# Synthesis of Single Crystalline Metal Oxide Nanowires Controlled by Crystal Growth Interfaces in a Vapor-Liquid-Solid Process

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論 文 名　：Synthesis of Single Crystalline Metal Oxide Nanowires Controlled by Crystal Growth Interfaces in a Vapor-Liquid-Solid Process
（気液固成長機構における結晶成長界面制御を介した単結晶金属酸化物ナノワイヤの構造・機能設計）

区　　分　：甲

# 論　文　内　容　の　要　約


Nanowires composed of single-crystalline metal oxide have unique properties that are difficult to obtain with conventional semiconducting materials. Therefore, the semiconducting metal oxide nanowires have been expected as functional materials, including electronic elements. Nevertheless, an electronic property of the nanowires has not been controlled precisely because of difficulties in the nanowire growth. Especially, $SnO_2$ nanowire, which is one of the well-known metal oxides as a gas sensor, has high electrical conductivity without intentional carrier doping despite its bandgap wider than 3 eV. The unintentional conductivity caused by crystal defects such as oxygen vacancies hinders us from controlling the electrical property precisely. Furthermore, the functional electronic elements need the precisely controlled surface property, while the crystal defects affect the electronic property at the nanowire surface. Therefore, intrinsic nanowire growth, which generates less unintentional crystal defects, are strongly required. Herein, this thesis focuses on the single-crystalline metal oxide nanowires grown by a vapor-liquid-solid (VLS) process, which is one of the nanowire growth processes. Especially, crystal growth interfaces, that is, a liquid-solid (LS) interface and a vapor-solid (VS) interface during the VLS process was focused on to control the electrical and surface properties on the nanowires. First, the electrical transport property of $SnO_2$ nanowires with controlled crystal growth interface was investigated. It was found that the unintentional electrical conductivity in the nanowires is attributed to the crystal grown via the VS interface (VS crystal). Whereas, the crystal grown via the LS interface (LS crystal) have significantly high electrical resistivity due to a stoichiometric $SnO_2$ crystal without the unintentional defects, which was revealed by scanning transmission electron microscope - electron energy loss spectroscopy (STEM-EELS) and a molecular dynamics (MD) simulation. Second, the electrical transport property influenced by oxygen partial pressures during the nanowire growth in the VLS process was investigated. It was found that the LS crystal grown under the low oxygen partial pressure has high electrical resistivity, which is an unusual phenomenon in the n-type metal oxide semiconductor. Observation by the STEM-EELS and the MD simulation clarified that the LS interface grows the stoichiometric $SnO_2$ crystal even under the low oxygen partial pressures due to the crystal growth close to thermal equilibrium. Third, the surface property of the nanowires with controlled crystal growth interfaces was investigated. Observation by electron microscopes found that the surfaces of the LS crystal and VS crystal have different structures whose exposed facets should be different, resulting in a lower desorption temperature of molecules-adsorbed $SnO_2$ nanowires composed of the LS crystal than that of the VS and the

LS crystals. Infrared spectroscopic measurement clarified that there is no significant difference in chemical reactions between the nanowire surfaces and the molecules both in the LS crystal and the VS crystal. These findings will provide not only the foundation on the electrical and surface properties of the nanowires but also the design strategy for the functional materials as the electronic elements.