PHYSICAL PROPERTIES OF INTERMETALLIC ADSORPTION SYSTEMS AND THE ELECTRONEGATIVITY OF THE SURFACE

Jules D. Levine
Radio Corporation of America
Elias P. Gyftopoulos
Massachusetts Institute of Technology

1. Introduction

This presentation is a brief summary of the key ideas of the chemical approach to the problem of understanding the physical properties of intermetallic adsorption systems. The details of the theory have been described in a sequence of previous publications[1-4] and will not be repeated here.

The problem under consideration is to predict theoretically the electron work function and the atom and ion desorption energies and desorption rates for metallic surfaces partially covered by metallic particles.

For this purpose, it is assumed that the adsorbate particles are chemisorbed as a single, mobile species and that they are held onto the substrate by partially ionic and partially covalent bonds. The chemical nature of the surface bonds is indicated by the magnitudes of the binding energies which are of the order of a few electron volts and it is also supported by the recent experimental results of Utsugi and Gomer.[5] The mixed character of the bonds is suggested by the difference in the absolute electronegativity of the substrate and adsorbate atoms present in intermetallic adsorption systems.

A consequence of these assumptions is that, under conditions of dynamic equilibrium, each surface site available for occupancy by an adsorbate particle, is fully interacting with all other sites on the surface and may be assigned an electronegativity value.

The extension of the concept of electronegativity from atoms to sites of intermetallic surfaces proves very expedient. The reason is that through this extension, a number of ideas, which have been introduced and tested in molecular physics can be readily adapted to adsorption systems.

The paper is organized as follows. First, a brief review of the relation between the electronegativity scale of elements and other physical properties is given. Second, the concept of electronegativity is extended to intermetallic surfaces and used to compute the electron work function. Third, the calculation of the desorption energies is summarized and finally the derivation of the desorption rates is briefly outlined.

2. Electronegativity and Other Properties

The property of electronegativity of an atom is characteristic of the power of the atom in a molecule to attract electrons to itself.[6] All elements can be assigned a value of electronegativity. Such values have been derived by a variety of chemical or quantum mechanical methods.

Apart from the affinity of a neutral atom in a stable molecule for electrons, the electronegativity is also related to a variety of other microscopic or macroscopic properties such as ionization potentials, nuclear electric quadrupole moments, nuclear magnetic moments etc.[6-10] Two of these relations are of particular interest to the purposes of this paper. First, as pointed out by Gordy and Thomas[10] there is a reasonably good correlation between the electron work function and the electronegativity of an element:

$$\emptyset = 2.27x + 0.34 , \tag{1}$$

where $\emptyset$ is the work function in eV and x is the electronegativity in the relative scale of Pauling.[6] It is evident that Eq. (1) is approximate since the electronegativity is a unique characteristic of the element while the work function depends on the crystallographic structure of the surface.

Second, as pointed out by Pauling[6] and Malone[11] a molecule, made of two dissimilar atoms of relative electronegativities x_1 and x_2, exhibits a dipole moment proportional to the difference in electronegativities

$$\text{Dipole moment} = k_p(x_1-x_2) . \tag{2}$$

The constant of proportionality can be estimated from data on diatomic molecules and it is $k_p = 1.15$ Debyes per unit relative electronegativity. This value does not account for self-depolarization effects.[12]

Equation (2) can be extended to surface bonds between identical substrate and adsorbate particles with $x_1=x_2$. The resulting zero surface dipole moment is consistent with a variety of independent experimental and theoretical data on pure metallic lattices. The implication of this extension, in conjunction with Eq. (1), is that for pure metallic surfaces the electronegativity may also be viewed as a property of the surface sites of the lattice.

3. Work Function of Composite Surfaces

To avoid numerical complexities, consider a homogeneous intermetallic composite surface. In other words, assume a surface on which the adsorbate is uniformly distributed over the substrate. Suppose that, as in the case of pure metals, each site of the composite surface can be assigned a relative electronegativity, $x(\theta)$, which is a function of the degree of coverage, θ. This electronegativity must be a function of θ because as the coverage changes so do the cooperative interactions between the different surface sites and therefore so does the chemical activity of the surface.

The electron work function, $\emptyset_e(\theta)$, for the composite surface would be proportional to $x(\theta)$ (Eq. 1) if there were no surface dipole moments. However, in general, the electronegativity of an adsorbate particle is different than $x(\theta)$ and if Eq. (2) holds also for composite surfaces then there must be surface dipole moments. Thus, the electron work function must consist of a contribution which is directly related to the electronegativity (Eq. 1) and another contribu-

tion which arises from the surface dipole moments. If the surface electronega-
tivity is written in the convenient form:

$$x(\theta) = x_f + (x_m - x_f)G(\theta) \, , \qquad\qquad (3)$$

where x_m and x_f are the relative electronegativities of the substrate and the
adsorbate, respectively, and $G(\theta)$ is a function of θ to be determined, then
addition of the two contributions to the electron work function (see reference
1) yields:

$$\frac{\phi_m - \phi_e(\theta)}{\phi_m - \phi_f} = 1 - G(\theta)\left[1 - \frac{0.76 \times 10^{-14}\sigma_f\theta\cos\beta}{(1 + \alpha/R^3)(1 + 9\alpha\sigma_f^{3/2}\theta^{3/2})}\right]\!, \qquad (4)$$

where ϕ_m (eV) is the electron work function of the bare substrate, ϕ_f (eV) is
the electron work function of the bulk adsorbate, σ_f (cm^{-2}) is the number of
sites available for adatom occupancy per unit substrate area to form a mono-
layer, α (cm^3) is the polarizability of the adsorbate, R (cm) is the sum of the
covalent radii of the substrate and the adsorbate, $\cos\beta = (1 - 1/2\sigma_m R^2)^{1/2}$*
and σ_m(cm^{-2}) is the apparent surface density of the substrate.

The exact dependence of $G(\theta)$ on θ is very difficult to compute from first
principles in the same sense that it is difficult to compute, say, the work
function of a given crystallographic face of a pure metal. Nevertheless, it
can be approximated by a simple power series expansion which at least satisfies
some obvious boundary conditions. Specifically: (a) at zero coverage the
electronegativity, $x(\theta)$, must be equal to the electronegativity, x_m, of the
substrate; (b) at coverage of one monolayer or more the electronegativity must
be that of the adsorbate (x_f) because it is experimentally observed that under
these conditions the surface exhibits the properties of the bulk adsorbate. For
example, the electron work function is within a few per cent of that of the bulk
adsorbate for the systems: Cs-W[13-14], Cs-Mo[15], Cs-Al$_2$O$_3$[16], Ba-W[17-19],
Si-W[17-18], Mg-W[18], Be-W[18-20], Th-Re[21], Ti-W[22]; (c) at half coverage
the electronegativity must be the same in both systems in which the roles of
substrate and adsorbate are interchanged. The analytical statement of condi-
tions (a-c) in terms of $G(\theta)$ is:

$$G(0) = 1 \; ; \quad G(1) = 0 \; ; \quad dG(\theta)/d\theta\Big|_{\theta=1} = 0 \; ; \quad G(1/2) = 1/2 \, . \qquad (5)$$

The simplest rational polynomial which satisfies Eq. (5) is:

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*This definition of $\cos\beta$ and the numerical value 0.76×10^{-4} in Eq. (4) are
applicable only for body centered cubic substrates (for details see refer-
ence 1).

$$G(\theta) = 1-3\theta^2+2\theta^3 \tag{6}$$

This approximation proves extremely satisfactory as evidenced by the comparison of experimental and theoretical results for a variety of intermetallic adsorption systems presented in references 1 and 23-24.

Many implications of Eq. (4) have been discussed in reference 1. For the purposes of this review, it suffices to emphasize that the equation does not involve any adjustable constants and that it applies to all intermetallic adsorption systems with body centered cubic substrates. For other substrates, the definition of $\cos\beta$ and the constant 0.76×10^{-4} are different. The various adsorption systems are characterized by the physical constants σ_m, ϕ_m, σ_f, ϕ_f, α and R.

The temperature dependence of the electron work function has been assumed negligible. In the context of the present formalism it could be readily accounted for through the temperature dependence of σ_m and σ_f due to thermal expansions.

4. Atom and Ion Desorption Energies

The desorption energy, $\phi_a(\theta)$, of atoms from a composite surface may be assumed as consisting of an ionic and a covalent part:

$$\phi_a(\theta) = H_{ii} + H_{cc} . \tag{7}$$

The computation of the two parts must be such that at least three conditions are satisfied. First, the ionic contribution, H_{ii}, must vanish for purely covalent bonds. Second, the covalent contribution, H_{cc}, must vanish for purely ionic bonds. Third, when material X is adsorbed on bulk material X, H_{cc} must reduce to the heat of sublimation of material X.

The ionic contribution arises from a fraction of charge, F, of the substrate which is transferred to the adsorbate. A simple thought experiment reveals (see reference 2) that:

$$H_{ii} = F\phi_e(\theta)\left[1+\delta\right] \quad ; \quad \delta = F\left[(e^2/R) - V_f\right] \tag{8}$$

where e is the electronic charge and V_f is the ionization potential of the adsorbate. The fraction of charge F can be estimated by using the concept of surface electronegativity and for body centered cubic substrates (see reference 2) it is:

$$F = \frac{0.42\times10^{-8}(\phi_m-\phi_f)G(\theta)}{R(1+\alpha/R^3)} . \tag{9}$$

The covalent contribution arises from pairing of valence charges. An estimate of this contribution is derived in reference 2 by considering the conditions stated above and also using different features of covalent bonds which have been established for molecular physics. Thus, it is found that:

$$H_{cc} = (\phi'_f \phi'_m)^{1/2} S_{fm} Q_{fm} \tag{10}$$

where ϕ'_f and ϕ'_m are the heats of sublimation of the adsorbate and the substrate, respectively, $S_{fm} = 2/[(S_f/S_m)+(S_m/S_f)]$, S_f and S_m are the angular strengths of the valence orbitals of the adsorbate and substrate, respectively, $Q_{fm} = (1-F^2/v^2)^{1/2}$ and v is the largest number of valence electrons participating in the covalent bond.

Thus, the atom desorption energy is

$$\phi_a(\theta) = F\phi_e(\theta)[1+\delta] + (\phi'_f \phi'_m)^{1/2} S_{fm} Q_{fm} \tag{11}$$

Note that it depends explicitly on the physical properties of the materials of the adsorption system and that it does not involve any adjustable constants. Comparisons of theoretical and experimental results are presented in references 2 and 23.

The ion desorption energy, $\phi_p(\theta)$, is readily calculated from the simple energy balance equation:

$$\phi_p(\theta) = \phi_a(\theta) + V_f - \phi_e(\theta) \tag{12}$$

5. Atom and Ion Desorption Rates

Atom and ion desorption rates can be easily computed by means of standard statistical mechanics methods. The adsorbed particles are assumed to have two degrees of translational freedom parallel to and one degree of vibrational freedom perpendicular to the surface. They are also assumed to be in equilibrium with the vapor phase. From the equality of the chemical potentials, it is found that (see reference 3):

Atom desorption rate: $\quad E_a = \omega_a \sigma_f \theta \, \nu \exp(\Delta S/k) \exp(-\phi_a(\theta)/kT)$, $\tag{13}$

Ion desorption rate: $\quad E_p = \omega_p \sigma_f \theta \, \nu \exp(\Delta S/k) \exp(-\phi_p(\theta)/kT)$, $\tag{14}$

where ω_i is the statistical weight of the ith species of vapor particles, ΔS is the configuration entropy change given by

$$\Delta S = k \ln\left[(A_t/A_f)\exp\theta \, \partial \ln(A_t/A_f)/\partial \theta\right] , \tag{15}$$

T is the surface temperature, $A_f/A_t = (1-\theta)^{1/2}(1-\theta^{1/2})$ is the fractional area available for translation, $\nu = \nu_1 \exp(\theta \partial \ln \nu_1/\partial \theta)$ is the effective vibration frequency and ν_1 is the vibration frequency. The computation of the vibration frequency ν_1 and comparisons of Eq. (13) with experiment are given in reference 3.

6. Conclusions

The chemical approach to the problem of understanding the physical properties of intermetallic adsorption systems, yields results which are in very good agreement with experimental data for a large variety of adsorption systems.

The theoretical results for the electron work function and the atom and ion desorption energies and rates can be combined with Richardson's equation to derive electron emission S-curves. This is done in reference 4 for several adsorption systems and again very good agreement is established between theory and experiment. Also, in reference 4 a parametric study of the sensitivity of S-curves with respect to the values of the physical constants ϕ_m, σ_f and ϕ_f is presented.

It is felt that the chemical approach to adsorption systems will also yield practical results for the case of gaseous adsorbates on metallic substrates. This problem is currently under investigation and the preliminary results are very encouraging.

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