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PHOTOELECTROCHEMISTRY OF MONOCLINIC ZnP_2: A PROMISING NEW SOLAR CELL MATERIAL

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ABSTRACT

For the first time monoclinic p-type ZnP_2 has been used as photocathode material in a photoelectrochemical cell. In 1M NaOH a saturation photocurrent of $8mA/cm^2$ is observed ($I = 120\ mW/cm^2$) while the dark current is negligible. The pH dependence of the photocurrent is similar to that of p-GaAs. Using the Cr^{3+}/Cr^{2+} EDTA redox system a photovoltage of 0.5 V is obtained from the shift of the photocurrent-potential curve with respect to the current-potential curve on a reversible Hg electrode. The spectral dependence of the photocurrent yields a value of 1.45 eV for the band gap in accordance with absorption measurements. These results show that an efficient liquid junction solar cell is feasible based on this material.

INTRODUCTION

The semiconductor (SC)/electrolyte interface has become of ever increasing importance in the last few years due to the growing interest in solar energy conversion devices. Being very similar in many respects with the metal/SC interface the former has some distinct advantages such as the ease of implementation of the junction (simple immersion of the SC into the electrolyte) and the great versatility in the choice of the redox system (i.e. the Fermi level in the elctrolyte). The band bending in the SC can thus be increased (at least in principle) to approach the value of the band gap, which is a necessary prerequisite for a high conversion efficiency.

The SC/electrolyte interface does, however, pose some formidable problems as well. Thus for example most n-type SC's with appropriate band gaps seem to be highly susceptible to photoanodic corrosion (1,2) while for p-type SC's surface states near the edge of the valence band tend to lower the fill factors and/or lead to Fermi level pinning (which lowers the achievable open circuit voltage) (3,4). Nevertheless, it has been demonstrated recently that these problems can be overcome. Thus substantially higher efficiences have been achieved in liquid junction solar cells as well as photoelectrolysis cells through improved surface treatments of p-InP photocathodes (5,6).

This clearly emphasizes the need for the development of new and possibly cheaper electrodes using less well known p-type SC's. Our own search for such compounds led us to consider monoclinic ZnP_2 (β-ZnP_2) as a possible candidate. According to the literature this material has a direct band gap at 1.3-1.5 eV (depending on the reference) (7,8,9) and is thus ideally suited for the efficient absorption of sunlight.

In this communication we report about the first photoelectrochemical investigation of p-type β-ZnP_2. Although necessarily of a preliminary nature the results clearly show that an efficient liquid junction solar cell based on this material should be feasible in the future.

EXPERIMENTAL RESULTS

Zinc phosphide compounds were described first by Stackelberg and Paulus. In their work they mentioned only the red α modification of ZnP_2 apart from Zn_3P_2 (10). The monoclinic β-ZnP_2 was first characterized by Hegyi et al. (7). In our synthesis we relied on the work of other authors as well, in particular on that of Finzel (11). The reaction between Zn and P took place in evacuated quartz ampoules (10^{-5} Torr) in a three zone furnace after sublimation of the starting materials. In a first stage Zn_3P_2 is obtained which sublimes congruently and can thus be purified by gas transport in a temperature gradient. Through a subsequent reaction with excess phosphorous Zn_3P_2 is transformed into ZnP_2 at pressures between 3 and 10 bars and at a temperature of 750-820° C. α and β modifications are both obtained in various proportions by this method. β-ZnP_2 crystals have a size of several mm^2 and are the more perfect the smaller the temperature gradient in the growth region. The lattice parameters are in good accord with the values cited in the literature (7). The calculated density (from X-ray data) and the measured density (by a buoyancy measurement) are equal within experimental error limits ($3.55 \pm 0.01\ g/cm^3$). The composition is stoichiometric within the accuracy of the chemical analysis (± 0.5 %). The latter was carried out by oxidative disintegration, the zink and phosphorous content being determined complexometrically.

The measurement of the thermopower of β-ZnP_2 showed the conduction to be p-type. The resistivity was measured with a four-probe technique which yielded 770 Ω cm at 300 K. Back contacts for use in the electrolytic cell were made with silver paint which resulted in usable though not strictly ohmic contacts. After encapsulation in epoxy the (100) front face of the crystals was polished with 1 μm diamond paste and finally etched in 1M HCl for typically 1-2 hours.

The electrochemical experiments were carried out with a rotating electrode, an AMEL potentiostat (under linear sweep conditions) a platinum sheet as counterelectrode and a saturated calomel electrode as reference.

Fig. 1 shows the current-potential curve measured in 1M NaOH with and without white light illumination by a tungsten halogen lamp (120 mW/cm^2). The electrode showed perfectly blocking behaviour up to -5V_{SCE} in the dark. The rise of the photocurrent around - 1V_{SCE} was accompanied by vigorous gas formation indicating the evolution of H_2 gas. The photocurrent saturated at 8mA/cm^2. The small shoulder in the anodic sweep in figure 1 is most probably associated with O_2 reduction proceeding through the valence band in the dark. It becomes the more pronounced the less perfect the electrode and can be totally eliminated by bubbling Ar through the cell. This effect will be more closely analysed in a forthcoming paper. First stability tests showed that continuous operation for several hours does not result in any appreciable decrease of the photocurrent nor did observation by an optical microscope reveal any signs of surface corrosion.

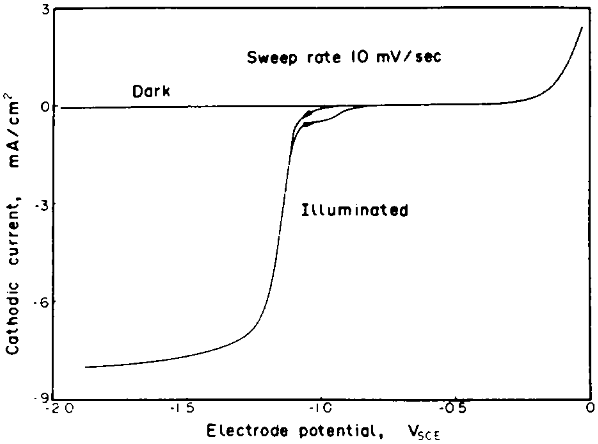

Fig.1 Current-potential curve for β-ZnP_2 photocathode in 1M NaOH. Broad band illumination intensity by a tungsten halogen lamp is 120 mW/cm^2.

First measurements of the pH dependence of the photocurrent reveal a rather similar behavior as has been observed for p-GaAs (12), i.e. the onset of the photocurrent shifts to more positive potentials for lower pH (0.6-0.8 V between pH 14 and pH 0.5, depending on the electrode quality). Most probably this is accompanied by a shift of the flatband potential V_{fb} with pH. All attempts to determine V_{fb} by a capacity measurement have failed so far, however, due to highly non-linear Mott-Schottky plots. A shift of V_{fb} as a function of pH can also be inferred from the use of different redox couples, such as Fe^{3+}/Fe^{2+} TEA (Triethanolamine) at pH 14 and Cr^{3+}/Cr^{2+} EDTA around pH 5 (reversible potentials at -1.0 and -1.2 V_{SCE}, respectively). Thus for the Cr^{3+}/Cr^{2+} EDTA redox couple the photocurrent-potential curves exhibit a shift of approximately 0.5 V with respect to the current-potential curves of a reversible Hg electrode (fig.2), indicating a photovoltage of 0.5 V. In principle the photocurrent in Fig.2 could be due to hydrogen evolution. In order to distinguish between hydrogen evolution and Cr^{3+} reduction the current potential curve was measured at a pH of 6.5, where the former can definitely be ruled out. At this pH a photovoltage of approximately 0.35 V was obtained. For the Fe^{3+}/Fe^{2+} TEA system on the other hand hardly any shift could be detected (< 0.1V). It should be stressed that the quality of the electrode used for the measurement in fig. 2 was substantially inferior to that used in the measurement of fig. 1. We are therefore convinced that the photovoltage measured with the former redox couple can yet be significantly increased by the use of more perfect crystals.

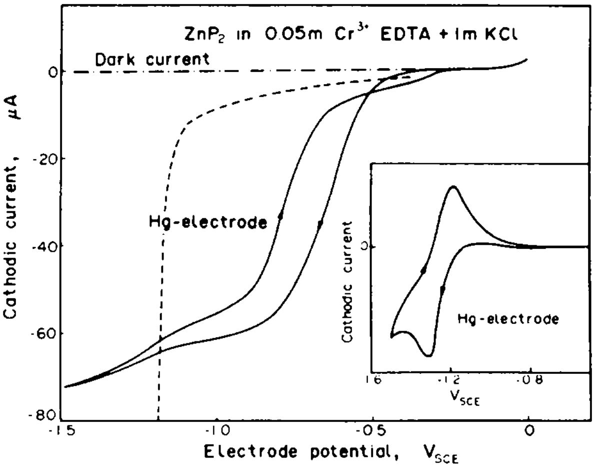

Fig.2 Current-potential curves for the Cr^{3+}/ Cr^{2+} EDTA redox system (sweep speed 10mV/sec, rotation rate 1750 rpm) with 0.05 MCr^{3+} EDTA in 1M KCl. Area of the ZnP_2 electrode 0.7 mm^2. The area of the Hg electrode is too large for current saturation to be seen on this scale. Insert: Cyclic voltammogram for Hg electrode (200mV/sec).

The spectral dependence of the photocurrent (at constant light intensity) was measured with standard LOCK-IN techniques. In fig. 3 this photocurrent is depicted together with the absorption coefficient K obtained through a transmission measurement on a thin crystal. From the

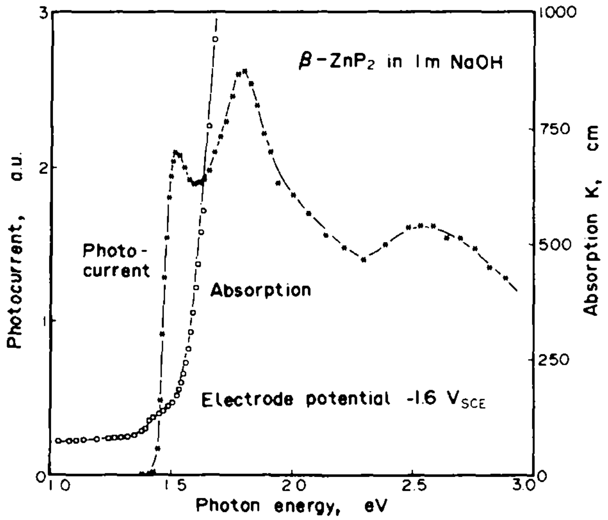

Fig.3 Photocurrent and absorption spectrum of β-ZnP_2.

steep rise of the photocurrent a band gap of 1.45 eV can be deduced in accordance with the absorption measurement. As is evident from fig. 3 the photoresponse is very good in the whole visible and near infrared region of the spectrum. The photocurrent was also found to depend linearly on the light intensity up to the highest intensity reached with a beam expanded Ar laser (80 mW/cm^2 at λ = 5145 A).

CONCLUSIONS

For the first time p-conducting β-ZnP_2 has been considered for use in a liquid junction solar cell. Its optical properties render this material ideally suitable for an efficient device. The feasibility of an efficient solar cell has been clearly demonstrated by the fact that a photovoltage of 0.5 V was obtained with Cr^{3+}/Cr^{2+} EDTA as the redox system. Naturally this constitutes but a first step towards the implementation of an efficient cell based on this material. Thus much work is required pertaining to improved crystal growth, doping as well as the exact determination of V_{fb}, etc., all of which will show what ultimate efficiency can be reached with this material.

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