Chemisorption on semiconductors: The role of quantum corrections on the space charge regions in multiple dimensions

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(Received 13 March 2012; accepted 11 April 2012; published online 3 May 2012)

The chemisorption of O$_2$ on nanoscale n-doped CdS semiconductors is computed in terms of a Wolkenstein isotherm coupled to the Schrödinger Poisson equation. Present numerical results show the dependence of the chemisorbed charge and the differential capacitance on oxygen partial pressure. A comparison against the classical Poisson-Boltzmann approach shows a higher chemisorbed charge in the quantum model, but a greater differential capacitance in the classical case. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4709483]

In this article, we are concerned with chemisorption of molecular oxygen on semiconducting surfaces and its effects on the measurable differential capacitance as a function of partial pressure of oxygen and sample size. In particular, we consider that the size of the semiconducting system is of the order of 10 nm. This size range is of interest since space charging in nanoscale systems is used for solar cells, and sensors, and electrochemistry on the nanoscale. We are in particular interested in the following chemisorption reaction:

$$\frac{1}{2} O_2(g) + e^- \rightarrow O^-(\text{ad}) \quad (1)$$

and its impact on the total absorbed charge and the measurable differential capacitance. This effect is investigated by coupling Wolkenstein’s isotherm, which describes the chemical adsorption process, with the nonlinear Poisson’s equation which describes the distribution of energy bands and charge density in the semiconductor sample. In the present article, we introduce a quantum mechanical correction accounting for the quantization of energy levels inside the semiconductor due to confinement of charge carriers that is usually neglected by models based on the classical parabolic density-of-states assumption. We focus on doped CdS and we evaluate the effect of oxygen adsorbates on one measurable electrochemical quantity, the differential capacitance $C_{\text{diff}}$. $C_{\text{diff}}$ is defined as the derivative of the space charge with respect to the surface voltage. This work couples chemisorption with a continuum space charge model accounting for quantum effects in multiple dimensions. In order to describe the adsorption process, we employ Wolkenstein isotherm. This is an alternative expression to Langmuir isotherm, and the main difference with the latter is the dependence of the adsorption coefficient with respect to the degree of coverage $\theta$ of chemisorbed species. The chosen isotherm also provides a relationship between $\theta$ and the oxygen partial pressure $p_{O_2}$ (Ref. 5) under non-dilute conditions thanks to the following expression:

$$\theta = \frac{\beta p_{O_2}}{1 + \beta p_{O_2}}. \quad (2)$$

In Eq. (2), $\beta$ is the adsorption coefficient given by

$$\beta = \beta_0 + \frac{1}{1 + \frac{1}{\alpha_1} e^{\frac{q_1}{k_B T}} \exp{\left(\frac{E_{\text{surf}}}{k_B T}\right)}} \left[1 + \frac{1}{\alpha_2} e^{\frac{q_2}{k_B T}} \exp{\left(\frac{E_{\text{bulk}}}{k_B T}\right)} \right], \quad (3)$$

where $\beta_0$, the adsorption coefficient from Langmuir’s isotherm is given by $\beta_0 = \frac{S_0}{\sqrt{2 \pi M_q T}} \exp{\left(\frac{q}{k_B T}\right)}$.

The parameter $\kappa$ is the sticking probability, $S_0$ is effective area of a chemisorbed adparticle, $M$ is the mass of one molecule of gas, $q_0$ is the adsorption heat of the neutral form of chemisorbed species, and $\nu^0$ and $\nu^-$ are oscillation frequencies of the neutral and the charged chemisorbed state, respectively. The symbol $E$ indicates energies, and as shown in Fig. 1, $E_F$ is the Fermi level and $E_{\text{surf}}$ is the energy level of the chemisorption-induced surface states and $E_{\text{surf}}$ is the energy level of the conduction band at the surface.

We assume that chemisorption is the only phenomenon responsible for surface charging and we further assume that each chemisorbed adion captures one electron. Then, the surface charge density $Q_{\text{surf}}$ is given by

$$Q_{\text{surf}}(\phi_{\text{surf}}, p_{O_2}) = -e f_A \bar{\theta} N^*, \quad (4)$$

where $N^*$ is the number of available chemisorption sites per unit area, $f_A$ is the Fermi-Dirac distribution that can be written as a function of $\phi^0$, and the electric potential at the surface as follows:

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The values of the physical parameters used in this work are reported in Table I along with the main definition of the quantities used. The overall charge that is absorbed on the surface of the material \( Q_{\text{surf}} \) needs to be matched by the charge that is stored inside the material \( Q_{\text{sch}} \), which is a function of the electric potential at the surface of the sample as follows:

\[
Q_{\text{surf}}(\phi_{\text{surf}}, P_{O_2}) + Q_{\text{sch}}(\phi_{\text{surf}}) = 0. \tag{6}
\]

By providing the \( \phi_{\text{surf}} \), one is able to determine the \( P_{O_2} \) that satisfies Eq. (6) as shown in the works of Rothschild and coauthors.11–14

The electric potential \( \phi(x) \) is related to the net charge density \( q(x) = \epsilon_0 n(x) \) by means of Poisson’s equation

\[
\nabla \cdot (-\epsilon_0 \nabla \phi(x)) = q(x), \tag{7}
\]

where \( \epsilon_0 \) is the dielectric constant of the semiconductor and \( \epsilon_0 \) is the permittivity of vacuum. Equation (7) is nonlinear because an additional expression relating \( n \) to \( \phi \) is required. The latter can be written as follows:

\[
n(x) = \int_{E_c}^{\infty} g(E, x) f(E, x) dE, \tag{8}
\]

where \( g(E, x) \) denotes the density of energy states (DOS) in the conduction band and \( f(E, x) \) state occupation probability. In this article, we assume the latter to be the Maxwell-Boltzmann7 distribution, while for the former, we consider two approaches described below. Either of these approaches allows the computation of \( Q_{\text{sch}} \) given \( \phi_{\text{surf}} \). Thanks to Eq. (6) the corresponding \( Q_{\text{surf}} \) and \( P_{O_2} \) are computed. The differential capacitance, which is a directly measurable quantity, can be computed as \( C_{\text{diff}} = \frac{\partial Q_{\text{surf}}}{\partial \phi_{\text{surf}}} \).

Even at the nanoscale, one typically assumes \( g(E, x) \propto E_c(x) - E_F \) in Eq. (8) which leads to the classical Boltzmann statistics,

\[
n(x) = N_e \exp \left( \frac{E_c(x) - E_F}{k_B T} \right), \tag{9}
\]

for the space charge distribution inside the sample.8,9 The effective density of states in the conduction band is given by

\[
N_e = 2 M_e \left( \frac{2 \pi m_e k_B T}{\hbar^2} \right)^{3/2},
\]

where \( M_e \) is the effective mass of electrons. Equations (7) and (9) are usually referred to as the Poisson-Boltzmann equation.

If the size of the sample along one or more directions is comparable with the Bloch wavelength of electrons, a continuum approximation for the DOS becomes inaccurate. A first order correction may by achieved using a quantum mechanical procedure where the DOS consists of a discrete set of subbands, so that the total electron concentration in Eq. (7) is given by10

\[
n(x) = \sum_{k=1}^{\infty} n_k |\psi_k|^2. \tag{10}
\]

The amount of charge in the \( k \)-th subband may be expressed as

\[
n_k = A_{N-D} N_e \exp \left( \frac{E_k - E_F}{k_B T} \right), \tag{11}
\]

where \( N \) denoting the number of unconstrained directions and

\[
A_{1-D} = \frac{m_e k_B T}{2 \hbar^2}, \quad A_{2-D} = \frac{\sqrt{m_e k_B T}}{2 \hbar}, \quad \text{and} \quad A_{3-D} = 1.
\]

The eigenvalues \( E_k \) and the eigenfunctions \( \psi_k \) appearing in Eqs. (10) and (11) are obtained by solving the following \( N \)-dimensional eigenproblem:15,17

\[
\left(-\frac{\hbar^2}{2m_e^*} \nabla^2 + E_c(x)\right) \psi_k = E_k \psi_k, \tag{12}
\]

where \( ||\psi_k|| \) and \( \psi_k = 0 \) at the boundaries of the sample. The latter condition is chosen for electrons to be confined inside the sample with zero probability of finding electrons at the...
boundary and should be modified if electrons can tunnel through. As stated above, we compare a classical parabolic DOS with DOS computed with quantum corrections using Schrödinger-Poisson’s approach for three geometries: a slab of varying thickness $L$, a cylinder of square cross section whose length is $L$, and a cube of side length $L$. We highlight the impact of quantum corrections on both the charge equilibrium from absorption-space charge region and the pressure sensitivity with respect to $C_{\text{diff}}$. The $Q = Q_{\text{ch}} - Q_{\text{surf}}$ is plotted against $p_{\text{O}_2}$ for all three cases 1-D (Fig. 2) and 3-D (Fig. 3) and varying length-scales $L$. We note that the classical case is shown in dashed red and corresponds to $\phi_{\text{surf}} < 0$, instead quantum case is shown in both blue and black. Black corresponds to $\phi_{\text{surf}} < 0$ and blue to $\phi_{\text{surf}} > 0$, indicating that in the quantum case for $\phi_{\text{surf}} = 0$, a small residual charge is present.

The gap between the charges stored in quantum and classical cases reduces if $L$ increases and if the dimensionality of the system is reduced, being greatest in the 1-D case and smallest in 3-D. As expected, the distance is smallest if one increases the size of the sample and if one consider higher $p_{\text{O}_2}$. In fact, higher $p_{\text{O}_2}$ corresponds to a greater surface potential $\phi_{\text{surf}}$. As clearly shown in the classical case, the sensitivity measured as the slope of $Q$ with respect to $p_{\text{O}_2}$ changes markedly with $L$. As $L$ decreases, the semiconductor becomes more sensitive at lower $p_{\text{O}_2}$.

While the quantum effects tend to increase the stored charge per unit volume, this is not reflected into the sensitivity with respect to $p_{\text{O}_2}$; it is consistently shown for the various dimensions that the sensitivity is greater at lower $p_{\text{O}_2}$ if compared to the classical case.

We note that the classical and quantum case converge at higher oxygen partial pressure but diverge at low partial pressure. The quantum case gives greater charge than the classical case at low $p_{\text{O}_2}$. This is consistently shown for 1D, 2D, and 3D.

In Figs. 4 and 5, the differential capacitance $C_{\text{diff}}$ is also shown and the value provided by the quantum model (solid line) is consistently lower than classical case, indicating that the classical approach could in principle over-predict its value. The gap between the two models is the greatest at low $L$ and low $p_{\text{O}_2}$. Sensitivity of the measurement depends on the $p_{\text{O}_2}$ at which the differential capacitance starts decaying. Size effect is such that for smaller $L$, the sensitivity occurs at lower oxygen partial pressure, and for the quantum case, the sensitive effect is shifted towards smaller $p_{\text{O}_2}$. As anticipated by direct inspection of the $Q$ plots, it is clear that at higher $L$, the quantum effects are not as marked and this is reflected on the $C_{\text{diff}}$ as well. Again, this effect is weaker for higher dimensional samples of larger size. For example, in the

FIG. 2. Volumetric space charge $Q = Q_{\text{ch}} - Q_{\text{surf}}$ as a function of $p_{\text{O}_2}$ for the classical and quantum case. In the quantum case, the black curve corresponds to $\phi_{\text{surf}} < 0$, while the blue curve corresponds to $\phi_{\text{surf}} > 0$.

FIG. 3. Charge per unit volume stored in the space charge region for 3-D for various lengths $L$ of the cube.

FIG. 4. Volumetric differential capacitance as a function of $p_{\text{O}_2}$ for the 1-D case at various slab thicknesses $L$. 
80 nm panel of Fig. 5, the quantum and classical approaches are hardly distinguishable. The two effects are, however, more marked on the analogous panel of Fig. 4.

In conclusion, a method that enables one to compute the stored excess charge on nanometer size semiconductor particles is presented. A precise control of the 3-D particle size and oxygen concentration can be used to initiate and modify electrochemical reactions. The study of nanometer colloidal CdS particles in contact with air (or O₂) described in terms of a Wolkenstein’s isotherm complements the investigation of small semiconductor particles in aqueous suspensions. We observe that quantum effects on the chemisorption of oxygen gas not only modifies the electronic properties of CdS but also affects the charge the semiconductor is able to store as a function of pO₂ and the measurable differential capacitance.

F.C. thanks HKUST for providing start-up funds. S.L. and F.C. thank the Marie Curie Reintegration Grant FastCell-256583. M.I.G. thanks funding from the University of Kentucky.

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