博士論文（要約）

Ta_3N_5 and $BaTaO_2N$ Thin Film Photoanodes for Solar-driven Water Splitting

(太陽光利用水分解のための Ta_3N_5 および $BaTaO_2N$ 薄膜光アノードの研究)

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Abstract

Photoelectrochemical (PEC) water splitting is one of the most promising approaches to convert and store solar light energy in the form of hydrogen. A typical p/n PEC device consists of a photoanode for oxygen evolution and a photocathode for hydrogen evolution. In order to achieve a high solar-to-hydrogen efficiency, the semiconductor material as photoelectrode used for PEC water splitting should have a narrow band gap (1.6-2.5 eV) to absorb sufficient part of visible light in the solar spectrum. (Oxy)nitride materials, such as Ta_3N_5, $BaTaO_2N$ and $LaTiO_2N$, absorb over a sufficient range of visible light wavelengths in the solar spectrum and have suitable band edge positions to allow for efficient PEC water oxidation.

The state-of-the-art (oxy)nitride photoanodes with high efficiency for PEC water oxidation were mostly fabricated based on metallic substrates by thermal nitridation process in a flow of NH_3 gas. Further improvements of PEC activities and stability were limited by the lack of suitable fabrication methods and the difficulties in controls over the electrode structures. In addition, effects of the back contact layers on the crystalline, structural and PEC properties of (oxy)nitride electrodes have not been explicitly investigated yet. The primary objectives of this thesis are to develop Ta_3N_5 and $BaTaO_2N$ thin film photoanodes with high efficiency and stability for PEC water oxidation by investigating the new fabrication methods, the properties of thin film layer, the semiconductor/substrate interface and electrode/electrolyte interface.

In chapter 2, a thin film transfer method was introduced for the fabrication of Ta_3N_5 electrodes with controllable film thicknesses and layered structures. Ta_3N_5 thin film was initially formed on Si substrate and subsequently transferred onto a conductive substrate via a mechanical exfoliation process with preserved phase purity and film structure. This new preparation method enabled the optimization for the PEC performance of Ta_3N_5 photoanodes by varying the film thickness and back contact layers. It was found that Ta_3N_5 photoelectrode with

a film thickness approximately 600 nm and a Ta back contact layer produced relatively high PEC activity. The photocurrent density at 1.23 V vs. RHE could be enhanced from 2.2 to 3.5 mA cm^{-2} in the presence of a buffer interlayer (NbN_x) between the Ta_3N_5 thin film and the back substrate.

Effects of the buffer interlayers on the crystalline structure and PEC performance of Ta_3N_5 photoelectrodes were studied in chapter 3. The layered structure of the Ta_3N_5/NbN_x/Ta/Ti sample is demonstrated by an observation of the sample's cross section. In the presence of NbN_x interlayer, the preference in the crystalline orientation of the Ta_3N_5 film was favored owing to the lattice spacing matching of Ta_3N_5 and Nb_4N_5 phases. An ordered growth for Ta_3N_5 film occurred and a 200 nm layer of highly grain-oriented Ta_3N_5 was formed near the Ta_3N_5/NbN_x interface. It is indicated that the formation of an oriented Ta_3N_5 layer could possibly promote the electron mobility in the Ta_3N_5 film near to the Ta_3N_5/NbN_x interface. Therefore, the photogenerated charges near the surface mainly contribute to the PEC water oxidation more effectively in the presence of a NbN_x interlayer, given that the migration distance required for holes to reach the surface is shorter in a disordered Ta_3N_5 layer. The introduction of the NbN_x interlayer thus enhances the PEC performance of Ta_3N_5 photoelectrode.

In chapter 4, the concepts of tuning film structures and employing buffer interlayers were applied for the carbon-based Ta_3N_5 photoelectrodes. It was found that the carbon substrate composed of graphite fiber structure can act as an effective substrate for (oxy)nitride electrode, owing to the high conductivity and resistance against thermal nitridation process. Herein, a new type of photoanode with a Ta_3N_5/TaN_x/Ta/C multi-layered structure was fabricated. The promoting effects of buffer interlayers on electron transport resulted in a significant increase in the photocurrent of the carbon-based Ta_3N_5 photoelectrodes. After the deposition of a $Co(OH)_x$ layer as a protective layer and an oxygen-evolution catalyst, the Ta_3N_5 photoelectrode could be

stabilized for more than 2 h for PEC water oxidation. Scanning electron microscopy (SEM) results demonstrated that the surface of Ta_3N_5 electrode was homogeneously covered with a $Co(OH)_x$ layer with a stacked sheet structure. As a consequence, the exposure of Ta_3N_5 layer to the electrolyte was ruled out and the photocorrosion of Ta_3N_5 electrode could be suppressed maximally in the presence of appropriate surface modifications.

In chapter 5, synthesis of nanostructured $BaTaO_2N$ thin films on Ta substrates and their applications as photoanodes for PEC water oxidation were studied. A $Ba_5Ta_4O_{15}$ layer with vertically aligned nanosheet structures was formed as a result of the hydrothermal reaction of Ta and $Ba(OH)_2$, and was subsequently transformed to $BaTaO_2N$ thin film by nitridation. The oxide nanosheets have been structurally altered to produce a $BaTaO_2N$ film at nitridation temperature of 1000 ℃. The layered structure $BaTaO_2N/Ta_4N_5/Ta$ was demonstrated by the SEM and EDX analyses. The formation of Ta_4N_5 interlayers was caused by Ta diffusion and reduction of $BaTaO_2N$ films. In the presence of a cobalt phosphate (CoPi) catalyst, the photocurrent density was significantly increased from 0.2 to 0.75 mA cm^{-2} at 1.23 V vs. RHE. The photocurrent decreased by only 3% during a 5 h measurement at 1.23 V vs. RHE, while the Faradaic efficiency for oxygen production remained almost unit. The CoPi layer acted not only as an oxygen-evolution catalyst, but also protected the surface of the $BaTaO_2N$ photoanode.

The (oxy)nitride photoelectrode configurations, prepared by thin film transfer method or by applying carbon substrates, can provide new approaches for the design of photoelectrodes toward efficient, stable PEC water splitting. The investigation of contact layer at the semiconductor/substrate interface can give a guideline for the controllable growth of oxynitride thin films with high electronic quality.