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Control of positive and negative threshold voltage shifts using ultraviolet and ultraviolet-ozone irradiation

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A B S T R A C T

The precise control of the threshold voltage (V_{th}) required to turn a metal-oxide semiconductor field-effect transistor on/off at the designed voltage was important to ensure that the V_{th} was constant for all the transistors in the circuit. In this study, V_{th} was adjusted in both the negative and positive directions by manipulating the number of O vacancies on the surface of an oxide nanowire channel using ultraviolet (UV) and UV-ozone (UVO) irradiation. UV irradiation shifted the V_{th} in the negative direction by an amount that increased with increasing exposure time (−0.96 V at 1 min, −1.42 V at 2 min, and −1.70 V at 3 min), whereas UVO irradiation shifted the V_{th} in the positive direction by an amount that increased with increasing exposure time (+0.37 V at 3 min, +0.69 V at 5 min, and +1.07 V at 10 min). The shifted values of V_{th} were maintained by passivating the channel region of the oxide nanowire with an octadecylphosphonic acid self-assembled monolayer.

1. Introduction

The use of metal-oxide nanowire transistors in display-pixel and digital-logic circuits such as those in transparent and flexible electronics is promising because of their numerous advantages — high mobility, low-voltage operation, mechanical flexibility, and optical transparency [1–4]. Since transistor circuits with reduced size and resolution are used in recently developed nanoscale circuits, the severe threshold voltage (V_{th}) shifts that result from short-channel effects [5,6], which are important for high-performance display-device applications, should be considered. In previous studies, precise control of the V_{th} in nanowire and thin-film transistors during and after the device fabrication process was demonstrated. For instance, to adjust the V_{th} during device fabrication, the following methods have been employed: impurity atom (*e.g.*, P or B) doping of a transistor's channel regions [7], adding additional gate (*i.e.*, double or floating gate) structures [8,9], using the bias-stress-induced method [10], and using self-assembly monolayers between the gate oxide insulators and semiconductors [11]. However, when transistors in a circuit exhibit significantly different V_{th} values after device fabrication, it is difficult to manipulate their V_{th} values to match those of the other transistors. Thus, it is necessary to develop a localized, easily reproducible, and more controllable method for adjusting the V_{th} in these transistors.

In this study, we investigated a simple and reproducible method for manipulating V_{th} shifts locally by controlling the surface properties of oxide nanowires using ultraviolet (UV) and UV-ozone (UVO) irradiation. The differences between the representative characteristics of an SnO_2 nanowire transistor before and after UV and UVO irradiation were observed. A passivation method involving a self-assembled monolayer (SAM) was introduced to prevent the V_{th} from recovering to its initial value over time.

2. Experimental

The SnO_2 nanowire transistor was fabricated on an SiO_2/Si substrate using the following photolithographic process: (*i*) a 100-nm-thick ITO gate electrode was deposited by a direct current magnetron sputtering system; (*ii*) a gate dielectric was formed from a 30-nm-thick Al_2O_3 thin film (dielectric constant of ~9) via the atomic layer deposition (ALD) method; (*iii*) a contact hole was formed using a dry etching system; (*iv*) a single SnO_2 nanowire (diameter ~60 nm, length ~3 μm) grown using a two-temperature-zone chemical vapor deposition system [12,13] as a semiconducting channel was dispersed on a gate insulator; (*v*) the source and drain electrodes were formed from a ~120-nm-thick Al thin film; and (*vi*) the semiconducting channel region of the SnO_2 nanowire transistor was exposed to UV radiation (wavelength 20 mW cm^{-2}, lamp

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power 253 nm) for various durations (1 min, 2 min, and 3 min) as well as to UVO radiation (3 min, 5 min, and 10 min); to generate UVO, O_2 gas was injected into an UV chamber at 5 L/min; and finally, (*vii*) an octadecylphosphonic acid (OD-PA) SAM was coated onto the channel region of the SnO_2 nanowire [14,15]. Note that when the devices were exposed to ozone, they were shielded from UV light, which is known to desorb oxygen species from oxide surfaces. Before applying the OD-PA self-assembly, the SnO_2 nanowire transistor was dipped and sonicated in a semiconductor-grade isopropyl alcohol for 3 min to remove the inorganic/organic contaminants on the surface of the SnO_2 nanowire. The device was immersed in the OD-PA (2 mM) solution for 30 min and rinsed with fresh IPA twice. The surfaces of the SnO_2 nanowires were functionalized with a SAM of OD-PA.

3. Results and discussion

Fig. 1 presents a schematic diagram of the UV/UVO irradiation of the SnO_2 nanowire transistor's channel region. The number of O vacancies on the surface of the oxide nanowire channel was controlled by adjusting the irradiation time. The left inset in Fig. 1 shows a field-emission scanning electron microscopy (FE-SEM) image of the channel area of the SnO_2 nanowire transistor, where the length of the channel between the source and drain electrodes was ~3 μm. The X-ray energy-dispersive spectrometry shown in the middle inset of Fig. 1 confirmed the presence of tin and oxygen. The changes in the transistor characteristics were monitored by measuring representative quantities such as V_{th}, the on-current (I_{on} with I_{ds} at $V_{gs} = V_{th} + 2$ V and $V_{ds} = 0.5$ V), the subthreshold slope (*SS*), and the field-effect mobility (μ_{eff}). The μ_{eff} was extracted from the gate-to-channel capacitance given by $C_i = 2\pi\varepsilon_0 k_{eff} L_{ch}/\cosh^{-1}(1 + t_{ox}/r_{nw})$ with $\mu_{eff} = dI_{ds}/dV_{gs} \times L^2{}_{ch}/C_i \times 1/V_{ds}$, where the effective dielectric constant of the ALD-deposited Al_2O_3 was ~9.0. Note that the V_{th} of the SnO_2 nanowire transistor was extracted using the linear extrapolation method, which is the common V_{th} extraction method.

Fig. 2 shows the X-ray photoelectron spectroscopy of the as-grown and OD-PA self-assembled SnO_2 nanowires. The surface chemical states in Fig. 2(a) show the main peaks of Sn $3d_{3/2}$ (494.8 eV), Sn $3d_{5/2}$ (486.6 eV), Sn 4d (26.8 eV), O 1s (531.8 eV) and C 1s (284.8.x eV) observed in the as-grown SnO_2 nanowire. However, after applying the OD-PA self-assembled monolayer, the peak C 1s at 284.5 eV dramatically increased along with the peaks of Sn $3d_{3/2}$ (494.5 eV), Sn $3d_{5/2}$ (486.5 eV), Sn 4d (26.5 eV), and O 1s (531.5 eV). An in-depth spectrum analysis of the C 1s peak shown in Fig. 2(b) revealed C–C (284.6 eV), C–H (284.6 eV), and C–O (286.1 eV). This result indicates that the OD-PA was self-assembled on the SnO_2 nanowire with the formation of a CH combination.

The drain-current gate voltage (I_{ds}–V_{gs}) characteristics of the SnO_2 nanowire transistor were measured after UV and UVO exposures of various durations. Fig. 3(a) shows the V_{th} shifts of the transistor after being exposed to UV irradiation for 1 min, 2 min, and 3 min. The fabricated device exhibited a V_{th} of 0.33 V, an I_{on} of 1.17×10^{-6} A, an on-off current ratio (I_{on}/I_{off}) of 1.35×10^5, and an *SS* of 0.1 V/dec before being irradiated. UV irradiation caused the V_{th} to shift in the negative direction by -0.68 V (1 min), -1.10 V (2 min), and -1.38 V (3 min) from its original value of 0.33. In addition, I_{on} increased by $+0.43 \times 10^{-6}$ A (1 min), $+0.91 \times 10^{-6}$ A (2 min), and $+3.81 \times 10^{-6}$ A (3 min) from its original value of 1.17×10^{-6} A. Meanwhile, the *SS* remained at 0.1 V/dec, demonstrating that the interface state between the nanowire channel and gate insulator was largely unaffected. O_2 molecules near the surface of the SnO_2 nanowire were adsorbed by the surface, and the electrons on the surface of the nanowire reacted with the adsorbed O_2 molecules (O_2 (gas) + $e^- \rightarrow O_2^-$ (ads.)). This process generated a depletion layer with low conductivity adjacent to the surface of the SnO_2 nanowire. After UV irradiation, the photo-generated carriers tended to migrate to the surface of the SnO_2 nanowire and discharge the adsorbed O_2^- ions (O_2^- (ads.) + $h^+ \rightarrow O_2$ (gas)). Thus, the conductivity of the SnO_2 nanowire increased and the V_{th} shifted in the negative direction [16–20].

With increasing durations of UVO irradiation time, the V_{th} shifted in the positive direction. The fabricated device exhibited a V_{th} of 0.07 V, an I_{on} of 1.39×10^{-7} A, an I_{on}/I_{off} of 2.77×10^4, and an *SS* of 0.2 V/dec before being irradiated. Fig. 3(b) depicts the I_{ds}–V_{gs} characteristics of the devices, illustrating the changes resulting

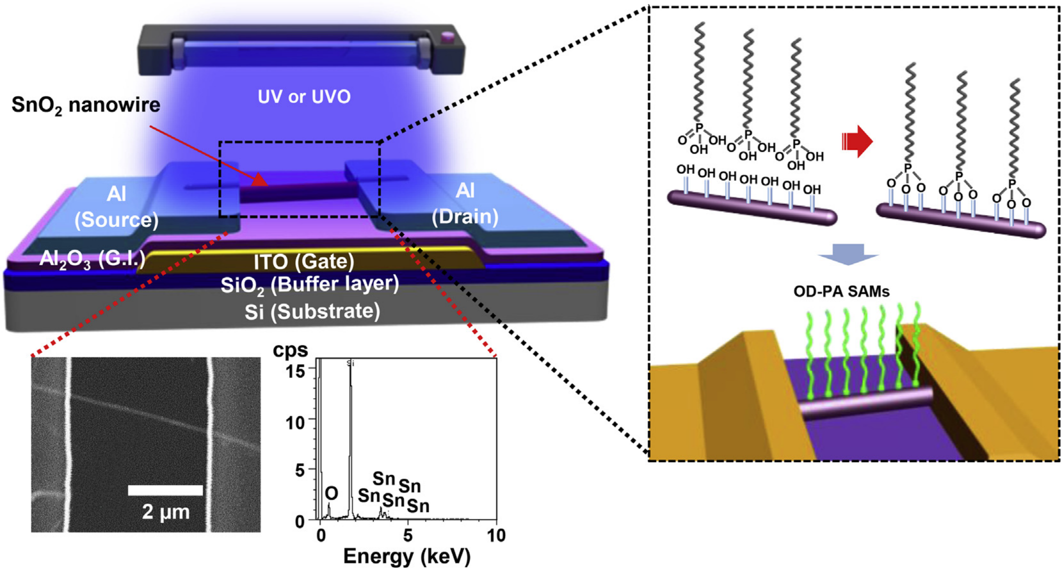

Fig. 1. Schematic diagram of an SnO_2 nanowire transistor during UV/UVO irradiation of the channel regions. The inset shows an FE-SEM image of the SnO_2 nanowire between the source and drain electrodes. The middle inset shows the X-ray energy-dispersive spectrometry of the SnO_2 nanowire. The right inset shows a schematic diagram of the formation of the OD-PA self-assembled monolayer on the surface of the SnO_2 nanowire.