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Thermodynamic Potential for the Anodic Dissolution of n-Type Semiconductors

A Crucial Factor Controlling Durability and Efficiency in Photoelectrochemical Cells and
an Important Criterion in the Selection of New Electrode/Electrolyte Systems

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ABSTRACT

We show that the standard potential for anodic dissolution, E_D° , of n-type semiconductors (e.g., E_D° for $\text{CdS} \rightleftharpoons \text{Cd}^{2+}(\text{aq}) + \text{S} + 2e^-$ is +0.08V vs SCE) plays a key role in ultimate efficiency of thermodynamically stable n-type semiconductor-based photoelectrochemical cells. The selection of redox active substances that can be used for competitive capture of photogenerated holes is limited to those systems where the product does not have the potential to oxidize the semiconductor. Where E_{VB} and E_{CB} represent the position of the valence and conduction band positions at the interface, respectively, we must conclude that E_D° is at a more negative potential (vs. a reference) than E_{VB} , if the semiconductor undergoes photoanodic dissolution. Quenching of the photoanodic dissolution by competitive hole capture by some electrolyte component, say A, is possible if $E_{\text{redox}}(\text{A}^+/\text{A})$ lies at a potential more negative than E_{VB} . But additionally, if the A^+ , the oxidation product, is to be incapable of oxidizing the semiconductor, $E_{\text{redox}}(\text{A}^+/\text{A})$ must be more negative than E_D° . Consequently, for the semiconductor to be thermodynamically stable in the A/A^+ electrolyte the maximum photovoltage output, $(E_{CB} - E_{\text{redox}})$, can be no greater than $(E_{CB} - E_D^\circ)$ for E_{CB} more negative than E_D° . Naturally, kinetic inertness of the semiconductor to an oxidant with E_{redox} more positive than E_D° may allow its presence and/or use in a more efficient cell. N-type CdS and TiO_2 semiconductors in aqueous electrolytes are treated in detail. Some preliminary comments are made concerning p-type materials.

Much attention has been focused recently on the use of certain redox active electrolytes to "quench" the photoanodic dissolution of small bandgap, nonoxide,

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n-type semiconductors (1-6). Broadly interpreted, the success realized can be attributed to the ability of the redox active species to capture photogenerated holes before the holes participate in oxidation reactions of the semiconductor. At present there is no detailed understanding of the factors controlling the competi-

tion between the interfacial electron transfer and the photoanodic dissolution, although clearly certain energetic requirements (7) must be met for any photo-induced interfacial charge transfer to occur.

Power efficiencies of $\sim 10\%$ can be obtained for the conversion of monochromatic visible light to electricity with "stabilized" n-type semiconductor-based cells (1-6). Even cells employing polycrystalline photoelectrodes appear to give good efficiencies (2, 3, 8-10). It is appropriate to enunciate criteria which will aid in (i) the selection of new electrolyte/electrode combinations and (ii) the determination of durability and conversion efficiency under operating conditions. The aim of this note is to point out the importance of the standard potential for the anodic dissolution, E_D° , of n-type semiconductors. For semiconductors which undergo photoanodic dissolution, the position of E_D° controls the ultimate efficiency and limits the redox active substances that can be used for competitive capture of photogenerated holes.

Theory and Discussion

According to Gerischer (7), the energetics of an n-type semiconductor/electrolyte interface at equilibrium in the dark are as sketched in Fig. 1, where the energy levels of importance, which can be expressed in volts *vs.* a reference electrode, are as follows: E_f is the Fermi level of the semiconductor, E_{CB} and E_{VB} are the conduction and valence band positions, respectively, at the interface, E_{BG} is the semiconductor bandgap, and E_{redox} is the actual redox potential of the chemical system ($A^+ + e = A$) in equilibrium with the semiconductor. In the following discussion we will generally assume that A^+ and A are at unit activity, so that $E_{redox} = E_{redox}^\circ$. However, if the redox system involves H^+ , e.g., the O_2/H_2O system, E_{redox} will be a function of pH. Moreover, all energy levels (given on some absolute scale in electron volts) will be expressed relative to a saturated calomel electrode, *i.e.* in volts *vs.* SCE.

Absorption of light within the depletion region corresponding to a $VB \rightarrow CB$ electronic transition results in separated e^-h^+ (electron-hole) pairs such that h^+ goes to the interface and the e^- moves to the bulk of the semiconductor. The h^+ rises to the top of the valence band, and, in the absence of surface states, is at a potential equal to E_{VB} . Thus, if E_{redox} is more negative than E_{VB} , interfacial electron transfer can occur to fill h^+ , thereby oxidizing some component of the electrolyte. However if the standard potential for the anodic dissolution of the semiconductor, E_D° , is more negative than E_{VB} , h^+ can also cause oxidation of the crystal. The primary oxidation product, then, will depend on the relative rate of the two competing h^+ reactions.

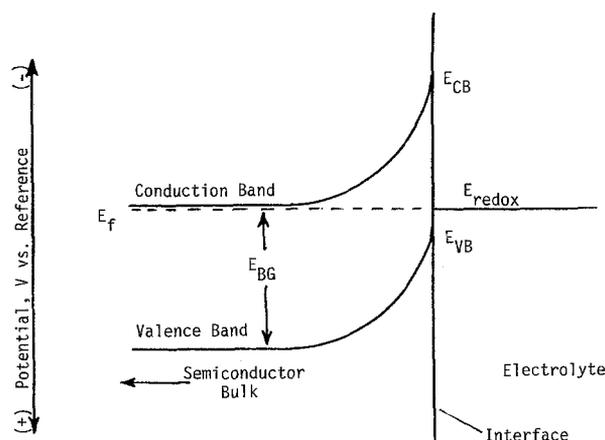


Fig. 1. N-type semiconductor at dark equilibrium

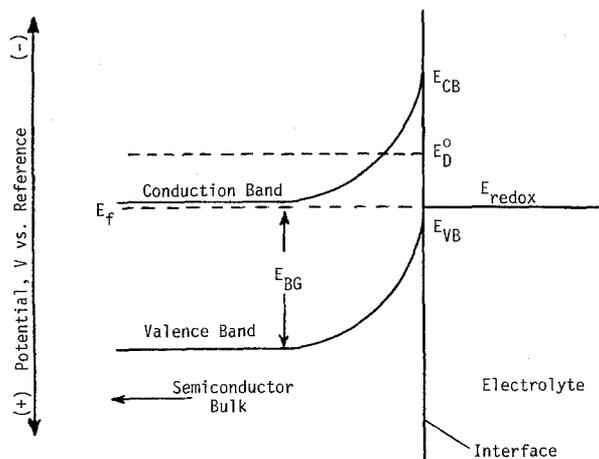


Fig. 2. E_{redox} more positive than E_D°

Significantly, though, the relative position of E_{redox} and E_D° is crucial to whether prolonged stabilization of the semiconductor is expected. In Fig. 2, we show a situation where E_{redox}° is more positive than E_D° . What is readily apparent is that the oxidized form of the redox couple with a potential E_{redox}° is capable, energetically, of spontaneously oxidizing the semiconductor in the dark. If the redox system is represented by A/A^+ and one starts with only the reduced form, A , present, then the photogeneration and to interfacial transfer to give the oxidized form, A^+ . But with the E_{redox}° level of A/A^+ situated more positive than E_D° , A^+ is capable of chemically oxidizing the semiconductor. Thus, the use of A as a reductant to capture competitively photogenerated h^+ is not attractive, because the primary oxidation product may, thermodynamically, oxidize the semiconductor.

Figure 3, shows the situation for E_{redox}° (A/A^+) more negative than E_D° . In this case the primary oxidation product, A^+ is not capable, thermodynamically, of oxidizing the semiconductor to an appreciable extent. Thus, if A can successfully capture 100% of the photogenerated h^+ , then the semiconductor could be stabilized to anodic dissolution for an indefinite period.

A comparison, though, of Fig. 2 and 3 suggests several other important comments. First, the amount of band bending in the dark ($E_{CB} - E_{redox}$) is

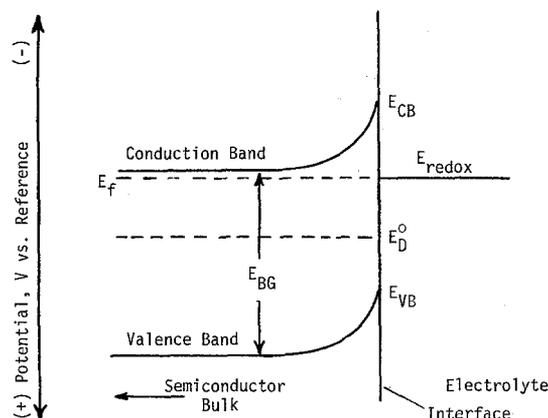


Fig. 3. E_{redox} more negative than E_D°

equal to the maximum open-circuit photopotential, and in Fig. 3 the amount of band bending is less than ideal. In fact, the position of E_D° will limit the amount of band bending to $E_{CB} - E_D^\circ$ for an electrolyte system which can stabilize the semiconductor. Thus, the maximum conversion efficiency with monochromatic light and for a thermodynamically stable system is just $E_{CB} - E_D^\circ / E_{BG}$.

Second, the position of E_{redox} may be required to be significantly more negative than E_{VB} . This may preclude effective overlap of filled levels of the redox active A and the valence band (containing the primary photogenerated h^+) of the semiconductor. Indeed, if the h^+ position is, at best, at the top of the valence band, stabilization of the semiconductor to photoanodic dissolution may not be possible, owing to the slow oxidation of A because of this lack of overlap. This consideration suggests that surface states or intermediate levels may be of importance in the transfer of holes to solution species whose E_{redox} is located in the band-gap region, and there may be merit in the controlled introduction of such states or levels so that the photo-generated hole can rise to a level more negative than E_D° .

Third, when E_{redox} is required to be substantially more negative than E_{VB} there may be substantial overlap of the filled levels in A and the conduction band (unfilled) levels of the semiconductor. This will result in significant dark anodic currents.

Finally, since E_D° must be closer to E_{VB} than E_{redox} , we can only be cautious about the prospects for finding a large number of redox active materials that will be capable of competing efficiently with photoanodic dissolution. The presence of surface states will alter the prospects considerably, and their role in the known cases of stabilization should be investigated in detail.

Consideration of a couple of examples will serve to reinforce the principles outlined here. Table I shows some pertinent information. Stabilization of CdS to photoanodic dissolution has been reasonably successful (1-6) and is a useful illustrative case. In aqueous electrolytes the energetics are as in Fig. 4, and are approximately independent of pH (6, 11). The value of E_D° is for the reaction $Cd^{2+} + S + 2e^- = CdS$ and is based on the thermodynamic data given in Latimer (12). From the foregoing discussion, E_{redox} must be more negative than $+0.08V$ vs. SCE. Consequently, and in retrospect, it is understandable that failure results in the attempted (13) use of I^- to capture competitively photogenerated h^+ . The primary oxidation product, I_2 , is capable of oxidizing CdS, since $E_{redox}(I_2/I^-)$ is $+0.25V$ vs. SCE (12). Indeed, it is well known that I_2 will oxidize CdS, and this reaction is used in an established analytical procedure (14). Since the oxidation of CdS by I_2 will occur at some finite rate, it may be possible to generate some reasonable concentration of I_2 at CdS. However, it is the long-term stability that is of importance here. Moreover, an axiom of inorganic photochemical systems is that, at the very least, the role of the light is to accelerate thermodynamically favorable chemical processes. Thus, irradiation of CdS in the presence of I_2 should increase its rate of spontaneous oxidation.

Table I. Calculated standard potentials for decomposition half-reactions of several semiconductors

Compound	Half-reaction	E_D° (V vs. SCE)
TiO ₂	$TiO^{2+} + \frac{1}{2} O_2 + 2e^- \rightleftharpoons TiO_2$	+1.18
ZnO	$Zn^{2+} + \frac{1}{2} O_2 + 2e^- \rightleftharpoons ZnO$	+0.65
	$Zn(OH)^+ + \frac{1}{2} O_2 + 2e^- \rightleftharpoons ZnO + OH^-$	+0.52
	$ZnO_2^{2-} + 2H_2O + \frac{1}{2} O_2 + 2e^- \rightleftharpoons ZnO + 4 OH^-$	+0.19
Fe ₂ O ₃	$2Fe^{3+} + 3/2 O_2 + 6e^- \rightleftharpoons Fe_2O_3$	+1.00
WO ₃	$WO_4^{2-} + 4H^+ + \frac{1}{2} O_2 + 2e^- \rightleftharpoons WO_3 + 2H_2O$	+1.40
SnO ₂	$Sn^{4+} + O_2 + 4e^- \rightleftharpoons SnO_2$	+1.11
CdS	$Cd^{2+} + S + 2e^- \rightleftharpoons CdS$	+0.08

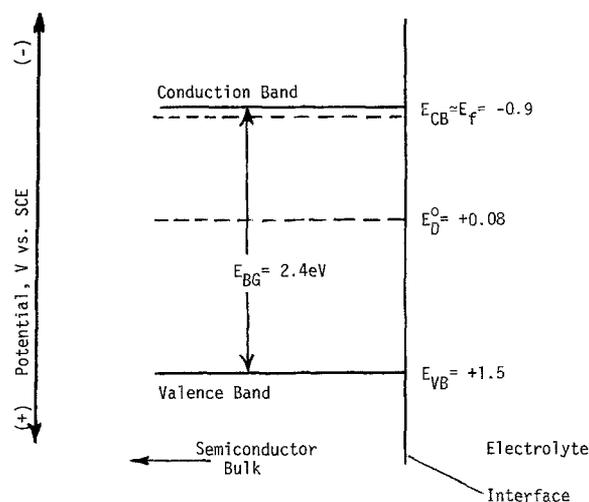
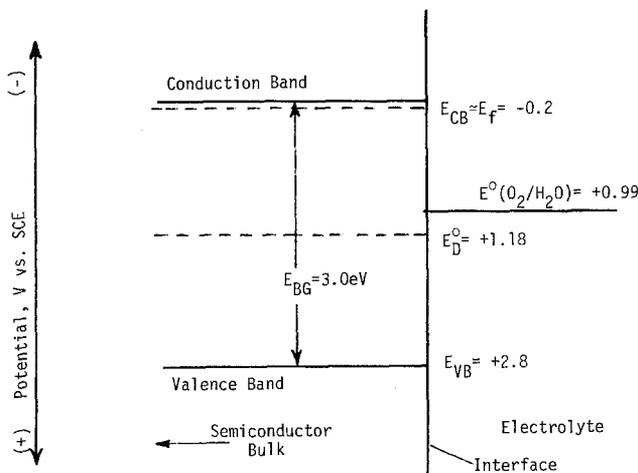


Fig. 4. CdS in aqueous solution

In the presence of X^{2-} ($X = S, Se, Te$) the positions of E_{CB} and E_{VB} for CdS are located at more negative potentials, but the E_{redox} values (12, 15) for X^{2-}/X_n^{2-} at $-0.7, -0.9,$ and $-1.1V$ vs. SCE for $X = S, Se,$ and $Te,$ respectively, are all sufficiently negative that the elemental chalcogen is incapable of oxidizing CdS. Thus, long-term stability can be expected provided the $X^{2-} \rightarrow X_n^{2-}$ oxidation is 100% efficient. Incidentally, it is worth noting that the lightest elemental chalcogen, O_2 , is thermodynamically capable of oxidizing CdS, since in H_2O the E for the O_2/H_2O couple under 1 atm of O_2 ranges from $+1.0$ to $+0.16V$ vs. SCE from $pH = 0$ to $pH = 14$ (12). Likely primary oxidation products from H_2O (such as $\cdot OH$ or H_2O_2) are certainly capable of spontaneously oxidizing CdS. However, the slow rate of the reaction of CdS with O_2 may make it possible to use this material as the photoanode in a cell for the electrolysis of H_2O , provided intermediates like $\cdot OH$ and H_2O_2 can be avoided.

The other n-type CdX photoelectrodes can be treated in the same way as CdS. At this time, the point to emphasize here is that the position of E_D° for CdS is significantly more negative ($\sim 1.4V$) than E_{VB} and, therefore, limits the immediately foreseeable output voltages in stable aqueous systems to about $1.0V$. This projection is clearly altered if the band positions can be moved substantially more negative by specific interactions with the electrolyte; e.g., in the presence of X^{2-} the bands move more negative by $\sim 0.5V$, while E_D° is presumably constant (6).

For a stable oxide semiconductor the value of E_D° lies at more positive potentials. For example, the energetics for TiO_2 (16) electrode immersed in a solution of $pH = 0$ are shown in Fig. 5, E_D° , calculated from available free energy data (12) for the half-reaction $TiO^{2+} + \frac{1}{2} O_2 + 2e^- = TiO_2$, is $+1.18V$ vs. SCE, which is $0.18V$ positive of the E for the O_2/H_2O reaction at $pH = 0$. At more alkaline pH's both the flatband potential and the E_{redox} for O_2/H_2O shift toward more negative values by about 59 mV/pH unit, while E_D° is independent of pH, as long as TiO^{2+} is the predominant Ti (IV) species in solution. Thus, the separation between E_D° and $E(O_2/H_2O)$ increases with increasing pH, leading to greater stability of the material. The value of E_D° is consistent with an equilibrium constant for the reaction $TiO_2 + 2H^+ \rightleftharpoons TiO^{2+} + H_2O$ of 2×10^{-7} . In sufficiently acidic solutions some small amount of dissolution of the TiO_2 may occur. Indeed, the change observed in surface morphology of a TiO_2 single crystal immersed in $1.0N$ H_2SO_4 under irradiation (17) may represent this light-catalyzed dissolution. At higher pH's the TiO_2 electrode is stable, even

Fig. 5. TiO_2 in aqueous solution at $\text{pH} = 0$

under prolonged irradiation, as predicted from the above discussion. Note, however, that E_D° lies quite negative of E_{VB} and, as discussed for CdS, may limit how positive the potential of an added redox active electrolyte can be, for use in a photoelectrochemical cell without encountering stability problems with the electrode. It is also of interest to consider the behavior of the electrode in a nonaqueous solvent, e.g., acetonitrile. E_D° will become more positive in a solvent which complexes or solvates the lattice metal ion to a smaller extent, yielding a more stable semiconductor with respect to photo-oxidation.

The behavior of ZnO in aqueous electrolytes is also an interesting case. For the half-reaction $\text{Zn}^{2+} + \frac{1}{2} \text{O}_2 + 2e^- = \text{ZnO}$, E_D° is $+0.65\text{V vs. SCE}$ (12). This lies near or negative of $E(\text{O}_2/\text{H}_2\text{O})$ at all pH's (when E_D° is calculated for the appropriate Zn(II) species, i.e., Zn^{2+} , $\text{Zn}(\text{OH})^+$, or ZnO_2^{2-}) and is consistent with the known instability of ZnO under irradiation, even though E_{CB} and E_{VB} are located at about the same positions for ZnO and TiO_2 (16, 18, 19). Thus, it is E_D° rather than E_{VB} which governs the long-term stability of the material. It is true that the position of E_{VB} is related to the bonding energy of the valence electrons and thus the stability of the lattice. However, in terms of half-reactions, E_{VB} represents the potential for the abstraction of one electron from the lattice (e.g., $\text{CdS}^+ + e = \text{CdS}$), whereas E_D° involves equilibrium constants and potentials involving the intermediate species which may be so thermodynamically favorable as to make E_D° quite negative of E_{VB} . Thus, while redox couples with potentials near E_{VB} clearly will cause decomposition of the lattice (7), in fact couples at even more negative potentials are capable of oxidizing the semiconductor. Ideally, E_D° should be at, or below E_{VB} . For the semiconductor materials investigated for which thermodynamic data are available, even the very stable ones (9), such as SnO_2 , WO_3 , and Fe_2O_3 , E_D° is negative of E_{VB} for an aqueous solution.

Though p-type semiconductors have received some attention as photocathodes, p-type semiconductor-based photoelectrochemical cells have not been found to be very efficient. We note that the systems studied, e.g., p-GaP, GaAs, CdTe, (20-23) all have n-type counterparts which undergo photoanodic dissolution in aqueous solution (1, 6, 24-26). This allows us to conclude that the E_D° in each case is situated at a potential which is more negative than E_{VB} . Since a heavily doped p-type material has $E_f \approx E_{VB}$ at the flatband potential, E_{FB} , the p-type material is thermodynamically unstable to anodic dissolution at E_{FB} in particular and at potentials more positive than E_D° . The flatband condition for a p-type electrode is shown in Fig. 6

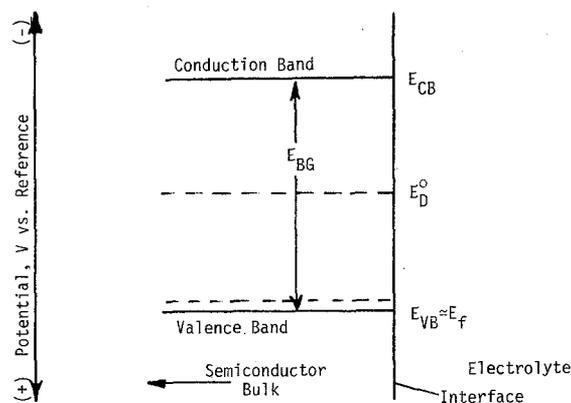


Fig. 6. P-type semiconductor at flatband potential

and since the majority of charge carriers are holes, it is apparent that the anodic dissolution may occur. At least, the dissolution will occur until the E_f at the surface is approximately E_D° . Consequently, in practice, p-type semiconductors having a fairly negative E_D° may give poor output photovoltages. Logically, other factors concerning p-type materials must be considered, including the standard potential for cathodic reaction, e.g., $\text{CdTe} + 2e^- \rightarrow \text{Cd} + \text{Te}^{2-}$. For p-type materials such a reaction should be feasible for E_{CB} more negative than such a potential. And again, whether the semiconductor is stable may depend in large measure on relative rates of minority carrier (e^-) interfacial transfer vs. the cathodic decomposition of the semiconductor.

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Photoelectrochemical Processes at Semiconducting WO₃ Layers

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ABSTRACT

The basic electrochemical properties of WO₃ electrodes are described. The influence of the preparation techniques on the photoelectrochemical behavior of the electrodes is reported. The results are discussed in view of applications in solar energy conversion systems.

The tungsten oxide (WO₃) is a transition metal oxide with a number of interesting optical and electrical properties (1, 2). During the last years new interest arose in it because of its potential use in small area displays (3). The subject of our interest, however, is its use as light-sensitive electrodes in a semiconductor/electrolyte solar cell.

Semiconductor/electrolyte cells are considered as potential solar energy converters [for a review see (4)]. In principle they allow a direct conversion into electrical and/or chemical energy. Few self-regenerative solar cells have been realized (5-8), and direct photoelectrolysis has been reported (9, 10). Problems arise from the photocorrosion [see, e.g., (11, 12)] of the semiconductor electrode. Most known semiconductor electrodes immersed in an aqueous electrolyte show this phenomenon, and other semiconductors (e.g., TiO₂) which are known to be stable have energy gaps which are too large to be used efficiently for solar energy conversion. In order to find suitable electrodes, it seems to be necessary to investigate less known semiconductor materials with respect to their photoelectrochemical behavior. In this paper we present results obtained from some investigations with WO₃ electrodes.

Different values of the bandgap energy of WO₃ have been reported ranging from 2.5 to 3.65 eV (2, 13). This scattering is probably due to a strong influence of the preparation technique on the electrical and optical properties. Tungsten oxide can be obtained in different colors from lemon yellow to dark blue. The color can be changed also by electric charge injection [electro-

and electrochromism, see, e.g., (3)]. For the coloration mechanism several models have been proposed; in any case the degree of disorder due to lattice defects seems to play an important role. Electrochemical investigations in relation to display applications were performed already by Chang *et al.* (17), and preliminary experiments in connection with solar energy conversion were reported by Hodes *et al.* (18) and by Butler *et al.* (27).

Experimental

Tungsten oxide layers were prepared by two different techniques:

(i) By sputtering WO₃ powder on tungsten sheet, films of thicknesses 0.4-0.7 μm were obtained which were transparent and showed typical interference colors. X-ray analysis revealed a diffraction pattern typical for a crystalline structure of composition WO_{2.98} (19). A heat-treatment in an oxygen atmosphere for only 10 min at 600°C effected a visible darkening of the films. The original greenish interference color turns into dark blue. Obviously the oxide reacts further with the tungsten substrate, leading to lower tungsten oxides.

(ii) By thermal oxidation of tungsten sheets (purity 99% in an oxygen atmosphere at 780°C) oxide layers of several μm thickness were obtained. If the oxidation time was shorter than ca. 15 min, the oxide layers assumed a dark blue color; for longer times a lemon yellow color was obtained. X-ray analysis also revealed here a diffraction pattern compatible with a