Quantum Adsorption of an Electron to Porous Silicon

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Abstract

Using the theory of Zhang and Clougherty [Phys. Rev. Lett. 108, 173202 (2012); arXiv:1012.4405], we provide detailed supporting information concerning the numerical calculations of the probability $s(E)$ for a low-energy electron with incident energy $E$ adsorbing to the surface of nanoporous silicon.
I. INTRODUCTION

The numerical values for the rate of sticking $R$ calculated in Zhang and Clougherty (ZC) [1] are obtained by using Eq. (33) in ZC,

$$R = 2\pi \left( \frac{z}{\hbar \omega_c} \right)^{\alpha} e^{\alpha} \frac{g_1^2 \rho}{\hbar^3} E_b \left( \frac{E_b}{E_b + \alpha \hbar \omega_c} \right)$$

(1)

In this supplementary note, we provide numerical values for the variables in this expression for $R$.

The coupling constant $g_1$, the strength of bath-assisted particle transitions between the continuum and the bound state, is given by Eq. (36) in ZC

$$g_1 = \left\langle k \left| \frac{\partial V_0(x)}{\partial x} \right| b \right\rangle = \int_0^\infty \phi_k^*(x) \frac{\partial V_0(x)}{\partial x} \phi_b(x) dx$$

(2)

where $V_0(x)$ is the static surface potential with ground state energy denoted by $E_b$. The coupling constant $g_3$ is similarly calculated

$$g_3 = \left\langle b \left| \frac{\partial V_0(x)}{\partial x} \right| b \right\rangle = \int_0^\infty \phi_b^*(x) \frac{\partial V_0(x)}{\partial x} \phi_b(x) dx$$

(3)

The coupling strength $\alpha$ was introduced in Eq. (5) in ZC

$$J(\omega) \equiv \sum_q \frac{g_1^2}{\hbar^2} \sigma(\omega_q) \delta(\omega - \omega_q) = \alpha \omega$$

(4)

where the frequency of the excitations is cut off from above by $\omega_c$. The exact form of $\sigma(\omega_q)$ for the case of coupling to Rayleigh phonons is given later in this note (see Eq. (25)).

Five fundamental variables $g_1, g_3, \alpha, E_b$ and $\omega_c$ are needed in order to calculate the numerical sticking rate given by Eq. (1). Once the numerical values of these fundamental variables are obtained, the other variables are calculated with the following formulae, which were also given previously in ZC.

The constant $\rho$ is calculated by

$$\rho = \frac{\alpha \hbar^2}{g_3^2}$$

(5)

The variable $z$ is given by Eq. (28) in ZC

$$z \approx K \left( \frac{eK}{\hbar \omega_c} \right)^{\alpha}$$

(6)

where $K$ is given by Eq. (29) in ZC

$$K \approx \frac{(g_1 g_3 \rho \omega_c)^2}{E + E_b + \alpha \hbar \omega_c}$$

(7)
The probability of sticking to the surface is the sticking rate per surface area per unit incoming particle flux,
\[ s = \sqrt{\frac{2\pi^2 m}{E}} R \]  
\hspace{1cm} (8)

In the following sections, we will take the example of an electron sticking to the surface of porous silicon (pSi) (porosity \( P = 92.9\% \)) by emission of a Rayleigh phonon to show how to calculate the five fundamental variables for the specific case of an electron sticking to porous silicon. The sticking probabilities displayed in Fig. 1 in ZC are calculated using Eq. (8).

II. FUNDAMENTAL VARIABLES: \( g_1, g_3 \) & \( E_0 \)

We adopt the commonly used model of an attractive image potential with a cut off at \( x_c = 0.05 \, \text{Å} \), plus a repulsive hard wall \cite{2, 3}:

\[
V_0(x) = \begin{cases} \frac{q_e^2}{4\pi\epsilon_0} \frac{\Lambda_0}{x+x_c} & x > 0 \\ \infty & x \leq 0 \end{cases}
\]  
\hspace{1cm} (9)

where
\[
\Lambda_0 = \frac{\kappa - 1}{4(\kappa + 1)} \]  
\hspace{1cm} (10)

and \( q_e \) is the charge of an electron, \( \epsilon_0 \) is the vacuum permittivity and \( \kappa \) is the relative dielectric constant. The average relative dielectric constant for pSi is found from the following three equations \cite{4},

Bruggeman approximation
\[
P \frac{\kappa_a - \kappa_{pSi}}{\kappa_a + 2\kappa_{pSi}} + (1 - P) \frac{\kappa_{cSi} - \kappa_{pSi}}{\kappa_{cSi} + 2\kappa_{pSi}} = 0
\]  
\hspace{1cm} (11)

Maxwell and Garnett approximation
\[
\frac{\kappa_{pSi} - \kappa_a}{\kappa_{pSi} + 2\kappa_a} = (1 - P) \frac{\kappa_{cSi} - \kappa_a}{\kappa_{cSi} + 2\kappa_a}
\]  
\hspace{1cm} (12)

Looyenga approximation
\[
\frac{\kappa_{pSi}}{\kappa_{pSi} + 2\kappa_a} = (1 - P) \frac{\kappa_{cSi}}{\kappa_{cSi} + 2\kappa_a}
\]  
\hspace{1cm} (13)

where the relative dielectric constant of bulk crystalline silicon (cSi) and air is respectively \( \kappa_{cSi} = 11.68 \) and \( \kappa_a = 1 \). We find for pSi \( (P = 92.9\%) \), \( \kappa \approx 1.2 \)
There are exact analytical forms for the continuum and bound state wave functions in $V_0(x)$. The relevant matrix elements are given by [3],

\[ g_1 = \langle b \left| \frac{dV_0(x)}{dx} \right| k \rangle = \frac{q_e^2}{4\pi\epsilon_0} \Lambda_0 Z_{b,k}^2 \tag{14} \]

\[ g_3 = \langle b \left| \frac{dV_0(x)}{dx} \right| b \rangle = \frac{q_e^2}{4\pi\epsilon_0} \Lambda_0 Z_{b,b}^2 \tag{15} \]

where

\[ Z_{b,k}^2 = \langle b \left| \frac{1}{(x + x_c)^2} \right| k \rangle \]

\[ = \frac{\sqrt{k_0}}{a_B^2 N_{\kappa_b}^2} \int_{x_c}^{\infty} dx' W_{\kappa_b,\frac{1}{2}} \left( \frac{2\Lambda_0 x'}{\kappa_b} \right) \frac{1}{x'^2} \sqrt{\frac{\pi}{1 + c^2}} \sqrt{2\Lambda_0 x'} \left[ J_1 \left( 2\sqrt{2\Lambda_0 x'} \right) - \tilde{c} N_1 \left( 2\sqrt{2\Lambda_0 x'} \right) \right] \]

\[ = \frac{1}{a_B^2 N_{\kappa_b}^2} \int_{x_c}^{\infty} W_{\kappa_b,\frac{1}{2}} \left( \frac{2\Lambda_0 x'}{\kappa_b} \right) \frac{1}{x'^2} W_{\kappa_b,\frac{1}{2}} \left( \frac{2\Lambda_0 x'}{\kappa_b} \right) dx' \tag{16} \]

\[ Z_{b,b}^2 = \langle b \left| \frac{1}{(x + x_c)^2} \right| b \rangle \]

\[ = \frac{\sqrt{k_0}}{a_B^2 N_{\kappa_b}^2} \int_{x_c}^{\infty} W_{\kappa_b,\frac{1}{2}} \left( \frac{2\Lambda_0 x'}{\kappa_b} \right) \frac{1}{x'^2} W_{\kappa_b,\frac{1}{2}} \left( \frac{2\Lambda_0 x'}{\kappa_b} \right) dx' \tag{17} \]

Here, $a_B$ is Bohr radius and $x_c = x_c/a_B$ is the lower limit of the integration. $\tilde{c}$ is given by

\[ \tilde{c} = - \frac{J_1 \left( 2\sqrt{2\Lambda_0 x_c'} \right)}{N_1 \left( 2\sqrt{2\Lambda_0 x_c'} \right)} \tag{18} \]

where $J_1(x)$ and $N_1(x)$ are the Bessel and Neumann functions of order one, respectively. $W_{\kappa_b,\frac{1}{2}} \left( \frac{2\Lambda_0 x'}{\kappa_b} \right)$ is the Whittaker function, whose expansion in terms of Laguerre polynomials $L_n(x)$ for positive non-integer $\kappa_b$ is used in the numerical integrations.

\[ W_{\kappa_b,\frac{1}{2}}(x) = \sum_{n=0}^{\kappa_b} \frac{\kappa_b(\kappa_b - 1) e^{-\frac{1}{2}x} L_n(x)}{\kappa_b - n)(\kappa_b - n - 1)\Gamma(2 - \kappa_b)} \tag{19} \]

$\kappa_b$ is the bound state quantum number and is found from the boundary condition at $x = x_c$ on the surface

\[ W_{\kappa_b,\frac{1}{2}} \left( \frac{2\Lambda_0 x_c'}{\kappa_b} \right) = 0 \tag{20} \]

The bound state energies are given by

\[ -E_{\kappa_b} = -hcR_y \frac{\Lambda_0^2}{\kappa_b^2} \tag{21} \]

where $h$ is Planck’s constant, $c$ is the speed of light and $R_y$ is the Rydberg constant. The ground state energy in $V_0(x)$ is $-E_b = -7.76$ meV. $k_0$ is a dimensionless number calculated
from the continuum incident energy $E$,

$$E = \hbar c R \frac{k_0^2 \Lambda_0^2}{\kappa_b}$$  \hfill (22)

$N_{\kappa_b}$ is the reciprocal normalization constant of the bound state wave function. Thus,

$$N_{\kappa_b}^2 = \int_{x_c}^{\infty} \left( W_{\kappa_b} \left( \frac{2 \Lambda_0 x'}{\kappa_b} \right) \right)^2 dx'$$  \hfill (23)

We obtain numerical values of the coupling constants $g_1$ and $g_3$ by numerical integration of Eqs. (14) and (15). We obtain $g_3 \approx 1.3$ meV Å$^{-1}$ for an electron bound to the surface of pSi ($P = 92.9\%$). $g_1$ varies with incident energy $E$ and has a range of $57.7 \mu$eV Å$^{-1} \leq g_1 \leq 1.826$ meV Å$^{-1}$ for incident energies in Fig. 1 in ZC.

III. FUNDAMENTAL VARIABLES: $\omega_c$ & $\alpha$

We consider particle-surface coupling through Rayleigh phonons. The cutoff frequency of Rayleigh phonons is approximated by its dispersion relation

$$\omega_c = \xi c_t Q_c$$  \hfill (24)

where $\xi$ is the ratio of speed of Rayleigh waves to transverse waves, $c_t$ is the transverse speed of sound and $Q_c$ is the maximum surface wave vector. We take for pSi ($P = 92.9\%$) $\xi \approx 0.88$ and $c_t/c_l \approx 0.694$, which follows from cSi data [6]. (Ref. [7] shows that $\xi$ and $c_t/c_l$, where $c_l$ is the longitudinal speed of sound, are largely independent of porosity $P$.) $c_l$ measured from high pSi with $P \approx 80\%$ is approximately 1680 ms$^{-1}$ [7]. Assuming $c_l$ and $c_t$ do not vary much for high pSi with $P \gtrsim 80\%$, we obtain $c_t \approx 1166$ ms$^{-1}$ for pSi ($P = 92.9\%$). We take $Q_c = 2\pi/a$, where $a = 5.43$ Å (the lattice constant of cSi) [8]. Hence from equation (24), we obtain $\omega_c \approx 1.19 \times 10^{13}$ s$^{-1}$.

The exact form for particle-surface phonon coupling is given in Ref. [5]. For Rayleigh waves,

$$\sigma(\omega Q) = \left( \frac{\hbar^2 F^2(\sigma)}{S^2 G \rho_0} \right)^{1/4}$$  \hfill (25)

where $Q$ is the surface wave vector of Rayleigh waves and $S$ is the surface area of the target. The shear modulus $G$ and the target’s density $\rho_0$ for pSi ($P = 92.9\%$) are approximated by
using Ref. [7],

\[
\rho_0 = \rho_{cSi} (1 - P) \approx 166 \text{ kg m}^{-3} \quad (26)
\]

\[
G = 0.482 \rho_0 c_t^2 \approx 230 \text{ MPa} \quad (27)
\]

We use a mass density of cSi of \(\rho_{cSi} = 2330 \text{ kg m}^{-3}\) [8].

The constant \(\tilde{F}(\sigma)\) is given by [5]

\[
\tilde{F}^{-1}(\sigma) = 8\xi^{-3} \left( \frac{2 - \xi^2}{2\sqrt{1 - \xi^2}} - \frac{2 - \xi^2}{\sqrt{1 - (\xi\tau)^2}} + \frac{(2 - \xi^2)^2 (2 - (\xi\tau)^2)}{8 (1 - (\xi\tau)^2)^2} \right) \quad (28)
\]

where \(\sigma\) is Poisson’s ratio, and \(\tau\) is given by

\[
\tau = \sqrt{\frac{1 - 2\sigma}{2 - 2\sigma}} \quad (29)
\]

For Rayleigh waves, \(\xi\) is determined by [5]

\[
\xi^6 - 8\xi^4 + 8\xi^2 (3 - 2\tau^2) - 16(1 - \tau^2) = 0 \quad (30)
\]

Thus for \(\xi = 0.88\), we obtain \(\sigma \approx 0.03\) and \(\tilde{F}(\sigma) \approx 0.24\).

Substituting Eq. (25) into Eq. (4) and taking the continuum limit of the sum over all the modes, we obtain for coupling through Rayleigh waves

\[
\alpha = \frac{g_3^2}{\hbar} \frac{1}{2\pi \xi^2 c_t^2} \sqrt{G\rho_0} \frac{\tilde{F}(\sigma)}{\sqrt{G\rho_0}} \quad (31)
\]

where the following vibrational density of states for Rayleigh waves is used

\[
D(\omega) = \frac{S}{2\pi \xi^2 c_t^2} \omega \quad (32)
\]

Using the numbers of \(g_3\), \(\xi\), \(c_t\), \(G\), \(\rho_0\) and \(\tilde{F}(\sigma)\) obtained above, we find \(\alpha \approx 0.008\) for an electron coupled to the surface of pSi through Rayleigh waves. The numerical values for the sticking probabilities \(s(E)\) contained in Fig. 1 in ZC are now calculated using Eqs. (1) and (8).

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