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Bond energies in alloys determined from underpotential deposition potentials

Abstract A procedure is presented to determine bond energies between the metal (Me) and substrate (S) components of binary alloys from characteristic underpotential deposition (UPD) potentials. The bond energy between Me and S atoms is one of the factors governing the deposition kinetics and structure of Me-S alloy deposits. The proposed procedure is based on the determination of the UPD potential for formation of a condensed two-dimensional (2D) phase of the less noble metal Me (the UPD metal) on the more noble metal S (the substrate). Making reasonable approximations, the sublimation enthalpy of the condensed 2D Me phase is obtained from the corresponding formation underpotential. From this sublimation enthalpy the bond energy of an atom of the UPD metal in a kink site position of the 2D Me phase is calculated. This value is used to calculate the bond energy ($\phi_{\text{Me-S}}$) between an Me atom and an S atom. The method is demonstrated using experimental data obtained in selected electrochemical UPD systems.

Keywords Alloys · Electrochemical deposition · Intermetallic compounds · Sublimation enthalpy · Underpotential deposition

Introduction

The electrochemical deposition of alloys is an established process in plating technology [1]. The typical deposit is either an eutectic mixture or a solid solution with full or limited miscibility. In the latter case, different intermetallic phases can develop. Much less is known about the formation of intermetallic compounds (ICs) during electrodeposition.

The structure of alloys is determined by five factors (Villars [2]): (1) size factor, e.g. radius; (2) valence electron factor, e.g. density of valence electrons in the elementary cell; (3) electrochemical factor, e.g. electronegativity; (4) cohesive energy factor, e.g. melting temperature; (5) atomic number factor (Mendeleev factor), e.g. position in the Periodic Table or a modified periodic listing of the elements. At least two of these factors determine the structure developing in a deposition process.

The first rules were given by Hume-Rothery et al. [3], with the definition of Hume-Rothery phases (determined by size and valence electron density) and rules on solubility (size and electronegativity). An additional driving force for the formation of the structure in an alloy is the bond strength between the components, which is represented by the corresponding bond energy. The bond energy combines the different bond characteristics (metallic, covalent, ionic). It is possible to calculate bond energies, either by the methods of quantum chemistry or by approximate procedures [4]. In the present paper, ways of experimental access to bond energies are described.
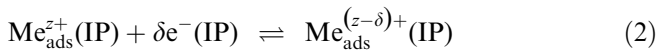
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Underpotential deposition of metal Me on metal S

In recent decades the phenomenon of underpotential deposition (UPD), i.e. deposition of a metal Me on a substrate S at electrode potentials, E, more positive than the Nernst equilibrium potential of the 3D Me bulk phase, E_{3DMe}, has been intensively investigated [5]. This phenomenon is induced by a strong Me–S interaction and can be considered as an electrosorption process described by the reactions [5]:

$$\text{Me}_{\text{solv}}^{z+}(\text{El}) \;\rightleftharpoons\; \text{Me}_{\text{ads}}^{z+}(\text{IP}) \tag{1}$$

and:

$$\text{Me}_{\text{ads}}^{z+}(\text{IP}) + \delta e^-(\text{IP}) \rightleftharpoons \text{Me}_{\text{ads}}^{(z-\delta)+}(\text{IP}) \qquad (2)$$

The first reaction (Eq. 1) describes the adsorption of metal ions Me^{z+} from the electrolyte phase (El) to the inner part of the electrochemical double layer located in the interphase (IP) at the S/electrolyte interface. The second reaction (Eq. 2) represents the interaction between adsorbed metal ions $\text{Me}_{\text{ads}}^{z+}(\text{IP})$ and the electrons e^- (IP) in the interphase, leading to formation of partially $(z > \delta > 0)$ or completely $(\delta = z)$ discharged ad-species $\text{Me}_{\text{ads}}^{(z-\delta)+}(\text{IP})$. The charge coverage $(q-\Gamma)$ stoichiometry of the electrosorption process is given by the so-called electrosorption valency [5]:

$$\gamma = \frac{1}{F}\left(\frac{\partial q}{\partial \Gamma}\right)_E \qquad (3)$$

In the absence of cosorption and/or competitive sorption of other electrolyte constituents, $\gamma = z$ and the UPD process can be described by:

$$\Delta E = E - E_{3\text{DMe}} = -\frac{RT}{zF}\ln a(\Gamma) \qquad (4)$$

where $a(\Gamma)$ is related to the adsorption isotherm, which depends on the atomic structure and homogeneity of the substrate surface and on the Me_{ads}–S and Me_{ads}–Me_{ads} interactions.

An alternative view on the UPD process provides the recently developed concept of substrate-supported formation of low-dimensional Me phases and systems [6, 7, 8, 9]. This theory is based on the stabilizing effect of substrates on agglomerations of atoms on the surface. Small clusters and linear chains of atoms formed preferentially at surface point defects and monatomic steps are considered as 0D and 1D systems, respectively. The UPD monolayers are considered as 2D phases, stabilized by the strong bond between substrate and UPD metal on atomically smooth substrate surface terraces. Generally, the thermodynamic stability of low-dimensional systems is described by quasi-Nernst equations:

$$E = E_{3\text{DMe}} - \frac{RT}{zF}\ln a_{i\text{DMe}} \qquad (5)$$

where $a_{i\text{DMe}}$ (with $i = 0, 1, 2$) represents the activities of metal atoms in corresponding iD systems (phases), which are smaller then the activity in the 3D Me bulk phase $(a_{i\text{DMe}} < a_{3\text{DMe}} = 1)$.

The formation of expanded (gas-like) 2D Me phases is characterized by a continuous increase of the equilibrium Me surface coverage Γ with the electrode potential E, and the activity of Me adatoms $a_{2\text{DMe}} = a(\Gamma)$ is expressed by Eq. 4. In the case of formation of a condensed 2D Me phase, however, $a_{2\text{DMe}}$ becomes a constant and E in Eq. 5 represents the corresponding equilibrium potential $(E = E_{2\text{DMe}})$.

In principle, a condensed 2D Me phase (condensed UPD layer) can be considered as a special modification of the metal Me. Then the difference $(E_{2\text{DMe}} - E_{3\text{DMe}})$ resulting from Eq. 5 can be defined as the thermodynamic formation underpotential, $\Delta_f E_{2\text{DMe}}$, of the condensed 2D Me phase:

$$\Delta_f E_{2\text{DMe}} \overset{\text{def}}{=} E_{2\text{DMe}} - E_{3\text{DMe}} = -\frac{RT}{zF}\ln a_{2\text{DMe}} \qquad (6)$$

This is illustrated with the electrochemical cell in Fig. 1. One electrode in Fig. 1 is the bulk metal Me (3D Me); the other electrode shows the condensed UPD Me layer (2D Me) on the substrate (S). The cell reaction of this electrochemical cell is the formation reaction of the UPD modification of the metal Me (condensed 2D Me phase) on the substrate metal S:

$$\text{Me}_{3\text{D}} \rightarrow \text{Me}^{z+} + z e^- \qquad (7)$$

and:

$$\text{Me}^{z+} + z e^- \rightarrow \text{Me}_{2\text{D}} \qquad (8)$$

Overall:

$$\text{Me}_{3\text{D}} \rightarrow \text{Me}_{2\text{D}} \qquad (9)$$

One can calculate the free energy of formation of the 2D Me phase $\Delta_f G_{2\text{DMe}}$ from the cell voltage corresponding to the formation underpotential $\Delta_f E_{2\text{DMe}}$:

$$\Delta_f G_{2\text{DMe}} = -zF\Delta_f E_{2\text{DMe}} \qquad (10)$$

The free energy of formation, $\Delta_f G_{2\text{DMe}}$, can be expressed as:

$$\Delta_f G_{2\text{DMe}} = \Delta_f H_{2\text{DMe}} - T(S_{2\text{DMe}} - S_{3\text{DMe}}) + \Delta G_{\text{dl}} + N_A \varepsilon \qquad (11)$$

where $\Delta_f H_{2\text{DMe}}$ is the formation enthalpy and $S_{2\text{DMe}}$ and $S_{3\text{DMe}}$ represent the entropies of the 2D and 3D Me
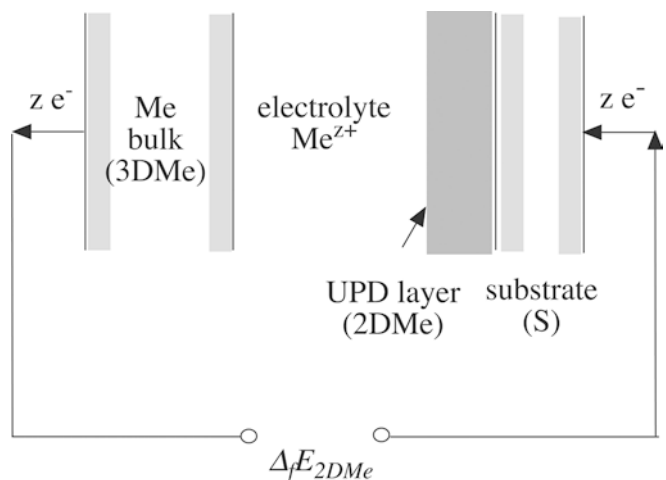
Fig. 1 Nernst cell between a condensed UPD metal layer (2DMe) on a substrate S and the bulk metal (3DMe). The free energy of formation, $\Delta_f G_{2\text{DMe}}$, of the UPD Me layer is calculated from the cell voltage: $\Delta_f E_{2\text{DMe}} = E_{2\text{DMe}} - E_{3\text{DMe}}$

Table 1 Sublimation enthalpies of substrates ($\Delta_s H_{3DS}$) and Me bulk phases ($\Delta_s H_{3DMe}$), and values for formation and sublimation enthalpies ($\Delta_f H_{2DMe}$ and $\Delta_s H_{2DMe}$) of condensed 2D Me phases, calculated from experimental data for the UPD systems Ag(111)/Pb^{2+}, Ag(111)/Tl$^+$ and Au(111)/Pb^{2+}

Substrate (S)	UPD metal (Me)	$\Delta_f E_{2DMe}$ (V)	$\Delta_f H_{2DMe}$ (kJ mol^{-1})	$\Delta_s H_{3DMe}$ (kJ mol^{-1})	$\Delta_s H_{3DS}$ (kJ mol^{-1})	$\Delta_s H_{2DMe}$ (kJ mol^{-1})
Ag(111)	Pb	0.15	−28.9	184.3	265.3	213.2
Ag(111)	Tl	0.25	−24.1	166.6	265.3	190.7
Au(111)	Pb	0.20	−38.6	184.3	337.2	222.9

phases, respectively. The double layer term ΔG_{dl} is related to changes of the double layer structure when the substrate/electrolyte interface is substituted by the 2DMe/electrolyte interface. The last term $N_A \epsilon$ (where ϵ represents the strain energy per atom) is included to take into account the strain of the condensed 2D Me phase, which for example can be induced by a strong Me–S interaction [5, 6, 10].

So far, the concept of interpretation of the UPD is not new, as summarized in [5]. However, with the separation of the free energy of formation into different terms, one has to discuss their relative significance. It can be shown in the following discussion that well-defined conditions exist when the entropy term, the double layer term and the strain energy term in Eq. 11 are small compared with the formation enthalpy.

Let us firstly discuss the entropy term ($S_{2DMe} - S_{3DMe}$) in Eq. 11. When the UPD process is more like an adsorption process, a considerable difference between the entropy values is possible. Otherwise, when the monolayers of the bulk metal and the condensed 2D Me phase have the same close-packed structure, this term will be very small. Under these conditions the package densities of both monolayers and the corresponding mean volumes of atom vibration in the layers, $\tilde{v}_{2DMe}$ and $\tilde{v}_{3DMe}$ [5, 11], are similar, which leads also to similar S_{2DMe} and S_{3DMe} values according to the equation:

$$S_{2DMe} - S_{3DMe} = R \ln\left(\frac{\tilde{v}_{2DMe}}{\tilde{v}_{3DMe}}\right) \qquad (12)$$

Deviations from complete epitaxy, tensions, misfits, etc., influence the energy of interaction between the substrate S and the UPD layer, but have less influence on the entropy.

The next term in Eq. 11 to be discussed is the double layer term ΔG_{dl}. If on both metals only solvent molecules are physisorbed and the anion chemisorption can be neglected (e.g. ClO$_4^-$), this term is very small. It will become a more important term if the specific adsorption of anions must be taken into account and if the specific adsorption differs between substrate and UPD metal.

The contribution of the strain energy term $N_A \epsilon$ can be estimated by considering a compressed close-packed (2D hcp) UPD monolayer, which behaves as an isotropic elastic medium [5, 10]. In this case the strain energy per atom, ϵ, can be expressed by the equation:

$$\epsilon = 2(\lambda + \mu)v\left(\frac{d_0 - d}{d_0}\right)^2 \qquad (13)$$

where λ and μ are the Lamé coefficients, v is the atomic volume in an uncompressed monolayer, and d_0 and d represent the nearest-neighbour distances in the uncompressed and compressed monolayers, respectively. The relative compression, $(d_0-d)/d$, of condensed 2D hcp monolayers obtained experimentally in many UPD systems ranges between 1% and 3% [5]. A value of $\epsilon = 1.2 \times 10^{-21}$ J is estimated from Eq. 13 for a relative compression of 2% using typical values of $v = 3 \times 10^{-29}$ $v = 3 \times 10^{-29}$ m^3 and $(\lambda + \mu) \approx 10^{11}$ N m^{-2} [5, 10]. The corresponding strain energy contribution $N_A \epsilon$ is about 0.7 kJ mol^{-1} and can also be neglected since the observed experimental values for $zF\Delta_f E_{2DMe}$ usually range from 10 to 100 kJ mol^{-1} (see Table 1).

If the entropy difference, the double layer term and the strain energy contribution can be neglected, $\Delta_f G_{2DMe}$ is approximately equal to the enthalpy difference between Me in the UPD modification and in the bulk form. This is the formation enthalpy of the condensed UPD monolayer:

$$\Delta_f G_{2DMe} = \Delta_f H_{2DMe} \qquad (14)$$

The formation enthalpy can be used to calculate other thermodynamic data for the UPD modification of the metal. From the Born–Haber cycle, shown in Fig. 2, a formula can be derived to calculate from the sublimation enthalpy of the bulk metal the sublimation enthalpy of the UPD modification:
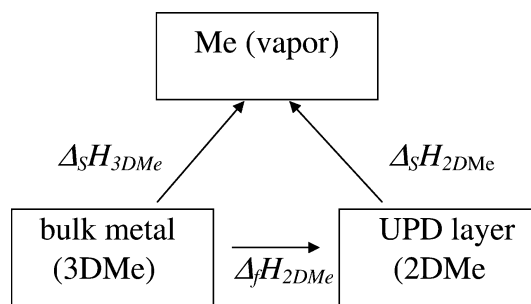
Fig. 2 Born–Haber cycle to derive the relation between the sublimation enthalpy of bulk Me phase, $\Delta_s H_{3DMe}$, and the formation and sublimation enthalpies of the condensed UPD Me layer

$$\Delta_s H_{2DMe} = \Delta_s H_{3DMe} - \Delta_f H_{2DMe} \qquad (15)$$

The comparison between the sublimation enthalpies of both components S and Me and of the UPD modification of Me on S provides a first insight into the structure-forming forces in the alloy.

Prerequisite to this discussion is that the condensed UPD layer is a close-packed layer of the same 2D structure as the corresponding monolayer of the bulk metal and consists of fully discharged atoms ($\delta = z$). Such a layer can be described as a condensed 2D Me phase, where atoms are bound to the substrate S by an average number of bonds depending on the crystallographic structure of S and the degree of 2DMe/S commensurability.

From sublimation enthalpies to bond energies

It was shown by Volmer [11] that the energy to separate an atom from a kink site position ("Halbkristallage"), i.e. the bond energy of an atom in the kink site position $\phi_{1/2}$, is obtained approximately by the following equation:

$$\phi_{1/2} = \frac{\Delta_s H}{N_A} + \frac{1}{2}kT \qquad (16)$$

where $\Delta_s H$ is the sublimation enthalpy, k is the Boltzmann constant and T the Kelvin temperature. For metals, however, the typical $\Delta_s H$ values amount to several hundred kJ mol^{-1} (cf. Table 1) and the contribution of the term $\frac{1}{2}kT$ in Eq. 16 can be neglected.

The structure of the kink site position differs with the crystal structure and the crystallographic face. Only low-index, atomically smooth G_I faces (equilibrium form faces) [12, 13, 14] with high atomic density and dominating energetic contributions from first nearest neighbors will be discussed.

In calculating the bond energy of atoms in the kink site position, contributions from second and third nearest neighbours are neglected. However, contributions of second and third nearest neighbours can be taken into account if the lattice type and the crystal structure demands this. The UPD layers formed on the G_I faces of the substrate are also subject to some restrictions. While a number of overlay structures is possible, in principle, only structures representing a high degree of compactness can be used for the anticipated purpose. This demands some degree of commensurability, as is shown in the following description of the most frequent substrate structures. The best fit is achieved when the atoms of the substrate and the atoms of the UPD metal have similar diameters. Then an approximately epitaxial UPD layer is formed.

For the face-centred cubic (fcc) lattice, which is a cubic close packed (ccp) structure, the number of nearest neighbours of an atom in the bulk is 12. An atom in the kink site position has six nearest neighbours and is characterized by a bond energy $\phi_{1/2}$ given by:

$$\phi_{1/2} = 6\phi_{Me\text{-}Me} \qquad (17)$$

where $\phi_{Me\text{-}Me}$ is the bond energy between nearest neighbours in the 3D bulk Me phase. For metal crystals with a fcc lattice, G_I faces are the (111) and (100) faces (cf. Figs. 3 and 4) [12, 13, 14].

In the hexagonal close-packed (hcp) crystal structure the number of nearest neighbours in the bulk is again 12 and the bond energy of an atom in the kink site position is again given by Eq. 17. The G_I face of metal crystals with this lattice is the (0001) face [12, 13, 14], which has the same atomic structure as the (111) face of metal crystals with a fcc lattice (cf. Fig. 3).

On foreign S(111) and S(0001) crystal substrates, condensed close-packed UPD Me layers consisting of Me atoms of similar size as the substrate S atoms have a 2D hcp Me structure (cf. Fig. 3). The bond energy of a Me atom in the corresponding kink site position can be expressed by:

$$\phi_{1/2} = 3\phi_{Me\text{-}S} + 3\phi_{Me\text{-}Me} \qquad (18)$$

where $\phi_{Me\text{-}S}$ is the bond energy between a Me atom and its closest S atom. In systems with similar sizes of Me and S atoms, a condensed UPD Me layer on a S(100) face of a fcc crystal has a quadratic S(100)–(1×1)Me structure (cf. Fig. 4) and the bond energy in the kink site position is given by the equation:

$$\phi_{1/2} = 4\phi_{Me\text{-}S} + 2\phi_{Me\text{-}Me} \qquad (19)$$

The terms $3\phi_{Me\text{-}S}$ and $4\phi_{Me\text{-}S}$ in Eqs. 16 and 17 represent the bond energies of isolated single Me adatoms on the corresponding crystal faces.

With increasing size of the UPD Me atoms, and particularly on S(100) substrates, a formation of less dense expanded UPD Me layers becomes possible at low coverage [5]. The interatomic distance in such layers is larger than the nearest neighbour distance in the 3D Me bulk phase and the lateral Me–Me bond energy in the UPD layer no longer corresponds to $\phi_{Me\text{-}Me}$. A similar
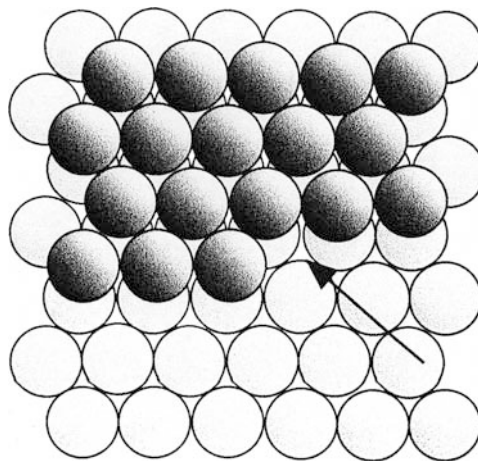

Fig. 3 Kink site on a (111) face of a fcc lattice and on a (0001) face of a hcp lattice
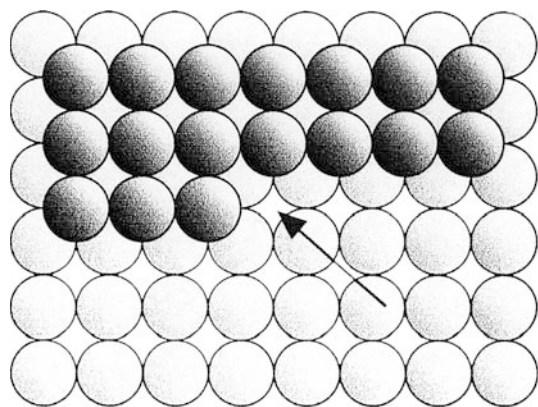
Fig. 4 Kink site on a (100) face of a fcc lattice

situation arises also if the UPD Me atoms are smaller then the S atoms. In this case the Me–Me distance between the nearest neighbours in the UPD Me layer again becomes larger than those in the bulk Me phase and the proposed analysis is no longer applicable.

Calculation of bond energies for some examples

In this section, some selected examples from the literature are used for the demonstration of the given analysis. The examples are based on UPD systems involving close-packed G_I faces as substrates and UPD metals forming condensed close-packed UPD layers consisting of completely discharged ($\delta = z$) Me atoms (cf. Table 1). All UPD systems are characterized by an electrosorption valence of $\gamma = z$ and an absence of specific adsorption of anions. The underpotentials $\Delta_f E_{2DMe}$ for the formation of the UPD layers are the average values between the corresponding cathodic and anodic peaks in cyclic voltammograms. The main characteristics of selected UPD systems are summarized below.

1. The system $Ag(111)/Pb^{2+}$ ($NaClO_4/HClO_4$ supporting electrolyte) [5, 6, 7, 15, 16, 17]. Both Ag and Pb have a fcc crystal structure. The diameter of Pb atoms ($d_{Pb} = 0.3500$ nm) is larger then those of Ag atoms ($d_{Ag} = 0.2890$ nm). A condensed UPD Pb monolayer with a 2D hcp structure is formed on the Ag(111) substrate at an underpotential of $\Delta_f E_{2DPb} = 0.15$ V. The Pb–Ag mismatch results in some incommensurability of the hcp Pb monolayer with the Ag(111)

substrate, but it can be assumed that this dos not significantly influence the bond energy calculation.

2. The system $Ag(111)/Tl^+$ ($NaClO_4/HClO_4$ supporting electrolyte) [5, 18, 19]. Thallium is characterized by a hcp crystal structure and an atomic diameter of $d_{Tl} = 0.3400$ nm. The UPD behaviour of Tl on Ag is very similar to Pb. A condensed UPD Tl monolayer with a 2D hcp structure is formed on Ag(111) at an underpotential of $\Delta_f E_{2DTl} = 0.25$ V. A second UPD Tl monolayer is deposited in this system at very low underpotentials.

3. The system $Au(111)/Pb^{2+}$ ($NaClO_4/HClO_4$ supporting electrolyte) [5, 20, 21]. This system has very similar characteristics to the system $Ag(111)/Pb^{2+}$. Gold has the same fcc crystal structure as Ag and a similar atomic diameter ($d_{Au} = 0.2884$ nm). Thus, a condensed UPD Pb monolayer with a 2D hcp structure is formed also in this system at an underpotential of $\Delta_f E_{2DTl} = 0.2$ V.

The values of the final calculation of the sublimation enthalpies $\Delta_s H_{2DMe}$ of condensed 2D Me phases using Eqs. 10, 14 and 15 are summarized in Table 1 together with the sublimation enthalpies $\Delta_s H_{3DMe}$ and $\Delta_s H_{3DS}$ of corresponding 3D Me and S bulk phases. Table 2 shows the bond energies $\phi_{1/2}$ of metal atoms in kink site positions as well as the Me–Me and Me–S bond energies ϕ_{Me-Me} and ϕ_{Me-S} determined from sublimation enthalpies using Eqs. 16, 17, 18.

The Pb–Ag bond energy ϕ_{Pb-Ag} can be estimated from results obtained in the UPD system $Ag(100)/Pb^{2+}$, ClO_4^- by applying a different analysis. An expanded UPD Pb layer with a Ag(100)–c(2×2)Pb structure is formed in this system at relatively low surface coverage by localized adsorption [5, 22]. In this case, each Pb atom in the compact adsorbed monolayer covers effectively two adsorption sites. Thus, the process was considered as a 1/2 adsorption on a square lattice and was studied by Monte Carlo simulation [5]. The fit of experimental coverage data with the Monte Carlo simulation data yields a value of $\phi_{Pb_{ads} - Pb_{ads}} = 2.5 \times 10^{-21}$ J for the bond energy between nearest neighbours in the adlayer [5]. This value is about one order of magnitude lower then the value for the Pb–Pb bond energy in the 3D Pb bulk phase (cf. Table 2), as could be expected from the much larger Pb_{ads}–Pb_{ads} distance in the expanded Ag(100)–c(2×2)Pb adlayer. The ϕ_{Pb-Ag} bond energy can be estimated from the value of the characteristic underpotential ΔE^* corresponding to a degree of coverage $\theta = 0.5$ using the following equation (cf. eq. 3.21 in [5]):

Table 2 Bond energies in kink site positions of substrates ($\phi_{1/2(3DS)}$), Me bulk phases ($\phi_{1/2(3DMe)}$) and condensed 2D Me phases ($\phi_{1/2(2DMe)}$), and single bond energies (ϕ_{Me-Me} and ϕ_{Me-S}) calculated from the data in Table 1

Substrate (S)	UPD metal (Me)	$\phi_{1/2(3DMe)}$ (J×10²⁰)	ϕ_{Me-Me} (J×10²⁰)	$\phi_{1/2(3DS)}$ (J×10²⁰)	$\phi_{1/2(2DMe)}$ (J×10²⁰)	ϕ_{Me-S} (J×10²⁰)
Ag(111)	Pb	30.6	5.1	44	35.4	6.7
Ag(111)	Tl	27.7	4.6	44	31.7	6.0
Au(111)	Pb	30.6	5.1	56	37	7.2

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$$\frac{\Delta_{\mathrm{des}}H}{N_{\mathrm{A}}} = 4\phi_{\mathrm{Pb\text{-}Ag}} = \frac{2F\Delta E^*}{N_{\mathrm{A}}} + \phi_{1/2(\mathrm{3DPb})} - 2\phi_{\mathrm{Pb_{ads}\text{-}Pb_{ads}}}$$
$$(20)$$

where $\Delta_{\mathrm{des}}H$ and $\phi_{1/2(\mathrm{3DPb})}$ represent the desorption enthalpy of an isolated single Pb adatom and the bond energy of a Pb atom in the kink site position of the 3D Pb bulk phase, respectively. With $\Delta E^* = 0.145$ V, $\phi_{1/2(\mathrm{3DPb})} = 30.6 \times 10^{-20}$ J, a Pb–Ag bond energy of $\phi_{\mathrm{Pb\text{-}Ag}} = 8.7 \times 10^{-20}$ J is obtained, which is close to the value of $\phi_{\mathrm{Pb\text{-}Ag}} = 6.7 \times 10^{-20}$ J (cf. Table 2) determined by applying the analysis described in earlier sections.

Conclusions

A procedure was suggested to determine bond energies between the components Me and S of an alloy. The procedure is based on measuring the characteristic potential for formation of a condensed close-packed UPD layer of the less noble metal Me on a densely packed crystal face of the more noble metal S as a substrate. Values for the Me–S bond energy were determined for selected Me/S UPD systems characterized by the absence of specific anion adsorption and by formation of close-packed UPD layers consisting of completely discharged metal atoms.

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