Space Charge Transfer in Hybrid Inorganic/Organic Systems

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The adsorption energy ($\Delta E_q^{\rm ads}$) of an adsorbate that receives q electrons from the electron reservoir with an electron chemical potential $\epsilon_{\rm F}$ can be written as

$$\Delta E_q^{\rm ads}(\epsilon_{\rm F}) = -E_q^{\rm surf/mol} + E_0^{\rm surf} + E_0^{\rm mol} + q\epsilon_{\rm F} + \Delta E^{\rm SC}. \quad (1)$$

$E_q^{\rm surf/mol}$ is the total energy of the adsorbate system computed in a supercell with q excess electrons. $E_0^{\rm surf}$ and $E_0^{\rm mol}$ are the total energies of the neutral bare substrate and the neutral molecule. This definition is similar to that used in calculations of defects in the bulk or at interfaces [1–3], but differs in the additional term $\Delta E^{\rm SC}$ that represents the energy correction for describing the space-charge layer.

For the bare substrate, $E_0^{\rm surf}$ is related to $E_q^{\rm surf}$ (the total energy in the charged state) by the definition of the Fermi level $\epsilon_{\rm F}^{\rm surf}(q) = dE_q^{\rm surf}/dq$. We thus have

$$E_q^{\rm surf} - E_0^{\rm surf} - q\epsilon_{\rm F} = \int_0^q {\rm d}q'[\epsilon_{\rm F}^{\rm surf}(q') - \epsilon_{\rm F}] = q\delta - q\Delta\epsilon_{\rm F}, \quad (2)$$

where $\epsilon_{\rm F}$ can be referenced to energy levels of the bare substrate, for instance, the conduction band minimum $\epsilon_{\rm CBm}$ for electrons and the valence band maximum $\epsilon_{\rm VBM}$ for holes.

For electrons,

$$\Delta\epsilon_{\rm F} = \epsilon_{\rm F} - \epsilon_{\rm CBm}, \quad (3)$$

and we obtain

$$\delta = \frac{\int_0^{\epsilon_{\rm F}^{\rm surf}(q)-\epsilon_{\rm CBm}} ED(E){\rm d}E}{\int_0^{\epsilon_{\rm F}^{\rm surf}(q)-\epsilon_{\rm CBm}} D(E){\rm d}E}, \quad (4)$$

where $D(E)$ is the density of states (DOS) of the bare substrate.

For holes,

$$\Delta\epsilon_{\rm F} = \epsilon_{\rm F} - \epsilon_{\rm VBM}, \quad (5)$$

and we obtain analogously

$$\delta = \frac{\int_0^{\epsilon_{\rm F}^{\rm surf}(q)-\epsilon_{\rm VBM}} ED(E){\rm d}E}{\int_0^{\epsilon_{\rm F}^{\rm surf}(q)-\epsilon_{\rm VBM}} D(E){\rm d}E}. \quad (6)$$

In the limit of small q, δ becomes zero. Combining Eq. (1) and Eq. (2), the adsorption energy becomes

$$\Delta E_q^{\rm ads}(\epsilon_{\rm F}) = (-E_q^{\rm surf/mol} + E_q^{\rm surf} + E_0^{\rm mol}) + (q\Delta\epsilon_{\rm F} - q\delta) + \Delta E^{\rm SC}. \quad (7)$$

Fermi level as a function of dopant concentration

The Fermi level position $\Delta\epsilon_{\rm F} = \epsilon_{\rm F} - \epsilon_{\rm CBm}$ of n-type semiconductors (ZnO here) is related by the bulk dopant concentration $N_{\rm D}$ by the relation [4]:

$$\frac{N_{\rm D}}{1 + 2\exp(\frac{\Delta\epsilon_{\rm F}}{k_{\rm B}T})\exp(\frac{E_{\rm d}}{k_{\rm B}T})} = N_{\rm C}\frac{2}{\sqrt{\pi}}F_{1/2}(\frac{\Delta\epsilon_{\rm F}}{k_{\rm B}T}). \quad (8)$$

$E_{\rm d}$ is the donor binding energy and $N_{\rm C}$ the effective density of states in the conduction band, which is given by

$$N_{\rm C} = 2(\frac{2\pi m^* k_{\rm B}T}{h^2})^{\frac{3}{2}}. \quad (9)$$

Here m^* is the density of state effective mass for electrons, $k_{\rm B}$ the Boltzmann constant, T the temperature and h the Planck constant. $F_{1/2}$ is a function defined as

$$F_{1/2}(\eta_{\rm F}) = \int_0^\infty \frac{\eta^{1/2}{\rm d}\eta}{1 + \exp(\eta - \eta_{\rm F})}. \quad (10)$$

For ZnO we used the following parameters: $E_{\rm d}$ = 30 meV [5], m^*=0.27 m_e (m_e: mass of free electron) [4], T = 300 K.

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