# Fundamental Study on Molecular Transformation and Discrimination on Single Crystalline Metal Oxide Nanowires

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https://doi.org/10.15017/2534472

出版情報：Kyushu University, 2019, 博士（工学）, 課程博士
バージョン：
権利関係：

（様式３）Form 3

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論 文 名　：単結晶金属酸化物ナノワイヤ表面における揮発性分子の変換・識別に関する基礎的研究

Title　　Fundamental Study on Molecular Transformation and Discrimination on Single Crystalline Metal Oxide Nanowires

区　　分　：甲

Category　　Kou

## 論 文 内 容 の 要 旨

## Thesis Summary

Metal oxide semiconductor gas sensors are the powerful tools to detect various gas molecules due to their many improved characteristics. The controllable synthesis of nanowires, the understanding of molecule-to-surface interaction and the design of novel sensor devices are all critical issues for the final sensor performance. In this thesis, we focus on these points aiming to get a deep understanding of the basic mechanism and accomplish the breakthrough in scientific and technological fields.

The molecular transformation behavior and mechanism of nonanal on single crystalline ZnO nanowire surface were well investigated by using optical spectroscopic (IR pMAIRS) and mass-spectrometric (TPD/GC-MS) techniques, as shown in Chapter IIV. The adsorption and desorption of nonanal itself as well as the aldol condensation and oxidation were all found on the ZnO nanowire surface. The thermal treatment had a significant influence on the surface reaction. The reaction rate could be increased with raising the annealing temperature or reducing annealing gas pressure. These results undoubtedly gave us a clear frame of molecule-to-surface interaction and provided a potential route for optimizing the applications in molecular sensing field by adjusting the surface activity of sensing material. For further controlling the surface behavior of nonanal, the inactive organic molecule MPA with robust thermal stability was modified on ZnO nanowire surface. As shown in Chapter IV, the aldol condensation reaction of nonanal on ZnO nanowire surface was drastically inhibited after carefully adjusting the MPA concentration. The single ZnO nanowire devices based on various degree of MPA modification were fabricated to explore the correlation between nonanal sensing properties and surface interaction, that the strong binding energy of 2-heptyl-2undecenal molecules induced the long recovery time during nonanal detection. The faster recovery process after MPA modification was observed due to the suppression of aldol condensation reaction. Fabricating cheap and disposable sensor devices can effectively solve the problem of deteriorating device performance in long-term use. In Chapter V, a paper-based disposable molecular sensor device comprised a cellulose nanofiber paper substrate, ZnO nanowires, and graphite electrodes, which was fabricated by two-step papermaking and pencil-drawing processes. This paper sensor device showed efficient sensing performance to $NO_2$ and could be cut-and-paste used and easily disposed. This strategy could be extended to a variety of oxide nanowires. In addition, for making flexible sensor device with high mechanical flexibility, ultralong $WO_3$ nanowires were synthesized by hydrothermal method. As shown in Chapter VI, the length of $WO_3$ could be up to millimeter range. We proved that monovalent sulfur oxoanions rather than $SO_4^{2-}$ substantially enhanced the anisotropic nanowire growth of hexagonal $WO_3$. The sensor device showed excellent property to nonanal molecules and good stability due to the enhanced textile effect.