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Photoelectrochemical Behavior of p-Type Boron Phosphide Photoelectrode in Acidic Solution

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The photoelectrochemical behavior of p-type boron phosphide (p-BP) in acidic solution was investigated. The p-BP photocathode was stable in sulfuric acid solution under irradiation, and the band gap deduced from the photocurrent action spectrum in acidic solution was 2.0 eV. The gas evolved from p-BP photocathode was hydrogen which was obtained with a current efficiency of *ca.* 100%. The photocurrent was markedly increased by suitable ruthenium treatment of the BP. A photoelectrochemical cell (PEC), Pt(H_2)/0.5 M H_2SO_4(1 M=1 mol dm^{-3})//0.5 M H_2SO_4/p-BP, was shown to have an open-circuit photovoltage of 0.45 V and a fill factor of 0.25.

The photoassisted electrolysis of water using semiconductor electrodes has been studied extensively in the last few years.[1–7] One of the major requirements in any practical application is that the semiconductor be stable. Because it is very difficult to find intrinsically stable materials, considerable effort has been expended on electrode modifications to improve stability and charge transfer properties. Some of the methods employed or suggested includes the use of stabilizing redox couples in the electrolyte,[8–10] overcoating of unstable semiconductors with noble metals,[11] stable semiconductors,[12,13] and conductive polymers.[14–18]

Although much work has been done on semiconductors, hardly any has been reported on boron phosphide (BP) behavior after Ginley *et al.*[13] reported that BP stabilized n-Si, n-GaAs photoanodes, and after Grantham's patent[19]. In this paper, we report the attainment of quite stable photocurrents resulting in hydrogen production that were obtained from a p-BP electrode in acidic solution. Also, we report a detailed study of the effects of ruthenium treatment of a p-BP electrode surface.

Experimental

A BP single crystal was prepared by a flux method[20] under high pressure either at 10 or 18 atms. The BP crystal was etched for 10 min in fused sodium hydroxide at 420 °C and then washed with distilled water. After an ohmic contact was made with an indium-gallium alloy, a copper wire was connected with silver paste, and then all surfaces except one side were covered with an epoxy resin.

The same cell was used for photoelectrolysis and for measurement of current-potential curves. This cell consisted of two compartments separated by a cation

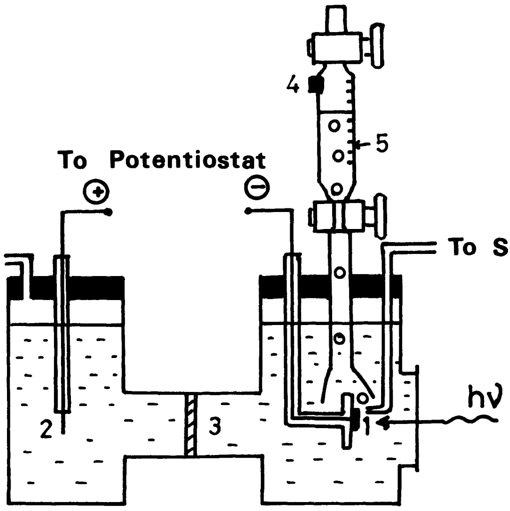

Fig. 1. Schematic of p-BP photoelectrolysis apparatus. 1: BP photoelectrode, 2: Pt counter electrode, 3: Cation exchange membrane separator, 4: Rubber stopper, 5: 2 ml calibrated burette.

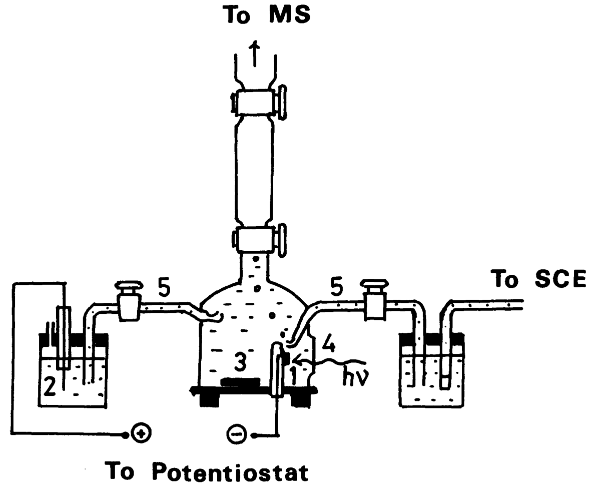

Fig. 2. Schematic of photoelectrolysis cell for mass spectrometric analyses.
1: BP photoelectrode, 2: Pt counter electrode, 3: Magnetic stirring bar, 4: Window for incident light, 5: Salt bridge.

exchange membrane (Selemion CMV, Asahi Chem. Co.) and a 2 ml burette in the catholyte chamber, as shown in Fig. 1. The volumes of catholyte and anolyte chamber were 100 and 80 ml, respectively. Another cell was used for mass spectrometric analysis, the volume of the catholyte of which was 1 ml, as shown in Fig. 2. These cells were equipped with the p-BP working electrode (av. surface area≈0.12 cm^2), a platinum wire counter electrode (dia. 1.0 mm × length 10 mm), and a saturated calomel electrode (SCE) as a reference electrode.

The light source was a 500W xenon lamp (Ushio Electric Inc.), and the light path included an infrared cut filter and quartz lens. Current-potential curves were taken by using a potentiostat/galvanostat system (Hokuto Denko Co.) in cojunction with an X–Y recorder. The hydrogen evolved was analyzed by means of a gas chromatograph (Hitachi model 163) and mass spectrometer (Ulvac YTP-150). The packing material of the column was molecular sieve 5A and the carrier gas for the gas chromatography was argon gas. Scanning electron microscopic and surface analyses were performed by means of a scanning electron microscope (Hitachi type S 550), X-ray detector (Kevex Co. type 7000-75), and a computer system (DEC Co. PDP 11/34). Ruthenium was applied to the BP surface by dipping the BP into ruthenium chloride solution [0.5—10% $RuCl_3$–methanolic solution (CH_3OH:H_2O=1:1)] and irradiating with 500W xenon lamp.

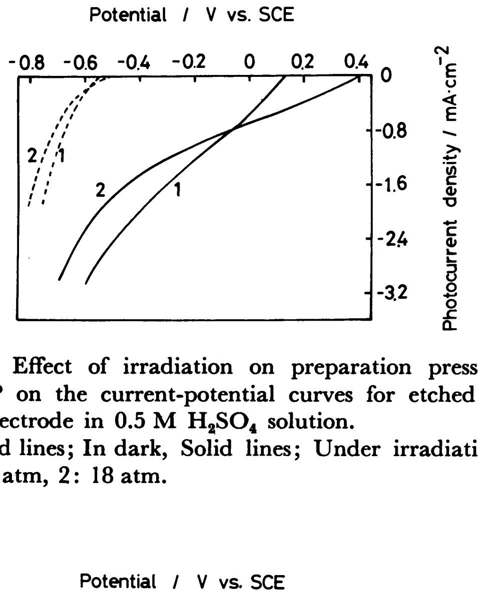

Fig. 3. Effect of irradiation on preparation pressure of BP on the current-potential curves for etched p-BP electrode in 0.5 M H_2SO_4 solution.
Dotted lines; In dark, Solid lines; Under irradiation, 1: 10 atm, 2: 18 atm.

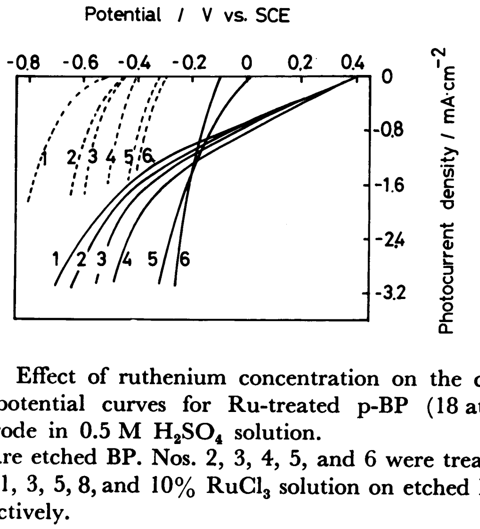

Fig. 4. Effect of ruthenium concentration on the current-potential curves for Ru-treated p-BP (18 atm) electrode in 0.5 M H_2SO_4 solution.
1: Bare etched BP. Nos. 2, 3, 4, 5, and 6 were treated with 1, 3, 5, 8, and 10% $RuCl_3$ solution on etched BP, respectively.
Dotted and solid lines have same meaning as in Fig. 3.

All chemicals were of reagent grade. Before all experiments, the electrolytic solutions were purged with nitrogen gas for more than 30 min.

Results and Discussion

Current-potential Characteristics. The effect of irradiation on the current-potential curves for an etched p-BP photocathode in 0.5M H_2SO_4 is shown in Fig. 3 for samples prepared at 10 and 18 atm pressure. The photocurrent was shifted about 0.9V in the anodic direction compared to the dark current value. Since the optical to electrical conversion efficiency was reported to be increased by applying ruthenium on semiconductor surfaces[21,22] we determined the effect of ruthenium concentration on the photocurrent-potential curves for the BP treated with ruthenium(III) chloride in 0.5M H_2SO_4, shown in Fig. 4. Increasing the concentration of ruthenium(III) chloride solution increased the photocurrent. In the case of treating the BP surface with concentrated ruthenium chloride solution or of long-term irradiation of the BP surface in diluted ruthenium solution, the photocurrent was markedly shifted in the cathodic direction. This phenomenon of cathodic shift can be explained by a decrease of characterization of semiconductor to be covered with ruthenium metal or ruthenium oxide.

Dependence of Photocurrent on Wavelength and the Stability of a BP Cathode. The wavelength dependence of the photocurrent for p-BP prepared under 18 atm pressure is shown in Fig. 5. The quantum yield was calculated by dividing the photocurrent at a certain wavelength by the number of photons incident on the BP electrode. The threshold of the photocurrent response was about

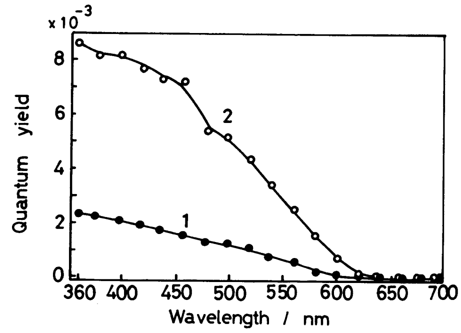

Fig. 5. Action spectrum of p-BP (18 atm).
Applied potential; −0.45 V *vs.* SCE.
1: Bare etched BP, 2: BP etched and treated with 3% $RuCl_3$ solution.

TABLE 1. ELECTROLYSIS RESULTS OF p-BP (18 atm) CATHODE UNTREATED AND WITH A $RuCl_3$ METHANOLIC SOLUTION (Electrolyte: 0.5 M H_2SO_4)

Set Pot. (V *vs.* SCE)	3% $RuCl_3$	Quantity of Electricity (Coulombs)	Electrolysis Time (min)	Av. Current Density (mA cm^{-2})	Hydrogen Gas Obtained (ml)		Current Efficiency (%) BP/Pt
					BP	Pt	
−0.6	Untreated	5.2	440	2.4	0.55	0.62	88.7
−0.6	Treated	5.2	365	2.9	0.62	0.62	100.0
−1.0	Untreated	10.0	140	14.4	1.20	1.25	96.0
−1.0	Treated	10.0	67	30.1	1.25	1.25	100.0

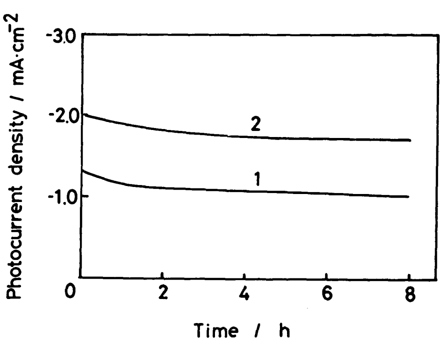

Fig. 6. Time dependence of photocurrent density at BP (18 atm) photocathode in 0.5 M H_2SO_4 solution. Applied potential; −0.4 V *vs.* SCE, Conditions of Nos. 1 and 2 were the same as in Fig. 5.

600 nm (2.0 eV), in agreement with the direct band gap calculation. As is evident from Fig. 5, the p-BP photocathode will respond to sunlight of wavelength shorter than 600 nm.

Figure 6 shows the photocurrent-irradiation time profile for a p-BP photocathode with and without a ruthenium treatment. As shown for a cell where the photocathode process was according to hydrogen evolution, there was no evidence that the photocathode deteriorated.

Hydrogen Evolution. The hydrogen evolution produced by the BP and the Ru-treated BP photocathodes during electrolysis was determined by measuring the quantity of electricity under constant set potential, and the results are shown in Table 1. For the purpose of calculating the current efficiency, the volume of gas evolved from the BP photoelectrolytic cell of Fig. 1 was compared with the volume of hydrogen evolved from the cathode of the Pt cathode/Pt anode electrolytic cell in 0.5M H_2SO_4. These two cells were connected in series with each other. The results in Table 1 show that the photoreaction on the BP photocathode in an acidic solution produced hydrogen, and the current efficiency of the process was almost 100% by comparison with the Pt cathode.

p-BP/H_2SO_4 Photoelectrochemical (PEC) Cell.

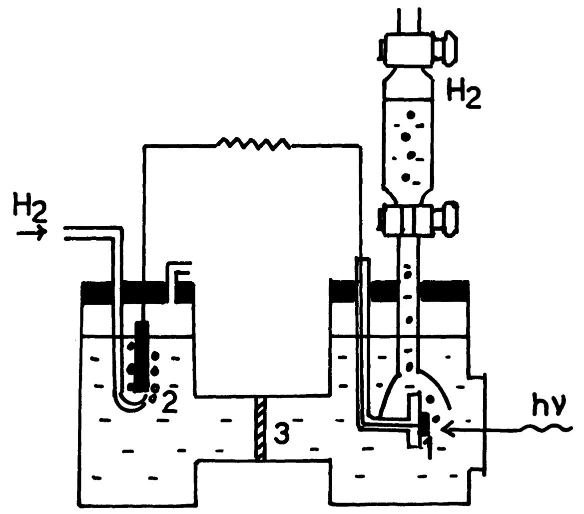

Fig. 7. Schematic diagram of PEC cell.
1: BP photoelectrode, 2: Platinized platinum electrode, 3: Cation exchange membrane.

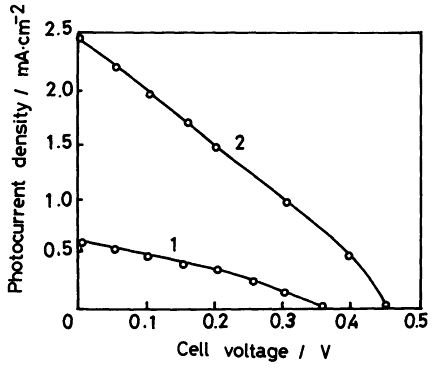

Fig. 8. Photocurrent-photovoltage characteristic of the cell Pt(H_2)/0.5 M H_2SO_4//0.5 M H_2SO_4/p-BP (1 atm). Irradiation source; 500 W xenon lamp.
1: Bare etched BP, 2: BP etched and treated with 3% $RuCl_3$ solution.

A PEC cell was made by connecting the p-BP semiconductor to a counter electrode by means of a variable resistive load in the external circuit. Schematic diagram of PEC cell is shown in Fig. 7. Figure 8 shows the power characteristic in the acidic solution obtained with and without ruthenium treatment on the BP electrode using light from a 500W xenon lamp. From curve 2 in Fig. 8, we estimate that the open circuit photovoltage was 0.45 V, the short-circuit photocurrent density was 2.4 mA cm^{-2}, and the fill factor was 0.25. The overall conversion efficiency of optical to electrical energy for the PEC photovoltaic cell was much increased by the ruthenium treated BP but it was still low with respect to the case of InP.

Examination of Surface State of BP. The surfaces of different BP specimens after etching and treating with ruthenium were observed by scanning electron micrographs. It was found that the p-BP surface without etching had a very smooth surface while the surface of etched p-BP had many blisters. The surface of etched BP, which had been treated by dipping in methonolic ruthenium(III) chloride solution for 1 min, washing with water, and irradiating for 1 min with the 500W xenon lamp, observed the white and black areas by the scanning electron microscope.

Analytical results of X-ray fluoresence of the average area have indicated, for example, that weight percents of each component were Si 3.09%, P 87.97%, and Ru 8.94%, where Si was surface impurities on the BP semiconductor. The amount of ruthenium was greater in the white areas than the black areas. Therefore, the surface layer was not a homogeneous coating, but rather there were islands of ruthenium on the BP. By dipping the BP in the ruthenium solution for 5 min a thick ruthenium covered the BP surface, not only in the white areas but also in the black areas. The thicker, homogeneous ruthenium layer on the p-BP is undesirable because the deposited ruthenium would absorb and reflect photons before they could reach the semiconductor, thereby decreasing the cell efficiency. Therefore, it is necessary that the surface treatment is carried out with a suitable concentration of ruthenium and treatment time.

Conclusion

The p-BP photocathode has a good wavelength response (E_g=2.0 eV), and is stable in an acidic solution under irradiation. The gas evolved from this BP photocathode under irradiation was hydrogen which was produced with a current efficiency of about 100%. The photocurrent was markedly increased by a suitable surface ruthenium treatment of the BP.

The overall conversion efficiency of optical to electrical energy for the PEC photovoltaic cell was low, that was, the open-circuit photovoltage was 0.45V, the short-circuit photocurrent density was 2.4 mA cm^{-2}, and the fill factor was 0.25. Therefore, to make a more practical device it is necessary to improve this conversion efficiency.

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