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VISIBLE-LIGHT INDUCED WATER SPLITTING ON NEW SEMICONDUCTOR ELECTRODES MADE BY PHOTOLITHOGRAPHY

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By making use of a photolithography technique, mosaic coating composed of thick metal films and a transparent silicon oxide film was applied to the surface of the small bandgap semiconducting electrodes such as Si electrodes with a p-n junction (p^+n-Si) or an MIS junction (MIS-Si), n-CdS/p-CdTe heterojunction electrodes. These electrodes are stable and evolve oxygen efficiently with visible light in concentrated alkaline solutions.

Since the work of Fujishima and Honda,[1] water splitting has been intensively investigated due to its importance regarding the chemical conversion of solar energy. However, the photocorrosion of small bandgap semiconductors has been a difficult barrier to the stable and efficient decomposition of water with visible light. In order to solve this problem, surface coatings with a uniform film,[2-9] a porous-metal film with a fine island structure,[10] or a thin metal film with a spotted structure[11] as well as new stable semiconductors such as RuS_2[12,13] have been investigated. However, several important problems still remain to be solved regarding water splitting, such as stability, efficiency and so on. In this letter we report a new type of semiconductor electrode and its application to water splitting, especially concerning oxygen evolution. The surface of an electrode is partially coated with thick metal films (nickel) and the rest of it is coated with a transparent metal oxide film (silicon oxide) by making use of a photolithography technique. We applied this technique to Si electrodes with a p-n junction or an MIS junction, and to n-CdS/p-CdTe heterojunction electrodes.

Single-crystal wafers of n-Si (Shin-Etsu Handotai Co., Ltd., 0.018-0.033 Ω cm) and p^+n-Si formed by thermal diffusion of boron (NEC; n-layer, 1 Ω cm; boron concentration, 10^{20} cm^{-3}; diffusion layer, 0.6 μm) were used. A CdS/CdTe heterojunction was prepared by the vacuum evaporation of p-CdTe (doped with Sb, 1.0×10^{18} cm^{-3}) on an n-CdS single crystal heated to 300 °C. For p^+n-Si and CdS/CdTe, SiO ($\approx$500 nm) was deposited by vacuum evaporation on the p^+-side of p^+n-Si or the CdTe-side of CdS/CdTe heated to 300 °C. For n-Si, a SiO_2 layer was grown by thermal oxidation at 1100 °C for 10 h in air. Figure 1A shows the photolithography procedure for the preparation of an electrode with a mosaic structure. The sample was baked at 210 °C for 1 h in air and coated with a photoresist (Tokyo Ohka Kogyo Co., Ltd., OFPR-800 or OMR-83) using a spin coater (5000 rpm for 30 s). It was immediately pre-baked at 75 °C in air for 30 min and then exposed to UV light through a photomask

and immersed in a developing fluid. After postbaking at 145 °C in N_2 for 30 min, it was etched with a 40% $NH_4F{\cdot}HF$ solution. A metal film (Ni, Fe, Ti, Au etc.) with a thickness of 20 to 100 nm was deposited by vacuum evaporation on an etched sample heated at 140 °C. Lastly, the photoresist and the metal layer on it were removed using a resist stripper (Tokyo Ohka Kogyo Co., Ltd., #502). Hereafter, we express this new type of electrode as a metal/SiO_2/semiconductor. The size of each metal island is typically 2 mm x 2 mm and the total area represents about 20% of the whole surface. We also applied a microscopic photolithography technique in order to prepare an electrode with a microstructure in which each metal island has a diameter of 12 μm and is isolated by 13.6 μm from each other. To prepare an MIS structure, a thin oxide layer was formed by heating the sample at 140 °C in the atmosphere for 5 to 20 h before evaporation of the metal (Au). A SEM picture of this electrode is shown in Fig. 1B. Shiny circles are metal parts which have an area of 13% of the whole surface. The rest of the surface was covered with SiO_2. For the preparation of electrodes, an In-Ga alloy was used for making an ohmic contact with the back side of the semiconductors. A 500 W Xenon (Ushio Electric Inc.), combined with a neutral-density filter or 150 W tungsten-halogen lamp was used as the light source.

Figure 2 shows typical photocurrent density(j)-potential(U) curves for Ni/SiO/p^+n-Si electrodes. When Ni and SiO were used as the metal and oxide parts, respectively, a weak photocurrent (less than 2 $mAcm^{-2}$ at +1.0 V vs. SCE) was observed in a dilute alkaline solution (pH 12.8)(curve a). However, the photocurrent increased dramatically in a concentrated alkaline solution (curve b). Bubbles evolved vigorously from Ni parts upon being subjected to visible light. The evolved gas was collected and identified as oxygen using a quadrupole mass spectrometer. The onset potential of the anodic current shifted to 0.5 V, more negative than the Ni electrode (dotted curve), due to the photovoltage of the p-n junction. At the potential of +0.8 V vs. SCE, the quantum efficiency of the photocurrent reached 45% over the whole wavelength region of 600-800 nm. For thicker Ni films (several μm thick) deposited by pulse electroplating (pulse width 200 ms) on

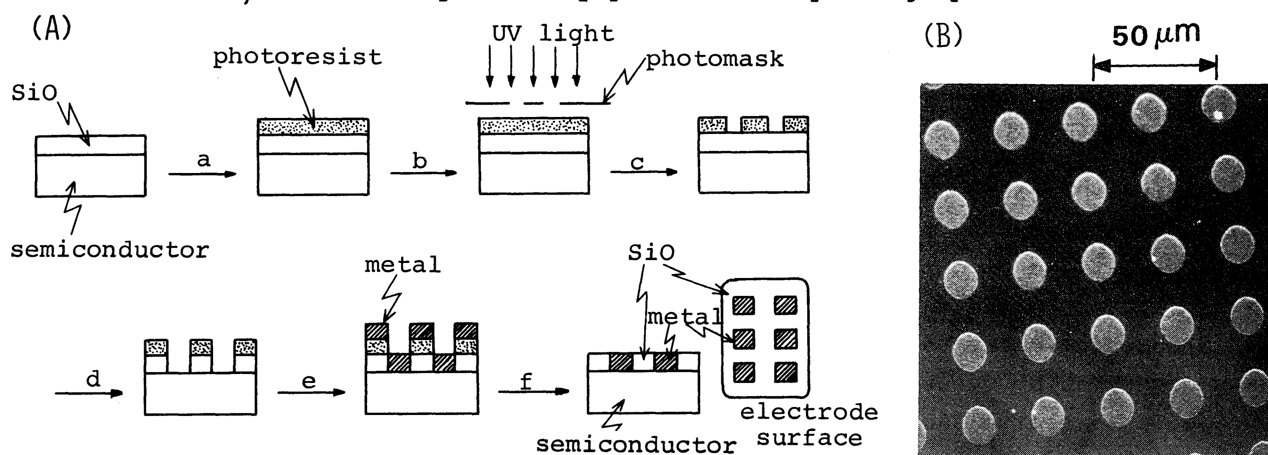

Fig. 1. (A) The photolithography procedure. (a)-(f) represent the process of each step as described below. (a) coating of the photoresist. (b) prebake. (c) developing and postbake. (d) etching. (e) metal evaporation. (f) removal of the photoresist. ; (B) A SEM picture of the Au/SiO_2/n-Si electrode surface produced by a microscopic photolithography technique.

a vacuum evaporated metal, a photocurrent of 20 $mAcm^{-2}$ was maintained for more than 100 hours. On the contrary, bare p^+n-Si electrodes completely degraded in 30 s. Among nickel, titanium, iron, and gold, nickel showed the best characteristics as a metal on p^+-Si.

The same method was applied to n-Si with an MIS (Metal-Insulator-Semiconductor) structure. Gold was used as the barrier metal. When Ni was pulse-electroplated on the Au parts, the electrodes were also stabilized in a concentrated alkaline solution. In this case, the microstructured electrode (shown in Fig. 1B) exhibited the best efficiency for oxygen evolution under the irradiation of visible light. The photocurrent density of this electrode was 2 to 5 times larger than that of the same MIS electrode having large metal islands (2 mm x 2 mm). This result might be explained by the following effect. A number of fine metal islands on the microstructure electrode could collect any photogenerated holes (in the case of an n-type semiconductor) more efficiently than for an electrode with a small number of large metal islands. This is because the hole diffusion length of our sample is 10 μm. From the view point of the ability of collecting carriers, this microstructure electrode would be advantageous for semiconductors with small diffusion length such as amorphous Si.

In order to confirm the effectiveness of the present method against the photocorrosion of II-VI compounds, CdS-CdTe heterojunction electrodes were prepared by electroplating Ni onto CdTe which was evaporated on a single crystal of CdS. This electrode was quite stable and oxygen bubbles evolved vigorously from the Ni parts. A photocurrent of 13 $mAcm^{-2}$ (+1.0 V vs. SCE) flowed for more than 40 hours in a concentrated alkaline solution.

All the above results clearly demonstrate that the present method is quite effective for the stabilization of a semiconductor surface and for preventing photocorrosion. The high stability of these electrodes must result from the thick

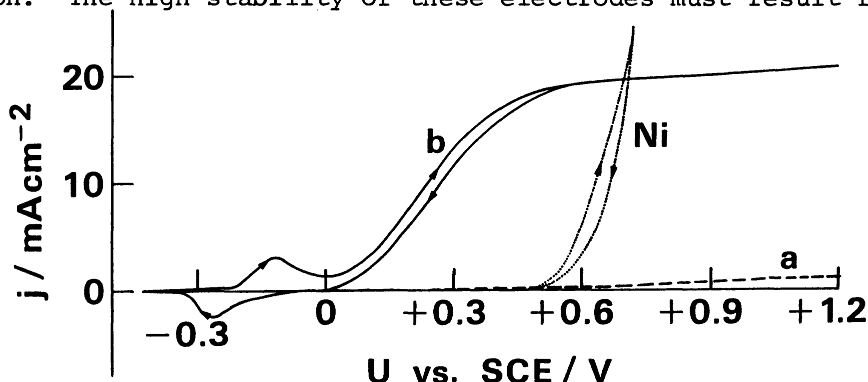

Fig. 2. Photocurrent density(j)-potential(U) curves for a p^+n-Si electrode and for a Ni electrode (dotted curve). This Si electrode was coated with a 500 nm thick SiO film and with 50 nm thick Fe films which were covered with electroplated Ni (several μm thick). The electrolytes are a 20% NaOH aqueous solution (curve b and Ni) and a 0.1 mol dm^{-3} Na_2SO_4 aqueous solution which was adjusted to pH 12.8 with NaOH (curve a). The scan rate was 100 mV/s and the light source is a tungsten-halogen lamp. Peaks at -0.1 V and -0.25 V correspond to the formation of nickel hydroxide and its reduction, respectively.

metal and oxide layers which are free from pinholes. Even when pinholes and cracks remained in the films (or at boundaries of metals and oxides), they were covered with Ni during electroplating. In these types of electrodes, the sites of chemical reactions and light absorption are completely separated from each other. Also, the photovoltage does not arise from the semiconductor-electrolyte junction, but rather from the semiconductor-metal junction, the MIS junction or the p-n junction which has begun to be applied to several photoelectrode reactions, such as the decomposition of hydrogen iodide.[4,5,11,14]

In some case, the microstructure electrode is expected to work more efficiently than solid solar cells. In solid solar cells, a comb type metal electrode is commonly used. It crosses over grain boundaries and etch pits on the semiconductor surface where leak current flows. This leak current is known to suppress the photovoltage and the conversion efficiency. Even if the number of grain boundaries and etch pits which are crossed over by the comb type metal electrode is small, it can lead to serious degradation of the cell, because all the lead wires of the comb are electrically interconnected. On the contrary, in the case of microstructure electrode, a large number of metal islands, through which current flows, are isolated from each other. Since most metal islands do not cross those grain boundaries and etch pits, the conversion efficiency would be improved for the microstructure electrode. This effect is expected to be especially marked for polycrystalline semiconductors. This is a new aspect of this micro-structure electrode.

We also confirmed that stable and efficient hydrogen evolution is possible by applying the present method to p-Si. This implies that complete and efficient water splitting using visible light is possible with the present method if suitable semiconductor electrodes with sufficient photovoltages for the photoanode and photocathode are chosen. A photoelectrode made by this method is also applicable to other important reactions, such as the reduction of CO_2 and N_2, Cl_2 evolution, and the photosynthesis of amino acids, by supporting appropriate catalysts on metal parts. Moreover, application of a submicron-photolithography, which is being developed for VLSI technology, would be important to make a more efficient photoelectrode.

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