The Influence of Contact Adsorbed Ions on the Photoelectrochemical Behaviour of α-HgS

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Results are reported to describe the influence of additives on the photoelectrochemical properties of the liquid junction α-HgS/electrolyte. The semiconductor electrodes were prepared by sublimation of α-HgS on Au substrates. The electrolyte was modified by additives such as Cl^-, Br^-, J^-, and CN^- ions. It was found that these anions play an important role in determining the flat band V_{fb} and the transition potential V_{tr}. Generally, both the nature and the concentration of the additives affect V_{fb} and V_{tr}. The results are interpreted in terms of contact adsorption of the used anions. It is further indicated that the adsorptive properties can be correlated to a possible chemical reaction of mercury cations with halide anions to form insoluble layers at the surface.

1. Introduction

The photoelectrochemical behaviour of a semiconductor electrode depends very strongly on the properties of the interface electrode/electrolyte [1—4]. Some contributions to its behaviour are attributed to the presence of intrinsic surface states and of specific adsorbed ions: They can promote dark processes with electrolyte species having a redox potential in the bandgap of the semiconductor, they may affect the recombination rate at the electrode and they can shift the bandedges, e.g. the flatband potential V_{fb}. The latter effect enhances reactions at the electrode with species whose redox potential is situated beyond the bandgap of the undisturbed electrode [5]. Consequently, these influences lead to a significant change in the properties of the system. Furthermore, adsorbed cations can stabilize n-semiconductor electrodes against anodic photodecomposition [6]. Finally, the more negative the value of V_{fb} the larger is the possible output voltage of the cell [7].

It is therefore of great interest to learn how to affect the flatband potential in a desirable way. One guide line for the preparation of suitable electrodes might be the use of semiconducting materials from constitutents with different electron affinities (EA). Correlations between EA and V_{fb} have been presented for many semiconductors. Conversely, the calculation of V_{fb} values from electron affinities

has turned out to be possible [8, 9]. On the other hand, it is known that chemical treatment of the electrode or changes in solvent/electrolyte combination can bring about modifications of the surface properties [10] that may lead to a change in flatband potential. But only very limited success has been achieved up to now to change V_{fb} into the desired direction.

In this work the influence is studied exerted by halide ions and by CN^- in the electrolyte on the behaviour of a model semiconductor electrode. As model substance the n-semiconducting red cinnabar (α-HgS) is used. α-HgS is chosen because of the well defined and gradual reaction behaviour of Hg^{2+} ions in aqueous solutions towards a great number of anions. It was expected that the reaction behaviour of Hg^{2+} can be correlated with the adsorptive behaviour of these anions at the HgS electrode surface. It was hoped to obtain this way more detailed informations on the contributions from interfacial processes.

It should be pointed out that detailed informations on the absorptive properties and on the photocurrent/potential behaviour of α-HgS electrodes can be found in an previous paper [11]. From the photoelectrochemical action spectrum the energy to promote an electron from conduction band into the valance band was determined to be 2.1 eV.

2. Experimental Set-up and Materials

The experimental set-up consisted of a potentiostat (PAR model 173), equipped with an uni-

versal programmer (PAR model 175), lock-in amplifier (Ithaco 393), a gain phase meter (HP 3575) and a high pressure Xe light source (Osram XBO 450 W 4) [12]. The voltage dependent capacity measurements (C/V) and photocurrent measurements (i_{ph}/V) were performed in an electrochemical cell containing the α-HgS working electrode, a platinum counter electrode and as reference a saturated calomel electrode (SCE). The semiconductor electrode were prepared on a gold substrate by a sublimation technique which allows the preparation of highly reproducible electrodes [11]. Electrolyte solutions were made up using destilled water and the potassium salts KNO_3, KJ, KBr, KCl, and KCN. All chemicals were obtained from Merck and were provided as reagent grade. Before measurement all electrodes were etched in 4 M HCl about 20 sec. All voltages mentioned in the text are against saturated calomel electrode (SCE).

3. Results

All measurements were carried out in 0.5 M KNO_3 aqueous solutions at pH values of 2.5 and 10.5, respectively. Prior to measurement nitrogen was bubbled through the electrolyte to minimize the concentration of desolved oxygen. The solutions were mixed with the additives to cover in some cases the concentration range from 10^{-7} M to 10^{-1} M for halide ions. Special experiments were performed to demonstrate that the presence of NO_3^- and K^+ ions did not influence the photoelectrochemical behaviour of the cinnabar electrode.

3.1. Photocurrent Measurements

Figure 1 shows some typical i_{ph}/V curves. They were taken with chopped light of the wavelength $\lambda = 570$ nm and a scan rate of 5 mV/sec. The curves show the following general pattern: i) In all cases negligible small dark currents were observed in the investigated range except in the presence of 0.1 M KCN solution. Using this additive a high dark current was observed. The obtained photocurrent saturates above 1 V_{SCE} at around 80% quantum efficiency [11] ii) The curves demonstrate the occurence of an anodic and a cathodic photoeffect. The cathodic photocurrent remains small. It becomes at most 5% of the anodic photocurrent at saturation. The potential at which the sign of the photocurrent inverts will be defined as transition
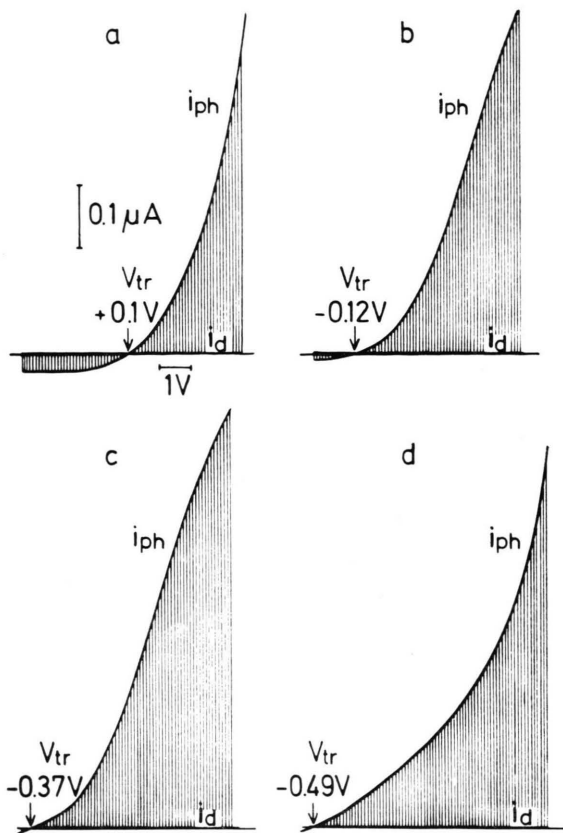

Fig. 1. Photocurrent/voltage curves on α-HgS taken in 0.5 M KNO_3/HNO_3 at pH 2.5. — a) oxygen-saturated solution, b) nitrogen-purched solution. The results obtained in nitrogen-purged solutions of 0.01 M KBr and 0.01 M KJ are denoted as c) and d), respectively.

potential V_{tr} [13]. The transition potential was found to depend on the concentration of the oxygen desolved in the electrolyte. It shifts from $+0.1$ V (cf. Fig. 1a) to -0.12 V (cf. Fig. 1b) at pH = 2.5 after deoxygenation of the electrolyte either by heating or by purging with nitrogen. At pH = 10.5 the transition occurs in a deoxygenated solution at roughly -0.3 V. iii) The curves show that the transition potential depends on both the nature and the concentration of the halide ions added. Even very small concentrations of J^- ions ($<10^{-5}$ M) yield a significant shift of V_{tr} to more negative values. A similar effect is found with CN^- ions as well in acid as in alkaline solution. The presence of Cl^- ions excerts only a small influence on V_{tr} at pH = 10.5. In alkaline solution no influence is observed at all. For all ions the tendency in the same: The influence on V_{tr} is stronger in acid than in alkaline solutions.

Finally it should be pointed out that the slopes of the i_{ph}/V curves close to V_{tr} are steeper in the presence of Br^- ions than in the presence of J^- ions, as shown in Fig. 1c and 1d. The strong deviation of the photocurrent/voltage curves from expectations according to Gaertner's formula [14] in the presence of J^- ions may be explained either by enhanced recombination rates or kinetic effects [15].

3.2. Capacity Measurements

To obtain linear Mott-Schottky plots a relatively high frequency of 5 kHz was required. Below this frequency nonlinearity was obtained [16]. It was also found that the use of frequencies higher than 5 kHz did not affect the slopes or the linearity of the plots. This can be understood from a frequency dependent impedance analysis, especially from an evaluation of the complex plane impedance and admittance data in the range of 20 Hz to 50 kHz [17, 18]. The analysis shows that the network of the investigated semiconductor/electrolyte interface can be evaluated best as an equivalent circuit consisting of at least one more RC element due to surface states. This element is bridged in parallel to the usual serial connection of the semiconductor's space charge capacitance C_{SC}, the ohmic resistances of the electrolyte R_{el} and of the semiconductor bulk R_{SC}. Assuming that the smallest time constant in the equivalent circuit is given by $t_S = (R_{el} + R_{SC}) C_{SC}$ then only at high frequencies the system will behave as a single capacitor and resistor connected in series. Under these conditions a simple evaluation of the measured data is indicated. Figure 2 represents a typical C^{-2}/V curve as obtained in a 10^{-1} M KCl solution. The donor concentration of the used electrodes was found to be in the range from 10^{13} to 10^{15} cm^{-3}.

The reported measurements suggest a strong influence of the halide ions added to the electrolyte on the flatband potential position of the used electrode. It was therefore decided to check whether the halide ions exert the same influence on V_{fb} as on V_{tr}. From a comparison it should be deduced to which extent the position of V_{tr} and V_{fb} depends on the adsorption of the monovalent halide ions at the interface.

Figure 3 demonstrates the shifts of V_{fb} and V_{tr} for the different halide ions used as function of their concentration. These shifts were evaluated as difference between the values of V_{fb} or V_{tr} obtained
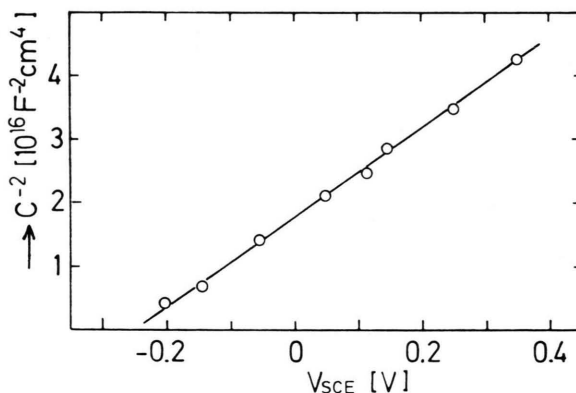

Fig. 2. Presentation of the capacitance/voltage data according to Mott-Schottky's relation. The data are taken in 0.5 M KNO$_3$/0.1 M KCl at pH 2.5. The applied frequency was 5 kHz. From the slope $N_D \cong 10^{13}$ cm^{-3} was calculated, assuming $\varepsilon_{HgS} \cong 100$.
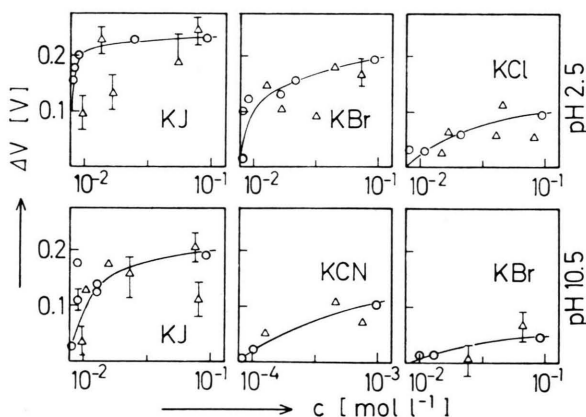

Fig. 3. Relative shifts of the transition potential ΔV_{tr} ($\circ$) and the flat band potential ΔV_{fb} ($\triangle$) referred to halide free nitrogen-purged 0.5 M KNO$_3$ solutions.

before and after the concentration change. They are denoted as ΔV_{fb} and ΔV_{tr}. The shifts refer to 0.5 M KNO$_3$ solutions at a pH value of 2.5 and 10.5. Before measurement the solutions were purged with nitrogen. A close agreement is established between ΔV_{fb} and ΔV_{tr}. In all investigated systems the absolute photocurrent transitions remain positive of V_{fb}. This results from the superposition of the cathodic and anodic photocurrent [13]. The transition potentials were obtained to lie within 0.10—0.15 V more positive than the extrapolated V_{fb} values. It should be mentioned that even at very small concentrations of J^- and CN^- the absolute values of V_{fb} and V_{tr} behave independent on the electrolyte pH. For Br^- ions present no changes in V_{fb} and V_{tr} with pH were obtained for concen-

trations $c \geq 10^{-2}$ M. The Cl$^-$ ions did not influence the small pH dependence of the halide free solution noticeably in the whole concentration range investigated.

4. Discussion

In this paper results are presented on the influence of small amounts of additives to the electrolyte on the contact α-HgS/electrolyte. It was generally stated that the used additives Cl$^-$, Br$^-$, J$^-$, and CN$^-$ shift the position of V_{tr} and V_{fb}. The most important result is that the observed shifts depend on both the nature and the concentration of the halide ions. The pattern of ΔV_{fb} and ΔV_{tr} as function of the amount of the various anions used behave similar within the accuracy of the measurements. It is assumed that the shifts of V_{fb} and V_{tr} can be interpreted by contact adsorption of the anions at the semiconductor/electrolyte interface. Kinetic or recombination effects seem to exert no influence on the V_{tr} position.

To discuss these observations the adsorption of ions at the electrolyte/semiconductor interface has to be considered first. The specific adsorption of charges at the interface results in a potential change $\Delta \varphi_H$ in the Helmholtz layer [19, 20] which is related to the flatband potential by (1)

$$V_{fb} = (EA - E_0 - \Delta f_c) - \Delta \varphi_H, \qquad (1)$$

where EA is the electron affinity of the semiconductor, $E_0 = 4.75$ V is the difference between the reference electrode SCE and the vacuum level, and Δf_c is a doping density dependent correction term for the energy difference between the bottom of the conduction band and the Fermi level. It is suggested that the correction term $\Delta \varphi_H$ is related to the net surface charge (Q_{ad}) of the adsorbed species through the following relationship

$$\Delta \varphi_H = - (\delta_H / \varepsilon_i) Q_{ad} + V_D', \qquad (2)$$

where δ_H is the thickness and ε_i is the permittivity of the Helmholtz layer. V_D' is the potential drop due to the oriented water molecules in the inner Helmholtz plane. Contributions to $\Delta \varphi_H$ from charge densities in surface states, Q_{SS}, and in the bulk of the semiconductor, Q_{SC}, are neglected. This leads to a direct relationship between V_{fb} and Q_{ad}

$$V_{fb} = (EA - E_0 - \Delta f_c) \\ + (\delta_H / \varepsilon_i) Q_{ad} + V_D'. \qquad (3)$$

If both ε_i and δ_H are considered to be independent on the nature and the density of the adsorbed species one obtains as a crude approximation the direct proportionality

$$V_{fb} \sim Q_{ad}.$$

Under this aspect the general shape of the curves in Fig. 3 may be interpreted in terms of Langmuir isothermes. Thus, for a qualitative description the adsorption of the halide ions can be considered to be ideal. Effects from the interactions between the adsorbed species — as taken into account e.g. by the BDM model [21] — are neglected.

The electrochemical free energy for the adsorption of halide ions hal is then given by

$$\overline{\Delta G} = \left[(\mu_{hal}^{0,ad} - \mu_{hal}^{0,s} - \sum_i (\mu_i^{0,ad} - \mu_i^{0,s}) \right] \\ + zF \Delta \varphi_H. \qquad (4)$$

$\mu_{hal}^{0,ad}$, $\mu_{hal}^{0,s}$ are the standard electrochemical potentials of the halide ions adsorbed at a standard surface or in solution; $\mu_i^{0,ad}$, $\mu_i^{0,s}$ are the respective standard potentials of all other species i either adsorbed or in solution, $zF \Delta \varphi_H$ represents the change in free energy due to potential changes in the Helmholtz layer initiated by the adsorption of halide ions. Equation (4) takes into consideration the possibility of adsorption of quite different species i, e.g. H_2O, H^+, OH^-, and O_2. It is argued that the shifts in V_{fb} and V_{tr} observed experimentally are related to an exchange of the added halide ions against species already adhering to the surface. The expression in brackets of Eq. (4) may be defined as the apparent standard free adsorption energy $\overline{\Delta G^0}$ [22].

A rough estimation of the apparent $\overline{\Delta G^0}$ for the halide ions shows that the adsorption of the anions increases gradually as follows: Cl$^- <$ OH$^- <$ Br$^-$ $<$ J$^- <$ CN$^-$. This sequence suggests a relation between the polarizability of the used anions and their adsorptive behavior. It is generally agreed, however, that electrostatic interaction of ions with semiconducting materials are of minor significance. This is because of the negligible polarisability of lightly doped semiconductors [23]. Therefore other forces should also be considered. It is well known that mercury forms strong covalent bondings with the halides. The compounds $HgX_2(X = J, Br, Cl)$ are insoluble in aqueous solution with the exception of $Hg(CN)_2$ [24]. Thus one can assume that the adsorption process is promoted by a strong bonding

Table 1.

X^-	$-\Delta G_r^0$ [kJ mol^{-1}]
CN^-	188
J^-	166
OH^-	129
Br^-	110
Cl^-	67
S^{2-}	326

of the halide ions to imperfections at the surface. It is suggested that the strength of this bonding might be correlated to the standard free energies ΔG_r^0 of the reactions $Hg^{2+} + 2 X_{aq}^- \rightarrow HgX_2$. In Table 1 the corresponding ΔG_r^0 values for the halides are listed. The table shows a satisfactory agreement between the sequence of the adsorption tendency and the standard free reaction energy. Doubtless, the formation of an insoluble layer at the semiconductor electrode surface is of great importance for the position of the flatband potential. This is corroborated by photoelectrochemical measurements made with CdS electrodes in the presence of $[Fe(CN)_6]^{4-}$, which shifts V_{fb} to more negative values. Cadmiumferrocyanide is insoluble in water [25].

The observed shifts of V_{fb} in acid and alkaline solution in the presence of the halide ions can be explained as follows: In alkaline solution more OH^- ions are adsorbed at the surface than in acid solution. Thus the exchange of the negative OH^- ions against the negative halide ions results in a small change of the net negative surface charge only.

On the other hand, the fact that the absolute value of V_{fb} in the presence of small amounts of J^- and CN^- and high concentrated KBr solutions are independent of the pH value indicates saturation of the α-HgS surface with these ions. The fact that no measurable changes of V_{fb} and V_{tr} are observed in the presence of Cl^- reveals the higher adsorptive nature of OH^- ions than of Cl^-. The influence of CN^- present in the electrolyte on the photo- and dark current behaviour as well as on V_{tr} seems to be caused by the good solubility of the very stable $Hg(CN)_2$ compound in water. From thermodynamic data one cau exclude a reaction with the gold substrate $(Au + 2p^+ \rightarrow [Au(CN)_2]^-)$ as an explanation for the observed high dark currents.

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