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学位論文題目	Growth of Transition Metal Dichalcogenides Layers by Chemical Vapor Deposition (CVD) and Investigation of their Photoresponse Properties （化学気相合成(CVD)法による遷移金属ダイカルコゲナイド層の成長とその光応答特性の評価）		
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論文内容の要旨

The transition metal dichalcogenides (TMDCs) layered materials have recently attracted significant attention due to their unique physical and chemical properties. Bulk TMDCs are normally indirect bandgap, whereas, monolayer TMDCs are direct band gap semiconductors, which has a lot of significant for device application. In this thesis, synthesis of monolayer TMDCs such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) by chemical vapor deposition (CVD), their environmental stability and fabrication of heterojunction optoelectronic device were investigated.

Chapter 1 describes the background of TMDCs materials and their unique properties. Then different synthesis methods of TMDCs layer, the characterizations of synthesized materials, identifying the layered structure, stability issues and current trend of device applications are discussed. The challenges in synthesis of monolayer TMDCs and their device fabrication process are addressed, in the motivation and objective part.

Chapter 2 deals with synthesis of TMDCs layer using a developed CVD technique particularly for this research work. The growth of ribbons, triangular crystals and continuous film of MoS_2 and WS_2 layers was achieved by the CVD method with specific parameters. The

MoS_2 ribbon structure with high edge density can be suitable for catalytic purpose. However, the ribbon shows poor photoluminescence (PL) than that of triangular crystals, hence further studies were performed for only triangular crystals and films. During the growth of the MoS_2 and WS_2 layers by the CVD method, some degradation was observed due to environmental exposure as explained in the next chapter.

Chapter 3 analyzes the detail degradation process of MoS_2 and WS_2 layers and subsequent encapsulation, which is an important aspect for practical device application of the TMDCs layers. Detailed analysis of degraded area showed that the degradation patterns appear due to oxidation and significant loss of sulfur from defective sites and edges. To prevent the dilapidation, dry encapsulation of TMDCs layer at room temperature with hydrophobic Teflon and carbonaceous layer was explored. The encapsulated dichalcogenide samples remained intact after heating at 200°C with stable photoconductivity. As in the encapsulation studies showed a foreign material can be directly deposited to reduce environmental degradation, heterostructure devices were designed by depositing a foreign semiconductor on top of the MoS_2 layer.

Chapter 4 discusses the possibility of fabricating unique germanium (Ge)-MoS_2 heterostructure device as both materials possess layered structures. Ge with a lower bandgap (0.66 eV) than that of silicon (1.1 eV) has been widely used for infrared (IR) photodiode. The Ge film was directly deposited by low pressure thermal evaporation on CVD synthesized MoS_2 layer. A thin interface was formed between the thermally evaporated Ge and chemical vapor deposited MoS_2 layers, considering the atomically smooth surface of MoS_2. It was realized that the demonstrated ultrathin heterojunction of Ge and MoS_2 layers can be significant for developing self-powered broadband photodetectors beyond silicon device wavelength.

Chapter 5 focuses on fabrication of a wide bandgap semiconductor and MoS_2 layer heterojunction. In this case, copper iodide (CuI) was chosen considering the p-type conductivity, where the counterpart MoS_2 layer is n-type. The CuI layer was deposited by two different methods, solid phase iodization and direct thermal evaporation. Significant quenching of PL peak for the MoS_2 layer in CuI/MoS_2 heterostructure was observed attributing a spontaneous charge separation. A CuI/MoS_2 heterojunction device was fabricated on sapphire substrate, which showed prominent photoresponsivity with light illumination. This suggests that a p-type halide can be very effective on MoS_2 layer for developing heterojunction device.

Chapter 6 summarizes this work and explores future prospects.

論文審査結果の要旨

The transition metal dichalcogenides (TMDCs) layered materials have recently attracted significant attention due to their unique physical and chemical properties. Bulk TMDCs are normally indirect bandgap, whereas, monolayer TMDCs are direct bandgap semiconductors, which has a lot of significance for device application. In this thesis, synthesis of monolayer TMDCs such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2) by chemical vapor deposition (CVD), their environmental stability and fabrication of heterojunction optoelectronic device were investigated.

Synthesis of TMDCs layer using a developed atmospheric pressure CVD (APCVD) technique particularly for this research work was investigated with respect to various parameters. The growth of ribbons, triangular crystals and continuous film of MoS_2 and WS_2 layers was achieved by the CVD method with specific growth conditions. The MoS_2 ribbon structure with high edge density can be suitable for catalytic purpose. However, the ribbon shows poor photoluminescence (PL) than that of triangular crystals, hence further studies were performed for only triangular crystals and films. After the growth of the MoS_2 and WS_2 layers by the CVD method, some degradation was observed due to environmental exposure.

The detailed degradation process of MoS_2/WS_2 layers and subsequent encapsulation were investigated, which is an important aspect for practical device application of the TMDCs layers. Detailed analysis of degraded area showed that the degradation patterns appear due to oxidation and significant loss of sulfur from defective sites and edges. To prevent the dilapidation, dry encapsulation of TMDCs layer at room temperature with hydrophobic Teflon and carbonaceous layer was explored. The encapsulated dichalcogenide samples remained intact after heating at 200°C with stable photoconductivity. As in the encapsulation studies showed a foreign material can be directly deposited to reduce environmental degradation, heterostructure devices were designed by depositing a foreign semiconductor on top of the MoS_2 layer.

The possibility of fabricating of unique germanium (Ge)-MoS_2 heterostructure device as both materials possess layered structures was investigated. Ge with a lower bandgap (0.66 eV) than that of silicon (1.1 eV) has been widely used for infrared (IR) photodiode. The Ge film was directly deposited by low pressure thermal evaporation on CVD synthesized MoS_2 layer. A thin interface was formed between the thermally evaporated Ge and chemical vapor deposited MoS_2 layers, considering the atomically smooth surface of MoS_2. It was realized that the demonstrated ultrathin heterojunction of Ge and MoS_2 layers can be significant for developing self-powered broadband photodetectors beyond silicon device wavelength.

Then, the possibility of combining the CVD synthesized MoS_2 layer with a wide bandgap semiconductor has been explored. In this case, copper iodide (CuI) was chosen considering the p-type conductivity, where the counterpart MoS_2 layer is n-type. The CuI film was deposited by two different methods, solid phase iodization and direct thermal evaporation. Significant quenching of PL peak for the MoS_2 layer in CuI/MoS_2 heterostructure was observed attributing a spontaneous charge separation. A CuI/MoS_2 heterojunction device was fabricated on sapphire substrate, which showed promising photoresponsivity with light illumination. This suggests that a p-type halide can be very effective on MoS_2 layer for developing heterojunction device.

Above-mentioned findings are significant in terms of TMDCs research, which will help world scientist to understand various structures of MoS_2 layer and their stability issues. From the understanding of growth and stability point of views, novel device structures were proposed in this thesis to overcome limitation of conventional technology. The research findings were published in reputed international journals that is enough worth for PhD thesis.