論文 / 著書情報
Article / Book Information

題目(和文)	電気化学的水分解およびCO2還元を目的としたSiC光電極の開発
Title(English)	The development of SiC photo-electrodes for electrochemical water-splitting and CO2 reduction
著者(和文)	宋浚太
Author(English)	Jun Tae Song
出典(和文)	学位:博士（工学）, 学位授与機関:東京工業大学, 報告番号:甲第9786号, 授与年月日:2015年3月26日, 学位の種別:課程博士, 審査員:波多野　睦子,小田　俊理,宮本　恭幸,河野　行雄,小寺　哲夫 ,藤井　克司
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第9786号, Conferred date:2015/3/26, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨
THESIS SUMMARY

専攻： Department of	電子物理　　　　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　Engineering　）
学生氏名： Student's Name	Song Jun Tae	指導教員（主）： Academic Advisor(main)	波多野睦子
		指導教員（副）： Academic Advisor(sub)	小寺哲夫

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

With importance of development for solar-fuel energy resource, photoelectrochemical (PEC) water-splitting and CO_2 reduction with 3C-SiC semiconductor which is fulfilling the basic requirements for the application was evaluated and additionally developed towards the improvement of solar conversion efficiency and stability. We approach to enhance the performance with the effect of Pt particles and graphene passivation layer. Also, PEC CO_2 reduction is demonstrated with analysis of gas products by 3C-SiC photo-electrode. As a result, it is clarified that 3C-SiC semiconductor is significant candidates as promising photo-active materials for the solution of practical PEC device. The summary of each chapter is described as following.

In Chapter 3, we evaluated the potential and current obstacles of 3C-SiC semiconductor as photo-electrode for both water-splitting and CO_2 reduction with investigation of ideal prospective as the beginning of this research. Through the evaluation in respect of ideal solar-conversion efficiency with considering free-energy loss, future prospective and limitation has been reviewed. In the result of PEC characteristic, it is found that overpotential to drive water-splitting at the SiC surface is estimated to be too high 1.2 ~ 1.4 V while general oxide materials generally show the overpotential of 0.2 ~ 0.4 V for oxidation evolving reaction. Also, surface corrosion during PEC reaction is also limited for long-term stability. In Chapter 4 and Chapter 5, the strategies to compensate the current limitation of 3C-SiC photo-electrodes have been proposed.

In Chapter 4, we fabricated Pt particles by sputtering and annealing at 400 ℃ in order to enhance the carrier transport at the interface and surface durability. Importantly, lower onset potential from 1.1 V to 0.7 V indicating reduced overpotential is realized with Pt particles. With facile carrier transfer by induced potential between 3C-SiC and Pt particles, solar-to-hydrogen (STH) conversion efficiency at applied bias of 1.1 V (vs. RHE) is greatly improved by 33 times while achieving 0.1 %. In addition, enhanced stability with Pt particles is shown by suppressing the corrosion reaction due to the preferential oxidation at the Pt particle sides. We also presented the variation of Pt particles effect by the different annealing temperature during fabrication process. From the result, it was revealed that the annealing process leads the Pt as particle formation and reaction of Pt and Si resulting in Pt_2Si which is beneficial to have a good contact between Pt and SiC. Specifically, 500 ℃ is considered to develop the optimal contact and particle structure. However, 700 ℃ and 900 ℃ cause the excessive Pt_2Si formation and carbon compounds at the interface, respectively, resulting in lower performance. The Pt particle effect provides a significant role to promote the oxidation with overcoming the limitation of SiC semiconductor.

In Chapter 5, epitaxial graphene was fabricated on the SiC substrate by high temperature annealing at 1450 ℃ with variation of time and atmosphere for passivation. Thin graphene layer in Ar atmosphere is obtained showing a degraded PEC property than bare sample probably due to the Fermi level pinning at interface originated from low interaction with substrate and hydrophobic property. In stability issue, while bare 3C-SiC is suffered from the surface corrosion in whole surface area, 47 % in whole surface for graphene-covered sample (5 min) is not damaged. However, the other areas for graphene-covered sample is corroded even faster than bare 3C-SiC. In the damaged area, 2D peak of Raman spectrum is blue-shifted indicating graphene layer is stressed by SiO_2 or etched line formation underneath graphene layer. It is considered that current flow might be blocked through the undamaged surface because lattice mismatch of 3C-SiC and graphene layer leads to the electrical decoupling. However, surface oxidation occurs on the damaged surface with

invasion of water molecules through grain boundaries than water-splitting due to the hydrophobic property of graphene. Herein, we note that graphene layer itself is not directly attacked from 2D peak intensity. Thus, graphene layer have potential for passivation layer with optimal treatments although these controversial discussion needs more supporting proof. Therefore, it is expected to be improved with solution for the enhanced interaction with substrate and introduction of Pt particles or oxidized graphene for better catalytic ability.

In Chapter 6, we presents the CO_2 reduction system with 3C-SiC photo-electrode with two different counter electrodes (Pt and Ag). The gas products from CO_2 reduction by photo-excited carriers in 3C-SiC photo-electrode were analyzed. Here, we note that gas analysis is performed at applied bias of 1 V between photo-anode and cathode with micro gas-chromatography with high detectivity and fast analysis time enabling the time-dependent measurement without syringe sampling. We confirmed both H_2 and CO gas evolve after PEC reaction. It means water-splitting easily occurs in condition of aqueous solution. However, the product rate is different for Pt and Ag counter electrode. For Pt, 4 times faster H_2 production rate is achieved than Ag, while one of the CO is 2 times faster by Ag. Also, the ratio of CO to H_2 is 22.5 times with Ag electrode indicating Ag counter electrode promotes CO_2 reduction than water-splitting as compared to Pt. It is significant that CO_2 gas is reduced with light-excited carriers of 3C-SiC photo-anode although gas analysis is performed at an external bias of 1 V due to the difficulty at no bias limited by low performance of bare 3C-SiC as we reviewed. These results suggest the importance of 3C-SiC for pathway to obtain chemical energies not only for H_2 but also to decrease greenhouse gas (CO_2).