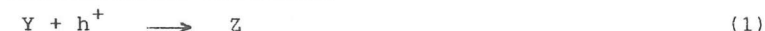


INFLUENCE OF ELECTROLYTE COMPOSITION UPON THE MECHANISMS OF
DECOMPOSITION AND STABILIZATION OF GaAs PHOTOANODES

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Gallium arsenide is an appropriate semiconductor material for photovoltaic solar energy conversion. The operation of an n-GaAs-based photoelectrochemical solar cell implies that the photogenerated positive holes oxidize a dissolved reducing agent Y at the semiconductor electrode:

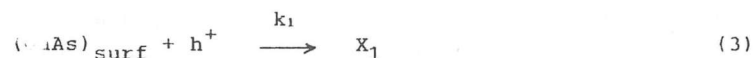


whereas Z is reduced back to Y at the counterelectrode. The long-term operation of such a cell is hindered however by a competing anodic hole reaction in which the semiconductor decomposes:

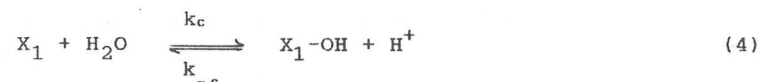


Since either oxyanions or oxides are among the products of reaction (2) (at low or high pH-values and in the intermediate pH range respectively), this process can be efficiently suppressed by working in non-aqueous medium. E.g., the n-GaAs photoelectrode appears to be quite stable in water-free acetonitrile as the solvent, with TMPD (tetramethyl paraphenylene diamine) added as the reducing agent Y. This conclusion was reached by Kohl and Bard⁽¹⁾ from the fact that the GaAs electrode showed neither a change in weight nor in surface appearance after the passage of a considerable charge in this medium, and was confirmed by the present work, in which the stabilization ratio, i.e. the fraction of the anodic photocurrent associated with reaction (1), was determined by rotating ring-disk (RRD) voltammetry and was found to be equal to one within the limits of error for the system under consideration. Residual water in the acetonitrile causes deterioration of the cell due to oxide formation on the semiconductor surface. In aqueous medium, the prevention of

anodic photodecomposition of n-GaAs by a competing stabilization reaction of the type (1) requires relatively high reducing agent concentrations. It is therefore clear that, in view of solar energy applications, the detailed knowledge of the role of water in the mechanism of the decomposition reaction (2) and in the kinetics of the competition between reactions (2) and (1) in aqueous medium as well as in mixed acetonitrile-water solvents is important. Recently, we have made a kinetic study, by RRD voltammetry, on the competition between the photoanodic oxidation of TMPD and the photodissolution of n-GaAs in acid aqueous medium⁽²⁾, and we have been able to interpret the results on the basis of the following mechanism. In the first electrochemical step of the six-equivalent oxidation reaction of GaAs, a mobile surface decomposition intermediate X_1 is assumed to be formed:



which can interact chemically with a water molecule to form an immobile intermediate X_1-OH according to the equilibrium reaction



(X_1 is positively charged, whereas X_1-OH is neutral); the second decomposition step is assumed to involve the reaction between an immobile X_1-OH and a mobile X_1 species:



whereas the stabilization reaction is supposed to take place by electron transfer between $TMPDH^+$ and X_2 . We have now made an analogous kinetic study in mixed acetonitrile-water solvents, the results of which are essentially as follows.

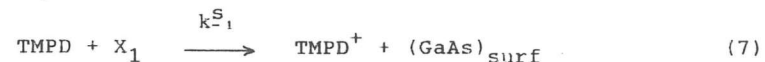
The stabilization ratio s was measured as a function of the analytical concentration c of TMPD, of the pH and of the total anodic photocurrent density (the latter being monitored by the light intensity) for the n-GaAs electrode in contact with acid acetonitrile-water mixtures containing 42 mol % CH_3CN . Qualita-

tively, the usual trends were observed, i.e. s increases with increasing c but decreases with increasing i . Quantitatively, the following relationship appeared to hold between s , c and i at given pH:

$$s^2/(1-s) = k.(c^2/i) \quad (6)$$

The rate constant k was found to be an increasing function of pH.

We have been able to interpret these data by assuming that the decomposition mechanism of GaAs is the same as that in aqueous medium, as expressed in the reaction eqns. (3), (4) and (5), but that the stabilization reaction now involves electron transfer from TPMD to the decomposition intermediate X_1 and hence the restoration of a partially broken surface bond:



In this interpretation, the rate constant k can be expressed as:

$$k = e.(k^S_{-1})^2.k_{-c}.c_{H^+}.[f(c_{H^+})]^2/6k_2k_c.c_{H_2O} \quad (8)$$

where e represents the elementary charge, c_{H_2O} and c_{H^+} represent the water and the proton concentration respectively, and $f(c_{H^+})$ the pH-dependent factor connecting the concentration of non-protonated TMPD molecules to the analytical TMPD concentration. It follows from eqns. (6) and (8) that as expected, decreasing the water content of the acetonitrile-water mixture influences the kinetics in the sense of improving the stability of the photoelectrode. The relatively poor stability in this medium as compared to that in purely aqueous solutions is due to the fact that in the latter case, $TMPDH^+$ instead of TMPD acts as the electroactive species, and that in the given pH range, the concentration ratio TMPD vs. $TMPDH^+$ is small. It should be remarked that not only the electroactive species in solution but also the surface decomposition intermediate involved in stabilization is different in water and in acetonitrile-water mixtures. This difference may be due to a difference in energy level positions in the redox electrolyte.

Analogous kinetic measurements on the interface illuminated n-GaAs/TMPD in acetonitrile-water mixtures containing 13 mol % CH₃CN lead to a different relationship between s, c and i:

$$[s/6 + s^2/(1-s)] = k' \cdot (c/i) \quad (9)$$

This kinetic law and the observed pH-dependence of the rate constant have led us to propose a reaction scheme, in which reactions (3) and (4) are followed by decomposition step (10) instead of (5):



and in which the stabilization reaction involves electron transfer from the TMPD molecule to the immobile decomposition intermediate X₁-OH. Hence, when lowering the acetonitrile concentration from 42 to 13 mol %, apparently free holes take over the role of the mobile reactive surface species from the intermediates X₁. This fact can be attributed to a drastic decrease in the X₁ concentration due to a shift in the equilibrium (4) which is thought to be caused by the stabilization of the proton in this medium. Indeed, it has been found (3) that the standard free enthalpy of transfer of the proton from water to acetonitrile-water mixtures exhibits a minimum around 22 mol % CH₃CN.

Summarizingly, it can be stated that changes in the composition of the medium may cause changes in the mechanisms of the decomposition and stabilization reactions at the n-GaAs/TMPD interface. It is conceivable that these different mechanisms operate simultaneously, and that their relative rates are influenced by medium effects by influencing the concentrations of the surface decomposition intermediates involved as well as the redox level positions.

References.

- (1) P.A. Kohl and A.J. Bard: J. Electrochem. Soc. 126, 603 (1979).
- (2) S. Lingier, D. Vanmaekelbergh and W.P. Gomes: J. Electroanal. Chem. 228, 77 (1987).
- (3) K.Das, A.K. Das and K.K. Kundu: Electrochim. Acta 26, 471 (1981).

ETUDE DU SYSTEME AgTlTe-HgTe DIAGRAMME D'EQUILIBRE ET CARACTERISATION PHYSIQUE

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L'étude du diagramme des équilibres de la coupe AgTlTe-HgTe a montré l'existence de trois solutions solides terminales ainsi que de deux phases intermédiaires. L'une d'elles, Ag₃HgTl₃Te₄, a été caractérisée par ses propriétés physiques.

INTRODUCTION

Le matériau AgTlTe est un semi-conducteur de type p présentant des propriétés thermoélectriques (1,2). A partir de ce composé, plusieurs expériences de dopage ont été réalisées de manière à obtenir une semi-conduction de type n. Notre choix s'est porté sur le mercure comme élément dopant par le fait que l'introduction du mercure divalent doit provoquer un déséquilibre des valences favorable à la création d'impuretés de type n (électrons). D'autre part, les rayons ioniques de Ag⁺ (1.16 Å) et de Hg²⁺ (1.10 Å) sont très voisins permettant l'insertion des atomes de mercure dans la matrice AgTlTe (3).

Nous avons, dans ce travail, procédé à l'étude des équilibres de phase du système AgTlTe-HgTe et à la caractérisation physique des phases mises en évidence.