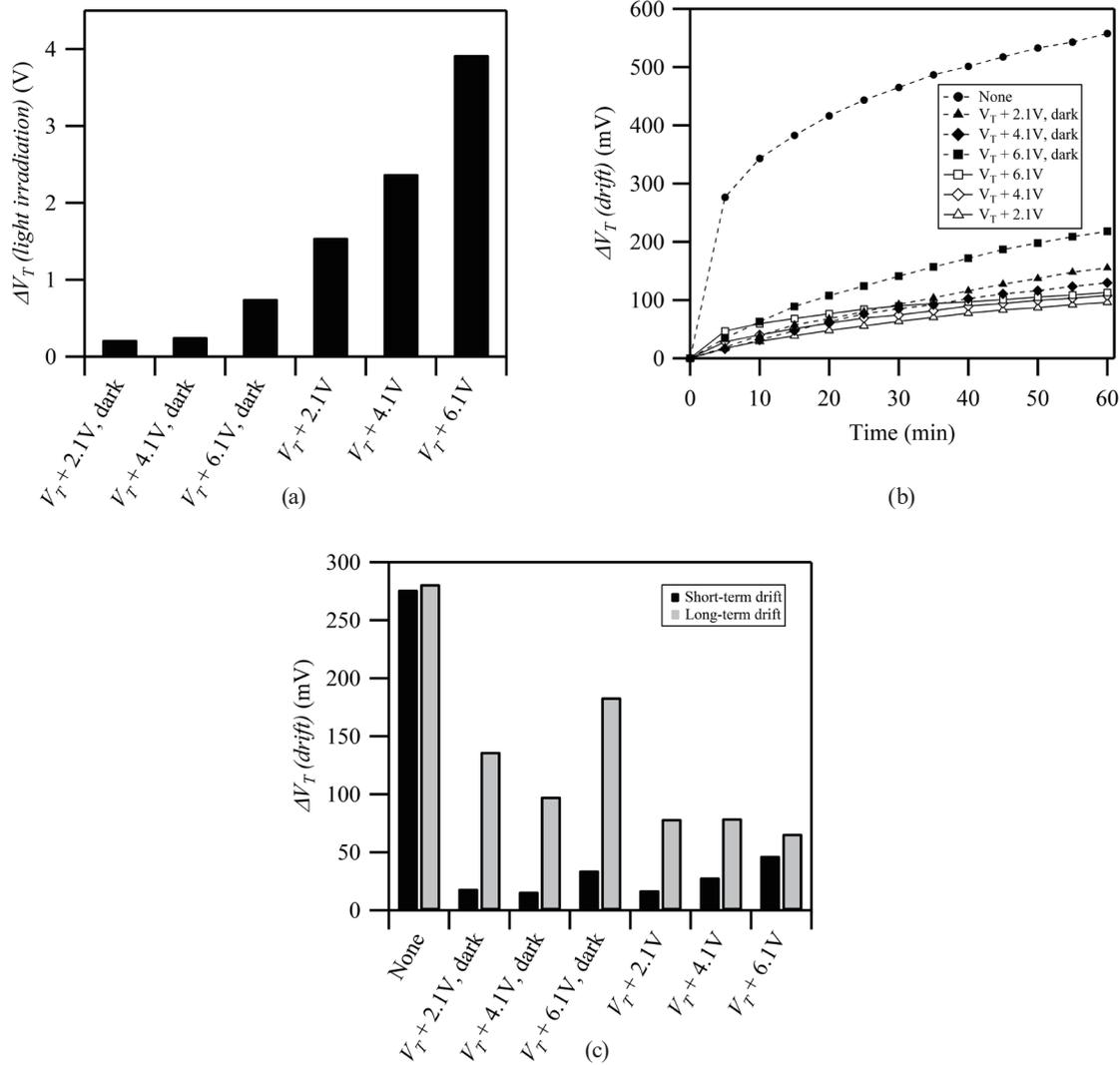


Fig. 4. Effects of UV light irradiation on drift. (a) ΔV_T induced by bias voltage application with or without light irradiation. (b) Drifts after bias voltage application. (c) Amounts of short-term and long-term drifts.

3.4 Effects of duration of light irradiation on drift

As suggested in Fig. 4(c), there may be an optimal light irradiation condition for the suppression of the short-term drift. To investigate the optimal condition, we examined the effect of the duration of light irradiation before the drift measurement. The duration was varied at 5, 30, 60, and 180 s. The bias voltage during light irradiation was set to V_T (2.864 V) + 6.1 V.

Figure 5(a) shows ΔV_T induced by light irradiation. ΔV_T induced by light irradiation for 5 min [Fig. 4(a), $V_T + 6.1$ V] is also shown for comparison. The ΔV_T values after light irradiation for 5, 30, and 60 s are found to be similar, whereas the longer duration of light irradiation induces a larger ΔV_T . This result indicates that the charge trapping induced by light irradiation includes at least two processes: the fast process that occurs in 5 s, and the slow process that occurs in 3 min. The drifts measured after light irradiation are shown in Fig. 5(b). This result shows that light

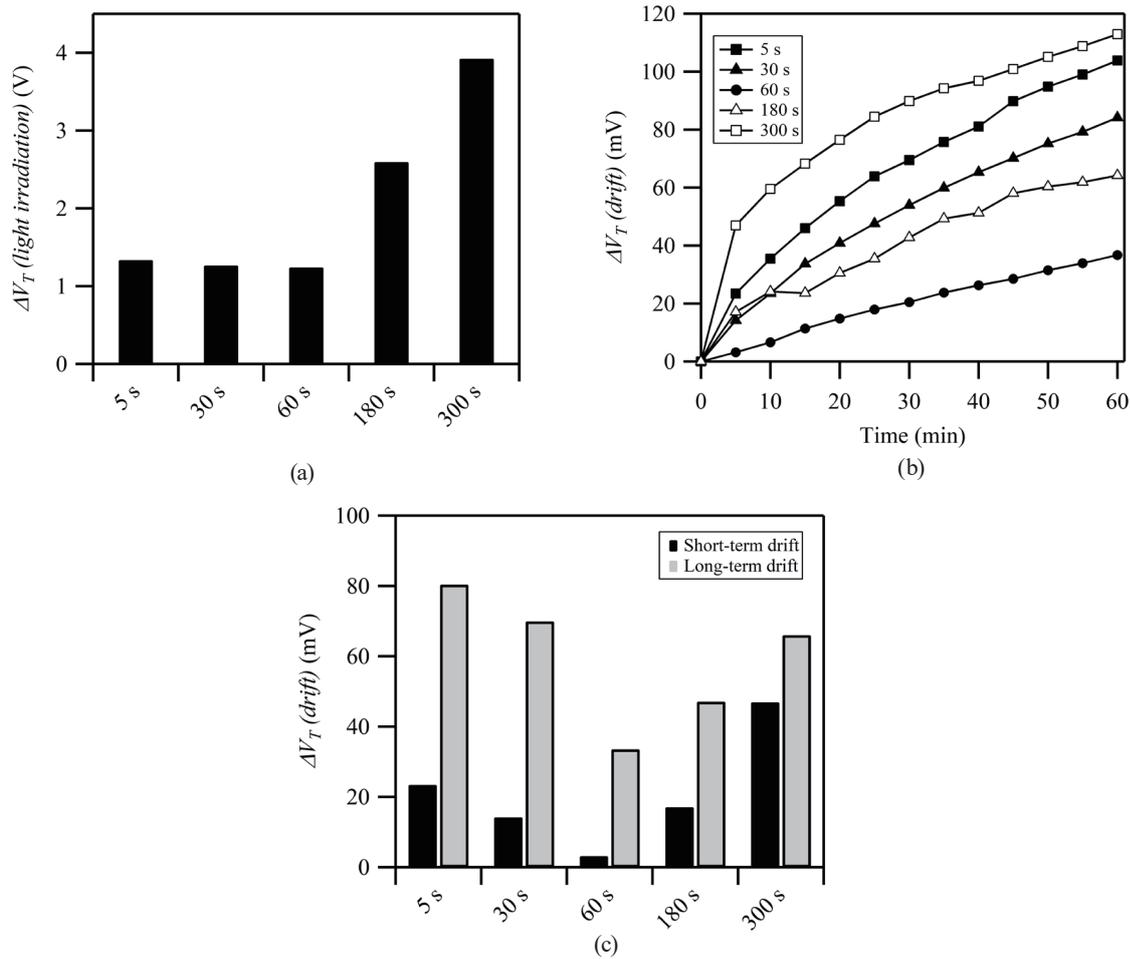


Fig. 5. Effects of duration of UV light irradiation on drift. (a) ΔV_T induced by UV light irradiation for different durations. (b) Results of drift measurements after UV light irradiation. (c) Amounts of short-term and long-term drift.

irradiation is effective for suppressing the drift even in the case of light irradiation for 5 s [Fig. 5(b), square]. It also shows that light irradiation for 60 s minimizes the subsequent drift. Figure 5(c) presents the short-term (black) and long-term (gray) drifts of each sample. It shows that both the short-term and long-term drifts become smaller with the increase in the duration of light irradiation up to 60 s. In contrast, the amounts of drifts increase in the longer light irradiation durations of 180 and 300 s. These results indicate that light irradiation for 60 s is optimal and that the optimal duration of light irradiation would be shorter than the moment at which the ΔV_T induced by the slow process becomes evident. The drift after light irradiation for 60 s was 37 mV/h, which is 6.6% relative to the drift under dark conditions (558 mV/h).

4. Discussion

As shown in Fig. 3(a), UV light irradiation induced a large positive ΔV_T and the shoulder of the CV curves in the depletion region disappeared with the increase in the duration of light

irradiation. These findings suggest that light irradiation induces the trapping of electrons and fills the trap levels near the interface between Al_2O_3 and Si. Since both the short-term and long-term drifts were affected by light irradiation, we consider that the main cause of these drifts is the gradual trapping of electrons under bias voltage application. We speculate that light irradiation suppressed the drift by filling the trap levels and decreasing the efficiency of charge trapping in the subsequent drift measurements. The existence of short-term and long-term drifts, which were affected by light irradiation through different mechanisms, and the existence of fast and slow processes during light irradiation suggest that the drift is caused by multiple charge trapping mechanisms. We consider that these mechanisms depend on the type of trap level (interface and border traps)⁽¹⁸⁾ and the distribution of border traps in Al_2O_3 .⁽³²⁾ Since light irradiation also affects the charge trapping and detrapping phenomena in the other types of metal oxide layers such as HfO_2 , SiO_2 , and SiN_x ,^(24,26–28) it is possible that light irradiation is effective for suppressing the drift of an ISFET, which uses those metal oxides as the sensing layer.

5. Conclusions

In this research, we investigated the effects of UV light irradiation on the drift in an ISFET with an Al_2O_3 sensing layer by fabricating a wafer sample with the same layer composition and measuring the drift by CV measurements. It was shown that light irradiation induces an increase in V_T and that the drift is suppressed after light irradiation. It was also shown that the shoulder in the CV curve, which is known to be related to the density of interface traps between Al_2O_3 and Si,⁽²⁹⁾ disappeared after light irradiation. These findings indicate that the main cause of the drift is the trapping of electrons by the trap levels in Al_2O_3 and that light irradiation reduced the efficiency of trapping by filling the trap levels. The smallest drift after light irradiation was 37 mV/h, which is 6.6% relative to the original drift (558 mV/h). These results suggest that the drift caused by charge trapping may not be negligible in ISFETs and light irradiation can be used as a method to suppress the drift.

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