ON THE ASYMMETRICAL ROLE OF INTRINSIC DEFECTS IN THE COMPLEMENTARY/OPPOSING OXIDE FORMATION/DISSOLUTION REACTIONS

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Rates of chemical dissolution (r) of anodic oxide films on Sb, W, Al, Ti, Zr and Hf were studied as a function of the energy of defect formation (E_f) in the respective oxide. The value of r was estimated from capacitance measurements. The relation between ln r and E_f is linear. The average value of the symmetry factor (α) for the dissolution reaction is 0.12. The deviation of α from 0.5 indicates that intrinsic defects play an asymmetrical role; in the present case their constructive action is about 7 times their destructive action.

Study of the electrochemical behaviour of anodic oxide films is still interesting from both the theoretical and technical points of views. These oxides are principal materials in different fields[1,2] e.g. electrical, electronic and display devices, catalysis, energy conversions, surface finishing and corrosion.

Many studies have been made to attribute the electrochemical behaviour of these oxides to their fundamental properties. Of these properties one can mention: (i) metal–oxygen bond energy[3], (ii) jump distance of the moving ion in the oxide[4], (iii) charge carriers types and concentrations[5], (iv) thickness of the space charge region within the film[6], (v) band gap energy and flat band potential[7], (vi) profile of defects in the oxide[8], (vii) microstructures of the oxide[9], (viii) multilayer nature of the film[10].

From the implications of the previous concise survey one may conclude that defects in the oxide affect its quality either positively or negatively. The nature of these defects are likely to be: positively charged metal sites, discontinuity of a given crystal face, oxygen vacancies or metal interstitials.

A defective site is an active center for several reactions. Some of these reactions are opposing, e.g., further growth or dissolution of the oxide in corrosive environments[11,12]. Another example for pairs of opposing processes are hole and electron generation and recombination.

The aim of the present study is the estimation of the percent weight of the enhancing effect made by a defective site towards the pair of the opposing reactions; dissolution and formation.

EXPERIMENTAL

A 50 nm oxide film was formed galvanostatically on the mechanically polished parent metal surface in 0.05 mol/dm^3 H_2SO_4 at 5 . 10^{-3} A/cm^2 till the appropriate formation voltage. Thereafter the oxide film was allowed to dissolve freely in 0.25 mol/dm^3 H_2SO_4. The aluminium oxide film was formed and dissolved in 1.0 mol/dm^3 H_3PO_4 whereas that on hafnium was dissolved in 1.0 mol/dm^3 HCl. The solutions were aerated and kept at room temperature. The course of the dissolution process was followed by capacitance measurements. The rate of dissolution was estimated following the procedure described in ref.[13]. The rates of dissolution of the different oxides reported here were calculated from previously published data[14–19].

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the rate of dissolution (r) on the energy of defect formation (E_f) in the oxides of the cited metals. The relation is linear. The break in the curve is due to the fact that the oxides of the first group (Sb, W and Al) are more defective than those of the second group[10] (Ti, Zr and Hf). This linear relation is theoretically justifiable.

It has been shown previously that r is proportional to the concentration of the intrinsic defects [D] in a given oxide[8] thus

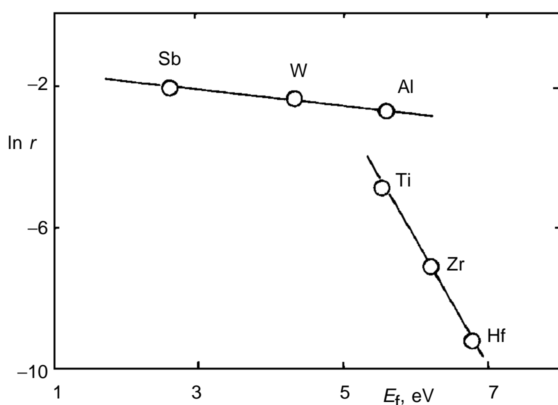

FIG. 1
Decrease of the logarithm of the rate of dissolution of a given anodic oxide film, ln r, with the respective metal–oxygen bond energy, E_f

$$r = k_1[\mathrm{D}] \quad . \tag{1}$$

[D] is related to E_f by the equation[20]

$$[\mathrm{D}] = k_2 \mathrm{e}^{-E_f/2\boldsymbol{k}T} \quad . \tag{2}$$

From (*1*) and (*2*)

$$r = k_1 k_2 \mathrm{e}^{-E_f/2\boldsymbol{k}T} \quad , \tag{3}$$

where k_1 and k_2 are proportionality constants, $\boldsymbol{k}$ is Boltzmann's constant and T is the absolute temperature.

The intrinsic defective site acts bifunctionally[11,12]; it enhances each of the two reverse processes; oxide formation and oxide dissolution. The oxide formation and oxide dissolution processes are complementary (occur simultaneously) with different rates to reach the equilibrium thickness under the prevailing condition[21]. So it is plausible to introduce a symmetry factor (α) to express the contribution of an intrinsic defective site towards each of the oxide dissolution and oxide formation reactions. Therefore Eq. (*3*) becomes

$$r = k_1 k_2 \mathrm{e}^{-\alpha E_f/2\boldsymbol{k}T} \quad . \tag{4}$$

From Fig. 1, α equals 0.015 and 0.22 for the oxides of the first and second group, respectively. The average value is 0.12.

If α is close to 0.5, it means that an intrinsic defective site enhances each of the oxide formation and oxide dissolution process equally. In the present case α is remote from 0.5, thus the intrinsic defects in the anodic oxide film enhance the dissolution process to a small extent (12%) whereas they enhance the reverse process, the oxide formation to a larger extent (88%) (average values).

From the results obtained it follows that the intrinsic defects in an anodic oxide film enhance the oxide formation (constructive) process 88/12 times the oxide dissolution (destructive) process. A question rises now: is this a general trend for the constructive role played by intrinsic defects in pairs of opposing reactions?

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