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# Charge regulation at semiconductor-electrolyte interfaces

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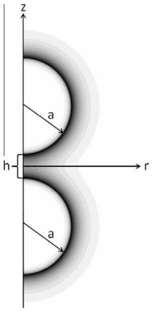
## GRAPHICAL ABSTRACT



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## ABSTRACT

The interface between a semiconductor material and an electrolyte solution has interesting and complex electrostatic properties. Its behavior will depend on the density of mobile charge carriers that are present in both phases as well as on the surface chemistry at the interface through local charge regulation. The latter is driven by chemical equilibria involving the immobile surface groups and the potential determining ions in the electrolyte solution. All these lead to an electrostatic potential distribution that propagate such that the electrolyte and the semiconductor are dependent on each other. Hence, any variation in the charge density in one phase will lead to a response in the other. This has significant implications on the physical properties of single semiconductor-electrolyte interfaces and on the electrostatic interactions between semiconductor particles suspended in electrolyte solutions. The present paper expands on our previous publication (Fleharty et al., 2014) and offers new results on the electrostatics of single semiconductor interfaces as well as on the interaction of charged semiconductor colloids suspended in electrolyte solution.

## 1. Introduction

The interface between a semiconductor material and electrolyte solution presents a very interesting system from both a fundamental and applied perspective. Both the semiconductor and the electrolyte phases have mobile charges (electrons and/or holes in the former and ions in the latter) that can redistribute in space depending on the global potential distribution. Bringing these two phases in contact induces an electrostatic interaction between them via the boundary conditions at the interface. This leads to a redistribution of the local charges that form electric double layers in both the electrolyte and the semiconductor phases. The interface itself can have a complex chemical structure due to the presence of a native oxide layer that forms in contact with water, or due to deliberate surface functionalization [1–3]. This surface layer determines the groups that are exposed to the electrolyte solution and through the surface chemical equilibrium determines the charge at the interface. This is known as charge regulation [4–10] and

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defines the only physically justifiable boundary condition for solving such electrostatic problems. Hence, the electrostatic properties of the semiconductor-electrolyte interfaces are obtained by the interplay between the charges in the two phases coupled to the specific interfacial chemistry. Any disturbance of the potential and charge density in one of the phases will induce a corresponding change in the other one. This has been experimentally demonstrated by Greenfield and Sivan [11] who developed a new type of force microscopy utilizing this effect. By measuring the conductivity variations in a semiconductor substrate these authors successfully measured the electrostatic interaction with an approaching charged object. Recently we performed a theoretical analysis of the interaction between two charged colloidal particles suspended in electrolyte solution [12]. It predicts that the electrostatic repulsion between the particles decreases with increased doping level. Hence, doped semiconductor colloids suspended in electrolyte solution should be less stable than undoped ones if the surface chemical groups are identical for the two cases. The latter condition is important because if the doping procedure also changes the nature of the surface chemistry, the stability may be shifted in the opposite direction [13–15]. As the electrostatic repulsion drops with doping, attractive forces such as van der Waals can dominate and lead to particle coagulation [16,17].

Colloidal systems that involve semiconductor-electrolyte interfaces or simply semiconductor particles suspended in electrolyte solutions are not only of significant fundamental interest but present opportunities for new applications [2,18]. The effect of charge density redistribution in the semiconductor in response to potential variations in the electrolyte near the interface has been exploited to perform force measurements [11,19] and to develop sensing techniques that use nanoscale semiconductors [20–24].

This study is a continuation of our previous work [12], where we presented a semi-quantitative analysis of the stability of charged semiconductor colloids suspended in an electrolyte solution. Here we present a detailed analysis of the electrostatics of an isolated semiconductor-electrolyte interface, and thoroughly examine the effects of surface chemistry, salt concentration, and a wider range of doping concentrations abandoning several approximations made in the previous analysis. New results for highly-doped semiconductors are presented, and the role of the surface chemistry is investigated in more detail.

## 2. Theory

Consider the interface between a semiconductor material in contact with an electrolyte solution. Many semiconductors will form an oxide layer when in contact with an aqueous phase, the formation of silica on silicon being a typical example. The oxide layer provides chemical groups that are exposed to the electrolyte and may be involved in chemical reactions with some of the dissolved species. Often (and particularly when oxides are involved) the important species in solution are hydrogen ions which can bind to or dissociate from the oxide surface, which can be considered as ideally amphoteric. Unless specified otherwise, most of the model systems analyzed below are based on n-doped Si covered with a layer of $SiO_2$.

### 2.1. Potential distribution at semiconductor-electrolyte interfaces

While the surface groups may be involved in many chemical processes, most oxides can be adequately described by the following two chemical reactions [6]

$$\begin{aligned} &\mathrm{AH_2^+} \rightleftharpoons \mathrm{AH} + \mathrm{H^+}, \quad p\mathrm{K}_+ = -\log_{10}\mathrm{K}_+, \\ &\mathrm{AH} \rightleftharpoons \mathrm{A^-} + \mathrm{H^+}, \quad p\mathrm{K}_- = -\log_{10}\mathrm{K}_-. \end{aligned} \tag{1}$$

The $-A^-$ groups are part of the solid material, typically the oxide. If the oxide layer is $SiO_2$, then $-A^- = -SiO^-$. The chemical equilibrium constants $K_-$ and $K_+$ determine the overall charge for a given value of the solution $pH$. This surface charge gives rise to an electrostatic potential $\Psi$, which can be obtained by solving the Poisson equation

$$\nabla^2 \Psi = -\frac{\rho}{\varepsilon_r \varepsilon_0}, \tag{2}$$

where $\rho$ is the charge density, $\varepsilon_r$ is the relative dielectric permittivity of the local medium, and $\varepsilon_0$ is the permittivity of vacuum. The entire system, however, consists of a semiconductor region, oxide layer and electrolyte solution. Hence, Eq. (2) has to be solved in each of these domains. The charge density for each domain is given as

$$\rho = \begin{cases} e\sum\limits_i n_i^0 z_i \exp\left(\frac{-z_i e\Psi}{k_B T}\right), & \text{electrolyte}, \\ eN_d\left[1 - \chi F_{1/2}\left(\frac{\mu - e\Psi}{k_B T}\right)\right], & \text{n-doped semiconductor}, \\ 0, & \text{oxide}, \end{cases} \tag{3}$$

where $n_i$ is the number concentration of the $i$th ionic component, $z_i$ is the valence of the $i$th ionic component, $k_B T$ is the thermal energy, $e$ is the fundamental unit of charge, $N_d$ is the donor concentration

$$F_{1/2}(x) = \frac{2}{\sqrt{\pi}} \int_0^\infty dt \frac{t^{1/2}}{1 + \exp(t - x)}, \tag{4}$$

is the Fermi integral of order 1/2 and $\mu$ is the Fermi level, (i.e., the chemical potential of the charged species in the semiconductor) [25,26]. The parameter $\chi$ is given by

$$\chi = \frac{1}{4N_d}\left(\frac{2m^* k_B T}{\pi \hbar^2}\right)^{3/2}, \tag{5}$$

where $m^*$ is the effective mass of the electron and $\hbar$ is the reduced Planck constant. The charge density inside the oxide layer is assumed to be zero.

At high temperatures and moderate doping levels the Fermi integral can be approximated by an exponential function

$$\chi F_{1/2}\left(\frac{\mu - e\Psi}{k_B T}\right) \to \exp\left(-\frac{e\Psi}{k_B T}\right). \tag{6}$$

This approximation breaks down below the Fermi temperature, which is defined by [27,28]

$$T_F = \frac{\hbar^2 (3\pi^2 N_d)^{2/3}}{2k_B m^*}. \tag{7}$$

Above the Fermi temperature, the Boltzman distribution is applicable, while deviation from the Boltzman distribution is noticeable below the $T_F$. Eq. (7) shows that the Fermi temperature increases with the doping level $N_d$, hence for heavily doped systems the approximation in Eq. (6) may break down. For example GaAs (with $m^* = 0.067\, m_e$, $m_e = 9.11 \times 10^{-31}$ kg) with doping level $N_d = 10^{19}\ \mathrm{cm}^{-3}$, exhibits a Fermi temperature of $T_F \approx 2900$ K [27]. Similar calculations for Si with the same doping level ($m^* = 0.28\, m_e$) gives $T_F \approx 700$ K. Hence, for higher doping levels the charge distribution in the semiconductor will be more accurately expressed by Eq. (3) rather than Eq. (6).

The surface charge density $\sigma_s$ at the oxide-electrolyte interface is simply defined as the sum of the positive charge density minus the negative charge density and is given as

$$\sigma_s = e\left([AH_2^+] - [A^-]\right), \tag{8}$$

and the surface charge density can be related to the potential through

$$\sigma_s = -\varepsilon_r \varepsilon_0 \nabla \Psi \cdot \mathbf{n} \tag{9}$$