Theoretical Studies Of Electron Transport Processes In Metal/Semiconductor Interfaces

دراسة نظرية لعملية الانتقال الالكتروني لسطح معدن ـ شبة الموصل

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Abstract

A quantum mechanical description of the dynamics of non-adiabatic electron transfer in metal/semiconductor interfaces can be achieved using simplified models of the system. For this system we can suppose two localized quantum vector states system with a conduction electron state vector $l\varphi_D^{et}\rangle$ interacting with an acceptor state vector $l\varphi_A^{et}\rangle$ of electron in band of metal with the interacting described by the coupling matrix element. Expression of rate constant 0f electron transfer for metal/semiconductor system derived upon Green function and quantum model and perturbation theory for transition between $l\varphi_D^{et}\rangle$ and $I\varphi_A^{et}$ state when the coupling matrix element coefficient smaller than k_BT . The rate of electron transfer evaluated with orientation free energy using aMATLAP program. The calculate of the electron transfer rate constant are compared with experimental results as well as with theoretical results obtained for our mode.

الخلاصة

ألوصف الكمي لحركية الانتقال الالكتروني غير الكظيم عند سطحي نظام معدن-شبه موصل أعتمد باستعمال أنموذج مبسط للنظام .لهذا النظام افترضنا حالتين كميتين متمركزتين هما حالة المانح.$|D\rangle$ وحالة المستقبل $|A>$ على التتابع.
علاقة ثابت معدل الانتقال الالكتروني لنظام سطح معدن-شبه موصل اشتقت اعتمادا لنموذج ميكانيك كمي ونظرية الاضطراب للانتقال مابين حالتي المانح-المستقبل عندما تكون معامل مصفوفة عناصر الازدواج اقل بكثير من معدل الانتقال الالكتروني حسبت مع الطاقة الحرة لاعادة التوصيل باستعمال برنامج ماتلاب.
حسابات معدل الانتقال الالكتروني قورنت مع نتائج عملية وأظهرت تطابق جيد مع نتائج الانموذج .

Introduction

Electron 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 theory of electron transfer reaction is the subject of persistent interest in chemical and biological physics[2] . Over the past several decades, researchers have investigated the transfer of electron through molecule and solid state structure at molecule/ metal interfaces [3], and metal semiconductors interfaces [4]. They showed the electron transfer from semiconductor to metal in the bleaching of surface Plasmon band and occur within the time frame of incident pulse laser in 2009 [5] Since the seminal work predicting dynamical of ET reaction in the early 1980's, a great deal of theoretical effort has gone into clarifying the dynamics of the electron transfer.[6]. The field of electron transfer has been greatly advanced by the detailed analytical theory in the past half century ago depending on the standards Marcus theory and also by the introduction of new technology, such as photochemical initiation [7].

Metal semiconductor contact from interfaces that give basic features of many metal – semiconductor devices .To construct the diagram of an metal/ semiconductor contact ,we consider the energy band diagram of metal /semiconductor , and align .These ET systems seen important from technological and biological , where a metal is placed in intimate contact with a

semiconductor , the electrons from the conduction band in one material ,which have higher energy ,flow into the other material until the Fermi level on the two sides are brought into coincidence [8-9] .the energy level in the two material are rearranged relative to the new common Fermi level [10] however ,the Fermi energy of the metal and semiconductor do not change right away. In this paper a theoretical description and studied of electron transfer at metal/semiconductor interface and will be calculated theoretically the rate constant for this transfer of electrons depending on the results of reorganization energy and coupling matrix element coefficient.

Theoretical model

The probability of electron transfer between the localized quantum states for the donor state vector $l\psi_D^{et}\rangle$ and acceptor state vector $l\psi_A^{et}\rangle$ are perturbs the energy between the metal state electron and semiconductor conduction electron state and electron can tunnel from donor to the acceptor state as shown in figure (1).

Near equilibrium, the exchange of electrons occurs mainly at interface, but a reduced species can denote an electron to any empty level on the metal. The probability the electron transfer rate constant of the semiconductor acceptor relation to the metal donor has been given by [13]:

$$\Gamma_{ET} = \frac{2\pi}{\hbar}\int_{-\infty}^{\infty}|T_{DA}(E)|^2(4\pi \mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}\mathrm{k_B T})^{\frac{-1}{2}} exp\frac{-(\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}+\Delta V)^2}{4\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}\mathrm{k_B T}}F_{(E)}dE \quad \text{.....(1)}$$

where ħ is the Planck constant divided to 2π, $|T_{DA}(E)|^2$ is the coupling coefficient between the electronic state of the metal and the conduction band at semiconductor ,$\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}$ is the reorganization energy ,$\mathrm{k_B}$ is the Boltzmann constant , T is absolute temperature ,and $F_{(E)}$ is the Fermi-Dirac probability distribution of the electrons in the electron metal-semiconductor interface and given by[14].

$$F_{(E)} = (1 + exp^{\frac{E}{\mathrm{k_B T}}})^{-1} \text{... .....(2)}$$

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 is given by[15].

$$\Delta\mathbb{V}^* = \frac{(\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}+\Delta V)^2}{4\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}\mathrm{k_B T}} = \frac{(\varphi_m-\chi_{\mathrm{se}})^2}{4\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}\mathrm{k_B T}} \quad \text{.....(3)}$$

Where φ_m the work is function of metal, and χ_{se} is the electron affinity of semiconductor

For the metal/semiconductor contact system the probability of electron transfer rate constant can be evaluated by substituting Eq.(2) ,and Eq.(3) in Eq.(1),and evaluated the integration Eq.(1) ,then gate[16].

$$\Gamma_{ET} = \frac{2\pi}{\hbar}(4\pi \mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}\mathrm{k_B T})^{\frac{-1}{2}}\frac{n_{in}V_{sem}}{\beta}\exp -\frac{(\Phi_{met}-\chi_{sem})}{4\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}\mathrm{k_B T}}\langle\left|\overline{\Lambda(0)}\right|^2\rangle\left[[\pi \mathrm{k_B T} - \frac{1}{4\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}\mathrm{k_B T}}\left(\frac{(\pi \mathrm{k_B T})^3}{4}\right) + \frac{1}{32\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}2}\mathrm{k_B}^2T^2}\left(\frac{5(\pi \mathrm{k_B T})^5}{16}\right) - \frac{1}{384\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}3}\mathrm{k_B}^3T^3}\left(\frac{61(\pi \mathrm{k_B T})^7}{64}\right) \text{... ...} + \frac{1}{\mathrm{n!}(4\mathrm{E}_{\mathrm{met}}^{\mathrm{sem}}\mathrm{k_B T})^{\mathrm{n}}}(\propto (\pi \mathrm{k_B T})^{2\mathrm{n}+1})\right] \quad \text{.....(4)}$$

where $E_{met}^{sem}(eV)$ is reorganization energy , Φ_{met}work function of metal, χ_{sem}affinity of semiconductor, n_{in}consentration of electron, V_{sem} volume of unit cellfor semiconductor, β petration factor and the coupling matrix element coefficient$\langle|\overline{\Lambda(0)}|^2\rangle$for metal and semiconductor.

The reorganization energy E_{met}^{sem} arises from the reorientation of the charge in the system .Its magnitude dependent on the radius of the donor and acceptor site, on its distance (d) ,and on the dielectric properties of the metal and the semiconductor . Its due to the electron transfer reaction for metal/semiconductor interface is given by [17].

$$E_{semi.}^{met} = \frac{q^2}{4\pi\varepsilon_0}[\frac{1}{2R_{met}}\left(\frac{1}{n_{met}^2} - \frac{1}{\varepsilon_{met}}\right) + \frac{1}{2R_{semi}}\left(\frac{1}{n_{semi}^2} - \frac{1}{\varepsilon_{semi}}\right) - \frac{1}{4D_{semi}}\left(\frac{n_{met}^2-n_{semi}^2}{n_{met}^2+n_{semi}^2}\frac{1}{n_{semi}^2} - \frac{\varepsilon_{met}-\varepsilon_{semi}}{\varepsilon_{met}+\varepsilon_{semi}}\frac{1}{\varepsilon_{semi}}\right) - \frac{1}{4D_{met}}\left(\frac{n_{semi}^2-n_{met}^2}{n_{semi}^2+n_{met}^2}\frac{1}{n_{met}^2} - \frac{\varepsilon_{semi}-\varepsilon_{met}}{\varepsilon_{semi}+\varepsilon_{met}}\frac{1}{\varepsilon_{met}}\right) - \frac{1}{R_{met-semi}}\left(\frac{1}{n_{met}^2+n_{semi}^2} - \frac{1}{\varepsilon_{semi}+\varepsilon_{met}}\right)] \quad \text{.......(5)}$$

Where $q=q_D - q_A$ the difference in energy in donor and acceptor , R_{met} and R_{semi} are the radius of metal and semiconductor ,$D_{semi} = R_{semi} + 1A^{\circ}$, $D_{met} = R_{met} + 1A^{\circ}$,and $R_{met-semi} = R_{met} + R_{semi}$ are the distance between metal,metal to interface and metal-semiconductor , n_{met}, $\varepsilon_{met}$are the optical and statistical dielectric constant and n_{semi} and ε_{semi} are the optical and statistical dielectric constant for semiconductor. The radius of the molecule can be estimated from the apparent molar volume using spherical approach [18]

$$R = \left(\frac{3M}{4\pi N\rho}\right)^{\frac{1}{3}} \quad \text{.......... (6)}$$

Where M is the molecular weight, N is Avogadro's number, and ρ is the mass density.

Results

A theoretical description of electron transfer at metal/semiconductor interface system are depending on many important parameter are dependent on many parameters such that; transfer rate constant Γ_{ET}, reorganization energy E_{met}^{sem}, and electronic coupling coefficient $\langle|\overline{\Lambda(0)}|^2\rangle$. Our model have been applied to known the behavior of electron transfer across interface metal/semiconductor, we have been evaluated the rate of electron transferΓ_{ET},

for Ge, and Si semiconductors contact with Al metal system depending on calculation of many parameters, such that: the reorganization energy $E_{met}^{sem}(eV)$, work function of metalΦ_{met}, affinity of semiconductorχ_{sem},concentration of electron n_{in},volume of unit cellfor semiconductor V_{sem},petration factor β and the coupling matrix element coefficient$\langle|\overline{\Lambda(0)}|^2\rangle$for metal and semiconductor. One Initially of the calculate of rate constant of electron transfer in Al/ Ge interface system is the calculation of the reorganization energy$E_{met}^{sem}(eV)$ depending on Marcus– Hush semi classical theory Eq.(5).,that's must be estimation radius for metals ,and semiconductors from Eq.(6) by inserting the values of Avogadro's constant $N = 6.02 \times 10^{23} \frac{Molecule}{mol}$,molecular weight

M=26.982 g/mole, and density $\rho = 2.7\text{g/cm}^3$ [19],for Al metal and M =28.09 , $and\ 72.60\ g.mol^{-1}$, and $\rho = 2.328, and\ 5{,}3267 g.cm^{-3}$ for Si ,and Ge semiconductor[20-21] in Eq.(6), we can estimate the values of radii for metals and semiconductor respectively. Reorganization energies for metal. Semiconductor interface can be calculated according to Eq.(5),with the values of the static dielectric constant ε , and optical dielectric constant$n$,for metal and semiconductor from table (1), and radii estimation of the metal and semiconductor, result are tabulated in table(2).

For next ,we can be calculation the electron transfer rate constant for Al / Si semiconductor interface system Eq.(4) with a Matlab program and substituting the reorganization energies data from table(2) ,and the matrix element coupling coefficient$\langle\left|\overline{\Lambda(0)}\right|^2\rangle = 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75,$ and
$0.8\text{x}10^{-11}(\ eV)^2$ [22], and temperature is taken depending on experimental T=300 K, results have been summarized in table (3).

Discussion

The electron transfer theory across metal/semiconductor interface has been studied 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 potential. To transfer of electron happened across interface ,when the metal bring to contact with semiconductor, the Fermi level for tow material much be coincident at equilibrium state and describe by Fermi distribution function . The electron upon driving force energy has to be rapidly transfer into the metal before it can fall back to its ground state.

The rate constant of electron transfer in tables (3) to (4) for two systems Al/ Si and Al/Ge indicate the rate constant dependent on the reorganization energy $\text{E}_{\text{met}}^{\text{sem}}(eV)$,and work founction $\varphi_m(eV)$,of metal and affinity of semiconductor$\chi_{se}(eV)$.

Consequently the rate of electron transport across metal/semiconductor system has large according with large reorganization energy and vice versa. this indicate the reorganization energy is large for large dielectric constant for semiconductor.

On the other hand the shift in the reorganization energy is≈0.033 and the ratio of rate$\Gamma_{ET}\frac{\text{Al/Si}}{\text{Al/Ge}} \approx 1.0$ thus agreement with result ≈ 1[28] ,indicated the system Al/ Si active media for applied in devices technology according with Al/ Ge system.

Conclusion

Theoretical model for electron transport across metal/semiconductor interface has been derived depending on quantum theory provided a good model that describe the fundamental electron transfer processes .also the rate constant of transfer at tow system for Al/ Si and Al/ Ge depending on the reorganization 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 $\exp -\frac{(\Phi_{met}-\chi_{sem})}{4E_{met}^{sem}k_BT}$,for more high, the rate is small.

In summary, it can be concluded from the results the Al/ Si system a good matching compare with the Al/Ge system.

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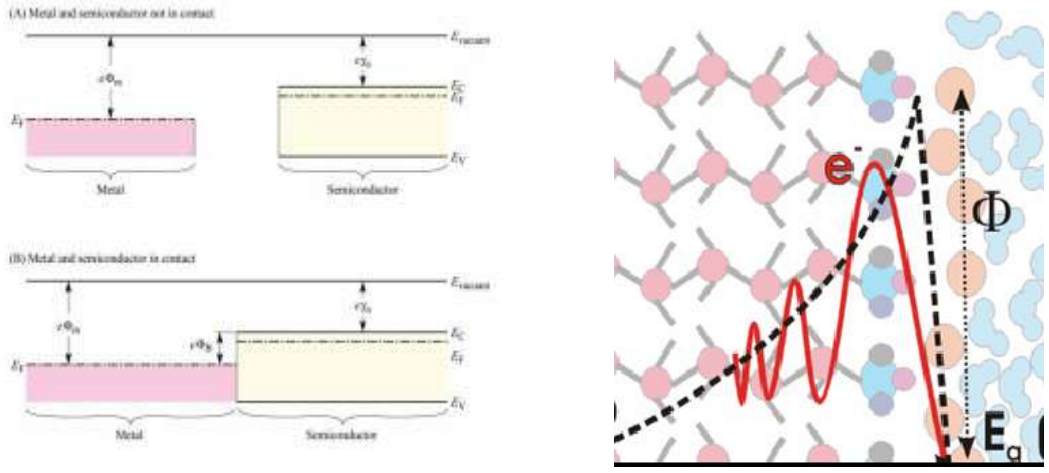

Figure (1): Schematic illustration of (a) model potential of electron transfer at band probability at the metal/semiconductor[11],and (b) tunneling process[12].

Table(1) :Common properties of semiconductor.

Properties	Semiconductor	
	Si[1]	Ge[1]
Atoms/cm^3	5.0x 10^{22}	4.42x 10^{22}
Atomic weight	28.09	72.60
Crystal structure	Diamond	Diamond
Density (g/cm^3)	2.328	5.3267
Refractive index	3.3	4.0
Dielectric constant	11.9	16.0
Effective density of states in conduction band, N_C (cm^{-3})	2.8x 10^{19}	1.04x 10^{19}
Effective density of states in valence band,N_v (cm^{-3})	1.04x 10^{19}	6.0x 10^{18}
Energy gap (eV) at 300K	1.12	0.66
Intrinsic carrier concentration	1.45x 10^{10}	2.4x 10^{13}
Intrinsic Debye length (μm)	24	0.68
Lattice constant (Å)	5.4310	5.6575
Melting point (ºC)	1415	937
Optical-phonon energy (eV)	0.063	0.037
Specific heat (J/gºC)	0.7	0.31
Electron affinity, □(V)	4.05	4.0

Table 2:Our results of the reorganization energy $E_{met}^{sem}(eV)$ for electron transfer at interface system

Material	Refractive index	Dielectric constant	Reorganization energy(eV)
Si semiconductor	3.3[20]	11.9[20]	
Al metal	1.02	1.6[20]	0.2252
	0.77		3.8068
	1.01		1.2933
	1		1.3635
Ge semiconductor	4[20]	16[21]	
Al metal	1.02	1.6	1.1965
	0.77		3.7761
	1.01		1.2646
	1		1.3347

Table(3):Data of the rate constant calculation for electron transfer at Al / Si semiconductor interface with variety coupling coefficient $\langle|\overline{\Lambda(0)}|^2\rangle$,at T= 300 K

Rate constant of electron transfer Γ_{ET} (Sec − 1)										
Coupling matrix element $\langle|\overline{\Lambda(0)}|^2\rangle$ x10^{-11}(eV)^2										
	re	0.4	0.45	0.5	0.55	0.6	0.65	0.7	0.75	0.8
Al-Si	1.224	1.582E+12	1.780E+12	1.978E+12	2.176E+12	2.374E+12	2.571E+12	2.769E+12	2.967E+12	3.165E+12
	3.803	9.052E+11	1.018E+12	1.132E+12	1.245E+12	1.358E+12	1.471E+12	1.584E+12	1.697E+12	1.810E+12
	1.292	1.541E+12	1.734E+12	1.926E+12	2.119E+12	2.312E+12	2.504E+12	2.697E+12	2.890E+12	3.082E+12
	1.362	1.502E+12	1.690E+12	1.877E+12	2.065E+12	2.253E+12	2.441E+12	2.628E+12	2.816E+12	3.004E+12
Al-Ge	1.195	9.096E+10	1.023E+11	1.137E+11	1.251E+11	1.364E+11	1.478E+11	1.592E+11	1.706E+11	1.819E+11
	3.776	5.164E+10	5.810E+10	6.455E+10	7.101E+10	7.746E+10	8.392E+10	9.038E+10	9.683E+10	1.033E+11
	1.264	8.854E+10	9.961E+10	1.107E+11	1.217E+11	1.328E+11	1.439E+11	1.549E+11	1.660E+11	1.771E+11
	1.334	8.624E+10	9.702E+10	1.078E+11	1.186E+11	1.294E+11	1.401E+11	1.509E+11	1.617E+11	1.725E+11