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Application of Ga_2O_3 as a substrate of GaN photo-electrode for CO_2 reduction

Masahiro Deguchi[1], Satoshi Yotsuhashi[1] Yoshihiro Yamashita[2], Shigenobu Yamakoshi[2], Kazuhiro Ohkawa[3], and Yuka Yamada[1]

[1] Advanced Technology Research Laboratory, Panasonic Corporation
3-4 Hikaridai Seika-cho Soraku-gun, Kyoto 619-0237, Japan
Phone: +81-774-98-2566 E-mail: deguchi.masa@jp.panasonic.com
[2] Tamura Corporation
2-3-1, Hirosedai,Sayama-shi, Saitama, 350-1328, Japan
3 Tokyo University of Science
6-3-1 Niijuku, Katsushika, Tokyo 125-8585, Japan

Abstract

Recent study shows that Gallium nitride (GaN) can be effectively applied to a photo-electrode for CO_2 reduction reaction. Here, we demonstrate that a single crystal Gallium oxide (Ga_2O_3) makes it possible to realize a vertical-current GaN photo-electrode. The photo-electrode consists of unintentionally doped AlGaN photo-absorbance layer and n^+-GaN electric conduction layer. From copper (Cu) counterpart-cathode electrode, formic acid (HCOOH) is mainly generated by light illumination alone.

1. Introduction

Gallium nitride (GaN) has attracted much attention during last two decades by its potential application to light-emitting diode (LED) or power device. Recently, its potential has been revealed to extend beyond solid devices: more specifically, that it can be used to generate hydrogen [1]and CO_2 reduction producing organic materials.[2-3] This means that GaN is effective not only for energy saving but producing energy resources. The authors showed that the photo-electrode can produce formic acid from CO_2 reduction efficiently by AlGaN/GaN hetero-structure.[3] In that case, since the device is fabricated on sapphire substrate, the electric current flows in lateral direction through n-GaN. If the current flow becomes vertical direction, the loss resistance will be reduced and the efficiency should be improved.

On the other hand, the capability of gallium oxide (Ga_2O_3) as a wide-gap semiconductor has been discussed recently, and the research for improvement of its crystal quality has been intensively progressed.[4-6] It may be one of the milestones that crystal level of Ga_2O_3 has been improved enough to construct and drive a metal-semiconductor field effect transistor (MESFET).[7]

In this study, we apply the GaN device on Ga_2O_3 single crystal substrate to the photo-electrochemical system of CO_2 reduction. Using a heavy-doping Ga_2O_3 substrate will enable us to realize a photo-electrode of vertical electric current. It is demonstrated that the AlGaN/GaN hetero-structure on Ga_2O_3 substrate actually acts as a photo-electrode for CO_2 reduction whose performance is almost as same as the conventional one.

2. Experimental and Results

Sn-doped β-Ga_2O_3 single crystal substrate was fabricated by edge-defined film-fed growth (EFG) method. The thickness of the substrate was 680 μm, and the carrier concentration was 6 x 10^{18} cm^{-3}. On the substrate, AlGaN/GaN photo-electrode layers were grown by Metal Organic Chemical Vapor Deposition (MOCVD). The photo-electrodes comprise an unintentionally doped (uid-) AlGaN and highly doped (n^+-) GaN layer. The n^+-GaN layer (Si-doped, n = 4.0 x 10^{18} cm^{-3}, d = 2.0 µm) acts as an electrically conductive region. The uid-AlGaN layer (Al concentration = 10.6 %, d = 78 nm) acts as a photo-absorbance region. NiO co-catalyst particles were appended to the surface of the photoelectrodes as is introduced in the previous study.[8] A Ti/Au layer, as ohmic contact, was evaporated on the reverse side of the β-Ga_2O_3 substrate. The brief illustration of the device is shown in Fig. 1 (a).

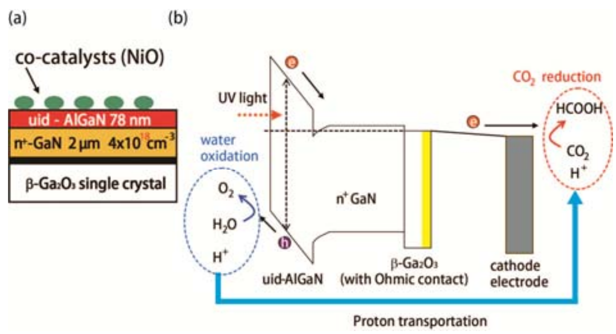

Fig. 1 Schematic illustration of (a) device structure of the photo-electrode and (b) reaction mechanism for CO_2 reduction.

For the photo-electrochemical measurement, we used so-called H-type cell which contains two chambers separated by cation exchange membrane (Nafion 117, Dupont) that prevents intercommunication of electrolytes. The electrons, excited illumination by light of the AlGaN layer, move to the cathode electrode, where they drive the CO_2

reduction reaction. The roles of photo-electrode and cathode electrode are shown in Fig 1 (b). For the cathode electrode, we use Cu plate of 99.9999% purity. The photo-electrode was immersed in 5 M sodium hydroxide (NaOH) electrolyte inside the anode chamber, and the cathode electrode was immersed in 3 M potassium chloride (KCl) inside the cathode chamber. The photo-electrode and the cathode electrode were electrically connected via an ammeter. An Ag/AgCl reference electrode was placed near the cathode electrode for the measurement of cathode potential.

A 300-W Xe arc lamp with a UV spectroscopic mirror was focused through a quartz optical fiber onto the surface of the cell. The cell for the cathode electrode was sealed, and CO_2 was introduced in the electrolyte by gas bubbling before the photo-electrolysis. Both the gas and liquid samples were analyzed, using gas and liquid chromatography respectively, after the photo-electrochemical reduction. Hydrogen was determined using a thermal conductivity detector (TCD) and CO, CH_4, C_2H_4, C_2H_6 were determined using the flame ionization detector (FID) attached to the gas chromatograph. Liquid chromatography was used for detecting HCOOH.

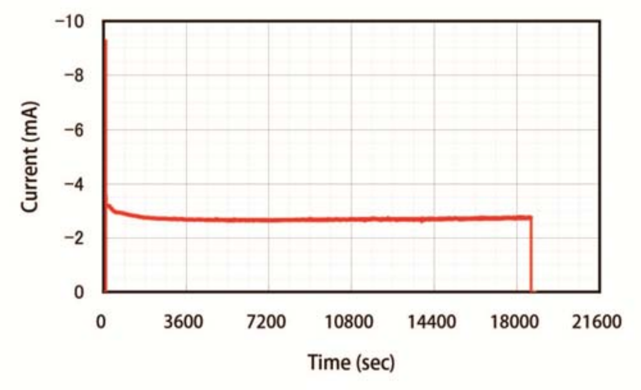

Fig. 2 Time course of photo-current by AlGaN/GaN photo-electrode on the β-Ga_2O_3 substrate. The photo-current is quite stable.

On illuminating the Ga_2O_3-based photo-electrode, the photo current was confirmed by the ammeter between cathode and anode. The measurement data for electric current are shown in Fig. 2. The average photo-current was -2.70 mA and the potential of cathode electrode was -1.38 V against the Ag/AgCl reference electrode. The photo-current was almost the same level with the previous study.[2] This means that the quality of single crystal Ga_2O_3 substrate and AlGaN/GaN thin film on that substrate is almost the same level as the photo-electrode on the sapphire substrate.

The comparative data for the product amount of each component are shown in Fig. 3. These data were obtained after 50 C of photo-electrolysis, and the Faradaic efficiencies are calculated by the total charge passed during electrolysis. The Faradaic efficiency for HCOOH was 41.32 %. The excited electrons are effectively used to CO_2 conversion, although it cannot be simply compared with the previous result[2] because the electrolyte is different in each case. The Faradaic efficiency for CO_2 conversion will be also increased furthermore if the performance of the photo-electrode is improved.

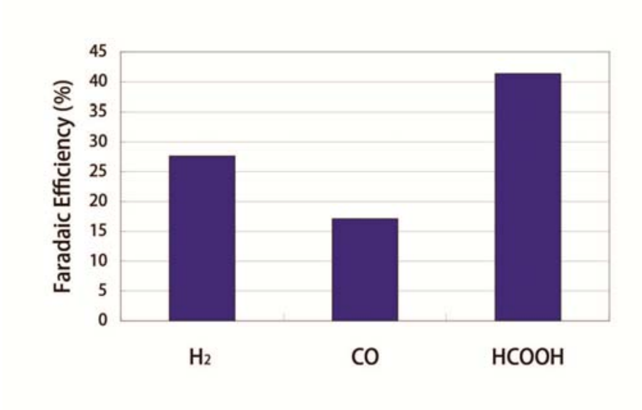

Fig. 3 Faradaic efficiencies for respective reaction products. Main reaction product is HCOOH whose efficiency is 41.32%.

3. Summary

It is shown that we have succeeded in realizing a vertical-current AlGaN/GaN photo-electrode with Gallium oxide (Ga_2O_3) single-crystal substrate. Both photo-current and CO_2 conversion were confirmed with almost the same level as the AlGaN/GaN device on the sapphire substrate. This indicates that the quality of single crystal Ga_2O_3 substrate and AlGaN/GaN thin film is also almost the same level as the AlGaN/GaN device on the sapphire substrate. In principle, the present device is expected to show higher performance than the conventional one. The performance is severely depends on the quality of the thin film and ohmic contact on the interface between GaN layer and Ga_2O_3 substrate, and so on. Further improvement will be promoted by the detailed analysis of those parameters.

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