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学 位 論 文 題 目	Crystal-phase and surface-structure engineering of MoS_2 for improving gas sensor performance at room temperature (室温でのガスセンサー性能の向上に資する MoS_2 の結晶相と表面構造エンジニアリング)
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論 文 内 容 要 旨

Molybdenum disulfide (MoS_2) has been widely acknowledged as a potential material for room temperature sensor devices. Good flexibility, good adsorption ability, and reactive at room temperature offer a potential possibility for wearable sensor device development. Various kinds of gasses have been successfully detected by using MoS_2 as a sensor material at room temperature which increases its possibility to be one of the suitable candidates for wearable sensor devices material. However, practically, MoS_2 still has a limitation due to the active sites only located on the edge of the layer, affecting the reactivity with gas molecules including low sensor response, slow response, and recovery speed. To increase the number of MoS_2 active sites, the surface structure and also phase structure of MoS_2 need to be modified to improve the reactivity of MoS_2 to detect various kinds of gasses molecules.

In this study, three different strategies to modify the surface structure and also phase structure of MoS_2 were conducted. The first strategy is the modification of the phase structure and also surface structure of MoS_2 through ethylene glycol intercalation techniques to detect toluene gas at room temperature. Since MoS_2 is a polytopic material, MoS_2 has several different structures. 2H-MoS_2 as the most stable structure of MoS_2 with tetragonal coordination has a semiconductor characteristic with band gap energy around 0.9 eV to 1.8 eV. On the other hand, the 1T-MoS_2 structure with orthogonal coordination has a metallic characteristic and is relatively less stable than 2H-MoS_2. In terms of chemical reactivity, 2H-MoS_2 is less reactive due to the inert conditions on the basal plane of MoS_2. On the other hand, 1T-MoS_2 is very reactive for chemical reactions. Based on these two different properties of 1T and 2H-MoS_2. The formation of 1T/2H-MoS_2 heterostructure offers good reactivity and good stability for gas sensor applications at room temperature.

Ethylene glycol was used as a solvent due to its strong reducing ability and also lower polarity than water which will modify the phase structure and also surface structure at the same time. The ethylene glycol intercalation techniques were conducted through a solvothermal reaction process. Three different conditions were investigated to understand the role of ethylene glycol on surface structure and phase structure modification. Water solvent (MoS_2 (W)), water and ethylene glycol (MoS_2 (EG:W)), and ethylene glycol (MoS_2 (EG) solvents. The use of ethylene glycol as a solvent shifts the (002) diffraction pattern to the lower angle which indicates the expansion of the (002) lattice plane. The expansion of the (002) lattice plane is due to the ethylene glycol exist in the interlayer of MoS_2. The infra-red absorption analysis and also thermogravimetric analysis revealed that ethylene glycol existed in the interlayer of MoS_2. The phase structure analysis of all prepared samples investigated by Raman and X-ray Photoelectron Spectroscopy analysis had shown that the heterostructure of 1T-MoS_2 and 2H-MoS_2 has successfully formed and the number of 1T phase structure was higher when ethylene glycol was used as a solvent. This phenomenon occurred due to the ethylene glycol act as a reducing agent which helps the transformation from the 2H phase into 1T phase. Moreover, the specific surface area is also increased after ethylene glycol was used as a solvent due to the smaller particle size. After ethylene glycol was used as a solvent, the conductivity of the sensor devices decreases due to the ethylene glycol act as an insulating layer which can decrease the conductivity of MoS_2. However, the toluene sensor performance has revealed that the MoS_2 (EG:W) shows the highest toluene detection performance followed by MoS_2 (EG) and MoS_2 (W). From this result, it can be confirmed that high 1T content and also the high specific surface area of MoS_2 are beneficial to improve toluene detection at room temperature.

The second strategy to modify the surface structure of MoS_2 is through O_2 plasma irradiation. O_2 plasma irradiation offers a green and rapid process to modify the MoS_2 properties. The O_2 plasma irradiation can control the crystal structure and also surface structure of MoS_2 including defects creation and morphology modification. Moreover, the oxygen plasma irradiation also gives additional advantages for MoS_2 properties because it can stabilize the transition metal dichalcogenide (TMDs) in the air atmosphere. In this study, the O_2 plasma irradiations of MoS_2 (EG:W) samples were conducted to modify the surface structure of MoS_2 for humidity detection devices. 0, 1, 5, and 10 minutes O_2 plasma irradiation were conducted to analyze the influence of O_2 plasma irradiation on MoS_2 structures. After O_2 plasma irradiation, the diffraction position of the (002) plane was gradually shifted to a higher angle which indicates the shrinking of the interlayer of MoS_2 after O_2 plasma irradiation due to the removal of ethylene glycol in the interlayer of MoS_2. The O_2 plasma irradiation successfully removed some of the sulfur species and also some impurities were produced due to the oxidation of Mo^{4+} into MoO_3 state. The surface structure of MoS_2 was greatly modified after O_2 plasma irradiation. The

specific surface area greatly increases from 28 To 185 m^2/g After O_2 plasma irradiation. This phenomenon occurred due to the change of the morphology of MoS_2 after O_2 plasma irradiation from the flower-like structure into a leaf-like structure. The humidity detection process was conducted at room temperature and also at different humidity values. The humidity sensor response of MoS_2 greatly improved after O_2 plasma irradiation from 24.32 % to 48.36 % at 95% RH. It indicates that the O_2 plasma irradiation successfully improved the humidity sensor performance of MoS_2. The high humidity detection performance of MoS_2 after O_2 plasma irradiation is due to several reasons. The first one is a high defect content such as S vacancy and O_2 doping which is effective to increase the reactivity of MoS_2. The second one is the higher specific surface area which is beneficial to increase the number of active sites for the humidity detection process. In practical applications, the humidity sensor has been applied for various kinds of applications such as breath monitoring, and also humidity skin monitoring.

The third strategy to modify the crystal structure and also surface structure of MoS_2 is through the doping process. The purpose of this doping process is to change the chemical bonding in the crystal structure (expand or shrink). The modification of the chemical bonding could act as active sites for gas adsorption due to the presence of strain in the crystal structure. Strain in the crystal structure of MoS_2 can increase the molecular adsorption ability including higher adsorption energy, closer adsorption distance, and better charge transfer ability. In this study, some part of S atom in the MoS_2 structure was substituted by Se atom to form MoSSe solid solution to detect NO gas at room temperature. The Se atom is also one of the chalcogen anions, therefore, the S substitution by Se ion will not significantly change the crystal structure. $MoS_{2-x}Se_x$ solid solution was prepared by hydrothermal reaction followed by annealing treatment. Different Se concentrations were prepared (x=0, 0.2, 0.5, 1.8, and 2.0) to understand the influence of selenium atom doping on the crystal structure of MoS_2. In the hydrothermal process, the selenium atom can decrease the nucleation process of MoS_2 crystal which induces a lower crystallinity and also smaller particle size. The low crystallinity of $MoS_{2-x}Se_x$ solid solution makes the conductivity of MoS_2 high. In these conditions, the NO detection sensitivity is low due to a small electrical signal. After the annealing process, the crystallinity significantly increases. The substitution of sulfur element by selenium element in the TMDs structure increased the lattice parameter a=b from 3.148(0.1) Å for x = 0 to 3.279 (0.08) Å for x = 2. The selenium addition does not only modify the crystal structure but also the particle size of MoS_2 decreased after selenium addition (from 500 nm for x = 0 to 80 nm for x = 2). The optical properties of MoS_2 are also modified after selenium addition, the band gap energy of MoS_2 decreases after selenium addition. The $MoS_{2-x}Se_x$ (x=1) exhibits the best NO detection response with a response percentage around 47 % at 3 ppm NO concentration. The highest NO detection

performance of x=1 is due to the small particle size, high adsorption energy, and high charge transferability. The $MoS_{2-x}Se_x$ solid solution nanoparticles were also stable at different humidity environment and also good selectivity upon NO gasses. Therefore, the $MoS_{2-x}Se_x$ solid solution nanoparticles can be potentially used as NO detection at room temperature.

Based on this research, it can be concluded that the crystal structure and surface structure modifications of MoS_2 layers are crucial to improve the gas sensor performance of MoS_2. Even though this research gives clear information about the important role of MoS_2 modifications for gas sensor improvement, however, another challenge still needs to be overcome to provided MoS_2 as a wearable sensor device such as selectivity, response, and recovery speed, and also long-term stability.

（別紙）

論文審査結果の要旨及びその担当者

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論　文　題　目	Crystal-phase and surface-structure engineering of MoS_2 for improving gas sensor performance at room temperature（室温でのガスセンサー性能の向上に資する MoS_2 の結晶相と表面構造エンジニアリング）
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論文審査結果の要旨

二硫化モリブデン（MoS_2）は、代表的な遷移金属カルコゲナイドの一種であり、優れた柔軟性、吸着能、室温での反応性を有し、ウェアラブルセンサーデバイスとしての利用が期待される。MoS_2 にはいくつかの幾何異性構造があり、2H-MoS_2 はバンドギャップエネルギーが約 0.9 eV～1.8eV の半導体相であるが、1T-MoS_2 は金属相となり、比較的低い安定性を有し、化学反応に対して高い活性を示すとされる。MoS_2 の層状構造の端サイトは活性部位とされており、材料表面を修飾することにより、センサーの応答値、応答速度、並びにガス分子との反応性に影響を与えることが期待される。本学位論文では、ソルボサーマルプロセスによる材料合成を行い、さらに様々な手法による MoS_2 の表面構造と相組成に対する修飾を行い、種々の環境ガスに対する室温検出性能の実現と高度化を目指した。

本学位論文は全５章から構成される。

第一章は、本研究のバックグランドや国内外の研究進展について紹介した。二次元(2D)マテリアルの合成、構造、応用についても紹介し、MoS_2 の相組成、物理化学特性、吸着特性、様々なガス組成に対する応答機能やメカニズム、表面修飾による材料機能向上等について解説し、優れた環境応答機能を実現するための材料設計指針について、最新の文献を引用しながら紹介を行った。

第二章は、ソルボサーマルプロセスにおけるエチレングリコールのインターカレーションによる MoS_2 の相組成と表面構造の修飾に関する調査を行った。エチレングリコールは、水よりも還元能力が高く、極性が低いため、溶媒として使用する際、相構造と表面構造に影響を与える。水、エチレングリコール（EG)、及び水と EG の混合溶媒等、異なる溶媒を用いたソルボサーマル条件下で MoS_2 を合成し、EG をインターカレートした MoS_2 は、インターカレーションなしの MoS_2 と比較し、より多くの 1T 相（金属相）を有し、異なる相対湿度での室温トルエン検知に応用できることを明らかにした。

第三章は、酸素プラズマ処理による MoS_2 の表面修飾及びガスセンシング機能に対する影響を検証した。酸素プラズマ照射を行い、水熱反応で合成した MoS_2 の層間に存在するエチレングリコールや硫黄の一部を除去することにより、硫黄欠陥が生じ、一部の Mo^{4+} が MoO_3 状態に酸化されたことを見出した。さらに、酸素プラズマ処理による比表面積の劇的増加をもたらし、MoS_2 の反応性を高め、応答サイトの数が増え、湿度に対する応答が大幅に改善されたことが分かった。こうした機能は、呼気生体ガスや皮膚中の湿度等瞬時にモニタリングすることに応用できることを提案し、デバイスとして優れたポテンシャルを示した。

第四章は、MoS_2 構造の S 原子の一部を Se 原子に置き換えて、ドーピングによる MoSSe 固溶体を形成し、室温で優れた NO ガス検出機能について検証した。セレンの添加により、MoS_2 の結晶構造や粒子サイズに影響を与え、 MoSSe は MoS_2 に比べ粒子サイズが小さく、比表面積が大きく、電荷移動性も優れており、さまざまな湿度環境でも安定し手織り、NO ガスに対して優れた選択性と高い感度を示すことが明らかにした。

第五章は、論文の総括である。

よって，本論文は博士(学術)の学位論文として合格と認める。