Ibn Al-Haitham Journal for Pure and Applied Science | مجلة إبن الهيثم للعلوم الصرفة و التطبيقية
No. 3 Vol. 25 Year 2012 | 2012 السنة 25 المجلد 3 العدد

Theoretical Calculation of Reorientation Energy in Metal /Semiconductor Interface

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Receired in:19June 2011 : Accepted in: 20 September 2011

Abstract

A theoretical calculation of the reorientation energy for non adiabatic electron transfer at interface between metal and semiconductor system was carried out. The continuum outer sphere theory of electron transfer reaction has been extensively used for electron transfer between metal/semiconductor interface .It is found that in these calculations the reorientation energy is proportional to the optical and statistical dielectric constant of semiconductor , properties of metal ,and the distance between metal and semiconductor .Results of reorientation energy show that ZnO semiconductor with metal Au possess a good matching as compared with ZnS and ZnSe . Theoretical calculation showed a good agreement with experimental value.

Key words:- theoretical calculation , reorientation energy, metal semiconductor, metal/semiconductor, Gold(Au),ZnO,ZnS,and ZnSe semiconductors.

Introduction

Electron transfer (ET) reactions plays an important role in a huge number of chemical and biochemical reactions[1]. The field of electron transfer has a rich history and continues to pose interesting problems for today researchers. Electron transfer theory predicts reorganization energy to be one factor that determines the electrochemical potential of a meta lion [2]. Reorganization energy, is the energy required to change the structure of the reactants, or activate them, from that of equilibrium to that of the products. Reorganization energy can be divided into two parts: an inner sphere component, λ_i , and an outer sphere component,. λ_o The inner sphere component encompasses hanging bond lengths and geometries orientation, while the outer Spherion compasses intermolecular electronic interactions such as alignment of a polar system dipole moment. The pioneering studies of Marcus considered a classical description of the solvent fluctuations, which were subsequently handled in terms of a quantum-mechanical theory of solvent modes, developed by Lavish and his school. Marcus' had also advanced a classical description of inner-sphere reorganization effects[3]. A quantum-mechanical treatment of non adiabatic ET processes is available, which provides a quantitative description of the effects of configurationally changes[4] The Marcus model of solvent reorganization represents the microscopic field of the acting on the transferred electron by a cavity field of a dielectric continuum. The model is very useful and provides many important insights into solvent effects on the activation barrier for ET and other types of reaction in polar liquids. It is exceptional to have a description of reorientation in terms of only two, the refractive index and the static dielectric constant. On the other hand, this concept suggests that ET reactions (and, more generally, reactions producing changes in multiple state), interact only with the macroscopic electric field in a polar medium. Clearly, the reaction proceeds on a molecular length scale and is coupled to specific molecular motions of the solvents well as to the macroscopic electric field[5].In our research we study

and calculate the reorientation energy for gold Au with ZnO ,ZnS, and ZnSe semiconductor interface.

Theory

Theoretical aspects of non adiabatic ET process are well established within the classical, semi classical, and quantum mechanical framework[6] .In all these theories the first step is the calculation of rate electron transfer which is the reorientation energy. The reorientation free energy is calculated for a reaction between a reactant and some semiconductors. We consider a no equilibrium system having some charge distribution, expressed in terms of equilibrium free energies, the free energy of formation[7].

$$\Delta G_n - \Delta G_o = m^2 \lambda = m^2 (\lambda_i + \lambda_o) \qquad \ldots\ldots\ldots \qquad (1)$$

where ΔG_o is the free energy for reactant , $\Delta G_n$is the free energy of product, λ, is the total energy of any vibration contribution of the reorientation energy from the reactants λ_i, due to changes in the equilibrium values of their vibration coordinates due to the reaction; λ_o, is given by [7]

$$\lambda_0 = \lambda_s + \lambda_m + \lambda_{m-s} + \lambda_{s-m} + \lambda_{sm} \qquad \ldots\ldots\ldots \qquad (2)$$

where λ_s, λ_m , $\lambda_{m-s}, \lambda_{s-m}$, and λ_{sm} are the contripution of reorientation for semiconductor ,metal ,metal-semiconductor semiconductor-metal, and semiconductor metal contact.

$$\lambda_o = \frac{\Delta e^2}{4\pi\varepsilon_o}\left[\frac{1}{2R_s}\left(\frac{1}{n_s^2} - \frac{1}{\varepsilon_s}\right) + \frac{1}{2R_m}\left(\frac{1}{n_m^2} - \frac{1}{\varepsilon_m}\right) - \frac{1}{4d_s}\left(\frac{n_m^2 - n_s^2}{n_m^2 + n_s^2}\ \frac{1}{n_s^2} - \frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + \varepsilon_s}\ \frac{1}{\varepsilon_s}\right) - \frac{1}{4d_m}\left(\frac{n_s^2 - n_m^2}{n_s^2 + n_m^2}\ \frac{1}{n_m^2} - \frac{\varepsilon_s - \varepsilon_m}{\varepsilon_s + \varepsilon_m}\ \frac{1}{\varepsilon_m}\right) - \frac{1}{R_{m_s}}\left(\frac{1}{n_s^2 + n_m^2} - \frac{1}{\varepsilon_s + \varepsilon_m}\right)\right] \qquad \ldots\ldots\ldots(3)$$

, ε_m, n_s^2, n_m^2, R_{ms}, R_s, R_m, d_s, and, $d_m$are the dielectric constant for semiconductor and ε_s metal,refrective index for semiconductor and metal ,distance between metal semiconductor, radii of semiconductor and metal and the distance for semiconductor and metal to electrode respectively.

Result

In this paper, our main theoretical calculation of reorientation energy in metal/semiconductor interface system .The tool is an outer inner sphere equation that given by Marcus.ET reactions from a no equilibrated initial state.

Semiconductor /metal interface system provide interfacial charge transfer processes. To study and calculate the rate constant of electron transfer in Au/ZnO, Au/ZnS, and Au/ZnSe system, first we calculate the reorientation energy λ(eV) for these systems. To calculate the reorientation energy we extensively the relation of Hsu-Marcus[7] that derived upon continuum sphere for two materials system. The reorientation energy for gold metal interface with ZnO, ZnS., and ZnSe semiconductor system are calculated using Eq.(3).

Inserting the values of radii R_{se}= 3.8025A^0,5.4100A,and 5.6600A^0 [10] for ZnO,ZnS,and ZnSe semiconductor , R_m= 1.6600A^o for Gold metal [8] for metal and the distance $d_m=a_m+1$, $d_{se}=a_{se}+1$, $R_{m\text{-}se}=a_m+a_{se}$ with the values of n_{se},n_m,ε_{se}, and ε_m are refractive index of

semiconductor and metal and static dielectric of semiconductor and metal from table(2). Results have been summarized in table(3).

Discussion

As for the metal/semiconductor system interface a reorientation energy that is given to rearrangement of the conduction electrons occurs at the interface. The results of reorientation free energy for Au/ZnO, Au/ZnS and Au/ZnSe system indicate illatively weak coupling coefficient when the distance d_m and d_{se} increase with R_m and d_{se} . These because of the barrier height in metal/semiconductor system large with increase of d, and have a reorientation free energy to arrangement system is large The value of λ(eV) observed large where a metal/semiconductor is not contact . This refers and investigates the barrier height in contact which is minimum. However, some electrons flow from the metal into the semiconductor because of potential height barrier and electrons accumulated at the interface instead of receding from it. The results of the Au/ZnO system possess a good matching as compared with Au/ZnS, and Au/ZnSe.Tabe (3) shows the results of the reorientation free energy for Au/ZnO system which is more effective to Au metal than ZnSe and ZnS for the same metal. This indicates that ZnO possess optical index smaller than ZnS and ZnSe also the crystal of structure is wurtzite[10], which is difference than ZnS and ZnSe have Zinc blend structure[10].On the other hand the energy gap of ZnO is about 3.4(eV)[10] with a better carrier of electron mobility, and electron affinity is larger than the other ZnS and ZnSe. This means that the density of electron in conduction band of ZnO is larger than the other semiconductor .It is leading to suggest that Au/ZnO is attraction and a good system obviously, a large value of reorientation energy in semiconductor /Au metal would give rise to large transfer of electron, however these value are good for three semiconductor but the ZnO is a better than two semiconductors . Our results are in good coincident with the other experimental and theoretical value in table(4).

Conclusion

When a metal is making intimate contact with a semiconductor , the reorganization energy in minimum, this indicates the Fermi levels in two materials must be coincident at equilibrium and that given which is arrangement of change carrier is suitable to transfer. In summary it can be conclusion depending on present results that the reorientation energy for change transfer across metal/semiconductor interface showed strong dependence on the type of semiconductor (properties of semiconductor).

For increasing the distance between gold metal and ZnO, ZnS, and ZnSe semiconductor the reorientation free energy is increasing proportional with distance that's mean the height of barrier is large that is formed between two materials.

We concluded from the present results that the reaction of electron transfer strongly depends on system. Large values of the reorientation energy in Au/ZnO system lead to suggest the ZnO is good matching reaction towards the gold meta as compared with other semiconductor ZnO and ZnSe.

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Table(1): Properties of metals

Metal / Properties	Gold(Au)
Atomic weigth	196.97[8]
Atomic volume(cm^3/mol)	10.2[8]
Atomic radius(pm)	144 [8]
Refractive index	1.658[11]
Crystal structure	Cubic face centerd
Lattice constant(A^0)	4.080 [8]
Electron work function(ev)	5.1 [8]
Density(g/cm^3)	19.32[8]
Fermi energy(eV)	7.32[9]

Table (2): Properties of semiconductors

Properties \ semiconductor	ZnO	ZnS	ZnSe
Crystal structure	Wurtzite[10]	Zinc blend[10]	Zinc blend[10]
Lattice constant(nm)	a=0.32495,c=o. 5206[10]	0.541 [10]	o.566[10]
Density(g/cm^3)	5.66 [10]	4.08 [10]	5.42[10]
Dielectric constant	8.5 [10]	8.3 [10]	9.2[10]
Refractive index	2.00337[11]	2.52226[11]	2.62408[11]
Energy gab(eV)	3.4[10]	3.6 [10]	2.6[10]
Electron affinity(ev)	4.5[12]	3.9[12]	4.09[13]

Table (3): The results of calculation of the reoreintation energy λ(eV) for gold metal/semiconductor interface system

System	Reorganization energy λ(eV)			
	$d=a_{s-m}+1.0(A^0)$	$d= a_{s-m}+1.2\ (A^0)$	$d= a_{s-m}+1.4(A^0)$	$d= a_{s-m}+1.6(A^0)$
Au-ZnO	o.71502218	o.71900496	0.722411668	o.725354107
Au-ZnS	o.670556312	o.682074705	o.69202476	0.700700169
Au-ZnSe	o.673663776	O.685728201	o.696178713	o.705299904

Table(4):comparing our results with theoretical and experimental of reorientation energy λ(eV)

	Our result	Experimental[9]	Theoretical[14]
Au/ZnO	0.715	0.8	1.2-2.3
Au/ZnS	0.67	0.6-1.2	
Au/ZnSe	o.67		

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No. 3 Vol. 25 Year 2012
العدد 3 المجلد 25 السنة 2012

الحسابات النظرية لطاقة اعادة الترتيب عند سطح شبه موصل /معدن

هادي جبار مجبل ، حسين خضيرمجبل
قسم الفيزياء ، كلية التربية ابن الهيثم ،جامعة بغداد
استلم البحث في: 19 حزيران 2011 قبل البحث: في 20 ايلول 2011

الخلاصة

الحسابات النظرية لطاقة اعادة الترتيب للانتقال الالكتروني غير الكظيم على السطح لنظام مابين المعدن–شبه الموصل استخرجت نظرية السطوح الكروية المستمرة لتفاعل الانتقال الالكتروني وصفت للاستعمال في الانتقال الالكتروني ما بين سطح المعدن وشبة الموصل.

وجد في الحسابات ان طاقة اعادة الترتيب تتناسب مع ثابت العزل الكهربائي والبصري لشبه الموصل ، خواص المعدن ، والمسافة الفاصلة بين شبه الموصل والمعدن.

اظهرت الحسابات لطاقة اعادة الترتيب أن شبه الموصل ZnO اكثر ملائمة مع معدن الذهب Au حيث يملك ملائمة جيدة مقارنة مع ZnS و ZnSe . واظهرت الحسابات النظرية تطابقا جيدا مع القيم العملية.

الكلمات المفتاحية:– حسابات نظرية، طاقة اعادة الترتيب، المعدن، شبه الموصل، معدن/ شبه موصل، الذهب(Au) ، اشباه الموصلات ZnO، ZnS,ZnSe.