Theoretical Model of Charge Transport Processes In Metal/ Semiconductor Interfaces

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Abstract

The dynamics of charge transport across metal/semiconductor interface system are studied using a model that derives according to the quantum theory. We suppose continuum level model for donor state $|\varphi_{\downarrow} D>$ and acceptor state $|\varphi_{\downarrow} A>$. Marcus– Hush semi classical theory adapted to evaluated the reorientation free energy. The rate constant of charge transfer are calculated with assume a continuum level model .Our result for calculation of rate constant of charge transfer show a good agreement with experimental data. the ratio of rate

$$K_{et}\frac{\frac{GaAs}{Au}}{\frac{InAs}{Au}} \approx 1.025$$

thus agreement with result ≈ 1 [28] ,indicated the system Au/ GaAs is active media for applied in devices technology according with Au/ InAs system.

Key Words: Charge Transport Processes, Metal / Semiconductor Interfaces

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أنموذج نظري لعملية انتقال الشحنة لنظام سطح معدن /شبه موصل

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الخلاصة

حركية انتقال الشحنة عبر نظام سطح معدن/ شبه موصل درس باستعمال أنموذج اشتق وفقا لنظرية الكم.افترضنا أنموذج الحالات المستمرة لكل من حالة الواهب وحالة المستقبل .نظرية ماركوس– هاش شبه الكلاسيكية تبنيت لحساب الطاقة الحرة لإعادة الترتيب. معدل انتقال الشحنة حسبت بافتراض الحالات المتصلة للطاقة. نتائج حسابات معدل انتقال الشحنة أظهرت توافقا جيدا مع الحسابات العملية. نسبة المعدل

$$K_{et}\frac{\frac{GaAs}{Au}}{\frac{InAs}{Au}} \approx 1.0\square5$$

مقاربة للمصدر [28] وهذا يشير إلى إن نظام Au/ GaAs وسط فعال للتطبيق في تكنولوجيا أجهزة النانو مقارنة بنظام Au/ InAs.

Introduction

Charge transfer is an integral part of many biophysics, physical chemistry processes and technology, which occurs in a large variety of molecules ranging from small ion pairs up to large biological system [1].The nature of charge transfer as a quantum mechanical electronicvibration transition was recognized early [2].

The field of charge transfer has a rich history and continues to pose interesting problems for today's researchers. charge transfer theory predicts by many factor that determines the electrochemical potential [3]. The Marcus-Hush theory of charge transfer CT reactions fully relies on the transition state formalism defining the CT activation barrier in terms of two thermodynamic parameters, the free energy gap and the nuclear reorganization energy [4]. The reorientation is a key factor of charge -transfer processes in media. The electrostatic response of the dipoles moment to a change in electronic charge distribution creates a basis for valence

trapping [5]. Photo induced charge transfer is one of the most pivotal processes in photosynthesis, photo-imaging, organic reaction mechanisms and optoelectronic devices [6].

In the present work the transfer of charge in metal/semiconductor is studies theoretically using quantum theory to derive an expression to calculate the rate constant of charge transfer. On the other hand the reorientation energies of charge transfer are calculated using a continuum sphere model of Hush-Marcus theory.

THEORY

A quantum theory used to the studies of dynamics of non-adiabatic charge transfer at metal/semiconductor interface system. For this theory we suppose donor state $|\varphi_{\downarrow}D>$ and acceptor state $|\varphi_{\downarrow}A>$ initially at t~0 independent of each other and interact for t›0 [7]. The complete set wave function that describe the system [8].

$$|\phi_1((r,t))>=\sum_1 n ⟦c_1((t))\,\varphi_1 r⟧ \qquad \ldots\ldots\ldots (1)$$

The Hamiltonians operator that used to satisfy the electron transfer in $|\varphi_{\downarrow}D>-|\varphi_{\downarrow}A>$ system is given by [9].

$$\mathcal{H}=\mathcal{H}_{DA}+T_{DA} \qquad \ldots\ldots\ldots (2)$$

Where [10],

$$\mathcal{H}_{DA}=|\varphi_D>\mathcal{H}_D<\varphi_D|+|\varphi_A>\mathcal{H}_A<\varphi_A| \qquad .(3)$$

And T_{DA} is the coupling coefficient between $|\varphi_{\downarrow}D>$ and $|\varphi_{\downarrow}A>$ system state.

The $\mathcal{H}$ operator obeys the time dependent schrodinger equation
$\mathcal{H}|\phi_1((r,t))>=i\hbar\, d/dt\ |\phi_1((r,t))>$ [11].

Results of mathematical treatment is.

$$c_{(t)} = \frac{1}{i\hbar}\int_0^t T_{DA}\, e^{\frac{i(E_D - E_A)t}{\hbar}}\, dt \qquad \text{.....(4)}$$

The total probability for electron transfer at time t in the final state $|\varphi_\downarrow A >$ is given by[12] .

$$\mathbb{p} = |T_\downarrow DA|^2\, 2\pi t/\hbar\; \delta(E_\downarrow D - E_\downarrow A) \qquad \text{........(5)}$$

For all space the total probability is .

$$\mathbb{p} = |T_\downarrow DA|^2\, 2\pi t/\hbar \int_{-\infty}^{\infty} \rho(E_\downarrow D - E_\downarrow A)\; \delta(E_\downarrow D - E_\downarrow A)\, dE_\downarrow \qquad \text{.....(6)}$$

The rate of the charge transfer per unit time when assume a discrete final state is aconitum is [13].

$$K_\downarrow et = d/dt\, \mathbb{p} = 2\pi/\hbar\; |T_\downarrow DA|^2\, \rho(E) \qquad \text{...... (7)}$$

Where, $\int_{-\infty}^{\infty} \rho(E_D - E_A)\delta(E_D - E_A)dE = \rho(E)$ [14],

For $|\varphi_\downarrow D - |\varphi_\downarrow A >$ system the matrix of density operator is written [15].

$$\rho = \begin{pmatrix} \sigma_{AA} & \sigma_{AO} \\ \sigma_{DA} & \sigma_{DD} \end{pmatrix} \qquad \text{.......(8)}$$

The basis complete set of donor and a acceptor state is $|\varphi_\downarrow(A, D) >$ that satisfy $H^\wedge\; |\varphi_\downarrow(A, D) > = E_\downarrow n\; |\varphi_\downarrow(A, D) >$

We introduce operator,

The expectation value of the operator $\hat{T}$ is written by.

$$< T^{\wedge} >= \sum_{\downarrow} d \left[\sum_{\downarrow} a \left[< \phi_{\downarrow}((r.t)) | \varphi_{\downarrow} D \right]_{\downarrow} > \right] < \varphi_{\downarrow} D | T^{\wedge} | \varphi_{\downarrow} A >< \varphi_{\downarrow} A | \phi_{\downarrow}((r.t)) > e^{\uparrow}((-(E_{\downarrow} D - E_{\downarrow} A))/(k_{\downarrow} B\, T))$$ …(9)

And

$$< \hat{T} >= \sum_{D} \sum_{A} \rho_{DA} > e^{-(E_D - E_A)/_{k_B T}} = N \sum e^{-(E_D - E_A)/_{k_B T}}$$ ……………………………..……..(10)

Then $\rho = Ne^{-(E_D - E_A)/_{k_B T}} = Ne^{-\Delta Q/_{k_B T}}$

Density operator with barrier height energy $\Delta Q = \frac{(\lambda + \Delta E)^2}{4\lambda}$ is become.

$\rho = Ne^{-(\lambda + \Delta E)^2/_{4\lambda k_B T}}$ Using $T_r \rho = 1$ [12], and evaluated to find N=$(4\lambda k_{\downarrow} B\, T)^{\uparrow}(-1/2)$

Insert ρ in the Eq.(7), that the charge transfer rate from $|\varphi_{\downarrow} D -$ state to $|\varphi_{\downarrow} A >$ state can be given as.

$$K_{ET} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} \left[f(E) \left| [T_{DA}| \right]^2 (4\lambda k_B T)^{-\frac{1}{2}} e^{-(\lambda + \Delta E)^2/_{4\lambda k_B T}} \right] dE$$ …….(11)

Where $f(E)$ the Fermi- Dirac function is can be related to electron by [16].

$$f(E, E_F) = \frac{1}{1 + \frac{\exp E}{k_B T}}$$ ………………………………………………………………(12)

Where $E_{□}$ is the level energy.

Inserting Eq.(12) in the Eq.(11) we gate .

$$K_{ET}=\frac{2\pi}{\hbar}\int_{-\infty}^{\infty}[\frac{1}{1+\frac{\exp E}{K_B T}}\Big|[T_{DA}|□]^2(4\lambda k_B T)^{-\frac{1}{2}}e^{-(\lambda+\Delta E)^2/4\lambda k_B T}dE]$$

...(3)

The free energy $\Delta□$ related to occupied energy E by [17]

$$\Delta Q=\Delta E_{\circ}-E \quad ....(14)$$

Where $\Delta E_{\circ}$ is the standard free energy of reaction.

Substituting Eq.(3-64) in Eq.(3-63),and $\frac{1}{1+\frac{\exp E}{k_{□}T}}\approx\frac{\exp(-E)}{K_B T}$ when $E\gg K_B T$ results

$$K_{ET}=\frac{2\pi}{\hbar}\int_{-\infty}^{\infty}□$$

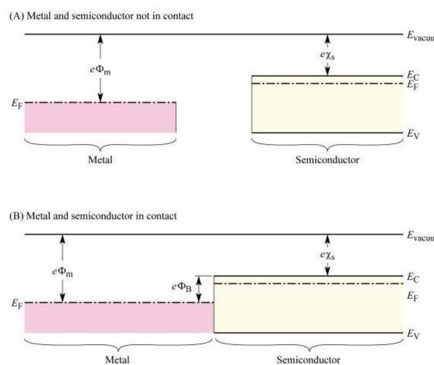
The exponent in the integral in the numerator of Eq.(15) can be written as[17].

$$e^{-(\lambda+\Delta E_{\circ}-E_{□})^2/4\lambda k_B T}=\exp-\left[\frac{(\lambda+\Delta E_{\circ})^2}{4\lambda K_B T}-\frac{(\lambda+\Delta E_{\circ})E}{2\lambda K_B T}+\frac{□^2}{4\lambda K_B T}\right]$$

First term in the right hand side of the above equation is independent of E and can remove from the integral. The second term varies much more slowly with E than the $\frac{E}{K_B T}$ in the exponent at the third term in the integral Eq.(15) becomes.

$$\mathbf{K_{et}} = \frac{2\pi}{\hbar(4\lambda k_B T)^{-\frac{1}{2}} \int_0^\infty [\frac{\frac{\exp((\lambda + \Delta E_\circ)^2)}{4\lambda k_B T} \exp(-E)}{K_B T} \Big| \frac{[T_{DA}|\square]^{\square} \exp(-\mathbf{E}^2)}{4\lambda \mathbf{k_B T}}] \, d\mathbf{E}} \quad ....(16)$$

When a metal and a semiconductor get into contact a barrier forms The barrier height is measured in eV The barrier height is equal to the difference of metal work function and semiconductor electron affinity figure(1) .



Figure(1) Metal and semiconductor (A) not in contact (B) in contact .

And barrier height energy is given by $\Delta Q = \mathbf{e}(\chi_m - \chi_{se})$ [18].

Where χ_m is the work function of metal, and χ_{se} is the electron affinity of semiconductor We assume the coupling coefficient of matrix element is given by polynomial.

$$|[T_{\downarrow}DA|]^{\uparrow}2 = |[T_{\downarrow}DA(O)|]^{\uparrow}2\,(1 + E^{\uparrow}1 + E^{\uparrow}2 + E^{\uparrow}3 + E^{\uparrow}4 + \cdots) \quad ....(17)$$

And $$\frac{\exp(-\mathbf{E}^2)}{4\lambda \mathbf{k_B T}} = \left(1 - \frac{\mathbf{E}^2}{4\lambda \mathbf{k_B T}} + \frac{\mathbf{E}^4}{16(\lambda \mathbf{k_B T})2} + \cdots .....\right)$$

Equation (16) with Eq.(17) become.

$$K_{et} = \frac{\frac{2\pi}{\hbar(4\lambda k_B T)^{-\frac{1}{2}} \exp(-e(\chi_m - \chi_{se}))}}{4\lambda k_B T} \int_0^{\infty} [\frac{\exp(-E)}{K_B T} \left| [T_{DA}(0)|]^2 (1 + E^1 + E^2 + E^3 + E^4 + \cdots) \left(1 - \frac{E^2}{4 k_B T} + \frac{E^4}{16(\lambda k_B T)2} + \cdots \ldots\right) \right] dE$$

..(18)

With mathematical treatment of integral Eq.(18),results

$$K_{et} = 4\pi/\hbar\,(4\lambda k_B T)^{((-1)/2)}\, [exp]^{-\, e(\chi_m - \chi_{se})/(4\lambda k_B T)}\, |T_{DA}(0)|^2\, k_B T(1 - (k_B T)/2\lambda + (3 + 2(k_B)^2 - \frac{6(k_B T)^3}{\lambda} + \ldots\ldots) \quad \ldots\ldots\ldots(19)$$

With first approximation, result

$$K_{et} \cong \frac{4\pi}{\hbar}(4\lambda k_B T)^{\frac{-1}{2}} exp - \frac{e(\chi_m - \chi_{se})}{4\lambda k_B T} |T_{DA}(0)|^2 k_B \left(1 - \frac{k_B T}{2\lambda}\right) \quad \ldots\ldots(20)$$

The rate constant of charge transfer k_{et} , and the barrier height energies ΔE effective free energy depends on the reorganization energy λ (eV) .That is the energy energy required to change the structure of the reactants, or activate them, from that of equilibrium to that of the products [19]. The Marcus –Hush theory of outer sphere electron transfer reaction in solvent predicts parabolic free energies for reaction and product pairs as functions of an appropriate reaction coordinate [20]. The energy λ (eV) arises from the reorientation of the charge in the medium .Its magnitude dependent on the radius of the molecular donor and acceptor site, on its distance (d) ,and on the dielectric properties of the metal and the semiconductor .For electron transfer between reactant metal and semiconductor , the medium reorientation energy is in many parts[21]:

$$n_{s} - n_m^2{}^{\dagger}$$

Where $\Delta e = e_D - e_A$ the difference in energy in donor and acceptor ,R is the radius of molecule dye, d is the distance between dye and semiconductor , D^{op}, D^{s} are the optical and statistical dielectric constant and $D^{s^2}{}_{se}$ and D^{s^2} are the optical and statistical dielectric constant for semiconductor .

Results

Theoretical model for charge transfer at metal/semiconductor interface system is formulated depending on quantum theory .Our model have been applied to the studies the dynamic of charge transfer at Au/ GaAs and Au/ InAs interface systems. The rate constant of charge transfer have been evaluated for GaAs, and InAs semiconductors contact with gold Au metal system depending on calculation of many parameters, such that: the reorientation free energy work function of metal, affinity of semiconductor, and the coupling matrix element coefficient .

Initially of the calculate of rate constant of charge transfer in Au/ GaAs interface system is the reorientation free energy that calculated depending on Marcus– Hush semi classical theory Eq(21).inserting the values a_s ,and a_m , are the radii of semiconductor ,and metal, and the distance $d_s = a_s + 1$, $d_m = a_m$ +1 , and $R_{m_s} = a_s + a_m$ with values of refractive index and static dielectric constant for semiconductor and metal n_s, n_m, ε_s, and ε_m respectively.The results of the reorganization energies are 0.63004eV for Au/ GaAs and 0.6630eV for Au/ InAs thus agreement with experimental result[28]. Substituting this values with work function of metal X_m ,and affinity of semiconductor X_{se} and value of coupling matrix element [27]in a Matlab designed program to evaluated the rate constant of charge transfer Eq(20).results are summarized in table (3)for Au/ GaAs and table(4) for Au/ InAs.

Discussion

A theory of charge transport across metal/semiconductor interface has been derived depending on quantum theory .In our theoretical model, we have been assuming the wave function for transfer of charge from donor to acceptor state describe in Hilbert space, and quantum well. When the metal bring to contact with semiconductor, the Fermi level for tow material much be coincident at equilibrium state. The charges upon excitation has to be rapidly transfer into the metal before it can fall back to its ground state .

The rate constant of charge transfer in tables (3) to (4) for two systems system Au/ GaAs and Au/ InAs indicate the rate constant dependent on the reorientation energy $\lambda_{\circ}(eV)$,and work founction $\chi_m(eV)$, of metal and affinity of semiconductor $\chi_{se}(eV)$.

Consequently the rate of charge transport across metal/semiconductor system has large according with large reorientation energy and vice versa.this indicate the reorientation free energy is large for large dielectric constant for semiconductor.on the other hand the shift in the reorientation free energy is≈0.033 and the ratio of rate $K_{et}\frac{\frac{GaAs}{Au}}{\frac{InAs}{Au}} \approx 1.025$ thus agreement with result ≈1 [28] ,indicated the system Au/ GaAs is active media for applied in devices technology according with Au/ InAs ystem.

Conclusion

A theoretical model with for charge transport across metal/semiconductor interface has been derived depending on quantum theory provided agood model that describe the foundmental charge transfer processes.also the rate constant of charge transfer at tow system for Au/ GaAs and Au/ InAs depending on the reorientation free energy that is necessary to alignment and oriented of the configuration system .this energy is limited the ability of transfer . The rate

constant is proportional exponentially with height barrier in $exp^{-\frac{e(\chi_m - \chi_{se})}{4\lambda k_B T}}$,for more high ,the rate is small.

In summary ,it can be concluded from the results the Au/ GaAs system agood matching compare with the other system.

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Table (1) Properties of metals

metal / Properties	Gold(Au)[22]
Atomic weigth	196.97
Atomic volume(cm^3/mol)	10.2
(Atomic radius(pm)	144
Refractive index	1.658
Crystal structure	Cubic face centered
Lattice constant(A^0)	4.08
Electron work function(ev)	5.1
Density(g/cm^3)	19.32
Fermi energy(eV)	7.32

Table (2) Properties of semiconductors

Properties / semiconductor	GaAs[23]	InAs
Crystal	cubic	Cubic
lattice constant	A=5.653	A=5.55[26]
Dielectric constant	13	15[25]
Refractive index	3.419	3.51[24]
Energy gab(eV)	1.5177	1.42[24]
Electron affinity(eV)	4.07	4.9[24]

Table (3) The rate constant of charge transfer for r for GaAs/Au interface system.

$\|T_{DA}\|^2 \times 10^{-11} (eV)$ [27]	$K_{et} \left(\frac{eV}{sec}\right)$
0.4	7.44352×10^2
0.45	8.3739×10^2
0.5	9.30441×10^2
0.55	1.023485×10^2
0.6	l,116529 $\times 10^2$
0.65	1.20957×10^2
0.70	I.30261 $\times 10^2$
0.75	1.39566×10^2
0.80	1.39566×10^2

Table (4) The rate constant of charge transfer for for InAs/Au interface system.

$\|T_{DA}\|^2$x10^{-11} (eV) [27]	$K_{et}\left(\frac{eV}{sec}\right)$
0.4	7.26196 $\times 10^2$
0.45	8.16971 $\times 10^2$
0.5	9.07746 $\times 10^2$
0.55	9.98520 $\times 10^2$
0.6	1.089 $\times 10^2$
0.65	1.18006 $\times 10^2$
0.70	1.27084 $\times 10^2$
0.75	1.36161 $\times 10^2$
0.80	1.45239 $\times 10^2$