Thermodynamic analysis of electrodeposition of copper from copper sulphate

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Abstract. The free energy of activation of copper electrodeposition from copper sulphate solution is derived in terms of the dehydration energy of copper sulphate, hydration number of copper sulphate, solvated work function of the host metal and coordination number of the host metal on which the copper deposition is carried out. The free energy of activation for copper electrodeposition on 31 different host metals had been evaluated. The trend in the free energy of activation on different metals is studied and feasible electrodeposition of copper for appropriate applications had been suggested. The methodology is extended to obtain the exchange current densities for copper electrodeposition on different surfaces of Pt in acid medium and compared with the existing literature.

Keywords. Copper sulphate; copper electrodeposition; thermodynamics; free energy of activation; work function.

1. Introduction

Due to miniaturization of electronic devices, the need for thin-film materials replacing bulk material becomes inevitable [1,2]. Microelectronic devices, solar cells and magnetic devices [3–5] are few applications that utilize thin films. Thin films gained importance in these devices due to their capability to improve electrical, magnetic, optical and mechanical properties that results in the increase of efficiency of the devices. As grain size increases in thin films, resistivity decreases, hardness reduces and stress becomes tensile [6,7]. There are different synthesis routes to develop these thin films and electrodeposition technique is one among them. It has various advantages over other techniques, such as electrodeposition of large number of pure metal and alloys, easy to control via tailoring electrodeposition parameters, low processing temperature, deposits onto complex shapes and the production of non-equilibrium materials that cannot be accessed by traditional processes [8–12].

The electrochemical phase formations are usually associated with the nucleation and growth processes. The 3D nucleation and growth process include many stages: diffusion of ions to the electrode, discharge on its surface with resulting ad atoms, critical nuclei formation, crystal growth and overlap as a result of diffusion and ion

discharge on the crystal surface and also rearrangement of ad atoms onto a crystal lattice [13–19]. The competition between the nucleation and growth processes determines the granularity of the deposit [18] and are influenced by the different operating parameters, such as bath composition, pH, bath temperature, over potential, bath additives, etc. [4,20–24].

In the present work, a phenomenological thermodynamic approach is employed to evaluate the free energy of activation and heterogeneous rate constant for electrodeposition of copper on 31 different host metal surfaces from CuSO₄ electrolyte solution. The free energy of activation is written in terms of work function of the host metal, coordination number of host metal, dehydration energy of CuSO₄, hydration number of CuSO₄ in bulk and interface and metal–Cu bond formation energy. The variation of free energy of activation and the heterogeneous rate constant for copper electrodeposition on various parameters have been evaluated. Calibration graphs for identification of ideal combination of host metal to attain low free energy of activation and high heterogeneous rate constant is identified and discussed. As a proof of concept, the methodology is utilized to calculate the exchange current density of copper deposition on different Pt surfaces in acid medium.

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2. Methodology

The free energy of activation for any reaction on a metal/electrolyte interface can be written as [25,26]

$$\Delta G^\ddagger = \frac{w_r + w_p}{2} + \Delta G_{\text{et}}^s, \quad (1)$$

where w_r and w_p are the work terms involved in the transport of the reactant and the product species from bulk of the solution to interface and metal/electrolyte interface to the bulk, respectively. ΔG_{et}^s denotes the free energy change involved in the electron transfer from the solvated electrode surface (in the present case, solvent is water) to the reactant species. Equation (1) is the reminiscent of Marcus theory [27].

The work terms for the transport processes can be written via the hydration behaviour of the electrolyte and the electrode surface. The electrolyte molecules diffuse from the bulk of the solution to the reaction zone (metal/electrolyte interface) by progressive shedding of their hydration sheath. In the reaction zone, the electrolyte molecules are almost dehydrated and hence, w_r and w_p can be written as

$$w_r = \frac{N_{\text{h inter}}^r}{N_{\text{h bulk}}^r} \Delta G_{\text{dehyd}}^r \quad (2)$$

and

$$w_p = \frac{N_{\text{h inter}}^p}{N_{\text{h bulk}}^p} \Delta G_{\text{hyd}}^p, \quad (3)$$

where $N_{\text{h inter}}^r$ and $N_{\text{h bulk}}^r$ denote the hydration number of the reactant species at the interface and the bulk, respectively. Analogously, $N_{\text{h inter}}^p$ and $N_{\text{h bulk}}^p$ are the hydration number corresponding to the product at the interface and bulk, respectively. The ratios $N_{\text{h inter}}^r/N_{\text{h bulk}}^r$ and $N_{\text{h inter}}^p/N_{\text{h bulk}}^p$ indicate the percentage variation of the hydration number of the reactant and the product species while getting transported from bulk of the solution to the metal/electrolyte interface. $\Delta G_{\text{dehyd}}^r$ and ΔG_{hyd}^p represent the dehydration and hydration energy of the reactant and product species, respectively.

The free energy change involved in the electron transfer process depends on the hydration behaviour and work function of the metal electrode under consideration. Thus,

$$\Delta G_{\text{et}}^s = -\frac{nF\Phi_M^s}{\text{CN}_M}, \quad (4)$$

where n being the number of electrons involved in the process, F denotes the Faraday constant, Φ_M^s represents the solvated work function of the metal electrode and CN_M is the coordination number (here the coordination number is a first-step approximation for coverage of copper on metal surface) of the metal electrode. The coordination number quantitatively takes account of the surface anisotropy of the

electrode surface. Therefore, the free energy of activation for any electron transfer process at the reaction zone is written as

$$\Delta G^\ddagger = \frac{N_{\text{h inter}}^r}{N_{\text{h bulk}}^r} \Delta G_{\text{dehyd}}^r + \frac{N_{\text{h inter}}^p}{N_{\text{h bulk}}^p} \Delta G_{\text{hyd}}^p - \frac{nF\Phi_M^s}{\text{CN}_M}. \quad (5)$$

Equation (5) is the general equation for electron transfer process, where there exists no adsorption of the product on the electrode surface. Assuming that the process is reversible, product formed on the electrode surface has two ways to proceed with: (i) get oxidized and return back to solution or (ii) irreversibly adsorb onto the metal surface. Equation (5) holds good for case (i); for case (ii), equation (5) is modified as

$$\Delta G^\ddagger = \frac{N_{\text{h inter}}^r}{N_{\text{h bulk}}^r} \Delta G_{\text{dehyd}}^r + \frac{N_{\text{h inter}}^p}{N_{\text{h bulk}}^p} \Delta G_{\text{hyd}}^p - \frac{nF\Phi_M^s}{\text{CN}_M} + \frac{\Delta G_{\text{M-p}}^{\text{form}}}{\text{CN}_M}, \quad (6)$$

where $\Delta G_{\text{M-p}}^{\text{form}}$ indicate the free energy of bond formation between the metal electrode 'M' and the product 'p'.

2.1 Free energy of activation for copper deposition from CuSO_4

The electrolyte is CuSO_4 and the electron transfer occurs in two steps: first, reduction of Cu^{2+} to Cu^+ and second, reduction of Cu^+ to Cu atoms on the plane site of the metal electrode. Although the mechanism suggested for copper deposition in the literature [28] is as follows:

the work terms involving Cu^+ ions are not included in the present methodology. (In the present case, the work done by reactants and products are written in terms of the corresponding free energies. As the product of step I is the reactant in step II, any work terms associated with Cu^+ will cancel out upon summation. Hence, we have shown only the involvement of Cu^{2+} and Cu species in the work terms. Hence, the mechanism assumed by us is not different from Newman *et al* [28] and is applicable for all metals.) The formed Cu atoms diffuse on the surface of the electrode and get deposited on the kink, edge and vacancies of the electrode surface. After the insertion of copper atoms into the lattice of the metal electrode (vacancy sites), the copper atoms completely dehydrates. Until then the copper atoms are hydrated, although not completely, but to a lesser extent. The free energy of activation for copper deposition process is visualized as three different steps: (i) the transport of the electrolyte as a molecule to the reaction zone, accounted by the hydration numbers

and dehydration energies, (ii) the reduction of the electrolyte into Cu atoms on the plane surface of the electrode via two single electron transfer steps and (iii) surface diffusion of the Cu atoms to kink, edge and vacancies of the electrode.

The free energy and work term contributions to the free energy of activation for copper deposition on the metal electrode employing CuSO_4 as the electrolyte can be written as

$$w_{\text{CuSO}_4} = \frac{N_{\text{h inter}}^{\text{CuSO}_4}}{N_{\text{h bulk}}^{\text{CuSO}_4}} \Delta G_{\text{dehyd}}^{\text{CuSO}_4} \quad (7)$$

and

$$w_{\text{Cu}} = \frac{N_{\text{h inter}}^{\text{Cu}}}{N_{\text{h bulk}}^{\text{Cu}}} \Delta G_{\text{hyd}}^{\text{Cu}}, \quad (8)$$

where w_{CuSO_4} and w_{Cu} denote the work done by the reactant CuSO_4 and the product Cu to reach the reaction zone from the bulk of the solution and vice versa. The free energy due to the electron transfer process (for $n = 2$) can be given as

$$\Delta G_{\text{et}}^s = -\frac{2F\Phi_M^s}{\text{CN}_M}. \quad (9)$$

Since there is chemisorption of the Cu atoms formed on the electrode surface, equation (6) is valid. Hence,

$$\begin{aligned} \Delta G^\ddagger = & \frac{N_{\text{h inter}}^{\text{CuSO}_4}}{N_{\text{h bulk}}^{\text{CuSO}_4}} \Delta G_{\text{dehyd}}^{\text{CuSO}_4} + \frac{N_{\text{h inter}}^{\text{Cu}}}{N_{\text{h bulk}}^{\text{Cu}}} \Delta G_{\text{hyd}}^{\text{Cu}} \\ & - \frac{2F\Phi_M^s}{\text{CN}_M} + \frac{\Delta G_{\text{M-Cu}}^{\text{form}}}{\text{CN}_M}. \end{aligned} \quad (10)$$

Equation (10) implies the explicit relationship between the hydration behaviour of reactant and product species, nature of metal electrode and the bonding characteristics of the copper atoms on the electrode surface with the free energy of activation of the electrochemical copper deposition process. The insertion of the formed copper atoms in the vacant sites of the electrode surface causes coordination variation in the lattice of the metal electrode which is taken into account via the inclusion of the parameter CN_M in equations (5 and 10).

Upon revoking the Arrhenius equation, the heterogeneous rate constant can be written as

$$k_{\text{et}} = C \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{k_B T}\right), \quad (11)$$

where C is the bulk concentration of the electrolyte, k_B the Boltzmann constant, T the temperature and h the Planck's constant.

3. Results and discussion

From equation (10), by employing parameters such as the concentration to be 6.023×10^{-5} molal, dehydration energy for CuSO_4 ($\Delta G_{\text{dehyd}}^{\text{CuSO}_4}$) as 712 kJ mol^{-1} , hydration number for CuSO_4 at bulk ($N_{\text{h bulk}}^{\text{CuSO}_4}$) to be 671, at interface ($N_{\text{h inter}}^{\text{CuSO}_4}$) being 346, the free energy of activation ($\Delta G^\ddagger$) for copper electrodeposition on 31 different host metals at room temperature is calculated. The obtained free energy of activation is provided in table 1. From equation (11), the heterogeneous rate constant is calculated for the process and tabulated in table 1.

3.1 Dependence of free energy of activation on metal–copper formation energy

Figure 1 shows the variation of free energy of activation with the M–Cu bond formation energy, as this parameter determines the stability of the coatings. From figure 1, it is clear that the variation of $\Delta G^\ddagger$ with $\Delta G_{\text{M-Cu}}^{\text{form}}$ to be linear as suggested in equation (10). The linear fitting of the plot leads to

$$\Delta G^\ddagger = 0.12 \Delta G_{\text{M-Cu}}^{\text{form}} + 3900. \quad (12)$$

Upon comparing equations (10 and 12), the physical significance of slope and intercept can be written from the following terms:

$$\text{Slope: } \frac{1}{\text{CN}_M}$$

and

$$\text{Intercept: } \frac{N_{\text{h inter}}^{\text{CuSO}_4}}{N_{\text{h bulk}}^{\text{CuSO}_4}} \Delta G_{\text{dehyd}}^{\text{CuSO}_4} + \frac{N_{\text{h inter}}^{\text{Cu}}}{N_{\text{h bulk}}^{\text{Cu}}} \Delta G_{\text{hyd}}^{\text{Cu}} - \frac{2F\Phi_M^s}{\text{CN}_M}.$$

Thus, slope represents the electrodeposition of Cu dependence on the coordination number of the host metal. CN_M represents the number of atoms of Cu that can be deposited on a lattice site (analogous to surface coverage θ). Whereas the intercept is the summation of all hydration terms of CuSO_4 , Cu and the solvated work function of the host metal. Thus, any change in the solvation characteristics of the electrolyte and electrode will be reflected in the intercept. Therefore, for any host metal, the free energy of activation can be deduced with the help of figure 1 and equation (12). Figure 1 can act as a calibration curve to pick and choose the host metal for copper electrodeposition depending upon its application.

3.2 Variation of free energy of activation for copper electrodeposition with work function of host metal

Figure 2 implies that the variation of free energy of activation for copper electrodeposition with the work function of host metal to be complex. Depending on the physical state of the metal, the free energy of activation for the process varies. Tantalum being the reactive metal, forms oxide on the surface and

Table 1. Free energy of activation for copper electrodeposition on 31 different metals at room temperature at 6.023×10^{-5} molal concentration with dehydration energy of 712 kJ mol^{-1} . The hydration number for CuSO_4 at bulk is 671 and at interface is 346.

Metal	Work function (eV)	Coordination number	Metal–Cu bond formation energy (kJ mol^{-1})	Free energy of activation (kJ mol^{-1})	Heterogeneous rate constant ($\text{mol cm}^{-3} \text{ s}^{-1}$)
Zn	3.63	6	412	454.56	4.71×10^{-18}
Tl	3.84	8	198	414.74	4.49×10^{-11}
Hg	3.9	6	202	418.08	1.17×10^{-11}
Mn	3.9	6	159	410.92	2.11×10^{-10}
Cd	4.08	6	305	434.26	1.70×10^{-14}
In	4.08	8	247	420	5.64×10^{-12}
Bi	4.1	8	289.5	425.11	6.83×10^{-13}
Ti	4.1	8	381	436.55	6.75×10^{-15}
Sn	4.15	8	401.3	438.88	2.63×10^{-15}
Pb	4.18	8	177	410.72	2.28×10^{-10}
Nb	4.2	8	177	410.64	2.35×10^{-10}
Ta	4.22	8	811.21	489.84	3.09×10^{-24}
Ga	4.25	8	138	405.56	1.83×10^{-9}
Ag	4.3	2	176	423.2	1.48×10^{-12}
Mo	4.3	6	197	415.06	3.95×10^{-11}
Cr	4.4	6	155	407.51	8.31×10^{-10}
Sb	4.55	8	277.4	421.76	2.65×10^{-12}
W	4.55	8	305	425.21	6.58×10^{-13}
Fe	4.65	8	172	408.17	6.37×10^{-10}
Co	4.7	8	162	406.72	1.15×10^{-9}
Cu	4.7	6	202	413.71	6.82×10^{-11}
Ru	4.71	8	397	436.05	8.27×10^{-15}
Re	4.72	6	280	426.6	3.75×10^{-13}
Ni	4.73	4	206	418.44	1.01×10^{-11}
Al	4.78	6	216	415.6	3.17×10^{-11}
Au	4.78	4	232	424.53	8.63×10^{-13}
Os	4.83	8	198	410.68	2.31×10^{-10}
Ir	4.97	8	352	429.36	1.23×10^{-13}
Rh	4.98	6	395	444.34	2.91×10^{-16}
Pd	5.01	6	234	417.35	1.57×10^{-11}
Pt	5.03	8	478	444.86	2.36×10^{-16}

hence its free energy of activation is the highest amongst the host metals considered in the present work. On the other hand, remaining d block metals (transition metals), such as Fe, Co, Ni, Au, Ag, Pt, Pd, Rh, etc. show lower free energy of activation than the reactive tantalum. From figure 2, the experiments involving copper electrodeposition can be designed based on the free energy of activation variation with host metal work function. The combination of low $\Delta G^\ddagger$ with Φ_M of the host metal can be identified from figure 2 and that can be utilized for easy and facile electrodeposition of copper depending on its applications.

3.3 Variation of free energy of activation with coordination number of the host metals

From equation (10), it is clear that as the coordination number increases, the free energy of activation for copper electrodeposition decreases. This decrease in free energy of activation

with increase in coordination number could be attributed to the inverse proportionality of CN_M in equation (10) to $\Delta G^\ddagger$. Thus, as coordination number increases, the effect of the host metal on the electrodeposition process decreases and consequently the energetic solvation predominates. Therefore, for metals, such as Zn, Mn, Cd, Hg and Mo, copper electrodeposition is fairly feasible upon comparison with rest of the host metals considered in the present work (figure 3).

3.4 Trend in the variation of heterogeneous rate constant with metal–copper bond formation energy

As suggested by equations (10 and 12), the heterogeneous rate constant depends on the M–Cu bond formation energy exponentially. As the M–Cu bond formation energy increases, the k_{et} varies from 10^{-9} to $10^{-18} \text{ mol cm}^{-3} \text{ s}^{-1}$, thus indicating the fact that the host metals with lower M–Cu bond formation

Figure 1. Dependency of $\Delta G^\ddagger$ (kJ mol^{-1}) with $\Delta G_{\text{M-Cu}}^{\text{form}}$ (kJ mol^{-1}).

Figure 2. Plot of work function of various metals with the activation energy of Cu electrodeposition.

energy will possess higher heterogeneous rate for copper electrodeposition. Thus, figure 4 can help the experimentalists to identify the host metal with higher heterogeneous rate constant for copper electrodeposition and hence, can be useful to design the experiment for the required specific applications.

3.5 Effect of work function of host metal on the heterogeneous rate constant of copper electrodeposition

Figure 5 implies complex trend and dependency of heterogeneous rate constant of copper electrodeposition with work function of host metal. As discussed in section 3.2, the

Figure 3. Trend in free energy of activation with coordination number of the host metal.

free energy of activation is very high for Ta and hence, the rate of deposition of copper will be very low. Thus, Ta possesses a heterogeneous rate constant of the order $10^{-18} \text{ mol cm}^{-3} \text{ s}^{-1}$. Analogously, metals belonging to the d-block in the Periodic Table, such as Au, Ag, Pt, Pd, Rh, Zn, Fe, Co, etc. possess lower free energy of activation and higher heterogeneous rate constants.

3.6 Effect of coordination number of host metal on the heterogeneous rate constant

From figure 6, it can be inferred that as the coordination number increases, the heterogeneous rate constant increases. Equation (10) indicates that as the coordination number increases, the contribution by host metal work function and M–Cu bond formation on the free energy of activation decreases. This makes the solvation effects predominant

Figure 4. Dependency with M–Cu bond formation energy.

Figure 5. Variation of heterogeneous rate constant with work function of host metal.

Figure 6. Effect of coordination number of the host metal on the heterogeneous rate constant.

at higher coordination numbers. Host metals with higher coordination numbers, such as Zn, Cd, Mn, Mo and Hg

will possess higher heterogeneous rate constant for copper electrodeposition on their surfaces. Higher coordination number leads to more vacant sites on the surface, hence, feasibility of copper electrodeposition is very high. In general, electrodeposition initiates on the voids or vacant sites or defects of the host metal, thus, increase in coordination number increases the rate of the electrodeposition.

3.7 Modified free energy of activation for copper electrodeposition from CuSO_4 in acidic medium

In general, copper electrodeposition experiments were carried out in the literature from the CuSO_4 electrolyte on polycrystalline and single-crystal platinum surfaces in acidic medium [29–33]. Hence, the above discussed mechanism to evaluate the electrode kinetics will not be applicable. Therefore, equation (10) is modified as below:

$$\Delta G^\ddagger = \frac{N_{\text{h inter}}^{\text{CuSO}_4}}{N_{\text{h bulk}}^{\text{CuSO}_4}} \Delta G_{\text{dehyd}}^{\text{CuSO}_4} + \frac{N_{\text{h inter}}^{\text{Cu}}}{N_{\text{h bulk}}^{\text{Cu}}} \Delta G_{\text{hyd}}^{\text{Cu}} - 2\theta F \Phi_M^s + \theta \Delta G_{\text{M-Cu}}^{\text{form}}, \quad (13)$$

where the assumed coordination number is replaced by surface coverage ' θ '. The calculated $\Delta G^\ddagger$ from equation (13) is substituted in equation (11) to obtain the rate of reaction. Analogously, the exchange current density reported in the literature can be compared with the values calculated from equation (14) as follows:

$$i_0 = \frac{n F k_{\text{et}}}{CA} \quad (14)$$

where C is the bulk concentration of CuSO_4 in mol cm^{-3} and A is the area of the electrode in cm^2 . The calculated i_0 from equation (14) is in satisfactory agreement with the literature (table 2) thereby supporting the assumptions made

Table 2. Comparison of the exchange current densities calculated using equation (14) for copper deposition in acidic medium on different Pt surfaces with the reported values. Pt–Cu alloy formation energy is taken as -27 kJ mol^{-1} from ref. [45].

Metal surface	Work function (eV)	Area of electrode (cm ²)	Concentration (M)		Surface coverage, θ	i_0 (mA cm ⁻²)	i_{0_total} (reported) (mA cm ⁻²)
			CuSO ₄	H ₂ SO ₄			
Pt	5.03	0.1256 [29]	0.02	0.5	0.198	3.10	3.2 [29]
Pt(111)	6.10 [41]	0.2826 [43]	0.01	0.05	0.98	8.68×10^{-5}	0.01 [32]
			0.025	0.05	0.40	0.0018	0.012 [32]
			0.05	0.05	0.18	0.0144	0.015 [32]
			2×10^{-4}	0.5	0.43	0.0041	0.006 [33]
Pt(955)	6.25 [42]	0.074 [44]	2×10^{-4}	0.5	0.4	0.0044	0.003 [33]
Pt(544)	6.80 [42]	0.076 [44]	2×10^{-4}	0.5	0.46	0.0096	0.008 [33]
Pt(322)	5.93 [42]	0.074 [44]	2×10^{-4}	0.5			

to derive the free energy of activation. It is noted that upon diluting the CuSO₄ solution, hydrogen evolution kinetics predominates over copper deposition kinetics and this observation is in agreement with the experimental conclusions (supplementary figure S1).

4. Conclusions

It is a known fact that the copper deposits obtained at high-current densities and overpotentials are technologically important [34]. Copper deposits with open and porous structures obtained at high-current densities are used as electrodes in electrochemical devices [34,35], such as fuel cells, batteries and chemical sensors, whereas those of high-surface area are appropriate for evaluating electrochemical reactions such as nitrate ion reduction [36] and for the reaction in which nitrate is reduced to ammonia (high yield) in the presence of aqueous acidic perchlorate and sulphate media [37]. As the dimensions of copper structures continue to scale down into the nanometre range, the initial stage of copper electroformation, i.e., nucleation becomes increasingly important [38]. The foregoing analysis has provided a simple framework whereby the energetics involved in the electrodeposition of copper can be computed efficiently. Several parameters such as the extent of variation of hydration numbers, coordination number, work function and dehydration energy are introduced and expressed parametrically in conjunction with intuitive chemical principles. In the present study, the formalism has been found to be valid for copper deposition from CuSO₄ solutions and several subtle features regarding the importance of using these electrolytes in the rate of reaction are pointed out. However, it can be reiterated that this formalism is essentially of a complementary nature to the existing literature [16,29–33,39,40] on electrodeposition of copper. The methodology itself is novel and different from other models reported in the literature. Metallic parameters like effect of anisotropy, porosity of the electrode can be included with significant variation in the present methodology by introducing (i) time dependency, (ii) connecting the free energy of activation to the flux via expression involving dc/dx , thermodynamic force, etc. as a future improvement in the methodology.

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References

- [1] Mararka S P and Gutmann R J 1993 *Thin Solid Films* **236** 257
- [2] Lane M W, Murray C E, McFeely F R, Vereecken P M and Rosenberg R 2003 *Appl. Phys. Lett.* **83** 2330
- [3] Zhang J M, Xu K W and Ji V 2002 *Appl. Surf. Sci.* **187** 60
- [4] Anderson J C 1972 *Thin Solid Films* **12** 1
- [5] Granneman E H A 1993 *Thin Solid Films* **228** 1
- [6] Yin K B, Xia Y D, Chan C Y and Zhang W Q 2008 *Scr. Mater.* **58** 65
- [7] Harper M E, Cabra C, Andricacos P C, Gignac L and Noyan I C 1999 *J. Appl. Phys.* **86** 2516
- [8] Wang H, Huang Y, Tan Z and Hu X 2004 *Anal. Chim. Acta* **526** 13
- [9] Podaha E J 2004 *Nano Lett.* **4** 413
- [10] Ibanez A and Fatas E 2005 *Surf. Coat. Technol.* **191** 7
- [11] Wijesundera R P, Hidaka M, Koga K, Sakai M and Siripala W 2006 *Thin Solid Films* **500** 241
- [12] Chatterjee A P, Mukhopadhyay A K, Chakraborty A K, Sasmal R N and Lahiri S K 1991 *Mater. Lett.* **11** 358
- [13] Mirkin M V and Nilov A P 1990 *J. Electroanal. Chem.* **283** 35
- [14] Ratsch C and Venables J A 2003 *J. Vac. Sci. Technol. A* **21** S96
- [15] Schmelzer J W P 2001 *J. Colloid Interface Sci.* **242** 354
- [16] Grujicic D and Pesic B 2002 *Electrochim. Acta* **47** 2901
- [17] Venables J A, Spiller G D T and Hanbucken M 1984 *Rep. Prog. Phys.* **47** 399
- [18] Budevski E, Staikov G and Lorenz W 2000 *Electrochim. Acta* **45** 2559
- [19] Scarifker B and Hills G 1983 *Electrochim. Acta* **28** 879
- [20] Zainal Z, Kassim A, Hussein M Z and Ching C H 2004 *Mater. Lett.* **58** 2199
- [21] Fenineche N, Coddet C and Saida A 1990 *Surf. Coat. Technol.* **41** 75
- [22] Dulal S M S I, Yun H J, Shin C B and Kim C K 2007 *Electrochim. Acta* **53** 934

- [23] Ruiz A M, Pardave M P and Batina N 2008 *Electrochim. Acta* **53** 2115
- [24] Ramirez C, Arce E M, Romo M and Pardave M P 2004 *Solid State Ionics* **169** 81
- [25] Harinipriya S and Subramaniam V R 2008 *J. Phys. Chem. B* **112** 4036
- [26] Harinipriya S and Sangaranarayanan M V 2002 *Langmuir* **18** 5572
- [27] Marcus R A 1956 *J. Chem. Phys.* **24** 966
- [28] Newman J and Alyea T K 2004 *Electrochemical systems*, chap 8, 3rd edn (New York: Wiley) p 207
- [29] Bozzini B, Mele C and D'urzo L 2006 *J. Appl. Electrochem.* **36** 87
- [30] Bozzini B, D'urzo L, Re M and De Richardis F 2008 *J. Appl. Electrochem.* **38** 1561
- [31] Bozzini B and Sgura I 2006 *J. Appl. Electrochem.* **36** 983
- [32] Markovic N M, Gasteiger H A and Ross P N Jr 1995 *Langmuir* **11** 4098
- [33] Nishihara C, Raspini I A, Kondho H, Shindo H, Kaise M and Nozoye H 1992 *J. Electroanal. Chem.* **338** 299
- [34] Nikolic N D, Popov K I, Pavlovic L J and Pavlovic M G 2007 *Sensors* **7** 1
- [35] Cheol S H, Dong J and Liu M 2003 *Adv. Mater.* **15** 1610
- [36] Dima G E, de Voos A C A and Koper M T M 2003 *J. Electroanal. Chem.* **15** 554
- [37] Pletcher D and Poorbedi Z 1979 *Electrochim. Acta* **24** 1253
- [38] Grujicic D and Pesic B 2005 *Electrochim. Acta* **50** 4426
- [39] Li X, Drews T O, Rusli E, Xue F, He Y, Braatz R D *et al* 2007 *J. Electrochem. Soc.* **154** D230
- [40] Rusli E, Xue F, Drews T O, Vereecken P, Andracacos P, Deligianni H *et al* 2007 *J. Electrochem. Soc.* **154** D584
- [41] Derry D N and Zhong Z J 1989 *Phys. Rev. B* **39** 1940
- [42] Buso-Rogero C, Herrero E, Bandlow J, Comas Vives A and Jacob T 2013 *Phys. Chem. Chem. Phys.* **15** 18671
- [43] Markovic N M, Gasteiger H A and Ross P N Jr 1995 *J. Phys. Chem.* **99** 3411
- [44] Nishihara C and Nozoye H 1995 *J. Electroanal. Chem.* **386** 75
- [45] Schroder U, Linke R, Boo J-H and Wnadelt K 1996 *Surf. Sci.* **352–354** 211