Characterization of Vertically Aligned MoS2 Thin Film on Mo Electrode for Hydrogen Evolution Catalyst

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Vertically aligned MoS2 (V-MoS2) thin film was investigated to achieve a cost-effective hydrogen evolution reaction (HER) catalyst. As a simple method, the V-MoS2 film was deposited by partial sulphurisation of RF sputtered Mo film. The residual Mo layer was used as a bottom electrode instead of an expensive conductive substrate such as a glassy carbon. Different thicknesses of V-MoS2 were deposited to investigate an HER catalyst characteristic for the V-MoS2/Mo structure. The crystallinity of V-MoS2 was maintained even though the thickness of V-MoS2 was controlled, and was confirmed by comparing the X-ray diffraction, Raman measurement, and estimated exchange current density. As the thickness of V-MoS2 was decreased to 50 nm, the overpotential and Tafel slope were reduced to 0.38 V at 10 mA/cm² and 87 mV/dec, respectively. Based on the theoretical tendency of Tafel slope decline, the estimated optimal V-MoS2 thickness was 40 nm for the V-MoS2/Mo structure. The fabrication process for V-MoS2 and the estimated result from the variation of the thickness of V-MoS2 could help to realise a cost-effective HER catalyst using MoS2.

Key Words
Vertically aligned, MoS2, Catalyst, HER

1. Introduction

Transition metal dichalcogenides (TMDs) make up one of the large groups of two-dimensional (2D) materials. TMDs are generally described by the formula MX2, where M represents a transition metal such as molybdenum (Mo), tungsten (W), or niobium (Nb), and X represents a chalcogenide such as sulphur (S), selenium (Se), or tellurium (Te). The electrical properties of TMDs vary from semiconducting to superconducting and include direct and indirect energy bandgaps, depending on the number of layers. MoS2 is a representative TMD semiconductor with a bandgap ranging from 1.3 eV in bulk to 1.9 eV in a monolayer. MoS2 is a representative TMD semiconductor with a bandgap ranging from 1.3 eV in bulk to 1.9 eV in a monolayer. Most research has focused on single and few-layer MoS2 because of the attractive potential of nano-electronic and optoelectronic devices. In contrast, less effort has concentrated on the edges of these layered materials. There are two representative edge sites: edges formed by the absence of atoms on a TMD layer’s terrace (D-edges) and the geometrical ends of a TMD layer (E-edges). The D-edges are chemically active to manipulate properties of layered materials (e.g., n-type doping for graphene). The E-edges are the active site for essential catalytic reactions such as hydrodesulphurization, hydrogen evolution, methane conversion, and oxygen reduction. MoS2 presents a suitable energy band structure for the redox potential for hydrogen evolution reactions (HERs) as its conduction band minimum lies above the electrostatic potential of H2 evolution. Moreover, the simulated Gibbs free energy of adsorbed atomic hydrogen for the edge of MoS2 was nearly equal to the Pt.

The vertically aligned MoS2 (V-MoS2) thin film has attracted interest in exposing the E-edge of MoS2. Although previous reports have demonstrated the catalytic behaviour of HER using V-MoS2, further systemic works are necessary to realise the cost-effective MoS2 catalyst. Much work has been carried out on an expensive conductive substrate such as glassy carbon because of limited selectivity with the high annealing temperature (over...
800 °C) for a MoS$_2$ crystallisation. In this experiment, the V-MoS$_2$ thin film was formed by partial sulphurisation of the Mo film. The residual Mo layer was used as a bottom electrode for a catalyst, to improve the freedom of substrate selectivity. Catalytic property variation with different thicknesses of V-MoS$_2$ was investigated to optimise the V-MoS$_2$/Mo structure.

2. Experimental methods

The 400 nm-thick Mo film was deposited by an DC sputter on the cleaned SiO$_2$ substrate. The SiO$_2$ substrate’s surface was first treated with a piranha solution (H$_2$SO$_4$:H$_2$O$_2$=3:1) to enhance the adhesion of Mo and the SiO$_2$ substrate. As a bottom electrode for electrochemical measurement, the Mo thin film was partially sulphurised to form the V-MoS$_2$/Mo structure. The annealing process was conducted in an Ar atmosphere of 1 kPa at 800 °C for 5 min in a furnace. After reaching the annealing temperature, the sulphur powder (3N) was evaporated at 160 °C from another furnace to supply the sulphur source. The adjusted quantity of sulphur controlled the thickness of the V-MoS$_2$. To characterise the crystallinity of the V-MoS$_2$ thin film, X-ray diffraction (XRD) measurement was performed using a Rigaku Ultima IV X-ray diffractometer at 40 kV and 40 mA with Cu K$_\alpha$ radiation. The morphology of the surface and thickness of V-MoS$_2$ were investigated using a field emission scanning electron microscope (FE-SEM S-4800, Hitachi). The nanostructure of V-MoS$_2$ was observed using a transmission electron microscope (TEM). The catalytic properties were investigated by the electrochemical analyser (ECstate-301, EC Frontier) using an Ag/AgCl reference electrode in 0.5M H$_2$SO$_4$ solution.

3. Results and discussion

The cross-section SEM images of the V-MoS$_2$/Mo/SiO$_2$ structure are shown in Fig. 1 (a). The V-MoS$_2$ layer formed by the partial sulphurisation of the Mo thin film is clearly shown. The boundary of the V-MoS$_2$ layer has almost the same level due to the uniform diffusion of sulphur. The diffusion length of atoms into a solid is dependent on annealing temperature, time, and the diffused atom density on the surface following Fick’s law. However, these parameters also affect the crystallinity of V-MoS$_2$ in the sulphurisation process. Thus, to maintain the crystallinity of V-MoS$_2$ with different thicknesses, the annealing temperature, time, sulphur evaporation temperature, and pressure in the chamber were maintained. Although further investigation on the growth mechanism of V-MoS$_2$ in a sulphurisation process is needed, the thickness of V-MoS$_2$ was controlled by the supply time of the sulphur source, which was adjusted by the quantity of sulphur powder. As a result, the thickness of the V-MoS$_2$ was decreased from 90 nm to 50 nm as the quantity of sulphur powder was reduced from 30 mg to 5 mg, as shown in Fig. 1 (b).

The crystalline structure of V-MoS$_2$ with different thicknesses was investigated by XRD and Raman spectroscopy. The XRD patterns of the V-MoS$_2$/Mo/Si structures with different V-MoS$_2$ layer thicknesses are shown in Fig. 2 (a). The diffraction of MoS$_2$(002) at 15°, in which the terrace of MoS$_2$ is parallel to the substrate, was not visible in all films. MoS$_2$(110) at 58.5° and MoS$_2$(100) at 32.6°, in which the terrace of MoS$_2$ is vertically aligned with the substrate, were observed. The diffraction peaks of MoS$_2$(110) at 32.6° were located near Si(002), as shown in Fig. 2 (b). Each calculated full width at half the maximum MoS$_2$(110) at 2θ=58.5° for the different thickness was almost the same as that of 2θ=0.8°. There are other peaks, such as MoO$_2$, which are not related to MoS$_2$. The Si substrate was treated with a piranha solution to enhance the adhesion of Mo before RF sputtering by hydroxide termination. In this process, the hydroxide produced SiO$_2$ on the interface between Mo and the Si substrate. Hence, MoO$_2$ was formed by reacting the oxygen in SiO$_2$ with Mo, not in the V-MoS$_2$ layer, during the sulphurisation process. The Raman spectra of V-MoS$_2$ thin films with different thicknesses are shown in Fig. 2 (c). For all films, the Raman
smaller than 2. Based on the XRD and Raman results, the prepared V-MoS$_2$ films of various thicknesses had similar crystallinities and vertically aligned structures.

The cross-section TEM image verified the vertically aligned structure of V-MoS$_2$. The V-MoS$_2$/Mo/SiO$_2$ structure is shown in Fig. 3 (a). A layered MoS$_2$ structure (interlayer space of 0.62 nm) was observed, as shown in Fig. 3 (b), even though the thickness of V-MoS$_2$ was much thicker than the samples in this experiment. The vertically aligned layers perpendicular to the substrate caused the surface of the V-MoS$_2$ thin film to have a predominant exposure to the edge site of MoS$_2$.

The catalyst is characterised by the Tafel equation as follows:

$$\eta = A^* \ln \left( \frac{J}{J_0} \right) \quad (1)$$

$$A = \frac{kT \alpha_c F}{e} \quad (2)$$

where $\eta$ is overpotential, $A$ is Tafel slope, $J$ is current density, $J_0$ is exchange current density, $k$ is the Boltzmann constant.
\( \alpha \) is the charge transfer coefficient at the cathode, \( F \) is the Faraday constant, and \( T \) is the temperature. For these parameters, the polarisation characteristics (current density-potential, or \( J-V \)) of the V-MoS\(_2\) with different thicknesses were measured, as shown in Fig. 4 (a). The overpotential at \(-10\) mA/cm\(^2\) was decreased from 0.8 V to 0.38 V with the reduction of V-MoS\(_2\) thickness. A relatively thicker V-MoS\(_2\) film had additional resistance as a result of a catalytic non-activated region causing a voltage drop to the active area. Hence, the thinnest V-MoS\(_2\) film resulted in the lowest overpotential. The exchange current density, which is the x-axis crossed point at 0 V with each line extended, can be estimated from the log \( J-V \) plot, as shown in Fig. 4 (b). Interestingly, the exchange current densities of all samples were nearly the same value, 2.0 \( \mu \)A/cm\(^2\), indicating that the reduction rate on the V-MoS\(_2\) surface was maintained even though the thickness was controlled.

The theoretical Tafel slope for HER ranges from 40–120 mV/dec. The Tafel slopes for the tested samples were determined to be 189, 153, and 87 mV/dec for 90, 75, and 50 nm thicknesses, respectively, by fitting the linear part of the Tafel plot, as shown in Fig. 4 (b). The Tafel slope (A) has the transfer coefficient (\( \alpha_c \)), as shown in Eq. (2), which is determined by a sequence of consecutive elementary electron transfer steps and chemical steps. The relatively thicker V-MoS\(_2\) has a larger bulk region, which could be a form of resistance, one that does not join an HER and interfere with a charge transfer from the electrode to a reactive site on an edge of MoS\(_2\). From the variation of the Tafel slope of V-MoS\(_2\) with decreased film thickness, the optimal thickness of a catalyst using V-MoS\(_2\) could be estimated to be roughly 32 nm, as shown in Fig. 4 (c), based on the theoretical limited Tafel slope of 40 mV/dec.

Although considerable work is still required to enhance the catalytic performance of V-MoS\(_2\), such as engineering a Mo-edge of MoS\(_2\), the results in this study serve as the first step towards realising a cost-effective HER catalyst.

4. Conclusions

In this study, the catalytic characteristics of V-MoS\(_2\) thin films with different thicknesses were systemically investigated as part of efforts to achieve a cost-effective HER catalyst. The thicknesses of V-MoS\(_2\) thin films were controlled by only the sulphur supply time. The different thicknesses of V-MoS\(_2\) showed a vertically aligned structure and no significant changes in crystallinity. Catalytic parameter variation following a reduction of V-MoS\(_2\) film thickness was shown for the V-MoS\(_2\)/Mo structure. Overpotential and the Tafel slope decreased as the thickness of the V-MoS\(_2\) was decreased since reduction of the V-MoS\(_2\) region that does not enter a chemical reaction might increase the charge transfer coefficient. We speculated that the optimal V-MoS\(_2\) thickness is 32 nm, but the merit of this figure is limited as it is based on a theoretical Tafel slope for an HER, used to construct the V-MoS\(_2\)/Mo structure for a catalyst. Although further investigation is required to enhance the catalytic performance of V-MoS\(_2\), this experiment could be a cornerstone to realizing a cost-effective HER catalyst.
effective and straightforward method for creating an HER catalyst using V-MoS₂.

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