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課題名（和文）	ペロブスカイト型酸化物の半導体光電極への応用
課題名（英文）	Photoelectrochemical Properties of Perovskite Flims
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研究成果の概要（和文）

現代社会が抱えるエネルギーと地球温暖化の問題の解決には，太陽光エネルギーを利用した水の分解の技術を実用化する必要がある。本研究は，製造コストが低いペロブスカイト型の金属酸化物を半導体光電極に利用した光エネルギー変換系を構築することを目指す。数あるペロブスカイト型酸化物の中で，ニオブ酸塩 $ANbO_3$（A = Na または K）は水の分解ができると報告されている。しかし，$NaNbO_3$ と $KNbO_3$ の固溶体である$(K,Na)NbO_3$（KNN）については光電気化学的な特性は全く調べられていなかった。そこで，本研究では KNN 薄膜を主にスパッタ法で作成し，KNN の光電気化学的な特性を明らかかにした。

研究成果の概要（英文）

Photoelectrochemical (PEC) processes are promising candidates to address environmental and energy issues. Previous studies have shown that Nb-related perovskite oxides such as $KNbO_3$ and $NaNbO_3$ have excellent photochemical (PC) activities. However, as for $(K,Na)NbO_3$ (KNN), nothing has been studied on its PEC and PC behaviour. This work studied PEC properties of a KNN thin film prepared mainly by a radio-frequency magnetron sputtering method. This work also studied PEC properties of a KNN thin film prepared by a chemical solution deposition method. The KNN films exhibited a PEC activity similar to a n-type semiconductor photoanode. We thus concluded that KNN is an active material for PEC water splitting.

1. 研究開始当初の背景

Photoelectrochemical (PEC) and photocatalytic (PC) processes driven by solar energy, e.g., PEC and PC water splitting, have been paid increasing attention because the processes are promising candidates to address environmental issues and energy shortages. For decades, considerable efforts have been made to find a suitable semiconductor material for the processes. Recently, sodium niobate ($NaNbO_3$) and potassium niobate ($KNbO_3$), which have typical ABO_3 perovskite structures, attract much interest in the field of photocatalysis because $NaNbO_3$ and $KNbO_3$ show excellent PC activities for H_2 generation. The band gap of $KNbO_3$ is 3.1 eV, which is slightly narrower than that of $NaNbO_3$ (3.4 eV), and thus $KNbO_3$ shows a higher PC activity than $NaNbO_3$ due to the narrower band gap and higher mobile charge carriers.

2. 研究の目的

The Nb-related perovskite oxides have other interesting properties in terms of ferroelectric, piezoelectric, dielectric, and optical properties. Moreover, they exhibit photovoltaic effects due to spontaneous electric polarisation. In these regards, potassium sodium niobate, $(K,Na)NbO_3$ (KNN), has also been studied extensively. However, nothing has been studied on its PEC and PC behavior. Thus, this work aims to demonstrate the PEC behavior of KNN thin films.

3. 研究の方法

The PEC properties of a KNN film, namely, the PEC activity, flat-band potential, and band gap of the KNN film, are examined by measuring cyclic voltammograms with and without UV-vis light irradiation, Mott-Schottky method, and Tauc method. The experiments were conducted in a glass cell with a quartz window using a three electrode system at room temperature. The electrolyte used was a 0.1 M NaOH solution prepared by dissolving NaOH in ultrapure water. A KNN thin film with a thickness of 2 μm was prepared on a $Pt/Ti/SiO_2/Si$ substrate mainly by a radio-frequency magnetron sputtering method.

4. 研究成果

We found that the KNN film showed PEC activity: the photoanodic current was observed on the KNN film photoelectrode in 0.1 M NaOH under irradiation of UV light. The oxidative photocurrent, which is likely to be due to the oxygen evolution reaction ($4OH^- \rightarrow O_2 + 2H_2O + 4e^-$), started to flow at -0.5 V *vs.* SHE and increased as the electrode potential increased. Mott-Schottky plots showed that the KNN film was an n-type semiconductor photoelectrode. The flat-band potential was estimated to be around -0.5 V from the onset potential of the photocurrent. The band gap of the KNN film was determined to be 3.27 eV from Tauc method. We think that PEC (and/or PC) activity increases in the following order: $NaNbO_3$ < KNN < $KNbO_3$. Furthermore, the film was hardly affected by potential cycles, i.e., it was stable during the PEC reaction. We can thus say that the KNN is an active material for the PEC water splitting

5. 主な発表論文等

〔雑誌論文〕（計 1 件）

① M. Kurohagi, Y. Mukouyama, D. Yoshinaka, I. Kanno, “Photoelectrochemical Properties of $(K,Na)NbO_3$ (KNN) Thin Film,” *ECSarXiv* (2019), Doi: 10.1149/osf.io/652fh

〔学会発表〕（計 1 件）

② M. Kurohagi, Y. Mukouyama, S. Ishii, H. Ohsaka, I. Kanno, “Photoelectrochemical Properties of $(K,Na)NbO_3$ (KNN) Thin Film,” 235th ECS Meeting,Dallas,USA,May,2019