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Effect of the surface polarizability on electrostatic screening in semiconductors

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Abstract

Following the Gibbs approach a general electrostatic model of heterogeneous systems with non-homogeneous interfaces is proposed. The intrinsic surface polarization is taken into account through the introduction of a surface dielectric constant and the electrostatic boundary conditions are generalized as two-dimensional Poisson equations. This model is applied to analysis of the electrostatic potential of charged defects on a semiconductor surface. As a result, a good theoretical fit of the experimental data is obtained. The fitting value of the surface dielectric constant is in good agreement with its theoretical estimation in the framework of the Gibbs approach.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The present paper offers an approach to the analysis of point charge potential distribution at a semiconductor surface strictly based on the Gibbs *excess* model of heterogeneous systems [1]. The term ‘heterogeneous media’ is used in the literature to denote material systems of various bulk phases divided by surfaces. Actually, the so-called surfaces do not exist, but correspond to nanoscopic transition zones in the real systems where the bulk material characteristics change sharply [2, 3]. A substantial problem with such a macroscopic model is the practically unknown distribution of the phenomenological characteristics (e.g. dielectric permittivity, refraction index, viscosity coefficient, etc) in the transition zone. For the case considered herein, this problem can be exemplified by the Maxwell equation $\nabla \cdot \mathbf{D} = \rho$, where the unknown space-dependent dielectric tensor components $\varepsilon_{ij}(x, y, z)$ defining the electric displacement field $\mathbf{D} = \varepsilon_0 \boldsymbol{\varepsilon} \cdot \mathbf{E}$; $\mathbf{E} = -\nabla\varphi$ make the entire mathematical model unsolvable. The traditional approach to electrostatics treats the real heterogeneous system as homogeneous coexisting bulk (3D) phases divided by boundaries, i.e. by surfaces, considered also as homogeneous (2D) phases. The benefit of this modelling is that the dielectric constant of a homogeneous phase is constant, thus making possible the solution of the Maxwell equation in the bulk, i.e. $\varepsilon_0 \nabla \cdot \boldsymbol{\varepsilon} \cdot \mathbf{E} \rightarrow \varepsilon_0 \varepsilon \nabla \cdot \mathbf{E} = \rho$ (see equations (6), (7)). However, a new problem related to

the so-called boundary conditions arises, namely how to model the distribution at the surface. In electrostatics, this modelling concerns the jump of the normal component of the electric displacement field. It takes the form $D_{+n} - D_{-n} = \rho_s$ where '+' and '-' denote the field on both sides of the surface. This boundary condition is derived from the Maxwell equation applying the Gauss theorem at the boundary [4]. Special attention should be paid here to the interpretation of the surface charge density ρ_s . Usually, ρ_s (defined simply as the surface charge per unit area, by analogy to the bulk charge density ρ) is thought of as an actual net charge density but, as will be clearly shown below, ρ_s is an *excess* quantity. The concept of excess quantities, originally introduced by Gibbs for restoring the real amounts of matter, energy, etc in an idealized system, has been exclusively employed in the thermodynamic analysis of surfaces [2]. At the beginning of the 20th century the study of the dynamics of dispersed systems (capillary waves, convection of bubbles, droplets, etc [5]) showed the need for generalization of the traditional boundary conditions, accounting (by analogy with bulk phases) for specific surface characteristics such as surface viscosity, surface diffusion coefficient, elasticity, etc.

This generalization formally results in the appearance of an additional term in the boundary condition, namely $D_{+n} - D_{-n} + \nabla \cdot \mathbf{D}_s = \rho_s$, transforming it into a surface analogue of the bulk Maxwell equation. Here, \mathbf{D}_s is the vector of the electric displacement field on the surface.

As any novel phenomenological parameter ε_s needs an experimental verification, two of us (TI and BR) recently studied the problem of nucleation in Langmuir monolayers at the air–water interface by introducing surface excesses of the charge density and the dielectric constant [6]. Thus, the difference in the surface polarizability of the heterogeneous surface phases was taken into account with the help of a definition of surface dielectric constants for each surface phase. The theory successfully described the suppression of the nucleation process with the increase in the water electrolyte concentration as a polarization effect analogous to the Thomson theory for 3D-phase transition [7].

In this paper we present results of a study of another system giving additional corroboration of the relevance of the surface dielectric permittivity and, very importantly, that the fitting of the theoretical curve to the experimental data yields expected values of the surfaces dielectric constant.

The paper is organized as follows. In section 2 we shall come to a complete system of equations describing the electrostatics of complex heterogeneous media with a new substantial element, namely the introduction of a surface dielectric constant ε_s . Section 3 analyses the effect of ε_s on the field of a point charge near the boundary of a semiconductor. The results of this analysis are used to interpret the experimental data obtained and discussed elsewhere [8, 9].

2. General theory

Consider two bulk phases in contact with each other. Their bulk properties are not homogeneous around the phase boundary even if both phases are homogeneous. To obtain the real behaviour of some bulk quantity (say a) one must know the microscopic structure of the boundary which is usually unknown. Therefore, Gibbs [1] suggested an approximate treatment which amounts to the following. The real continuous behaviour of $a_{\text{real}}(z)$ (z is the coordinate normal to the phase boundary, see figure 1) is replaced by an idealized quantity $a_{\text{ideal}}(z)$ which has a step-like behaviour across the phase boundary. The difference between the real and the idealized quantity is ascribed to the interface surface as a surface (excess) quantity a_s defined as follows:

$$a_s = \int_{-\infty}^{\infty} [a_{\text{real}}(z) - a_{\text{ideal}}(z)] dz. \quad (1)$$

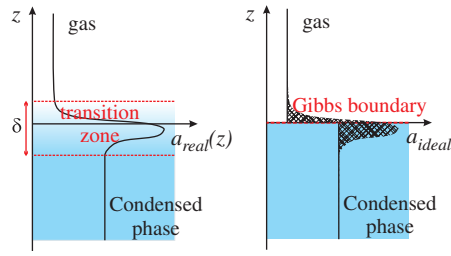


Figure 1. Left panel: the real behaviour of some bulk quantity across the transition zone between two bulk phases. Right panel: the idealized distribution of the quantity with a Gibbs phase boundary between the bulk phases. The shaded area is proportional to the excess quantity a_s .

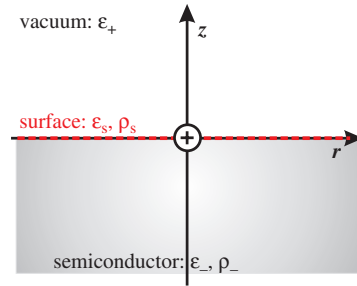


Figure 2. Schematic of the system under consideration in the text.

Thus, the distribution of a in both bulk phases and the boundary is given by [10–12]

$$a(z) = a_+\theta(z) + a_-\theta(-z) + a_s\delta(z), \quad (2)$$

where a_+ and a_- are the idealized characteristics of the two bulk phases (in the simplest case they are constants), $\theta(z)$ is the Heaviside step-function and $\delta(z)$ is the Dirac function. Examples of widely used surface properties defined in this way are absorption as an excess of the bulk concentration, surface viscosity as an excess of the bulk one, etc [13, 14].

Let us turn now to the derivation of the equations and the boundary conditions for the electrostatic potential in a heterogeneous system. Let us assume that the phase boundary surface is situated at $z = 0$ (figure 1). Following [12, 15] we assume the following expressions for the charge density and the dielectric constant

$$\varepsilon(z) = \varepsilon_+\theta(z) + \varepsilon_-\theta(-z) + \varepsilon_s\delta(z), \quad (3)$$

$$\rho(z) = \rho_+\theta(z) + \rho_-\theta(-z) + \rho_s\delta(z). \quad (4)$$

Here, ε_s , ρ_s are the surface dielectric constant and the surface charge density defined via equation (1) and ε_{\pm} , ρ_{\pm} are the corresponding quantities for the two bulk phases (situated at $z > 0$ and $z < 0$). Also, the vector of the electric displacement field is given by [12]

$$\mathbf{D} = \mathbf{D}_+\theta(z) + \mathbf{D}_-\theta(-z) + \mathbf{D}_s\delta(z). \quad (5)$$

Assuming that the Maxwell equations are valid for the above singular field, the equations for the electrostatic potential and the corresponding boundary conditions are obtained in the form

$$\varepsilon_-\Delta\varphi_- = -\frac{\rho_-}{\varepsilon_0}, \quad (6)$$

$$\varepsilon_+\Delta\varphi_+ = -\frac{\rho_+}{\varepsilon_0}, \quad (7)$$

$$\varepsilon_+ \frac{\partial \varphi_+}{\partial z} \Big|_{z=0} - \varepsilon_- \frac{\partial \varphi_-}{\partial z} \Big|_{z=0} + \varepsilon_s \Delta_s \varphi_s = -\frac{\rho_s}{\varepsilon_0}, \quad (8)$$

$$\varphi_-|_{z=0} = \varphi_+|_{z=0} = \varphi_s. \quad (9)$$

Here, ε_0 is the permittivity of vacuum; the indexes ‘s’, ‘+’, ‘-’ are used to denote the electrostatic potential at $z = 0$, $z > 0$, and $z < 0$, respectively. Equation (8), the classical boundary condition for the jump of the normal component of the electrostatic displacement field at the surface, is generalized as a Poisson equation on the surface, as it is modified with the term $\varepsilon_s \Delta_s \varphi$, which takes into account the surface polarization. The Laplacian Δ_s is taken only with respect to the surface coordinates. This approach is applicable to non-homogeneous surfaces as well and one can define line excesses of the surface properties [15].

Using the definition (1), one can estimate the value of ε_s to be

$$\varepsilon_s = \int_{-\infty}^{\infty} [\varepsilon_{\text{real}}(z) - \varepsilon_{\text{ideal}}(z)] dz \sim \varepsilon_{\text{bulk}} \delta, \quad (10)$$

where $\varepsilon_{\text{bulk}}$ is the bulk dielectric constant and δ is the width of the transition zone which is of the order of the average interparticle distance. As shown at the end of the next section, this theoretical estimation is confirmed by the fit to the experimental results.

3. Point charge on the semiconductor surface

The problem of the field caused by a point charge near the boundary of two continuous media (figure 2) is usually given in the textbooks as a demonstration of the so-called image forces [4]. Such systems have many other both fundamental and applied aspects and an interesting phenomenon in this respect is the interaction between defects in semiconductors. In [8], experimental determination of the electric potential around P vacancies on a In $P(110)$ surface is reported. To interpret the data from [8], Krčmar and Saslow (KS) studied a model of this system with free surface charges [9]. The main features and assumptions in [9] are as follows: (i) the approach is applicable to distances that exceed the atomic scale, i.e. only the macroscopic parameters of the semiconductor are needed; (ii) the defects are treated as point charges with charge $+e$ [8]; (iii) an unspecified local relationship between the chemical potential and the surface charge density is assumed; (iv) both bulk and surface charges are taken into account in the calculation of the screening of the additional charge. KS solved the standard electrostatic equations with the traditional boundary conditions and obtained the electrostatic potential due to an isolated charge on the semiconductor surface. Their theoretical results are in good agreement with the experimental data [8].

Our approach to the same problem is based on the model equations (6)–(9) where, as has already been pointed out many times, the most important new moment is that the effect of the surface polarization is taken into account. The first step is to define the charge density distribution.

In the semiconductor ($z < 0$), the equilibrium density of free carriers with effective mass m is given by the well-known expression [16, 17]

$$c(\mu) = 2N \Phi_{1/2}(\mu^*) \quad (11)$$

where N is the effective density of states

$$N = 2 \left(\frac{2\pi mkT}{(2\pi\hbar)^2} \right)^{1/2} \quad (12)$$

(k is the Boltzmann constant and T is the temperature). $\Phi_{1/2}(\mu)$ is the Fermi–Dirac integral

$$\Phi_{1/2}(\mu^*) = \frac{2}{\pi} \int_0^{\infty} \frac{\sqrt{x}}{1 + \exp(x - \mu^*)} dx \quad (13)$$

with $\mu^* = \mu/kT$. The charge density ρ_- is

$$\rho_- = e[c(\mu + \varphi_-) - c(\mu)]. \quad (14)$$

Here, e is the charge of the free carriers. We assume that the linear approximation holds and develop the expression for ρ_- in powers of φ_- retaining only the linear term

$$\rho_- = -\varepsilon_0\varepsilon_- \kappa_-^2 \varphi_- \quad (15)$$

where the inverse bulk screening length κ_- is defined by the expression

$$\kappa_-^2 = \frac{e^2 N}{\varepsilon_0 \varepsilon_- k T} \Phi'_{1/2}(\mu^*). \quad (16)$$

In the bulk of the semiconductor, the free carriers are holes with concentration p . The holes form a non-degenerate gas and according to [16, 17]

$$\kappa_-^2 = \frac{e^2 p}{\varepsilon_0 \varepsilon_- k T}. \quad (17)$$

The surface carrier concentration Γ is introduced as a Gibbs excess using equation (1). Consequently, the surface charge density is defined as

$$\rho_s = e[\Gamma(\varphi_s + \varphi_{s,\infty}) - \Gamma(\varphi_{s,\infty})] \quad (18)$$

where $\varphi_{s,\infty}$ is the so-called surface potential [16]. In linear approximation, we obtain

$$\rho_s = -\varepsilon_0 \varepsilon_s \kappa_s^2 \varphi_s \quad (19)$$

and κ_s^{-1} is the surface screening length. The expression for κ_s is given by

$$\kappa_s^2 = \frac{e^2 \alpha c_p}{\varepsilon_0 \varepsilon_s k T} \quad (20)$$

where c_p is the surface concentration of the phosphorus vacancies and α is a factor between 0 and 1 which measures the number of free surface carriers per phosphorus vacancy. As a quantitative characteristic of the surface screening KS used the constant K_{s0} [9] which is related to our inverse surface screening length through the expression $K_{s0} \equiv \varepsilon_s \kappa_s^2$.

Finally, the density of a point charge ρ_+ in a vacuum is given by

$$\rho_+ = \frac{q}{2\pi} \delta(z - z_0) \frac{\delta(r)}{r}. \quad (21)$$

To obtain the potential due to a point charge on the semiconductor surface we let $z_0 \rightarrow 0$ in the final expression (see below).

Next we solve the system equations (6)–(9) with the corresponding expressions for the charge densities obtained above. The solution for the potential of a point charge on the semiconductor surface ($z_0 = 0$) is cast into the form

$$\varphi_+(r, z) = \int_0^\infty \xi \hat{\psi}_s e^{-\xi z} J_0(\xi r) d\xi, \quad (22)$$

$$\varphi_-(r, z) = \int_0^\infty \xi \hat{\psi}_s e^{\sqrt{\xi^2 + \kappa_-^2} z} J_0(\xi r) d\xi, \quad (23)$$

$$\varphi_s = \int_0^\infty \xi \hat{\psi}_s J_0(\xi r) d\xi, \quad (24)$$

where

$$\hat{\psi}_s = \frac{q}{2\pi \varepsilon_0} \frac{1}{\xi + \varepsilon_- \sqrt{\xi^2 + \kappa_-^2} + \varepsilon_s (\xi^2 + \kappa_s^2)}. \quad (25)$$

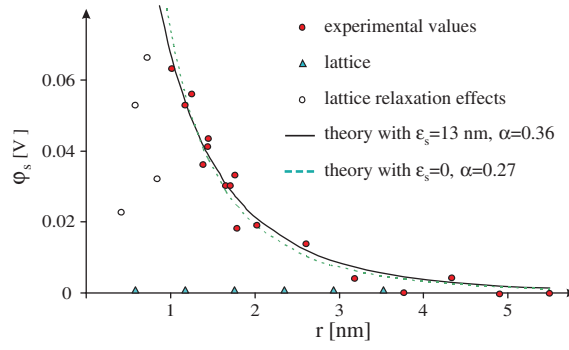


Figure 3. Surface potential φ_s of a point charge on the surface. The first four experimental points (those with no fill) are not taken into account because at distances less than two lattice constants the macroscopic theory is no longer valid.

Compared to the theoretical results of KS, equation (25) differs by the term $\varepsilon_s \xi^2$ in the denominator under the integral.

The numerical computations were performed with the following set of parameters. The bulk hole concentration is $1.3\text{--}2.1 \times 10^{18} \text{ cm}^{-3}$ [8, 18]. The surface density of the phosphorus vacancies is $c_p = 3.9 \times 10^{16} \text{ m}^{-2}$ [19]. For the bulk screening length $R_- = 1/\kappa_-$ (at 297 K and with $\varepsilon_- = 12.5$) we used the value 3.2 nm. The surface dielectric constant ε_s and the parameter α were used as fitting parameters.

The results of our calculation are shown in figure 3. The best fit gives the values $\varepsilon_s = 1.3 \times 10^{-8} \text{ m}$ and $\alpha = 0.36$; the standard deviation is 0.0041. If $\varepsilon_s = 0$ we obtain $\alpha = 0.27$ with standard deviation 0.0048. If we use the estimation (10) for ε_s , the obtained value for the width of the transition zone δ is of the order of one to two lattice constants (for $\ln P - 0.6 \text{ nm}$), which is a reasonable result. We must point out that in a different way Krčmar and Saslow [9] have estimated α to be 0.40. They have assumed that the surface screening dominates over the bulk one and the estimate for α was obtained by fitting the experimentally inferred surface screening length 1.1 nm [8].

An important feature of our approach is the behaviour of the surface potential as r tends to 0. From equations (24) and (25) we obtain as $r \rightarrow 0$

$$\varphi_s(r \rightarrow 0) \approx \frac{q}{2\pi\varepsilon_0 r} \int_0^\infty \frac{J_0(\xi)}{r(1 + \varepsilon_-) + \varepsilon_s \xi} d\xi. \quad (26)$$

The integral is performed to give the result [20]

$$\varphi_s(r \rightarrow 0) \approx \frac{q}{2\pi\varepsilon_0 r} \frac{\pi}{2\varepsilon_s} \left[H_0\left(\frac{1 + \varepsilon_-}{\varepsilon_s} r\right) - Y_0\left(\frac{1 + \varepsilon_-}{\varepsilon_s} r\right) \right] \quad (27)$$

where $H_0(x)$ is the zeroth-order Struve function and $Y_0(x)$ is the zeroth-order Bessel function of the second kind [21]. Finally, using the properties of these functions we obtain the $r \rightarrow 0$ behaviour of φ_s

$$\varphi_s(r \rightarrow 0) \approx -\frac{q}{2\pi\varepsilon_0 \varepsilon_s} \ln\left(\frac{1 + \varepsilon_-}{\varepsilon_s} r\right). \quad (28)$$

For comparison, according to the KS theory, $\varphi_s \sim 1/r$ as $r \rightarrow 0$. One sees that the inclusion of the surface dielectric constant drastically changes the behaviour of the electrostatic potential near the point charge. This difference in the small- r behaviour of φ_s may seem not very important as far as the experimental data for the potential of charged defects on a

semiconductor surface is concerned. As shown in [8] the interaction between charged defects less than two lattice constants apart is dominated by lattice relaxation and cannot be simply described as interaction of point charges. Nevertheless, the approach we adopted in the present work correctly takes into account the surface polarizability and has proved to be of crucial importance for systems like thin films [12] or Langmuir monolayers [6] where it is the only adequate approach.

In conclusion, we have developed a theory for the electrostatics of heterogeneous systems with non-homogeneous phase boundaries based on the Gibbs approach. A surface dielectric constant is introduced in order to take into account the intrinsic surface polarizability of the phase boundary. The potential of a point charge on a semiconductor surface is computed within this framework. The surface dielectric constant is determined by fitting to the existing experimental results for the potential of charged defects on a semiconductor surface. Its value is found to be of the correct order of magnitude.

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