

HYDROGEN EVOLUTION FROM AQUEOUS SOLUTIONS ON INDIUM PHOSPHIDE PHOTOCATHODES

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Hydrogen evolution from aqueous solutions on the p-indium phosphide photocathodes was studied. The efficiency of this process is affected by the crystallographic orientation of the photocathode surface. The influence of platinum metal additives in the electrolyte on water photolysis is discussed.

Key words: p-Indium phosphide; Photocathodes; Photolysis.

In the last period, photochemical evolution of hydrogen on semiconductor electrodes has been the object of intensive research focused on the development of alternative, ecologically clean energy sources. Indium phosphide (InP) photocathodes have been receiving much attention for several decades due to the applicability of these electrodes in photoelectrochemical (PEC) solar cells.

To reach the sufficient efficiency of water photolysis, it is necessary to specify the optimum material properties of photocathodes and to optimize the conditions of the electrolysis as well.

In a semiconductor-electrolyte junction exposed to the radiation with the energy equal or greater than the band gap energy of the semiconductor E_g , the absorption of a photon allows an electron to be transferred from the valence band to the conduction band. When the conversion efficiency is evaluated for semiconducting materials with different band gaps, the maximum efficiency of about 30% can be found around $E_g = 1.6$ eV (ref.¹). From this point of view, indium phosphide p-InP ($E_g = 1.34$ eV) appears to be one of the best candidates²⁻⁴.

The stability of an electrode material in the electrolyte is also a very important criterion. In the case of InP, the occurrence of native surface oxide (oxygen monolayer) is a positive factor which decreases losses in photocurrent, photovoltage and fill factor⁵⁻⁶.

Generally, the photocorrosion of semiconducting photocathodes with lower forbidden gap energy is possible to be restrained by covering of their surfaces by noble metals which act as photocorrosion inhibitors^{5,7-8}.

The application of electron mediators enabling electron transfer is another way to increase the hydrogen evolution efficiency. Solutions of molybdenum and tungsten heteropolyacids have been used in reaction systems with p-InP photocathodes as well as ruthenium and/or rhenium complexes^{9,10}.

A significant increase of photocathode activity is expected using more complicated semiconductor structures composed of materials with different E_g (tandem photoelectrodes). According to the theoretical predictions, they can absorb light in a broad range of the sun spectrum and their efficiency is estimated to be about 30% at air mass conditions $AM = 1.5$ (ref.¹¹). For example, the binary structure n-InP/p-In_{0.5}Ga_{0.5}P is currently investigated as one of the most promising structures^{11,12}.

The aim of this study is to report some new experimental data concerning the influence of the crystallographic orientation of the p-InP photocathode surface and noble metal additives in electrolyte on the efficiency of hydrogen evolution during water photolysis.

EXPERIMENTAL

Preparation of p-InP Photocathodes with Various Surface Crystallographic Orientation

Polycrystalline InP was synthesized from indium (5N5) and phosphorus (6N) by the horizontal Bridgman method combined with the high temperature zone¹³.

The p-InP single crystal doped by zinc was grown using the liquid-encapsulated Czochralski technique in the MSR6R apparatus (Metal Research Ltd., G.B.). Parameters of the single crystal were the following: The specific resistivity of $7.8 \cdot 10^{-2} \Omega \text{ cm}^{-1}$, the Hall mobility of $29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the hole concentration of $2.39 \cdot 10^{18} \text{ cm}^{-3}$.

To prepared electrodes with various surface crystallographic orientations, the single crystal was oriented with the accuracy of 0.3° by means of X-ray technique and sliced. The average thickness of an electrode plate was $440 \pm 15 \mu\text{m}$. After slicing, the frontal electrode plane was brushed and polished mechanically and chemically in solutions containing colloid SiO_2 , NaOCl and HCl . The back electrode plane was etched in a mixture of HCl , HNO_3 and H_3PO_4 (ref.¹³).

The $(111)_a$ and $(111)_b$ surface orientations were discerned by etching in a mixture of HCl and HNO_3 , where the more reactive $(111)_b$ surface plane is polished while only dislocations are etched on the $(111)_a$ surface plane.

Finally, the ohmic contact Au/Zn/Au was made by the sequential vacuum evaporation and its resistance was found to be of about $10^{-1} \Omega$.

The photocathodes of the surface orientations (100) , $(111)_a$, $(111)_b$, and (110) were prepared by this procedure.

Deposition of Noble Metal Catalysts

Essentially, there are two ways how to introduce catalysts into the reaction system. The first of them, the ex situ covering, is performed by the deposition of a platinum metal on the photocathode surface outside the cell. For this purpose p-InP (100) electrodes were platinised in a solution of hexachloroplatinic acid using current density of 1 mA cm^{-2} for 120 s at 90°C . A Pt film of the thickness of about 10 nm was formed.

The second method, the in situ covering, was carried out directly in the photoelectrolyser by addition of a platinum metal compound (e.g. aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$, PdCl_2 , RuCl_3 and $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$, respectively) into the electrolyte.

Electrochemical Measurements

Photoelectrochemical experiments were carried out at a room temperature in a cell consisting of two compartments separated by a glassy frit. A working electrode together with a reference saturated calomel electrode (SCE) was placed in the first and a platinum counter electrode in the second compartment (Fig. 1). Aqueous solutions of 1 mol l^{-1} and 3 mol l^{-1} HCl , H_2SO_4 , HClO_4 , H_3PO_4 and NaOH in double distilled water were used as working electrolytes.

The light source was a 50 W tungsten-halogen lamp operating at 4 A current. The light beam was passed through a water filter to absorb heat radiation.

The cell was placed in a metallic chamber to eliminate any exposition by light from other sources.

The electrochemical behavior was studied using a potentiostat PS 4 (Forschungsinstitut Meinsberg), function generator TR 0452 Orion EMG, and X-Y recorded Endim 620.02. The cyclic voltammetry was chosen as a main method for the investigation of the influence of the surface orientation of photocathodes, the presence of platinum metals in the reaction system, and electrolyte on the hydrogen evolution. The photocathode potential was cycled between 150 and -300 mV vs SCE at the scan rate of 100 mV s^{-1} .

RESULTS AND DISCUSSION

Influence of the Crystallographic Orientation of Photocathodes on the Hydrogen Evolution Efficiency

The surface anisotropy of $\text{A}^{\text{III}}\text{B}^{\text{V}}$ compounds is well known and its influence on photochemical reaction can be expected.

InP crystallizes in the zincblende-type structure formed by two face centered cubic sublattices mutually shifted by the translation $t \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4} \right)$. Three kinds of the crystal-

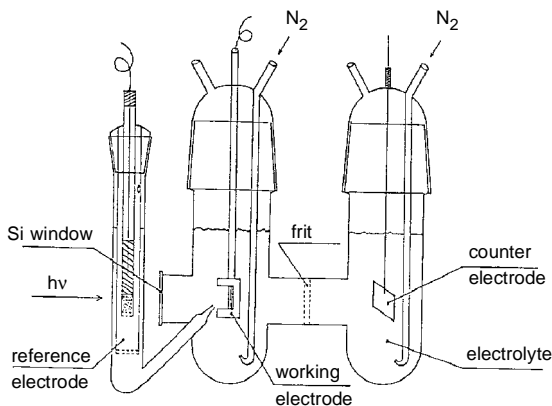


FIG. 1
Laboratory three-electrode cell used for the hydrogen evolution on p-InP photocathodes from aqueous solutions

lographic orientation of surface planes, namely tetraedrical (111), cubic (100) and rhombo-dodecaedrical (110) which are shown in Fig. 2 were chosen to study the influence of the photoelectrode surfaces orientation on the hydrogen evolution. For the (111) orientation, two types of the surface plane occupation are possible. The surface planes could either contain only indium $(111)_a$ or phosphorus $(111)_b$, and atoms of the other kind are hidden.

The effect of the photoelectrode surface orientation on the hydrogen evolution was studied by means of cyclic voltammetry. Typical voltammograms of the $(111)_a$, $(111)_b$, (100) and (110) oriented photocathodes are shown in Fig. 3.

The efficiency of the hydrogen evolution on the $(111)_a$ photocathode seems to be rather poor. Under illumination, the photocurrent onset is observed at about -200 mV and the photocurrent density does not exceed -1.5 mA cm $^{-2}$ at -350 mV.

In the case of the (100) and $(111)_b$ electrodes, the marked waves indicate some simultaneous surface processes, most probably the corrosion, at -100 mV and -270 mV, respectively. If cycling is repeated, the position of the waves shifts towards more negative potential values. The photocurrent onset is observed at about 0 mV and its density reached up to -5 mA cm $^{-2}$ at -350 mV.

Undoubtedly, the optimum surface orientation was found for the (110) electrode. It exhibits no corrosion wave on the voltammogram even at the repeated cycling. An outstanding increase of the photocurrent density in the cathodic region to the value of about -8 mA cm $^{-2}$ at -350 mV was observed.

In general, the very low activity of the $(111)_a$ electrode can be related to the prevailing occupation of the surface by indium. With regard to a well known sorption of

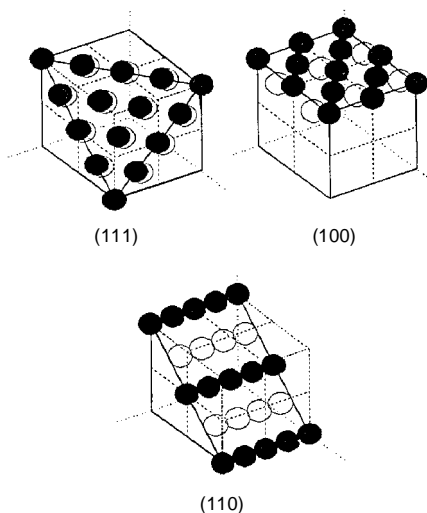


FIG. 2
Crystallographic orientation of (111), (100) and (110) surface planes in InP single crystal

hydrogen on $A^{III}B^V$ compounds we should expect that the energy of hydrogen sorption on the surface under formation of P-H bonds is just the optimum. It is in accordance with the theory of hydrogen evolution on materials where the photoelectrochemical deposition of H_2 is easy supported by the standard potential -111 mV of reaction $P + 3 H^+ + 3 e \rightarrow PH_3$ (ref.¹⁴).

Platinum Group Metal Catalysis

Ex situ deposition. The p-InP (100) electrode was covered by platinum as described above and its photochemical activity was investigated in 3 M HCl under illumination by the cyclic voltammetry. A comparison of the voltammograms for the platinized and nonplatinized (100) photocathodes, respectively, shows the absence of the typical corrosion wave at -140 mV on the descending part of voltammogram for the former electrode. Thus it can be deduced that the covering of the electrode surface by platinum significantly restrains the photocorrosion.

In situ deposition. The effect of platinum catalyst concentration in the working electrolyte on the photolysis was studied by the cyclic voltammetry under the same conditions as in the previous case. A gradual inhibition of the photocorrosion is obvious from a comparison of the voltammograms in Fig. 4. It becomes perceptible for addition of $8.8 \cdot 10^{-5}$ mol l^{-1} Pt and it is satisfactory for concentration of $2.9 \cdot 10^{-4}$ mol l^{-1} where the photocorrosion wave disappears.

The efficiency of hydrogen evolution increases with the increasing concentration of platinum in the electrolyte up to the value of about $5.7 \cdot 10^{-4}$ mol l^{-1} . Further increase

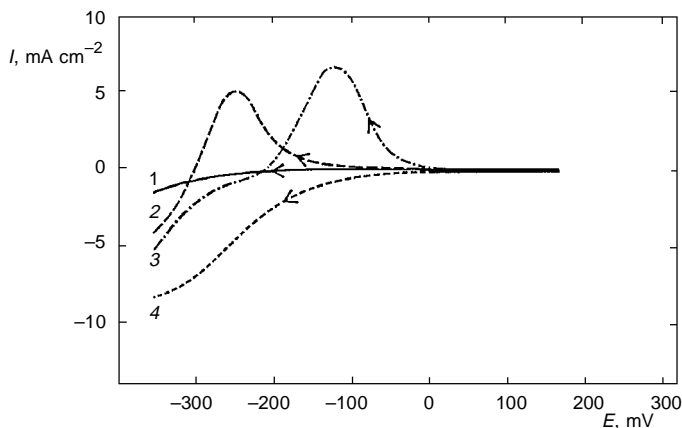


FIG. 3

Influence of crystallographic orientation of p-InP photoelectrode surface planes on the efficiency of hydrogen evolution. Electrolyte 3 M HCl, $2.9 \cdot 10^{-5}$ mol l^{-1} Pt, scan rate 100 mV s^{-1} . Electrode orientations: 1 (111)_a, 2 (111)_b, 3 (100), 4 (110)

of the platinum concentration up to $2 \cdot 10^{-3} \text{ mol l}^{-1}$ has no influence on the photocurrent. In this case, the photolysis of water starts at about +150 mV vs SCE and the photocurrent density rises with the decreasing potential up to the value of approximately -14 mA cm^{-2} .

To compare the catalytic activity of platinum with another metal catalysts from the platinum group, the subsequent measurements in the presence of ruthenium, rhenium and palladium salts were carried out under the same conditions. As we can see in Fig. 5, the

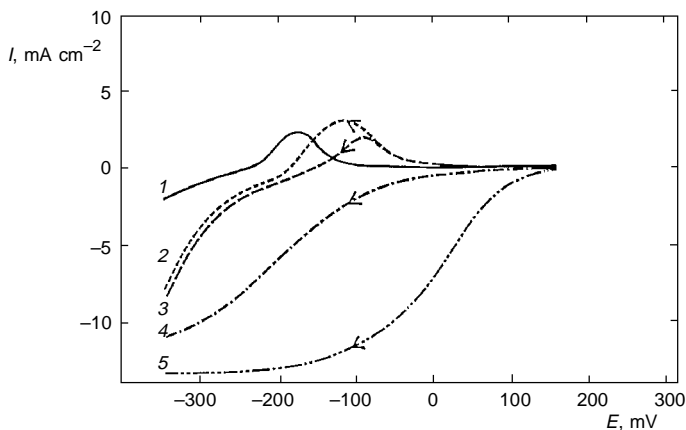


FIG. 4

Influence of platinum additives on the water photolysis on p-InP photocathodes, electrode orientation (100), electrolyte 3 M HCl, scan rate 100 mV s^{-1} ; platinum concentration: 1 0, 2 $2.9 \cdot 10^{-5}$, 3 $8.8 \cdot 10^{-5}$, 4 $2.9 \cdot 10^{-4}$, 5 $5.7 \cdot 10^{-4} \text{ mol l}^{-1} \text{ Pt}$

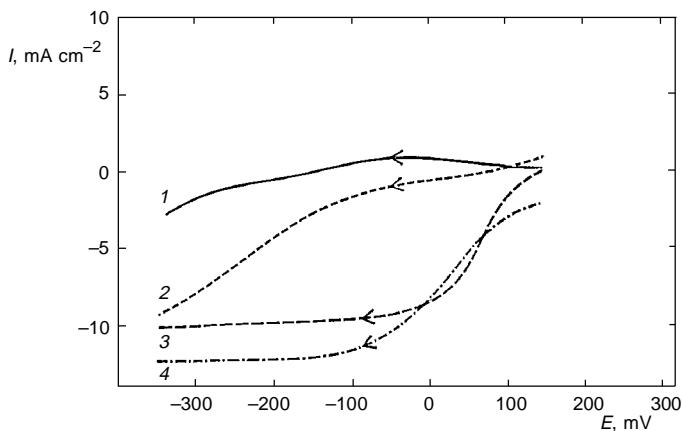


FIG. 5

Influence of platinum metal additives on the water photolysis on p-InP photocathodes, electrode orientation (100), electrolyte 3 M HCl, scan rate 100 mV s^{-1} ; concentration of platinum metals: 1 $1.2 \cdot 10^{-3} \text{ mol l}^{-1} \text{ Ru}$, 2 $1 \cdot 10^{-3} \text{ mol l}^{-1} \text{ Pd}$, 3 $1 \cdot 10^{-3} \text{ mol l}^{-1} \text{ Rh}$, 4 $1 \cdot 10^{-3} \text{ mol l}^{-1} \text{ Pt}$

catalytic activity increases in direction of $\text{Ru} < \text{Pd} < \text{Rh} < \text{Pt}$ but only rhodium seems to be as efficient as platinum. The catalytic activity of rhodium, however, appears to be much less stable during repeated voltammetric cycling.

In any case, the presence of noble metals in reaction system restrains photocorrosion processes. During the repeated cycling, the potential of the maximum of corrosion wave, if any, shifts towards more negative values.

Optimization of the Electrolyte

The all measurements described above were performed in 3 M HCl aqueous solution. To compare the efficiency of hydrogen evolution on p-InP photocathodes in other aqueous electrolytes, we carried out a series of experiments in solutions of 1 M hydrochloric acid, 1 M sulfuric acid, 1 M perchloric acid, 1 M phosphoric acid and 1 M sodium hydroxide results of which are summarized in Table I.

Essentially, the best results with regard to the photocurrent density were obtained in HCl solutions. Neither alkaline solution nor other acids with exception for perchloric acid yielded a sufficient photocurrent. Apparently, these electrolytes do not accept indium in the form of trivalent ion. Therefore we suppose the formation of a thin passivating layer on the surface of the electrode. On the contrary, hydrochloric acid keeps the surface free from corrosion products, and the photocurrent is high.

However, the corrosion is rather high and indium ions can be detected in the electrolyte after few hours. In the case of perchloric acid the activity of working electrode rapidly decreases and the reproducibility of the reaction is very poor.

TABLE I
Influence of composition of electrolyte on properties of the (100) oriented InP photocathodes

Electrolyte	Corrosion wave $E_{1/2}$, mV	Photocurrent density mA cm^{-2}	Potential onset of photolysis, mV
3 M HCl	-140	2	0
1 M HCl	-	1.8	0
1 M H_2SO_4	-120	0.5	-300
1 M HClO_4	-	1.3	-100
1 M H_3PO_4	-	-	-
1 M NaOH	-	-	-

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