

論文の内容の要旨

論文題目 Ta₃N₅ and BaTaO₂N Thin Film Photoanodes for Solar-driven Water Splitting
(太陽光利用水分解のためのTa₃N₅およびBaTaO₂N薄膜光アノードの研究)

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World energy demand and consumption have been increasing rapidly for the past decades. Solar light energy, as a clean and renewable energy source, serves as an alternative to replace the traditional fossil energy. Photoelectrochemical (PEC) water splitting is one of the promising approaches to convert and store solar light energy via the formation of hydrogen. A typical p/n PEC device consists of a separate photoanode for oxygen evolution and a photocathode for hydrogen evolution. In order to achieve a high solar-to-hydrogen efficiency, the semiconductor material used for a photoelectrode should have a proper band gap (1.6-2.5 eV). (Oxy)nitride materials, such as Ta₃N₅, BaTaO₂N and LaTiO₂N, 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, mostly fabricated based on metallic substrates via thermal nitridation process in a flow of NH₃ gas, have been demonstrated to exhibit high efficiency of PEC water oxidation. However, the 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. Effects of the back contact layers on the crystalline, structural and PEC properties of electrodes have not been explicitly investigated yet. The primary objectives of this thesis are to develop Ta₃N₅ and BaTaO₂N 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 Ta₃N₅ electrodes with controllable film thicknesses and layered structures. Ta₃N₅ 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 Ta₃N₅ photoanodes by varying the film thickness and back contact layers. It was found that Ta₃N₅ 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 Ta₃N₅ thin film and the back substrate.

Effects of the buffer interlayers on the crystalline structure and PEC performance of Ta₃N₅ photoelectrodes were studied in chapter 3. The layered structure of the Ta₃N₅/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 Ta₃N₅ film was favored owing to the lattice spacing matching of Ta₃N₅ and Nb₄N₅ phases. An ordered growth for Ta₃N₅ film occurred and a 200 nm layer of highly grain-oriented Ta₃N₅ was formed near the Ta₃N₅/NbN_x interface. It is indicated that the formation of an oriented Ta₃N₅ layer could possibly promote the electron mobility in the Ta₃N₅ film near to the Ta₃N₅/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 Ta₃N₅ layer. The introduction of the NbN_x interlayer thus enhances the PEC performance of Ta₃N₅ photoelectrode.

In chapter 4, the concepts of tuning film structures and employing buffer interlayers were

applied for the carbon-based Ta₃N₅ 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 Ta₃N₅/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 Ta₃N₅ photoelectrodes. After the deposition of a Co(OH)_x layer as a protective layer and an oxygen-evolution catalyst, the Ta₃N₅ photoelectrode could be stabilized for more than 2 h for PEC water oxidation. Scanning electron microscopy (SEM) results demonstrated that the surface of Ta₃N₅ electrode was homogeneously covered with a Co(OH)_x layer with a stacked sheet structure. As a consequence, the exposure of Ta₃N₅ layer to the electrolyte was ruled out and the photocorrosion of Ta₃N₅ electrode could be suppressed maximally in the presence of appropriate surface modifications.

In chapter 5, synthesis of nanostructured BaTaO₂N thin films on Ta substrates and their applications as photoanodes for PEC water oxidation were studied. A Ba₅Ta₄O₁₅ 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 BaTaO₂N thin film by nitridation. The oxide nanosheets have been structurally altered to produce a BaTaO₂N film at nitridation temperature of 1000 °C. The layered structure BaTaO₂N/Ta₄N₅/Ta was demonstrated by the SEM and EDX analyses. The formation of Ta₄N₅ interlayers was caused by Ta diffusion and reduction of BaTaO₂N 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 BaTaO₂N 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.