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Improvements of Electrical Characteristics of Single-Crystalline ZnO Nanowire Field-Effect Transistors via Self-Assembled Monolayer Modification

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We have developed a rational method to improve electrical characteristics of oxide nanowire field-effect transistors (FET) performance using self-assembled monolayer (SAM) modification. Octadecylphosphonic acid (ODPA) was utilized as the SAM because of its chemical reaction with oxide surface which removes -OH groups from the channel surface of FETs. The long alkyl chain of ODPA SAM is also effective to prevent adsorption of H_2O molecules on oxide nanowire surfaces. By utilizing ODPA SAM modification, the drain current versus gate voltage characteristics of back-gate hydrothermally grown ZnO nanowire FETs are improved: reduction of hysteresis in vacuum condition and improved switching characteristics in atmospheric condition. Present results could be useful to achieve stable characteristics of oxide-based nanowire FETs.

Key words: *ZnO, Nanowire, self-assembled monolayer, field-effect transistors, octadecylphosphonic acid, surface modification, adsorption, passivation*

1. Introduction

Nanowire field-effect transistors (FETs) have attracted a growing interest due to their ideal electrostatics for transistor operations and ultra-low power consumption.[1)] Among various kinds of semiconducting nanowires, metal oxide nanowires have been intensively studied due to their unique electrical and optical properties.[2)] However, actual performance of oxide nanowire FETs is limited mainly due to adsorption of ambient H_2O and/or O_2 on their channel surface. The absorption of these molecules on the FET channel surface causes the large hysteresis which slow down switching speed and decline the on/off ratio.[3)] Solving these issues is crucial to achieve applications based on the functionalities of oxide nanowire FETs.

Kim et al. have reported that one-dimensional nanotube FETs show large hysteresis characteristics in their transfer curves.[3)] H_2O molecules are considered as the cause of the hysteresis characteristics which observed in passivation-free nanotube FETs.[3)] By removing the surrounding H_2O via vacuum annealing or PMMA passivation, the hysteresis of nanotube FETs can be eliminated. Similar results have been also reported by using Ga+ ion beam treatment, laser annealing, and inorganic passivation.[4)-6)] Recently, Lim et al. utilized SAM modification on various oxide nanowire FETs to achieve stable device performances.[7)] However, these studies mainly focused on achieving the stability of transfer curves of FETs, and the mechanism of the hysteresis characteristics of nanowire FETs has not been fully understood.

In this study, we demonstrate the improvement in electrical characteristics of hydrothermally grown ZnO nanowire FETs via ODPA modification. By utilizing ODPA SAM modification, the drain current versus gate voltage characteristics (transfer curve) of back-gate hydrothermally grown ZnO nanowire FETs are improved: reduction of hysteresis in vacuum condition and improved switching characteristics in atmospheric condition. The impacts of O_2 and H_2O on electrical characteristics are also discussed.

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2. Experimental

2.1 ZnO Nanowire Growth

ZnO nanowires were grown by hydrothermal method on a Si(100) substrate. A 5 nm Ti buffer layer and a 100 nm ZnO thin film were sequentially deposited on the Si substrate using a conventional sputtering technique. The substrate was dipped into 200 mL of aqueous solution containing 25 mM zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Wako, 99.0%), 25mM hexamethylenetetramine (HMTA, Wako, 99.0%), and 2.0 g branched polyethylenimine (PEI, Mn = 1800, Aldrich, 50 wt. % in H_2O). The solution was kept at 95 °C for 24 h to grow the ZnO nanowires, followed by rinsing with water.

2.2 Device Fabrication

The grown ZnO nanowires were first treated by ultrasonic dispersion in isopropanol and dropped on a 100 nm SiO_2/p-type Si substrate. Electrode patterning was performed using electron-beam lithography and lift-off techniques.[8] Ti/Pt of 20/100 nm was deposited using radiofrequency (RF) sputtering. The distance between the source and drain electrodes was typically 3-5 μm. All devices were annealed in air at 200 °C for 10 min to remove surface adsorbed water.

2.3 Self-Assembled Monolayer Modification

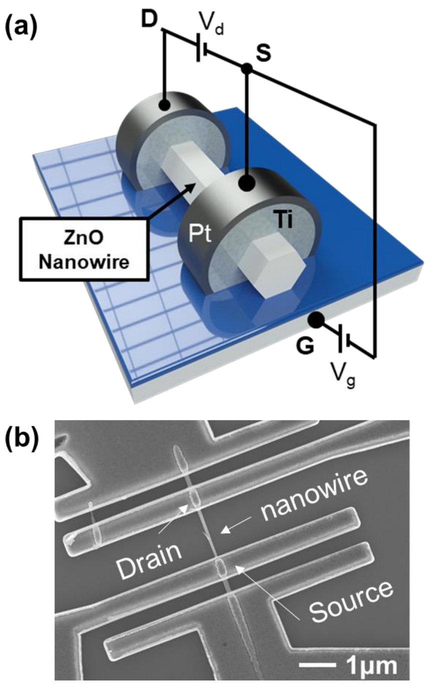

Fig.1 (a) Schematic of single nanowire FETs structure. (b) Field Emission SEM image of ZnO nanowire FETs

ODPA solution was first prepared with the concentration ranges from 0.01 mM to 10 mM in toluene at 60 °C, both ZnO nanowire array substrates and single nanowire devices were immersed and kept in the solution for 1 h. ODPA was self-assembled onto the surface of ZnO nanowires. Then the substrates were rinsed twice in toluene and dried by dry air blow.

2.4 Electrical Characterizations

All electrical characteristics were measured using a semiconductor parameter analyzer (Keithley 4200 SCS) with a probe station in various conditions from vacuum to ambient pressure at room temperature.

3. Results & Discussion

3.1 Device Structures

Fig.1(a) shows a schematic of a typical back-gate FETs, where a 100 nm SiO_2 layer is used as gate dielectric layer and a heavily doped Si substrate are served as a back gate. Fig.1(b) shows the SEM image of fabricated ZnO nanowire FET. The channel length is 2 μm and the diameter of ZnO nanowire is 100 nm.

3.2 Surface Modification on ZnO nanowires

Fig.2(a) shows the SEM image of ZnO nanowires growth by hydrothermal method. The average diameter of nanowire is about 100 nm. Fig.2(b) shows the relationship between the concentration of ODPA solution and contact angle of water on the ODPA-modified ZnO nanowires. At the lower concentration, the ZnO nanowires show hydrophilic properties because the surface of hydrothermally grown ZnO nanowires has -OH groups which have high affinity to H_2O. By increasing the concentration of ODPA in the modification solution, the contact angle increases due to the hydrophobic long carbon chain of ODPA. Since the contact angle saturates at 1 mM ODPA modification, this concentration was used for further single nanowire FET modifications. Fig.2(c) shows Fourier transform infrared spectroscopy (FTIR) data of ODPA-modified ZnO nanowires. Due to the long carbon chain of ODPA (C18), both $-CH_2$ symmetric vibration at 2850 cm^{-1} and its antisymmetric vibration at 2918 cm^{-1} are clearly observed and the absorbance of these vibrations is stronger than $-CH_3$ antisymmetric vibration at 2958 cm^{-1}. These

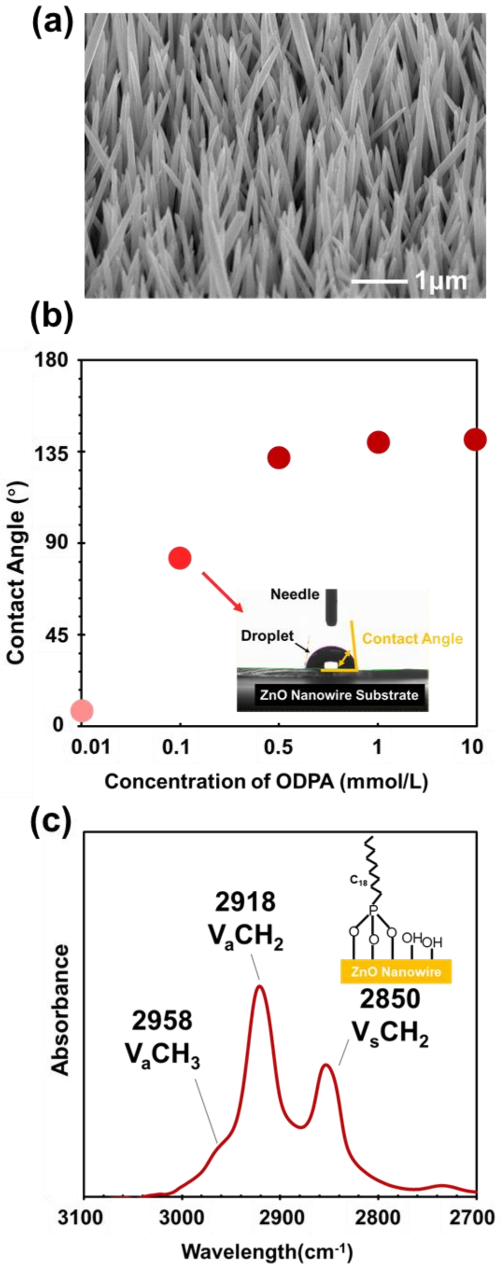

Fig.2 (a) SEM image of hydrothermally grown ZnO nanowires. (b) Relationship between ODPA concentration in modification solution and contact angle. The inset shows an image of the contact angle obtained at 0.1 mM ODPA modification. (c) FTIR data of ODPA modified ZnO nanowires. Inset shows schematic of ODPA SAM on ZnO nanowires.

results indicate that ODPA is successfully modified on ZnO nanowires.

3.3 Role of -OH groups on FET Characteristics

Due to oxygen vacancies in oxide materials, ZnO nanowires are generally n-type semiconductor. Therefore, ZnO nanowire FETs

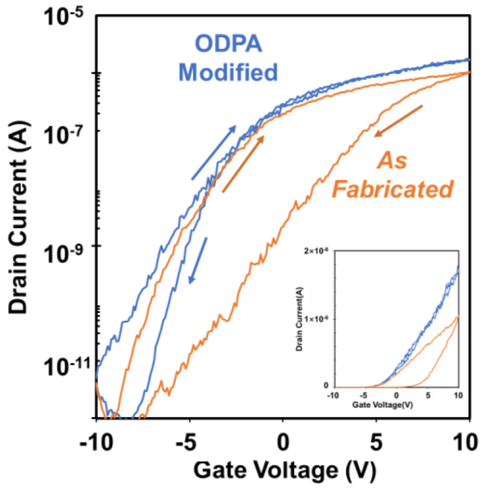

Fig.3 Drain current versus gate voltage characteristics of the single ZnO nanowire FETs with and without ODPA modification. The inset shows the linear scale graph of the characteristics.

turn on by applying positive gate voltage. Fig.3 shows the drain current versus gate voltage characteristics (transfer curve) in vacuum (<10^{-4} Pa). For the as-fabricated FETs without ODPA modification, hysteresis characteristics are observed. For the ODPA-modified FETs, on the other hand, the hysteresis characteristics are suppressed.

The obtained results in Fig.3 seem to be different from the previous works. In the nanotube FETs, it has been reported that hysteresis characteristics can be suppressed by removing surrounding H_2O.[3)] The as-fabricated devices were thermally annealed and measured under vacuum chamber where H_2O effect on electrical characteristics can be suppressed. Therefore, the observed hysteresis characteristics of as-fabricated FETs indicate that surrounding H_2O might not be the only cause of the degradation of FET performances.

For the ODPA-modified FETs, the anchor group of ODPA plays an important role to reduce the hysteresis characteristics. Wang et al. have shown that the surface of hydrothermally grown ZnO nanowires have hydroxyl ($O_{(OH)}$) species.[5)] These hydroxyl groups can trap carriers (electron) in the nanowire channels and degrade electrical characteristics. The charge/discharge behavior of electron traps causes hysteresis characteristics during voltage sweeping.[9)] ODPA can remove the surface -OH groups by the chemical reaction during the modification process, which is effective to reduce the H_2O adsorption on the nanowires. Moreover, the long alkyl chain of ODPA shows good hydrophobic behavior which prevents H_2O molecules from touching oxide nanowire surface. Due to the dual effects, electrical characteristics of ODPA-modified FETs are greatly improved in terms of less hysteresis characteristics and higher ON/OFF ratio of the drain current.

3.4 Role of O_2, H_2O on FET characteristics

Fig.4 shows drain current versus gate voltage characteristics of as-fabricated and ODPA-modified FETs under varied air pressure. As shown in Fig.4(a), the as-fabricated FET without ODPA modification shows a large degradation in ON/OFF ratio of the transfer curve when air pressure increases from 10 Pa to 10^5 Pa, indicating air (O_2, H_2O) has strong impacts on the electrical properties, such as carrier density and/or mobility, in ZnO nanowires. In addition to the ON/OFF ratio, the slope of transfer curve, which generally correspond to carrier mobility, degrades as air pressure increases. As shown in Fig.4(b), on the other hand, the ODPA-modified FET shows much better transfer curves than that of the as-fabricated FET even at the higher air pressure. The good ON/OFF ratio in the transfer curve of the ODPA-modified FET indicates that SAM modification is useful to achieve stable oxide nanowire transistor operation in air.

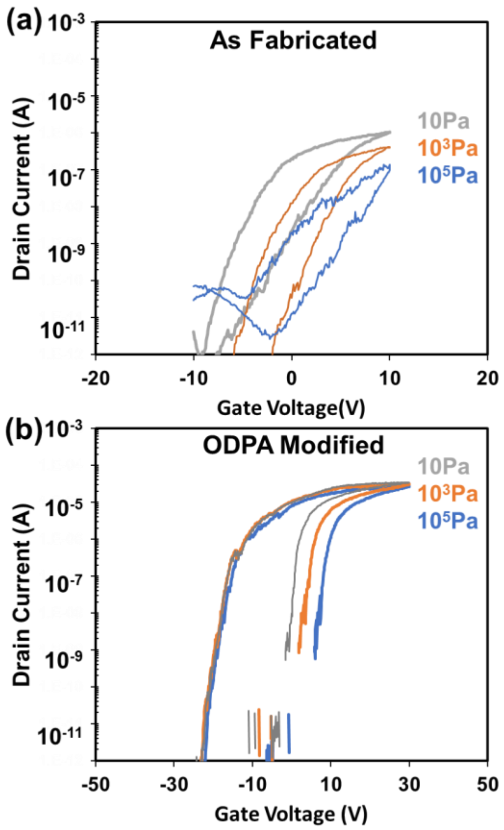

Fig.4 Drain current versus gate voltage characteristics for (a) as-grown and (b) ODPA-modified ZnO nanowire FETs at varied air pressure.

As discussed above, ODPA prevents H_2O adsorption on ZnO nanowire surface. Therefore, the differences in the transfer curves of the as-fabricated and ODPA-modified FETs can be understood through impacts of H_2O on electrical characteristics. Since the slope of the transfer curve degrades at higher air pressure only for the as-fabricated FET (Fig.4(a)), H_2O adsorption decreases carrier mobility through an increase in carrier scattering at nanowire surface.

Although the slope of transfer curve is stable for ODPA-modified FETs, hysteresis characteristics still remain and enhanced at higher air pressure (Fig.4(b)). The hysteresis characteristics are considered to originate in O_2 adsorption on ZnO nanowire surface through ODPA SAM. Dipole moment induced by absorbed O_2 is a possible model of the hysteresis.[10] Further investigations such as surface analysis and calculations of electronic structures are needed to clarify the origin of the hysteresis.

4. Summary and Conclusion

We demonstrated the improvements in electrical characteristics of hydrothermally grown ZnO nanowire FETs via ODPA modification. By utilizing ODPA SAM modification, the transfer curve characteristics of ZnO nanowire FETs were greatly improved: reduction of hysteresis in vacuum condition and improved switching characteristics in atmospheric condition. The impacts of -OH, O_2, and H_2O on electrical characteristics of ZnO FETs were separately discussed based on the results of the atmosphere-controlled electrical characterizations. It is clarified that H_2O and O_2 degrade ON/OFF ratio and hysteresis characteristics of the transfer curve of FETs, respectively. Present results could be useful to achieve nanowire-based FETs made from various oxide materials.

Acknowledgments

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References

1) D. Kaïblein et al., *ACS Nano*, **8**, pp. 6840-6848, 2014.
2) T. Kawanago and S. Oda, *Appl. Phys. Lett.*, **108**, p. 041605, 2016.
3) W. Kim et al., *Nano Lett.*, **3**, pp. 193-198, 2003.
4) W. Li et al., *Nano Res.*, **7**, pp. 1691-1698, 2014.
5) J. Maeng et al., *Nanotechnology*, **20**, p. 095203, 2009.
6) M. Zervos et al., *Mat. Sci. Eng.: B*, **198**, pp. 10-13, 2015.
7) T. Lim et al., *ACS Appl. Mater. Interfaces*, **7**, pp. 16296-16302, 2015.
8) K. Nakamura et al., *ACS Appl. Mater. Interfaces*, **11**, pp. 40260-40266, 2019.
9) C. Wang et al., *Nano Lett.*, **19**, pp. 2443-2449, 2019.
10) J. I. Sohn et al., *Nanotechnology*, **20**, p. 505202, 2009.