CO₂ conversion with light and water by GaN photo-electrode

Satoshi Yotsuhashi¹, Masahiro Deguchi¹, Yuji Zenitani¹, Reiko Hinogami¹, Hiroshi, Hashiba¹, Yuka Yamada¹, and Kazuhiro Ohkawa²

¹. Advanced Technology Research Laboratory, Panasonic Corporation, 3-4 Hikaridai, Seikacho, Sôraku-gun, Kyoto 619-0237, Japan
Phone: +81-98-774-2566 E-mail: yotsuhashi.s@jp.panasonic.com
². Department of Applied Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

1. Introduction
As atmospheric carbon dioxide (CO₂) has risen to a critical level due to high rates of combustion of hydrocarbon fuels, it is highly desirable to realize an energy conversion system reducing the CO₂. One of the main research targets for chemical conversion from solar energy is an inorganic photo-catalyst which has been a focus of considerable research interest since evolution of hydrogen was demonstrated using a TiO₂ photo-electrode.[1] Here, semiconductor photo-electrode is used as an anode to create separate electrons and holes by photo-absorption. The holes assist with the oxidation of water and the residual electrons move to the cathode, leading to the reduction reaction, such as hydrogen generation or CO₂ reduction. The schematic picture is described as Fig. 1 (a). The researches for photo-catalysts have been mainly focused on the direct water splitting generating hydrogen.[2-4] Meanwhile, there have been a few approaches for CO₂ conversion by photo-catalyst.[5-6] This is because it is difficult to satisfy the conditions for accommodating high energy required for CO₂ reduction. For CO₂ reduction, calculating the energy required for the reaction is somewhat complicated, since it depends on which products the reaction involves. For example, a cathodic potential of approx. –0.61 V (vs. SHE) is needed to produce formic acid (HCCOH) from protons and electrons. This energy cannot be reached by most oxide materials, including TiO₂, whereas it can be accommodated in the band gap of GaN as shown in Fig. 1 (b).

In this study, we report on direct CO₂ conversion by using gallium nitride (GaN) photo electrode. CO₂ reduction is realized without extra power input except for illumination with light. GaN has attracted attention for its potential application to highly efficient optical and power devices for energy saving; but recently, its potential has been revealed to extend beyond solid devices: more specifically, that it can be used to generate hydrogen.[7-9] In a chain of experiments, it has turned out that the energy of conduction band of GaN is higher than that of most oxides, which is preferable for CO₂ reduction. Here, we show that this material can be adapted to a system for CO₂ conversion by light and water.

2. Methods and Results
The engine of the reaction is the photo-absorption process that leads to electron-hole separation. High crystalline quality is needed to facilitate the reaction efficiently. Single-crystal GaN was grown by atmospheric-pressure metal organic vapor-phase epitaxy (MOVPE) on (0001) sapphire substrate with low-temperature GaN buffer layers. Silicon was chosen as the dopant for n-type GaN. The growth temperature of the n-type GaN was 1025 °C. The GaN layer thickness and carrier concentrations at room temperature were 3.0 µm and \(n = 3.0 \times 10^{17} \text{ cm}^{-3}\), respectively. The thickness was measured using a secondary electron microscope. The van der Pauw method was adopted for measuring electrical properties. The crystalline quality was confirmed by full width at half maximum of an X-ray rocking curve for the (0002) reflection of the GaN layer.

![Fig. 1 Schematic illustrations for (a) the mechanism of CO₂ reduction empowered by the photo electrode and (b) band structures of several oxides and GaN. The reduction energy of CO₂ is higher than that of hydrogen generation.](image)

The electrons, excited illumination by light of the GaN, move to the counter electrode, where they drive the CO₂ reduction reaction. For the counter electrode, we use Cu plate of 99.9999% purity. In the electrochemical reduction of CO₂, copper is the only transition metal that delivers a range of reaction products, such as CO, HCOOH, CH₄, etc.[10-11]

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 CO₂ 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 detec-
tor (TCD) and CO, CH₄, C₂H₄, C₂H₆ were determined using the flame ionization detector (FID) attached to the gas chromatograph. Liquid chromatography was used for detecting HCOOH.

Fig. 2 Comparison of the production amount of each component is shown. The values are normalized by electric charge passed during the electrolysis. Faradic efficiency of HCOOH is ~ 3%.

The comparative data for product amount for each component are shown in Figure 2. These data were obtained after 10°C of photo-electrolysis. The Faradic efficiency for HCOOH was 3.2%. We calculated the Faradic efficiencies from the total charge passed during electrolysis. It should be noted that the main product from CO₂, formic acid, is potentially a renewable energy source for transport and storage. Whereas recent studies are based mainly on various materials such as complex molecules [12-13] or silica-based materials,[14-17] our system uses only inorganic materials.

3. Conclusions

We have shown the direct CO₂ conversion using Cu and GaN electrodes. With this system, we realized CO₂ reduction without extra power input except for illumination with light. The generation of formic acid (HCOOH) from CO₂ and H₂O with 3% Faradic efficiency was confirmed by light illumination alone. This result demonstrates a possibility for direct CO₂ conversion in a system comprising only inorganic materials. GaN can be widely expanded due to its tunable band gap and carrier concentration. A well-defined and quantitative band engineering of this material will be relevant for improving the ability to control the ratios of its reaction products.

References