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# Efficient Photoelectrochemical Reduction of Carbon Dioxide on a p-Type Silicon (p-Si) Electrode Modified with Very Small Copper Particles

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The photoelectrochemical reduction of $CO_2$ was performed with p-type silicon (p-Si) electrodes modified with very small Cu particles. Hydrocarbons such as methane and ethylene were produced together with CO and HCOOH similar to the case of a Cu-metal electrode, but at potentials ca. 0.4 V more positive than the Cu-metal electrode, clearly showing that the photovoltage generated in the p-Si is effectively utilized for the $CO_2$ reduction. On the contrary, p-Si electrodes coated with continuous Cu layers as well as naked p-Si electrodes showed no such photo-shifts in potential.

Photoelectrochemical reduction of carbon dioxide ($CO_2$) on semiconductor electrodes, which is regarded as a kind of artificial photosynthesis, has recently been attracting much attention from the viewpoint of the global environment problem. Many studies have been made using naked and/or surface-modified p-CdTe,[1-3] p-Si,[1,4] p-GaP,[1,5] p-InP,[1,6,7] etc., and the production of compounds such as HCOOH and CO has been reported. However, the electrode potentials for the electrolysis in these studies were still highly negative even under illumination. Thus it is important to find a way to effectively utilize light energy for the $CO_2$ reduction.

According to the results of semiconductor photoelectrochemistry thus far studied, naked semiconductor electrodes in general generate fairly high photovoltages but have low catalytic activity for the electrode reactions. On the other hand, semiconductor electrodes coated with continuous metal layers can have high catalytic activity for the reactions but generate low photovoltages due to the presence of Fermi-level pinning and surface recombination. This dilemma can be solved if we use semiconductor electrodes modified with very small ($\lesssim 5$ nm) and sparsely scattered metal particles, owing to a new effect that we found through studies of n-type silicon photoelectrochemical solar cells.[8] In our previous work, electrodes of such a new type were applied to hydrogen photoevolution.[9,10] In the present work, the electrodes of the same type have been applied for the first time to the photoelectrochemical reduction of $CO_2$. The schematic cross section and expected electronic processes at the surface are shown in Fig. 1.

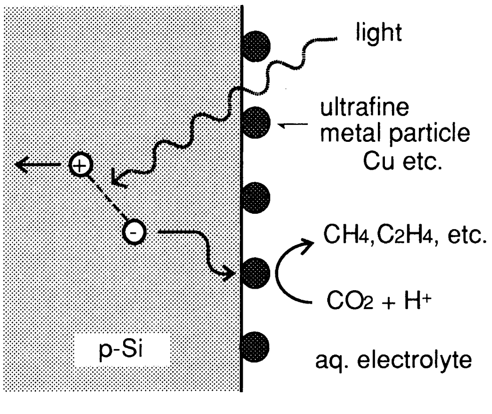

Fig. 1. Schematic cross section and electronic processes of the electrode surface.

Single crystal p-Si wafers [CZ, (100), 1.3 - 1.75 Ωcm, Shin-Etsu Handotai Co., Ltd.] were cut into pieces (0.6 - 1.0 $cm^2$), washed with boiled acetone and water, etched in a 33%-diluted CP4A (a mixture of $HNO_3$, HF and $CH_3COOH$ in a volume ratio of 5 : 3 : 3), and finally etched again with 12% HF. Ohmic contacts were made indium-gallium-zinc alloy. The p-Si piece was mounted in a Teflon holder to get a p-Si electrode (effective area: 0.25 or 0.5 $cm^2$). Photoelectrochemical measurements were performed using a potentiostat, a function generator, a digital coulomb meter and an X-Y recorder. Copper particles were deposited photoelectrochemically in a 10 mM (M = $moldm^{-3}$) copper sulfate aqueous solution at -0.1 V vs. SCE by illumination with a tungsten-halogen lamp. The electricity passed was 80 $mCcm^{-2}$. Figure 2 shows a scanning electron micrograph of the electrode thus prepared (hereafter called particulate-Cu/p-Si). Copper is deposited sparsely as small particles of hundreds nm or less in diameter.

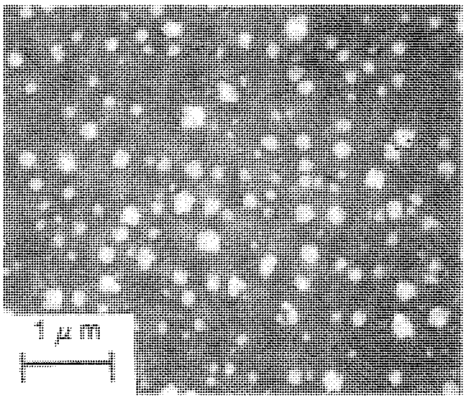

Fig. 2. Scanning electron micrograph of the particulate-Cu/p-Si electrode.

In order to check how well the Cu particles are deposited or how high photovoltages are obtained, we first measured photocurrent-potential curves for hydrogen evolution in 1 M HCl. The particulate-Cu/p-Si electrode showed an efficient photocurrent and its onset potential lay about 0.45 V more positive than that for the Cu-metal electrode, as shown in Fig. 3. On the other hand, a p-Si electrode coated with a continuous copper layer (continuous-Cu/p-Si) behaved rather similar to the Cu-metal electrode, with no photoshift, suggesting that the Cu/p-Si contact is nearly ohmic. A naked p-Si electrode showed only a little photoshift most probably due to the low catalytic activity of the p-Si surface for the hydrogen evolution.

Figure 4 shows the photocurrent-potential curves for the $CO_2$ reduction in a $CO_2$-saturated aqueous 0.1 M $KHCO_3$ solution. The photocurrents increase gradually with the potential compared with the case of hydrogen evolution probably due to the slow kinetics of the $CO_2$ reduction. Similar to the case of hydrogen evolution, the photocurrent-potential curve for the particulate-Cu/p-Si lay about 0.4 V more positive than that for the Cu-metal electrode, whereas the naked p-Si electrode and the continuous-Cu/p-Si electrode showed almost no photoshifts. These results clearly show that the coating with very small metal particles is of key importance for

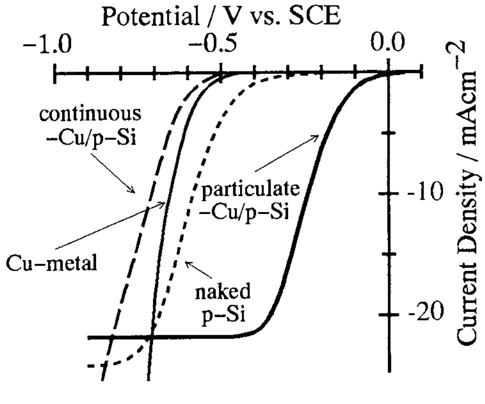

Fig. 3. Photocurrent-potential curves in a 1 M HCl.

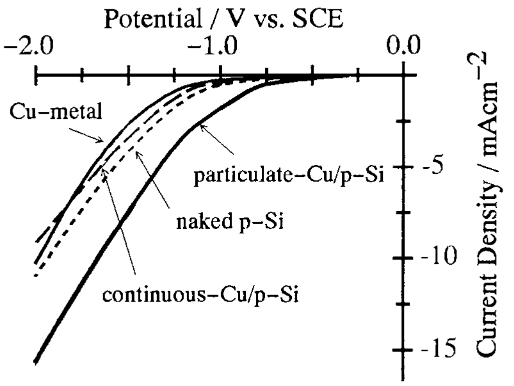

Fig. 4. Photocurrent-potential curves in a $CO_2$-saturated aqueous 0.1 M $KHCO_3$ solution.

obtaining high photovoltages as reported in our previous work.[8)]

The analysis of the reduction products was performed as follows: An H-shaped pyrex cell, equipped with the particulate-Cu/p-Si electrode and a platinum plate counter electrode, was used, the cathode and anode compartments being separated with a cation exchange membrane (Nafion 417). The electrolyte solutions were prepared using special-grade chemicals and water purified with a Milli-Q water purification system (Nihon Millipore Kogyo). $CO_2$ (99.99%) was bubbled into the stirred catholyte (aqueous 0.1 M $KHCO_3$) until the air in the cathode compartment was completely substituted for $CO_2$, and the compartment was sealed. Photoelectrolysis was then carried out potentiostatically under illumination by a tungsten-halogen lamp. The catholyte was stirred throughout the electrolysis. The reduction products in the gas phase were analyzed with Shimadzu gas chromatographs with MS-5A and MS-13X columns. Organic acids in the electrolyte solution were analyzed with a Tosoh high performance liquid chromatograph with a TSK-gel SCX($H^+$) column, and alcohols in the electrolyte with an Ohkura steam gas chromatograph with an A-1-3 glass column.

The electrolysis at -1.2 V vs. SCE on various electrodes has shown that the particulate-Cu/p-Si electrode produces hydrocarbons like $CH_4$ and $C_2H_4$ as well as HCOOH and CO, whereas the continuous-Cu/p-Si electrode produces only HCOOH and CO at this potential, apart from hydrogen. $CH_4$ and $C_2H_4$ are produced at potentials more negative than ca. -1.4 V for the continuous-Cu/p-Si. A naked p-Si electrode produced HCOOH, CO and no hydrocarbons at any potentials, indicating the importance of the catalytic effect of the surface copper particles.

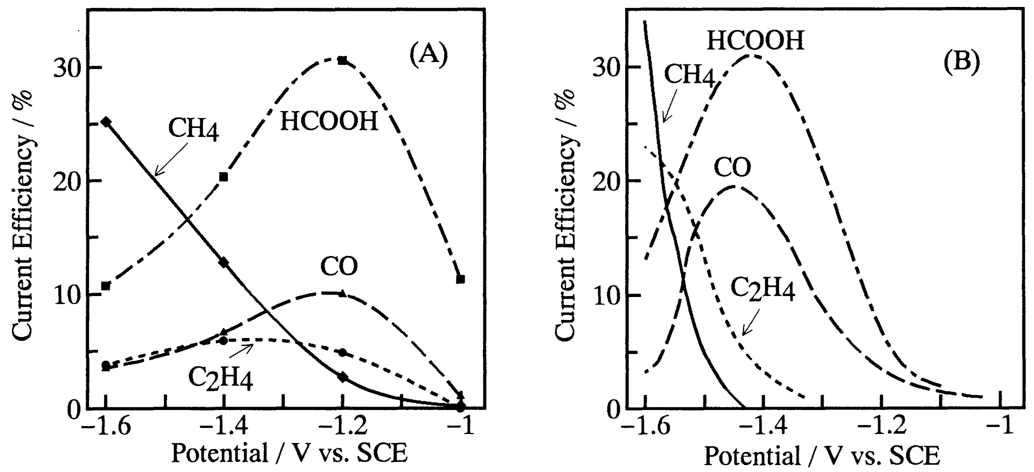

Fig. 5. Potential dependences of the current efficiencies of various reduction products for the particulate-Cu/p-Si (A) and the Cu-metal electrode (B).[11)]

Figure 5 shows the potential dependences of the current efficiencies of the various reduction products for the particulate-Cu/p-Si (A) as compared with those for a Cu-metal electrode (B) reported by Hori et al.[11)] For the particulate-Cu/p-Si, hydrocarbons like $CH_4$ and $C_2H_4$ start to be produced at -1.0 V vs. SCE, the current efficiencies for these compounds being 0.3 and 0.05% respectively, whereas they are produced only at potentials more negative than ca. -1.4 V vs. SCE for the Cu-metal electrode, thus indicating about 0.4 V shifts of the potentials for the formation of hydrocarbons. Also, similar shifts were observed for the production of HCOOH and CO, though the amounts of the shifts seem to become smaller, about 0.2 V as estimated from the potential of the highest current efficiency.

The production of $CH_4$ and $C_2H_4$ at -1.0 V vs. SCE for the particulate-Cu/p-Si electrode can be explained on the basis of our previously proposed model for such an electrode.[8] The most important is that the particulate-Cu/p-Si electrode generates a much higher photovoltage than the continuous-Cu/p-Si electrode. The flat-band potential of p-Si at pH 6.8 in the dark is determined to lie at ca. -0.1 V vs. SCE from the onset potential of the photocurrent under chopped illumination. When the electrode is illuminated in the presence of band bending, the photogenerated electrons in the conduction band come to the p-Si surface and to the Cu particles, and accumulate there. This induces the upward shifts of both the surface band energies of p-Si and the Fermi level of Cu, until the electrochemical reduction of $CO_2$ on the Cu particle starts. Under a photostationary state with the electrode potential of p-Si at -1.0 V, the Fermi level of Cu reaches, due to the photovoltage of 0.4 V, -1.4 V vs. SCE, where the $CO_2$ reduction can occur on Cu, as shown in Fig. 6.

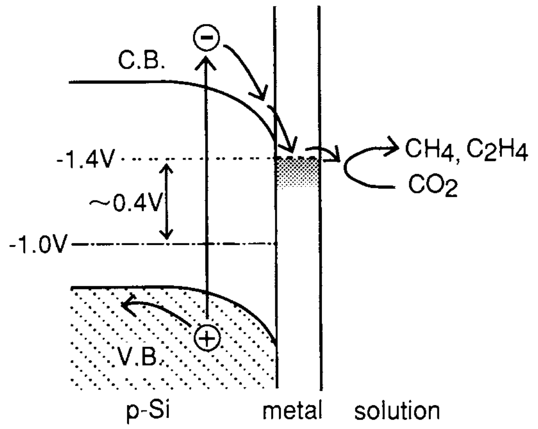

Fig. 6. Schematic energy band diagram explaining the production of $CH_4$ and $C_2H_4$ at -1.0 V vs. SCE for the particulate-Cu/p-Si. C.B. : conduction band, V.B. : valence band, ⊖ : electron, ⊕ : hole.

In conclusion, it has been shown that the p-Si electrode modified with very small Cu particles is effective for the photoelectrochemical reduction of $CO_2$. The improvement in the energy efficiency and the current efficiency may be achieved by further studies on the use of other metal particles, the control of the particle size, etc. Detailed studies on the reaction mechanism are also necessary including the contribution of the reaction on the naked Si surface. Such studies are now in progress.

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