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Controlling charge-transfer processes at semiconductor/liquid junctions

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Abstract

The interfacial kinetics of charge transfer at n-GaAs/liquid junctions were controlled by anchoring positively charged species, such as tetra(-4-pyridyl)porphyrinatomanganese(III), with the semiconductor surface. Unlike earlier adsorption techniques, the charges have been chemically anchored to the semiconductor surface, in this work, via a ligand. The number of charges per site (attached molecule) ranged from +1 to +5. The positive charges shifted the band-edges towards more positive potential values. The degree of shift increased with surface charge density. In the dark, the flat band potential (measured by Mott–Schottky technique) and the onset potential were shifted by up to 300 mV depending on surface charge density. Relatively less of a shift was observed during illumination of the system. Other surface characteristics, such as conversion efficiency and photoluminescence intensity, have been enhanced. The basis for these shifts and their implications with respect to control of interfacial processes are discussed.

Keywords: Semiconductor; Metalloporphyrins; Band-edges; Flat-band potential; Open-circuit potential

1. Introduction

Surface modification is known to improve the semiconductor properties, at the solid/liquid interface, in solar photoelectrochemical applications [1–16]. Semiconductor stability at the solid/liquid interface, together with the open circuit potential, has been improved by covering the surface with different conducting polymers [1–4]. It may become necessary, sometimes, to control the semiconductor band-edge positions. By doing so, it is then possible to control the kinetics of charge transfer at the semiconductor/liquid interface, Scheme 1. Such techniques are important in photoelectrochemical processes. For example, n-$GaInP_2$ is a promising photocatalyst for water splitting in visible light, since its band gap (~1.8 eV) is suitable for such purposes [17,18]. Unfortunately, n-$GaInP_2$ has a valence band-edge slightly higher than needed for water oxidation to produce O_2. Therefore, it is wise to shift the n-$GaInP_2$ valence band-edge slightly in order to enable holes to oxidize H_2O, Scheme 1. Band-edges, are known to be shifted by adsorption of charged species at the semiconductor surface. Negatively charged ions, such as I_3^- or Cl^- adsorbed or at the semiconductor/liquid interface, induce negative shifts in the semiconductor band-edges [8,19]. Such effects are rationalized by the tendency of the anions to adsorb onto the semiconductor surface. Adsorption of metal cations on semiconductor surfaces has also been known to affect characteristics at solid–liquid interface [10,11]. Surface charges formed onto GaAs surface also cause V_{fb} shifting [20]. The work described here is different from these and other earlier reports [8–11,13–17,19]. A new technique is presented here to create primary chemical bond formation between charged ions and the surface via anchoring ligands, using quaterinization reactions. It is also anticipated to see how increasing charge density at the surface may further increase V_{fb} shifting.

n-GaAs was employed here as a model semiconductor. n-GaAs surface was first reacted with 3-chloropropyltrimethoxysilane as reported for other metal, metal oxide and silica surfaces [12,21–26]. The silylated surfaces were then reacted with pyridyl groups via quaternization reactions to produce the positively charged pyridinium ions [27–30]. Different pyridyl group carrier species were used. Tetra(-4-pyridyl)porphyrinatomanganese(III and II) [$Mn^{III/II}$(TPyP)], un-metallated 5,10,15,20-tetra(-4-pyridyl)-21H,23H-porphine, H_2TPyP and 2,2′-bipyridine were reacted with the silylated n-

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