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# The structure and stoichiometry of anodic films on V, Nb, Ta, Mo and W

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Anodic films on Nb were found to have the expected amorphous structure for all formation voltages starting at 6 volts. Films on V, Ta, Mo, and W, on the other hand, were amorphous only when thick, with films below 9 to 30 nm (6 to 10 volts) showing a polycrystalline pattern by reflection electron diffraction. Although the patterns of the thin films were difficult to identify because of their poor quality, the following assignments are proposed: not $V_2O_5$, $TaO_z$ plus $\delta - Ta - O$, $MoO_2 \cdot H_2O$, $WO_2$. To get information on the stoichiometry of thick anodic films on V, Mo, and W, specimens were crystallized by heating them at 300 to 500° C in air, but it was shown that the resulting observation of $V_2O_5$, $MoO_3$, and $WO_3$ has no relevance, as oxidation is both thermodynamically and kinetically possible. Vacuum crystallization was shown to be quite unsatisfactory with V and Mo, though is possibly acceptable with W; the information obtained from a comparison of film weights with metal-removal weights, namely that the stoichiometries were close to $V_2O_5$, $MoO_3$, and $WO_3$, is more relevant. The stoichiometries $TaO_z$, $MoO_2 \cdot H_2O$, and $WO_2$ in the thin films are thermodynamically understandable. A greater problem arises in explaining the state of crystallinity of these as well as other anodic films. A parallel is proposed between anodic and ion-bombarded oxides, for in both cases the state of crystallinity tends to be the same and, furthermore, correlates with the ratio (crystallization temperature)/(melting temperature). A model based on crystallization due to energy deposition is discussed.

## 1. Introduction

Anodic films are found to be either amorphous or crystalline, depending on the material and on the conditions of anodizing. In particular, those on Hf, Sn, Zn and Zr are believed to be invariably crystalline [1–5], those on Ge, Mo, Si, V, and W are believed to be invariably amorphous [5–9], while those on Al, Be, Nb, Ta, Ti and U have been found to have a variable structure [5, 10–15]. If we regard amorphous films as the norm in the last 6 cases, then crystalline films can be said to appear under the following conditions:

| | |
|---|---|
| high anodizing temperature | Al, Nb, Ta, Ti |
| particular electrolytes | Be |
| small film thicknesses | U |
| large film thicknesses or long anodizing times | Al, Nb, Ta, Ti. |

In those instances where the films were crystalline, the stoichiometry could be determined directly by electron diffraction, the results being as follows for the metals considered in this paragraph: $HfO_2$, $SnO_2$, ZnO, $ZrO_2$, $Al_2O_3$, BeO, $Nb_2O_5$, $Ta_2O_5$, $TiO_2$, $UO_2$. In the other cases the films would have to be crystallized thermally before the stoichiometry could be established by diffraction, and while this has been done in many cases, we do not regard the results as necessarily meaningful: as will be shown in what follows, the heatings will often alter the stoichiometries.

To get further information on the nature of anodic films on V, Nb, Ta, Mo, and W, four approaches will be used: the examination of very thin films, air crystallization, vacuum crystalliz-

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ation, and the comparison of film weights with metal-removal weights.

Somewhat unexpectedly, the most interesting approach turns out to be the examination of very thin films, as such films were found in 4 cases (V, Ta, Mo, W) to be crystalline. The only precedent for this result known to the authors was of U [15], where the first formed films (up to 15 to 28 nm) were crystalline $UO_2$. A similar claim for Nb [16] is open to serious doubt as the anodic oxide was profiled with an ion beam and the observation of NbO next to the metal can be understood either in part or in totality as related to the bombardment-induced stoichiometry change, $Nb_2O_5(s) = 2NbO(s) + 3 \cdot O(g)$ [17].

## 2. Experimental

Anodic films can be formed on V and Mo only in exceptional cases, including electrolytes based on acetic acid [7, 9, 18], acetone [19], and ethylene glycol [20]. We have chosen the acetic-acid based electrolyte, which contains 0.02 moles of $Na_2B_4O_7 \cdot 10H_2O$ and 1.0 mole of additional water per litre of acetic acid. W can be anodized in a wider range of electrolytes, including dilute $HNO_3$ [21] and the acetic-acid based electrolyte [22] mentioned above. We have chosen the latter for W. Nb and Ta can be anodized in virtually any liquid which conducts, though can be anodically sectioned only when the elctrolyte consists of a 1 : 3 mixture of $H_2SO_4$ and $(C_2H_5)_2SO_4$ [22]. Since film structure is often important in the application of anodic sectioning (as in the measurement of ion depth distributions) we have confined attention to this $H_2SO_4$-based electrolyte for Nb and Ta. It should be stressed, however, in view of the evidence that electrolytes, even those which are relatively dilute, may contribute anions other than oxygen to an anodic film [23–25], that the results for Nb and Ta on structure and stoichiometry should not necessarily be generalized.

Other details on film formation are as described previously [7, 9, 22]. Reflection electron diffraction was carried out using a Philips EM-300 microscope operated at 60 or 80 kV. Air heatings were carried out in normal laboratory air. Vacuum heatings were carried out in a quartz tube separated by a liquid-nitrogen trap from an oil-diffusion pump. Film weights and metal-removal weights, discussed in detail in previous work [7, 9, 22], were obtained gravimetrically in the case of thick films and by using techniques linked to the depth distributions of implanted $^{85}Kr$ in the case of thin films.

## 3. Results

### 3.1. Thin anodic films

Anodic films were grown on V, Nb, Ta, Mo, and W at voltages down to 4 volts (except with Nb, where the lowest convenient voltage was 6 volts due to the unusually small value of thickness/volt) and were then examined by reflection electron diffraction. In agreement with previous work [4, 5, 7, 9]

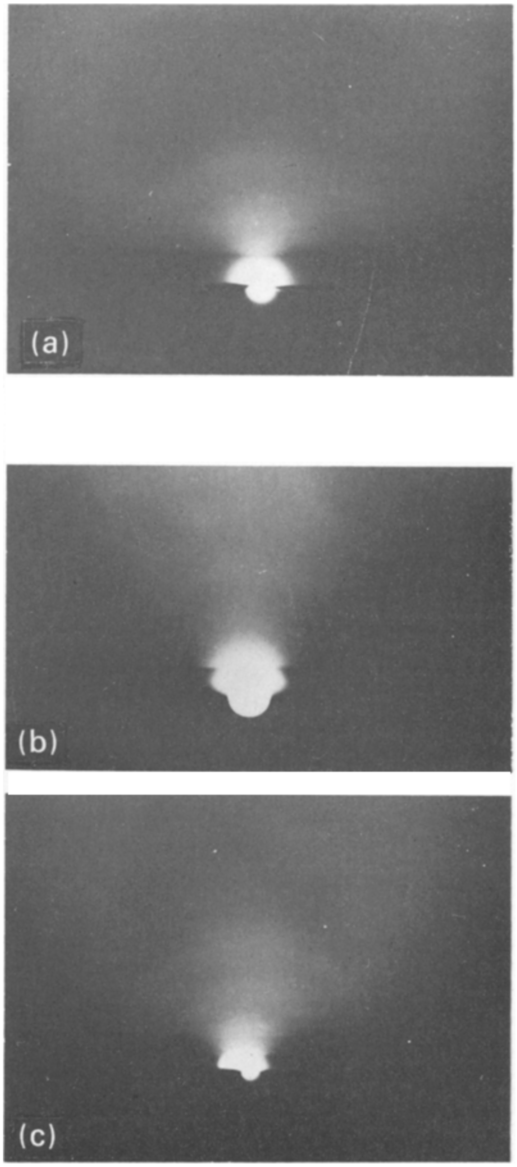

*Figure 1* Reflection electron diffraction patterns taken at 80 kV of anodic films formed at 10 or 12 volts on Ta, Mo, and W. Haloes as for an amorphous structure are in each case evident. (a) Ta, (b) Mo, (c) W.

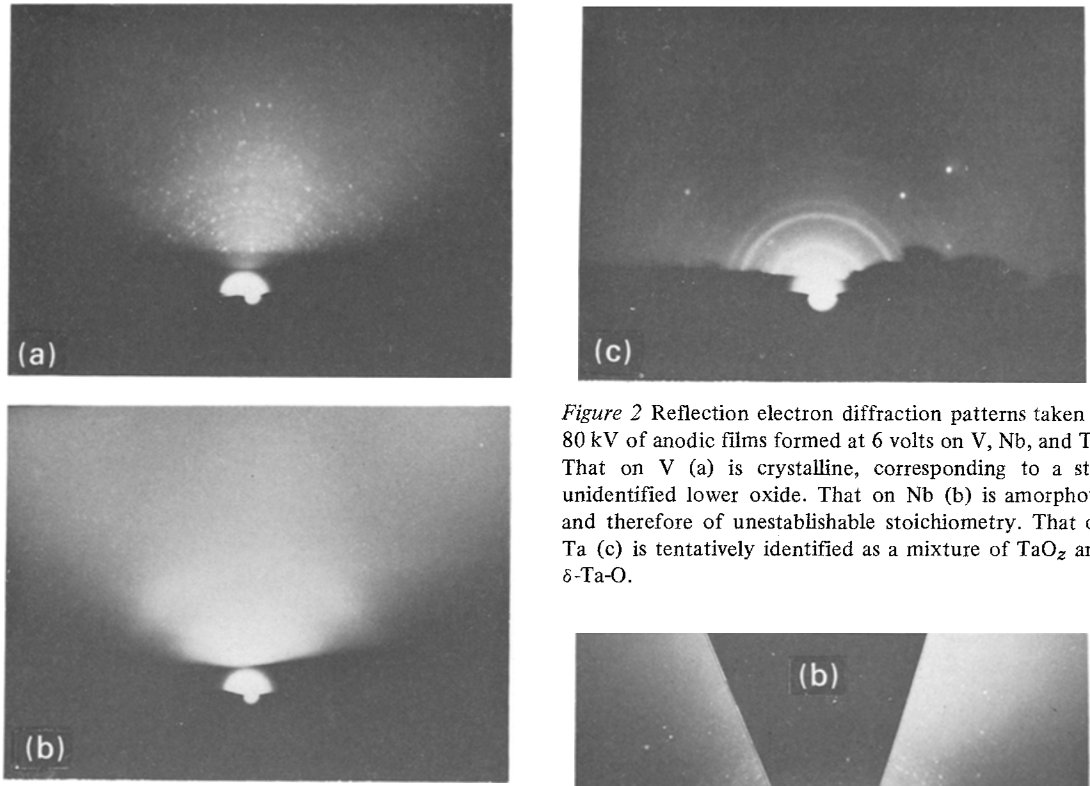

*Figure 2* Reflection electron diffraction patterns taken at 80 kV of anodic films formed at 6 volts on V, Nb, and Ta. That on V (a) is crystalline, corresponding to a still unidentified lower oxide. That on Nb (b) is amorphous and therefore of unestablishable stoichiometry. That on Ta (c) is tentatively identified as a mixture of $TaO_z$ and $\delta$-Ta-O.

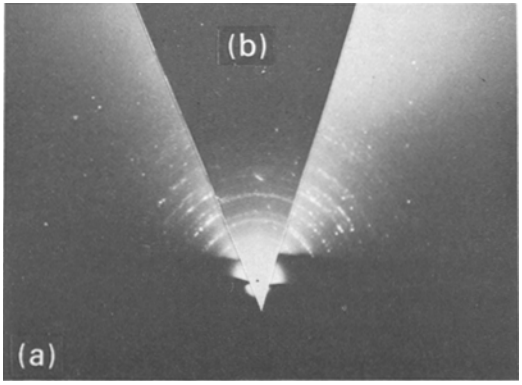

*Figure 3* Comparison of diffraction pattern (80 kV electrons) of a 6 volt anodic films on Mo (a) with that of $MoO_2$ (b). The $MoO_2$ was prepared by subjecting an $MoO_3$ pellet to $4 \times 10^{17}$ ions cm$^{-2}$ of 40 keV Kr [75]. The comparison suggests that the anodic film is not $MoO_2$ but more likely $MoO_2 \cdot H_2O$.

the thicker films showed haloes (Fig. 1) and could be concluded to have an amorphous structure. However, when very thin films were examined, all except those on Nb showed ring patterns (Fig. 2 to 4) and were concluded to be crystalline (Table I). The result that the thinnest films are crystalline is similar to that which was obtained previously for anodic films on U [15] but is otherwise a basically new aspect of anodizing; in fact, it is normally thick films which are found to be crystalline [11, 13, 14], due to field crystallization.

An analysis of the thin-film diffraction patterns was made difficult by the indistinctness of the images and the faintness of *d*-spacings exceeding ~0.4 nm. The thin film on V was certainly not $V_2O_5$. That on Ta could be tentatively identified as a mixture of $TaO_z$ (~ $Ta_2O$) and so-called $\delta$-Ta-O (~ $TaO_2$) by comparing the *d*-spacings with those found elsewhere [26] for Ta oxides (Table II). The similarity to a thermally formed film on

TABLE I Summary of electron-diffraction results

| Metal | Anodizing voltages yielding crystalline films (Volts) | Anodizing voltages yielding amorphous films (Volts) | Approximate thicknesses of films when structures change (nm) |
|---|---|---|---|
| V | 4, 6 | $\geqslant 10$ | ~ 30 |
| Nb | . . . | $\geqslant 6$ | < 9 (if at all) |
| Ta | 4, 6, 8, 10 | $\geqslant 12$ | ~ 13 |
| Mo | 4, 6 | $\geqslant 10$ | ~ 30 |
| W | 4, 6, 8 | $\geqslant 10$ | ~ 30 |

TABLE II Comparison of diffraction patterns relevant to Ta (s = strong, m = medium, w = weak).

| 6 volt anodic film (present work)* | | $TaO_z$ [26] | δ-Ta-O [26] | Thermal film formed at 700° C [27]† | Metallic Ta (ASTM 4-0788) |
|---|---|---|---|---|---|
| *d* (Å) | Character | *d* (Å) | *d* (Å) | *d* (Å) | *d* (Å) |
| ~ 3.58 – 3.20 | broad, s | 3.88 | 3.88<br>3.14 | 3.87<br>3.15 + 3.09 | |
| ~ 3.01 | spots, w | | | | |
| ~ 2.74 | spots, w | 2.73 | | | |
| ~ 2.51 | spots, w | | 2.44 | 2.46 + 243 | |
| (2.32)‡ | spot, m | | | | 2.34 |
| 2.12 – 1.98 | broad, s | 2.12 + 2.02 + 1.94 | 1.94 | 2.11 + 2.02 + 1.95 | |
| 1.84 | spots, m | | 1.81 | 1.83 | |
| 1.75 – 1.67 | broad, m | 1.67 | 1.65 | 1.66 | 1.65 |
| 1.58 | spots, w | 1.58 | 1.57 | 1.58 | |
| ~ 1.43 | broad, w | 1.43 | 1.46 | 1.46 | |
| ~ 1.31 | broad, w | 1.32 | 1.32 + 1.29 | 1.34 + 1.32 + 1.30 | 1.35 |
| 1.21 | spot, s | | | | |
| 1.19 – 1.16 | broad, m | | 1.22 + 1.20 | 1.24 + 1.23 + 1.20 | |
| (1.17)‡ | spot, m | | | | 1.17 |
| | | | | | 1.05 |
| (0.95)‡ | spot, s | | | | 0.95 |
| (0.88)‡ | spot, s | | | | 0.88 |
| (0.71)‡ | spot, m | | | | 0.71 |

* Reflection electron diffraction at 80 kV.

† X-ray diffraction.

‡ Due to Ta substrate.

Ta at 700° C by Calvert and Draper [27] (Table II). The similarity to a film formed thermally on to be similar to δ-Ta-O. Likewise, the thin film on Mo could be tentatively identified as $MoO_2 \cdot H_2O$ by comparison with the somewhat related pattern of $MoO_2$ (Fig. 3), while that on W could, with somewhat more certainty, be identified as $WO_2$ on the basis of its close similarity to $MoO_2$ (Fig. 4). We will avoid any further comments until more work is completed except to emphasize that the patterns were in all cases totally distinct from those of the underlying metals. For example, it follows from the last column of Table II that there is no possibility that the supposedly crystalline anodic films on Ta were in reality being confused with the metallic substrates.

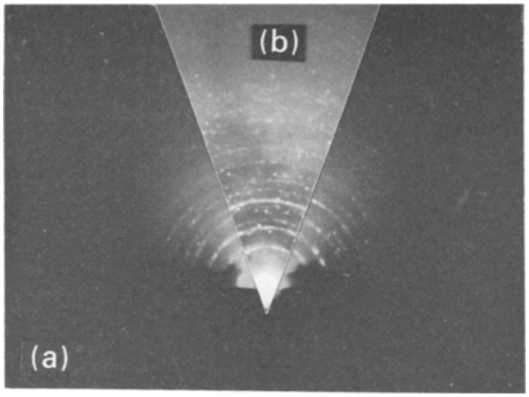

*Figure 4* Comparison of diffraction pattern (80 kV electrons) of a 6 volt anodic film on W (a) with that of $MoO_2$ (b), the $MoO_2$ having a similar origin as in Fig. 3. The similarity is not perfect but suggestive of the anodic film being $WO_2$.

## 3.2. Thick anodic films: air crystallization

The stoichiometry of thick films on Nb and Ta is not in doubt as there is in each case only one stable oxide which is fully insulating and could therefore support a large field. For example, $Nb_2O_{4.998}$ has a room-temperature conductivity of $\sim 10^{-1}$ ohm$^{-1}$ cm$^{-1}$ [28], $NbO_2$ has a room-temperature conductivity of $\sim 10^{-4}$ ohm$^{-1}$ cm$^{-1}$ [29], while $Ta_2O_{4.73}$ is metallic [30]. We therefore assign thick films on Nb and Ta the stoichiometries $Nb_2O_5$ and $Ta_2O_5$.

Simple reasoning of this type is not possible with V, Mo and W. While it is true that amorphous $V_2O_5$ [31] is much less conducting than $V_6O_{13}$ [32], $MoO_3$ [33, 34] much less than $MoO_{2.89}$ [35], and $WO_3$ [34] much less than $WO_{2.90}$ [36], not all the relevant phases have been studied. We therefore prepared anodic films on V, Mo, and W at 40 volts and crystallized them by heating the specimens at 300 to 500° C for 10 min in air in

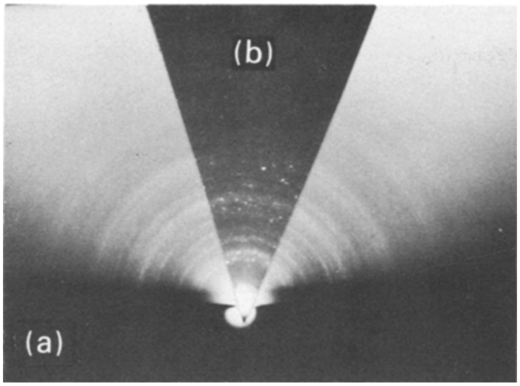

*Figure 5* Comparison of diffraction pattern (60 kV electrons) of a 40 volt anodic film on Mo which was heated in air at 450° C for 5 min (a) with that of an $MoO_3$ pellet (b). The patterns are both of poor quality, though are clearly identical.

order to facilitate a diffraction analysis. Analysis of the electron diffraction patterns [37] showed the films to consist of $V_2O_5$, $MoO_3$, and $WO_3$ in their normal structural modifications. The structures were further confirmed in the case of $V_2O_5$ and $MoO_3$ by direct comparison of the patterns with those of sintered pellets (Fig. 5).

It is easy to show that air heatings as carried out here are both thermodynamically and kinetically able to oxidize the lower oxides of V, Mo and W and are therefore of no use of inferring film stoichiometries. For the thermodynamic argument it is sufficient to consider the highest oxide pair which can exist in equilibrium (e.g. $V_3O_7 + V_2O_5$ rather than $V_6O_{13} + V_3O_7$ [38]). The relevant information is in Table III and enables one to conclude that, from a thermodynamic point of view, oxidation is inevitable for air heatings as carried out.

Whether the oxidation of a film is kinetically possible depends on two aspects, the supply of oxygen and the diffusivity of oxygen in the film. Both aspects are taken into account when a lower oxide in thin-film form is heated in air and the temperature of re-oxidation is determined. Fig. 6, based on unpublished work by Naguib [39], shows that for a ~ 100 nm film of $MoO_2$ oxidation begins and proceeds to completion over the range 100 to 250° C, well below the minimum crystallization temperature (~ 325° C). A similar result follows from experiments in which 40 volt anodic films were formed on V and Mo and then heated, first in vacuum (300–450° C, $10^{-4}$ Pa), then in air (425° C). The vacuum heatings gave lower oxides which we will avoid commenting on, whereas the air heating restored $V_2O_5$ and $MoO_3$. Corresponding information is not available for $WO_3$, but behaviour similar to $MoO_3$ would be expected in view of the diffusivity of oxygen in the two oxides being similar [40].

TABLE III Oxidation of lower oxides of V, Mo, and W at 700 K

| Reaction | Equilibrium oxygen pressure (atm) | Reference |
|---|---|---|
| $2V_3O_7 + \frac{1}{2}O_2 = 3V_2O_5$ | $1 \times 10^{-9}$ | [76] |
| $MoO_2 + \frac{1}{2}O_2 = MoO_3$ | $2 \times 10^{-16}$ | [77] |
| $WO_{2.96} + 0.02O_2 = WO_3$ | $2 \times 10^{-22}$ | [77] |

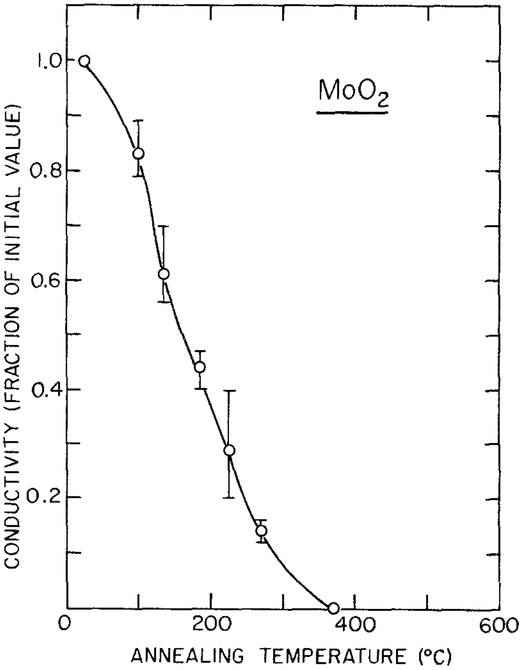

*Figure 6* Conductivity versus annealing temperature for a ~ 100 nm thick film of $MoO_2$ which was prepared by subjecting an $MoO_3$ pellet to $4 \times 10^{17}$ ions $cm^{-2}$ of 40 keV Kr and was then heated in air with 10 min hold times. The temperature range over which oxidation of $MoO_2$ begins and goes to completion for the particular time and distance scale can be identified with the range over which the conductivity is lost, 100 to 250° C (Naguib [39]).

One concludes that it is not possible to gain information on the nature of anodic films on V, Mo, and W by crystallizing them in air.

## 3.3. Thick anodic films: vacuum crystallization

In the next group of experiments, the thermal crystallizations were carried out at 300 to 500° C for 10 min in a vacuum of about $10^{-4}$ Pa. Analysis of the electron diffraction patterns [37] showed that the anodic films were not $V_2O_5$, $MoO_3$, or $WO_3$ and were by necessity therefore deficient in oxygen.

At least three processes other than direct evaporation can take place when oxide films on V, Mo, and W are vacuum annealed. Direct loss of oxygen, governed by the same thermodynamic information as in Table III, will be impossible with all three metals. Direct gain of oxygen is governed by the number of $O_2$ molecules striking the surface, namely [41]

$$\text{molecules cm}^{-2}\,\text{sec}^{-1} = 2.64 \times 10^{20} P M_g^{-1/2} T^{-1/2} \eta, \qquad (1)$$

where $P$ is the pressure in Pa, $\eta$ is the sticking coefficient and $M_g$ is the molecular weight of the gas. For a 10 min exposure at $10^{-4}$ Pa and 700 K to gas which is 20% $O_2$, Equation 1 yields about $13\eta$ collisions per substrate atom but since $\eta$ is probably low ($< 0.1$) when an oxide film is already present [42] the gain of oxygen may be assumed to be unimportant. This leaves the third process: reaction of the oxide with the metal substrate. It is thermodynamically possible for all three of $V_2O_5$, $MoO_3$, and $WO_3$, though whether it is kinetically possible can be judged only from experiment.

We have therefore prepared 40 volt anodic films on V and Mo and, in experiments similar to those described in Section 3.2, heated them at 300 to 500° C first in air and then in vacuum ($10^{-4}$ Pa). (The heatings were thus in the reverse order.) The initial heating in air gave $V_2O_5$ and $MoO_3$, as would be expected. The crucial step is the vacuum heating. The same oxygen, deficient phases appeared as when the initial heating was in vacuum, showing reaction of the oxides with the metal substrates to be kinetically possible. That $MoO_3$ will react with Mo at temperatures as used here has been shown also by Hickman and Gulbransen [43]. They found that thin films of $MoO_3$ on Mo reduced to $MoO_2$ when heated above 300° C in an unspecified vacuum. Corresponding information is not available for $WO_3$. Even the work of Hickman and Gulbransen [43] does not help, for although thin films of $WO_3$ on W did indeed reduce to $WO_2$ above 600° C if the films were thin enough, such a temperature is rather higher than those used here.

One concludes that it is not possible to gain information on the nature of the anodic films on V and Mo by crystallizing them in vacuum. With W, vacuum heating may or may not be acceptable and further work is required.

## 3.4. Film weights

Both film weights and metal-removal weights, expressed as relations of the type

$$\text{weight } (\mu\text{g})/\text{cm}^2 = A + B \times V(\text{volts})$$

and valid for specified current densities and anodizing times, are known accurately for V, Mo, and W [7, 9, 22, 37]. The constants $B$ correspond to weight slopes which have the important property of being largely independent of the existance of a lower stoichiometry in the film next to the metal, of interfacial potentials, as well as of the fact that metal dissolution occurs during film formation in the case of V and Mo. Further details on the use of the constants $B$ will be given in a companion article [44] concerned with the kinetics of anodizing V, Mo, and W, and we will here merely reproduce the most important information. This is done in Table IV. Evidently the stoichiometries are much closer, respectively, to $V_2O_5$, $MoO_3$, and $WO_3$ than to $VO_2$, $MoO_2$, and $WO_2$. The main qualifications lie in the facts that more subtle distinctions, as between $WO_3$ and $WO_{2.90}$, cannot be made with gravimetric information and that the films will be doped to an unknown extent with ions from the electrolyte and therefore be too heavy. This problem is evidently not too great with W [22],

TABLE IV Stoichiometries of anodic films as obtained from film weights (from Arora and Kelly [44])

| Metal | Slope of experimental metal-removal weight ($\mu$g cm$^{-2}$ V$^{-1}$) | Slope of inferred film weight ($\mu$g cm$^{-2}$ V$^{-1}$) | Slope of experimental film weight ($\mu$g cm$^{-2}$ V$^{-1}$) | Conclusion regarding stoichiometry |
|---|---|---|---|---|
| V | 0.63 ± 0.01 | 1.03 ± 0.02 if $VO_2$<br>1.13 ± 0.02 if $V_2O_5$ | 1.15 ± 0.04 | similar to $V_2O_5$ |
| Mo | 1.05 ± 0.03 | 1.40 ± 0.04 if $MoO_2$<br>1.58 ± 0.05 if $MoO_3$ | 1.58 ± 0.02 | similar to $MoO_3$ |
| W | 1.09 ± 0.03 | 1.28 ± 0.04 if $WO_2$<br>1.37 ± 0.04 if $WO_3$ | 1.38 ± 0.05 | similar to $WO_3$ |

whence by inference V and Mo, for all of which the same electrolyte was used.

## 4. Discussion

Overall results relating to the crystallinity of anodic films on V, Nb, Ta, Mo, and W were summarized above in Table I. Likewise, Table V summarizes the results relating to stoichiometry. We will now comment on these two aspects of anodic films with the object of establishing the plausibility of the results.

TABLE V Summary of anodic film stoichiometries

| Metal | Thin as-formed films | Thick as-formed films |
|---|---|---|
| V | not $V_2O_5$ | similar to $V_2O_5$ |
| Nb | unestablishable since amorphous | $Nb_2O_5$ |
| Ta | $TaO_z$ plus δ-Ta-O (tentative) | $Ta_2O_5$ |
| Mo | $MoO_2 \cdot H_2O$ tentative) | similar to $MoO_3$ |
| W | $WO_2$ (more certain) | similar to $WO_3$ |

## 4.1. The problem of film stoichiometry

### 4.1.1. Vanadium

The films first formed on V due to thermal oxidation at or below 400° C have been identified variously as $V_2O_3$ [45], VO or $V_2O_3$ [46], and phases containing $V^{IV}$ and $V^{V}$ [47], the main point being that one or more lower oxides is involved. A somewhat better deifned approach for determining the first formed film is to ion-implant V with $O_2^+$,in which case VO is readily identified by high-energy electron diffraction [48]. We have avoided making a definitive identification of the thin films on V, though we propose that they will probably be found to consist of a lower oxide in either anhydrous or hydrated form. The reason for a lower oxide is in all case probably the same: the tendency for the first formed film, including the phase arising by ion implantation, to be in thermodynamic equilibrium with the metal.

It is appropriate, in the case of V, to comment also on the thick-film stoichiometry. Mackintosh and Plattner [49] have recently used He backscattering, $(d, p)$ analysis, and film weight to show that the films formed on V at about 50 volt were close to $V_2O_5$, namely $V_2O_{5.0 \pm 0.25}$. This, as well as the present evidence for $V_2O_5$, contradicts evidence by Keil and Salomon [18] that 50 volt as-formed films are close to $VO_2$. We regard the techniques used here and by Mackintosh and Plattner [49] as more direct.

### 4.1.2. Niobium

Excluding the formation of suboxides, the first formed thermal films on Nb due to oxidation in air have been identified in two separate studies as $Nb_2O_5$ [50, 51]. Of closer relevance here is the corresponding work carried out at reduced pressures, where the first formed films were found to be NbO [50] or $NbO_2$ [51], as well as work in which Nb was ion-implanted with $O_2^+$ and NbO was identified [48], and work in which the resistance of anodic films on Nb was found to be low near the film–metal interface [52]. Nevertheless, no comparison with the present work is possible due to the anodic films on Nb persisting in an amorphous state down to 6 volt. We regard this as a surprising result in view of the behaviour of the other four metals and requires further work to be done. For example, it would be interesting to see the results of a structural study on films formed below 6 volt, though the very small thicknesses of these films might render examination difficult. We reiterate here that the work of Gray [16] does not necessarily supply the missing information, as an ion probe must not be used with an oxide such as $Nb_2O_5$ which is subject to preferential oxygen sputtering [17].

### 4.1.3. Tantalum

Kudrak and Sienko [30] have attempted to prepare intermediate Ta oxides with simple stoichiometries such as TaO or $TaO_2$ and concluded that such phases do not exist as solids. Their existence in the gas phase [53] is not relevant here, while the claim to have identified $TaO_2$ in O-implanted Ta [54] was apparently influenced by misleading information on ASTM card 17-709.* The evidence, in an infrared reflectance study of anodic films on Ta, for unspecified lower oxides [58] is regarded here as somewhat indirect. This means that the only well documented lower oxides other than extreme suboxides ($TaO_x$ and $TaO_y$ [26, 57]) are $TaO_z$ i.e. $\sim Ta_2O$ (formed both by thermal oxidation [26] and by ion-implanting Ta with $O_2^+$ [48]), δ-Ta-O i.e. $\sim TaO_2$ [26, 59], and $Ta_2O_{4.73}$

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* ASTM card 17-709 gives $d$-spacings for $TaO_z$ due to Norman [55], who estimated the composition using an electron microprobe to be $TaO_z$. Subsequently Steeb and Renner [56] deduced the structure of $TaO_z$ and found it to correspond to a composition $Ta_2O$. The problem is reviewed by Biebuhr [57], where the composition $Ta_2O$ is adopted.

TABLE VI Metal-removal weights for thin and thick anodic films (mainly from [37] and [44])

| Metal | Slope of metal-removal weight at low voltages ($\mu$g cm$^{-2}$ V$^{-1}$) | Slope of metal-removal weight at high voltages ($\mu$g cm$^{-2}$ V$^{-1}$) | Voltage of discontinuity (Volts) | Thickness at discontinuity (nm of oxide) |
|---|---|---|---|---|
| V | 1.45 | 0.63 | ~ 4 | ~ 10 |
| Nb | 0.46 | 0.42 | ~ 15 | ~ 22 |
| Ta | 0.64 | 0.455 | ~ 15 | ~ 13 |
| Mo | 1.75 | 1.05 | ~ 10 | ~ 37 |
| W | 1.33 | 1.09 | ~ 7 | ~ 40 |
|  | 1.13 [64] | 1.02 | ~ 12 | ~ 36 |

[30], and that our tentative identification of thin anodic films on Ta as consisting of a mixture of TaO$_z$ and $\delta$-Ta-O is both experimentally and thermodynamically reasonable.

### 4.1.4. *Molybdenum*

Ikonopisov [20] found that very thin anodic films on Mo are semiconducting and believed, on the basis of their dark color and the reluctance of the anodizing voltage to rise, that they consisted of a lower oxide. Beyond a critical thickness, however, this semiconducting film was argued to be converted into $MoO_3$ since the latter is the only known oxide of Mo which has a low enough conductivity to permit film growth. Daly and Keil [60] have found, by comparing the number of coulombs passed with chemical analysis of dissolved films, that the Mo in anodic films has an average oxidation state of 5.5. Thermal oxide formed on Mo at about 10 Pa was shown by Hickman and Gulbransen [43] to exist in layers, such that $MoO_2$ was next to the metal and $MoO_3$ on the outside. In other work only $MoO_2$ was identified [61], while ion-implanting Mo with $O_2^+$ also led to $MoO_2$ [48]. Our identification of thin films on Mo as consisting of $MoO_2 \cdot H_2O$ is thus compatible with previous experimental work. In addition, since $MoO_2$ is the lowest stable oxide other than the suboxide $Mo_3O$, it is thermodynamically reasonable.

### 4.1.5. *Tungsten*

Brandon *et al.* [5] stripped 50 nm anodic films from W and found them to be amorphous as formed but to crystallize to a mixture of $WO_2$ and a disordered form of $WO_{2.90}$ by pulse heating in an electron microscope. Since the films were free of the substrate, oxide-substrate reactions of the type $W + 2WO_3 = 3WO_2$ were avoided. On the other hand, reactions such as that between $WO_2$ and $WO_3$ or the disproportionation of $WO_{2.72}$, which is stable only above 548° C [62], were not avoided, so the results should be taken only as demonstrating an average stoichiometry lower than $WO_3$. Studies on the thermal oxidation of W [62, 63] have shown that the only oxides other than the suboxide $W_3O$ which are stable below 416° C are $WO_2$ and $WO_3$, while ion-implanting W with $O_2^+$ leads to a still unidentified lower oxide [48]. The overall conclusion is that the present evidence for thin anodic films on W having stoichiometry $WO_2$ is both experimentally and thermodynamically reasonable.

As a further precedent for finding thin anodic films to be different from thick films, we point out that plots of metal-removal weight versus voltage are normally found to show a discontinuity when the films are 10 to 40 nm (4 to 15 volt) thick (Table VI). Although such discontinuities could in principle be related to changes in the mechanism of film growth, they could also arise from a change in the nature of the films themselves. With Nb, both thin and thick films were found to be amorphous and a discontinuity should not occur. A closer examination of the information in Table VI shows that the change in slope is here only marginal and possibly not real.

## 4.2. The problem of film crystallinity

The question of why the various anodic films encountered in the present work were amorphous or crystalline still remains to be considered. We propose in what follows to draw a tentative parallel between anodically formed oxides and oxides which have been subjected to high-dose ion bombardment. Such a comparison is not necessarily unreasonable, for just as an anodic oxide is created at low temperatures and is therefore unable to equilibrate, so particle impact causes disordering similar to the liquid state which in many instances is preserved by quenching. As shown elsewhere [65], the quenching is likely to succeed whenever the following criterion is met:

$$\text{(crystallization temperature)/(melting temperature)} = T_c/T_m \gtrsim 0.30$$

A comparison will splat quenching is less valid, as the relevant quenching rate is much lower than that following ion impact and many phases, including $Nb_2O_5$ and $Ta_2O_5$, fail to amorphize [59].

As seen in Table VII, there is a remarkable parallel between anodically formed and bombarded oxides. Firstly, for 18 of the 20 cases for which complete information is available the state of crystallinity is the same. The exceptions are anodic $TiO_2$, which is amorphous only for a cooled electrolyte or possibly when not too thick [5, 11], and anodic $SnO_2$, which was found to be consistently microcrystalline [2]. A second similarity is that the state of crystallinity correlates in both cases with the ratio $T_c/T_m$. The two exceptions, $TiO_2$ and $SnO_2$, turn out to have intermediate values of $T_c/T_m$, and so in some respects cease to be exceptions.

An explanation for the crystal state of bombarded solids was developed in previous work [65, 71]. Briefly stated the argument was this. During ion bombardment of a crystalline solid, displacement cascades will form and consist of a compact liquid-like region surrounded by crystal, provided the ion is sufficiently heavy. For incident ion energy $E_1$, $x$-straggling $\Delta x$, $y$-straggling $\langle y^2 \rangle^{1/2}$, mean atomic spacing $\lambda$, and heat capacity $3k$, the initial temperature of the cascade will be given approximately by

$$T \approx E_1 \lambda^3 / \Delta x \langle y^2 \rangle 3k,$$

or about 3000 K [72]. The cascade cools rapidly with a $t^{-3/2}$ cooling law and crystallization begins when the temperature falls below the melting point ($T_m$). The total distance moved by the crystallization front follows as

$$x_c = (1/\lambda) \int_{t_1}^{t_2} D_c dt, \tag{2}$$

where $t_1$ is the time when $T = T_m$, $t_2$ is any sub-

TABLE VII Summary of anodic film crystallinity (cr = crystalline, am = amorphous).

| Oxide | State when formed anodically | State when ion-bombarded [65] | $T_c/T_m$ (K/K) [65] |
|---|---|---|---|
| $ZnO$ | cr [3] | cr | 0.17 [66] |
| $BeO$ | cr$^{*}$ [12] | cr | 0.21 |
| $HfO_2$ | cr [1] | cr | ~ 0.25 |
| $ZrO_2$ | cr [4, 5] | cr | 0.27 |
| $UO_2$ | cr [15] | cr | 0.30 |
| $TiO_2$ | am$^{\dagger}$ or cr [5] | am | 0.35 |
| $Ta_2O_5$ | am$^{\dagger}$ (This work) | am | 0.38 – 0.46 |
| $SnO_2$ | cr$^{\ddagger}$ [2] | am | ~ 0.41 |
| $Nb_2O_5$ | am$^{\dagger}$ This work) | am | 0.42 – 0.49 |
| $Fe_2O_3$ | [68] | am | ~ 0.43 |
| $Al_2O_3$ | am$^{\dagger}$ [10] | am | 0.43 |
| $WO_3$ | am (This work) | am | 0.43 |
| $Bi_2O_3$ | am [69] | am | 0.49 |
| $MoO_3$ | am (This work) | am | 0.49 |
| $SiO_2$ | am [8] | am | 0.57 |
| $V_2O_5$ | am (This work) | am | 0.61 |
| $GeO_2$ | am [6] | am | 0.65 |
| $MoO_2$ | cr (This work i.e. $MoO_2 \cdot H_2O$) | cr | |
| $TaO_z$ plus $\delta$-Ta-O | cr (This work) | cr [48, 70] | |
| ~ $U_3O_8$ | am$^{\S}$ | am | |
| $WO_2$ | cr (This work) | cr$^{\P}$ | |

$^{*}$ With most electrolytes, though not "electrolyte A" of [12]. The latter introduces significant P and S [67].

$^{\dagger}$ With unheated electrolytes and/or low current densities, particularly in the case of $TiO_2$.

$^{\ddagger}$ Borderline between being amorphous and crystalline.

$^{\S}$ All that is known structurally about thick anodic films on U is that they are amorphous [15]. We have assigned them a stoichiometry near $U_3O_8$ as this is thermodynamically reasonable and would point out that whether the real stoichiometry is $U_4O_9$, $U_3O_8$, or $UO_3$ is unimportant to the argument.

$^{\P}$ $WO_{2.72}$ is known to remain crystalline when bombarded [65]. $WO_2$ has yet to be studied but will most likely remain crystalline in view of being more ionic [65] than $WO_{2.72}$.

sequent time when $T$ is somewhat greater than $T_\infty$ (the ambient temperature), and $D_c$ is the diffusion coefficient for crystallization. If $D_c$ is taken as proportional to $\exp(-\Delta H_c/kT)$ and $T$ is given by $T_\infty + At^{-3/2}$, Equation 2 can be evaluated. The final result is that $x_c$ is less than $\lambda$, i.e. crystallization is avoided, if the following is true:

$$T_c/T_m \overset{\sim}{>} 0.30.$$

Here $T_c$ is the crystallization temperature as measured in a typical thin-film experiment with a 2 to 15 min time scale.

We would propose that an anodic film can be treated in a similar way. Analogous to the energy deposited by the incident ion is the field-imparted energy. If $q$ is the charge number of the mobile defect, $e$ the electronic charge, and the film formation field, the latter energy is just

$$E = qe\lambda\mathcal{E}.$$

This energy will dissipate in roughly $10^{-11}$ to $10^{-12}$ sec, as can be seen by writing $\kappa t = r^2$ and taking $\kappa$, the thermal diffusivity, as $10^{-2}$ to $10^{-3}$ $\mathrm{cm^2\,sec^{-1}}$ [70] and $r$ as 1 nm. The next jump of the defect occurs after a much longer time. For example, for a film with thickness $x$ the number of defects that jumped per $\lambda^2$ of surface is about $x^2/2\lambda^2$. This number is deduced by noting that the first $\lambda$ of film required 1 jump, the second $\lambda$ required 2 jumps and so on, so that a film having a final thickness of $x/\lambda$ atomic spacings required

$$1 + 2 + 3 + \ldots + x/\lambda \approx x^2/2\lambda^2$$

jumps. This amounts to $5 \times 10^3$ jumps for $x = 100\lambda$ so that if the total anodizing time is 3 min the average time for a jump (per $\lambda^2$ of surface) is 0.04 sec. The mobile defect thus behaves, following each field-assisted jump, like a displacement cascade of point dimensions and with temperature

$$T = qe\lambda\mathcal{E}/3k.$$

The remainder of the argument fully parallels that for a true displacement cascade, such that anodic films for which $T_c/T_m \overset{\sim}{>} 0.30$ will tend to avoid crystallization and therefore be amorphous.

The main weakness in the argument relates to the dimensions of the heated region. The heat deposited by an impacting ion is distributed over a sufficient volume, $\Delta x\langle y^2\rangle$, for heat conduction theory to have a reasonable chance of being valid, whereas that due to anodizing is localized to a single atom. On the other hand, an anodic film with thickness $x = 100\lambda$ suffers, as shown above, about $5 \times 10^3$ defect jumps per $\lambda^2$ surface, so there are $5 \times 10^3$ chances for crystallization to initiate per $\lambda^2$ of surface. Another problem is that such oxides as $MoO_2$ and $WO_2$ are metallic conductors [74] and should not support a large field. The argument can thus be disputed on a quantitative basis, though we would emphasize that the parallel between anodically formed and bombarded oxides as summarized in Table VII will still remain.

## 5. Conclusions

(1) Anodic films on V, Ta, Mo, and W are crystalline below a critical thickness which lies in the range 9 to 30 nm (6 to 10 volt). The crystalline films could in the cases of Ta, Mo, and W be tentatively identified using reflection electron diffraction as *not* $V_2O_5$, $TaO_z$ plus $\delta$-Ta-O, $MoO_2 \cdot H_2O$, and $WO_2$; the assignments are far from definitive, owing to the poor quality of the diffraction patterns and the lack in some cases of a reference pattern. We would note that the results for Ta were obtained with an unusual $H_2SO_4$-based electrolyte and are not necessarily generally valid, but are, nevertheless, both experimentally and thermodynamically reasonable.

(2) Thicker films on V, Ta, Mo and W, as well as all films on Nb, were amorphous and therefore could not be studied directly by diffraction. Nevertheless the assignments $Nb_2O_5$ and $Ta_2O_5$ could be made on the basis of these being the only stable oxides of Nb and Ta which are fully insulating.

(3) In an attempt to identify the thick films in the case of V, Mo, and W, air and vacuum crystallizations were carried out. Those in air are shown to be in general unsatisfactory due to oxidation being both thermodynamically and kinetically possible. Those is vacuum are unsatisfactory in the case of V and Mo due to the occurrence of reactions of the type

$$\text{higher oxide} + \text{metal substrate} = \text{lower oxide.}$$

But vacuum heating of W is possibly acceptable, with further work being required.

(4) By considering the ratio of film weights to metal-removal weights as given in previous work [37, 44], it was possible to establish stoichiometries close to $V_2O_5$, $MoO_3$, and $WO_3$ for thick films on V, Mo and W.

(5) The appearance of lower stoichiometries

with first formed anodic films is regarded as a normal consequence of thermodynamic equilibrium between the film and the metal substrate. In particular the phases in equilibrium with Ta, Mo, and W should be $TaO_z$, $MoO_2$, and $WO_2$, essentially as observed. The failure of thin films on Nb to consist of crystalline NbO or $NbO_2$ is regarded as surprising and requiring further work.

(6) The fact that the anodic films encountered here, as well as those described in other work, are variously amorphous or crystalline has a close parallel with ion-bombarded oxides. In 18 of the 20 cases for which complete information is available, the state of crystallinity is the same and, furthermore, correlates with the ratio $T_c/T_m$. The two exceptions, $TiO_2$ and $SnO_2$, turn out to have intermediate values of $T_c/T_m$. A model based on crystallization due to the energy deposited either by an impacting ion or by a defect moving in an electric field is discussed.

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