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## Discussion

The results presented in the previous sections shall now be summarised and their physical significance discussed. In particular, the following points will be of interest in this chapter:

- The comparison of the different  $\text{Au}_2\text{O}_3$  samples as to be deduced from the EXAFS analysis. Degree of order, symmetry effects and influence of the preparation will be discussed.
- The discussion of the growth and decomposition behaviour of electrochemically prepared gold(III) oxide.
- The thermodynamical data obtainable from TPD measurements, its relation to other works and interpretation.
- The electronic structure of the surface layers and its change due to different oxidation procedures as analysed *via* XPS.

### 4.1 EXAFS Results

Before going into details, it should be mentioned that the commercially available  $\text{Au}_2\text{O}_3$  exhibits the same structural features as the electrochemical compound. For this reason, only the difference between the electrochemical and the crystalline material will be discussed. Unfortunately, no information on the preparation of the commercial  $\text{Au}_2\text{O}_3$  is available. It is, however, reasonable to assume that the preparation will somehow involve precipitation from a  $\text{Au}^{3+}$  solution, e.g. tetrachloroauric acid. If this is the case then the similarities between the two materials can be understood. It is known from catalytic experiments [27, 28] that the precipitation of Au from  $\text{Au}^{3+}$  solutions yields small particles (approx. 3 nm in size). As the electrochemical growth procedure consists of the sum of a dissolving and an oxidation process it is not astonishing that the particles obtained *via* the two routes are nearly identical concerning the structure. The first obvious difference between the crystalline and the electrochemically prepared oxide is the degree of order. From the

EXAFS analysis of crystalline gold oxide one can deduce a high degree of crystallinity, which is in line with XRD results. This conclusion can be drawn from the facts that (i) the  $S_0^2$  value is greater in the case of the crystalline compound than in the electrochemical (0.87 vs. 0.72) and (ii) that more significant scattering paths can be included in the fit for the crystalline material. Furthermore, for the 1<sup>st</sup> shell oxygen atoms, the Debye Waller (DW) factors are slightly higher in the case of the electrochemically prepared oxide. The EXAFS analysis of electrochemical  $\text{Au}_2\text{O}_3$  yields essentially the square planar arrangement of oxygen atoms around the central gold absorber while the crystalline compound shows contributions from all important single scattering paths up to 4 Å. Hydrogen atoms cannot be detected with this method, but it is likely that the terminating oxygen atoms are saturated with this element. Three of the four oxygen atoms show no evidence of neighbouring atoms in the EXAFS analysis. The fourth is coordinated with a second gold atom, which in turn has two additional oxygen atoms as nearest neighbours. This picture is in line with the dominating structure of crystalline  $\text{Au}_2\text{O}_3$ , being a unit of two  $[\text{AuO}_4]$  units linked *via* common vertices which are detectable in the EXAFS analysis of the electrochemical material. The overall analysis gives rise to a model of at least two linked  $[\text{AuO}_4]$  units with no significant long-range order. More atoms of the covalent network in the crystalline compound are not detectable. Therefore, only the nearest Au atom and some of the oxygen atoms of the second shell can be observed. This structure corresponds to a chemical formula of  $(\text{OH})_3\text{Au-O-Au}(\text{OH})_3$ , which is contrary to the results described in [60]. Peuckert *et al.* describe the gold oxide obtained from electrochemical methods there as  $\text{AuOOH}$  species. This result cannot be confirmed within this thesis. It should be mentioned that the studies by Dickinson *et al.* [11] and Peuckert [60] have all been carried out under UHV conditions. These reductive conditions can lead to dehydration of the samples and therefore change the chemical composition of the oxides. This is critical especially for hydrated samples as the electrochemically prepared oxides. Additionally, the DW factors are larger in the case of the electrochemically grown material which points to a stronger damping of the EXAFS amplitudes by thermal disorder. The inclusion of cumulants with the FEFFIT algorithm yielded no significant fitting improvement. The static disorder is therefore higher in the electrochemical system. The crystalline oxide serves as a good example for a compound with low symmetry and its EXAFS analysis. As already pointed out, the EXAFS shows only contributions from single scattering paths, while high symmetry compounds (e.g.

Au metal) show large contributions of multiple scattering pathways to the EXAFS.

#### 4.2 Comparison between EXAFS and XPS Experiments

The first point which has to be discussed is that throughout all EXAFS experiments, only  $\text{Au}_2\text{O}_3$  and Au could be detected in the phases under investigation. This is true for both growth and decomposition process and also for the decomposition of commercial and crystalline  $\text{Au}_2\text{O}_3$ . Compared with the XPS studies (which will be discussed later in this chapter), this is a discrepancy which can be understood *via* the surface sensitivity of both methods. The XPS experiments (which exhibit two Au states and up to three oxygen states in the electrochemically oxidised samples, see below) are surface sensitive to  $\approx 10\text{-}20$  Å, while the EXAFS analysis has a depth sensitivity of  $\approx 1000$  Å. This fact is due to the escape depth of the produced electrons. In XPS, Au 4f and O 1s electrons are released from the material. With Mg  $K\alpha$  radiation as excitation source, this corresponds to kinetic energies of  $\approx 1100$  and 500 eV. From theoretical calculations [62, 81–84] it can be deduced (using the TPP-2 formula) that these electrons have an inelastic mean free path (IMFP) of 15 to 25 Å. For EXAFS in TEY mode, the situation is different. The excitation energy (11919 eV at the Au  $L_3$  edge) is much higher than in the case of the XPS studies. The main electrons originating from a source irradiated with photons of this energy are Auger LMM electrons. For these, an escape depth of 315 and 545 Å (for  $\text{Au}_2\text{O}_3$  and Au) can be calculated *via* Monte Carlo simulations [68]. It is obvious, that this fact imposes a large change in the surface sensitivity of both methods. Grazing incidence XAFS measurements could enhance the sensitivity, but were not available in this case due to difficulties in the experimental setup required for such measurements.

#### 4.3 Growth and Decomposition Process

The growth and decomposition of  $\text{Au}_2\text{O}_3$  has been intensively studied using electrochemical methods [9, 40, 49, 74], XPS [11, 60] and photometry [39]. Frankenthal *et al.* [15] investigated the corrosion of gold plates in electronic circuits while Whitton *et al.* [92] proposed a controlled removal procedure of gold. Lohrengel *et al.* summarised that the growth of anodic oxide layers on gold proceeds according to a high field mechanism at low overpotentials; at high overpotentials, a linear growth was found [4, 36, 75, 79]. They pointed

out that this growth mechanism differs significantly from that on other noble metals, where only monolayers are formed due to passivation processes. It was the aim of this thesis to provide more details on the structural changes during the growth and decompositions of anodically formed oxide layers. The literature provides little structural data. In this thesis, the linear growth of  $\text{Au}_2\text{O}_3$  at high overpotentials was confirmed (fig. 3.6). Furthermore, the linear growth was also borne out by the evaluation of EXAFS data presented here (figs. 3.13, 3.14, 3.17). It is important to state that (i) no other species than gold(III)oxide and gold metal were detected during the growth process. The agreement between the electrochemical and the EXAFS experiments is almost quantitative. Both methods yield growth constants in the same order of magnitude.

The decomposition of gold(III)oxide was previously studied mainly by XPS [38, 60]. It was concluded that the amount of  $\text{Au}^{3+}$  continuously falls during thermal treatment of the sample. The EXAFS studies presented in this thesis show that no other species than gold(III) oxide and gold metal are formed during the decomposition. This is in line with the statements of Jansen [35], who finds that for the oxide chemistry of gold, no other oxidation state than 3+ is stable. The comparison of the decomposition of the different samples (fig. 3.20), i.e. electrochemically prepared oxide, commercial oxide and crystalline oxide, shows that the decomposition proceeds at different rates. A direct correlation of the data presented here with a mechanism is difficult as more data would be needed. The fact that the oxides show different decomposition rates can be attributed to two possible factors:

- The degree of order in the samples. The electrochemical oxide shows a high degree of disorder as the crystalline substance is highly ordered. This could result in the fact that the oxygen atoms are more tightly bound in the lattice in the crystalline material (lattice energy).
- The degree of hydration. In the electrochemical case, water and OH groups are present in the substrate, which could mediate the decomposition process.

From the experiments carried out in this thesis, no decision can be made whether only one of these factors or both account for the change in the decomposition rates. It is likely that both factors play a role in this process.

#### 4.4 TPD Results

Concerning the gold/oxygen system one can generally say that most data published on this system mainly stems from TPD or XPS analysis of oxygen/gold systems, where mainly single crystals have been analysed. The main focal points of interest in the first published studies were:

1. Is oxygen capable of adsorbing on a clean gold surface, a question basically reviewed by Saliba *et al.* [65].
2. The nature of the chemisorption barrier for oxygen on gold and how to overcome this problem. The main techniques used to overcome this barrier are:
  - thermal dissociation of oxygen [10, 66]
  - use of microwave discharges [48]
  - sputtering of  $O^+$  ions [18, 61]
  - $NO_2/H_2O$  application [91]
  - ozone application [41, 47, 59, 65]
  - electrochemical oxidation [60]
  - electron bombardment of physisorbed  $O_2$  [19].

In this thesis the aim is to correlate the results obtained in my experiments with the literature. As can be seen from the previous chapter, electrochemically grown  $Au_2O_3$  exhibits one TPD peak. The analysis of the heating rate variation experiment yields a desorption energy of 133 kJ/mol ( $T_{des}=570$  K at  $\beta=3.71$  K/s). It is also obvious that no dioxygen peak appears if the oxidation potential is chosen to be lower than a critical value of 1.6 V. Below this value, only OH and  $H_2O$  signals are visible in the TPD. A strong  $H_2O$  and OH background is always observed which can be attributed to the experimental conditions (transfer of a highly hydrated sample into UHV). The fact that no dioxygen peak appears in the TPD spectra below  $U_{ox}=+1.6$  V is in line with results from literature which claim that above this value, bulk oxidation sets in. To correlate this behaviour with UHV experiments, systematic  $O_2$  plasma oxidation studies have been carried out. These show the existence of up to four TPD signals depending mainly only on the exposure time to the dioxygen plasma. These four signals are mainly (i) a slight increase of the baseline setting in at 360 K, (ii) a sharp desorption signal at 510

K, (iii) a shoulder at 565 K which corresponds to the desorption signal of O<sub>2</sub> from an electrochemically oxidised sample and (iv) a broad peak at T=670 K. For all these signals, a heating rate variation as well as a Redhead analysis has been carried out. All data summarised in table 4.1 have been calculated

Table 4.1: Summary of TPD data obtained in this thesis. All values listed here have been determined with the heating rate variation technique, except the value for the  $\gamma_1$  peak.

Experiment	State	T <sub>des</sub> [K]	$\beta$ [K/s]	E <sub>d</sub> [kJ/mol]
O <sub>2</sub> plasma exposure (300 s, p=8·10 <sup>-3</sup> mbar)	$\gamma_1$	367	3.71	43
	$\gamma_2$	511	3.71	114
	$\beta_2$	550	3.71	135
	$\gamma_3$	659	3.71	116
Potentiostatic oxidation (E=1.8 V vs. SCE, 600 s)	$\beta_2$	550	3.71	135
Galvanostatic oxidation (I=50 $\mu$ A, 300 s)	$\beta_2$	561	3.71	135

using the heating rate variation technique as well as the *Redhead* equation. It should be mentioned, that especially for the  $\gamma_1$  and  $\gamma_3$  state, the heating rate variation seems to yield incorrect results (for  $\gamma_1$ , no exact peak positions can be determined and for  $\gamma_3$  the value calculated is too low). Therefore, it is likely that the Redhead approximation - although imposing a lot of simplifications - yields the better result in these cases. To compare these results with the literature, table 4.2 lists some selected published data on different Au/O TPD experiments. The interesting aspect of these data is the similarity to results found on Au(111) single crystals. This is in line with the fact that gold foil exhibits mainly (111) facettes, which has been proved by XRD measurements. A further point which has to be discussed is the relation to the results found in the studies of activated O species on Au(110) [19]. Gottfried *et al.* find that by irradiating UV light or electrons on a sample of physisorbed oxygen on Au(110) yields TPD states above 550 K which seem to be similar to the  $\beta_2$  state found in this study. The state Gottfried finds increases in intensity with increasing electron/UV exposure time and reaches a maximum value. This similarity suggests that activated oxygen compounds are

Table 4.2: Summary of TPD data provided in the literature.

Experiment	States ( $T_{des}$ [K])	$\beta$ [K/s]	Reference
electrochemical oxidation (0.5 M H <sub>2</sub> SO <sub>4</sub> )	$\alpha$ (400)	5.00	Peuckert <i>et al.</i> [60]
	$\beta$ (600)	5.00	
	$\gamma$ (890)	5.00	
O <sub>3</sub> exposure 0.03 - 1.0 ML	$\beta_1$ (520)	8.50	Saliba <i>et al.</i> [65]
	$\beta_2$ (550)	8.50	
reactive sputtering of Au in oxygen plasmas	$\gamma_1$ (473)	0.17	Maya <i>et al.</i> [51]
	$\gamma_2$ (603)	0.17	
	$\beta$ (623)	0.17	
exposure of Au (110)-(1x2) to oxygen/hot filament	$\beta_1$ (525)	15.00	Sault <i>et al.</i> [66]
	$\beta_2$ (575)	15.00	
exposure of Au to oxygen/hot filament	$\beta_1$ (650)	21.50	Canning <i>et al.</i> [10]
	$\beta_2$ (680)	21.50	
exposure of Au(111) to O <sub>3</sub>	$\beta_1$ (525)	8.50	Parker <i>et al.</i> [59]
	$\beta_2$ (550)	8.50	
physisorbed O <sub>2</sub> on Au(100)-(1x2)	$\alpha_1$ (38 K)	2.35	Gottfried <i>et al.</i> [19]
	$\alpha_2$ (44 K)	2.35	
	$\alpha_3$ (51 K)	2.35	
	$\mu$ (35 K)	2.35	
physisorbed O <sub>2</sub> after e <sup>-</sup> bombardment	$\beta$ (530 K)	2.35	

able to oxidise gold surfaces even at low temperatures. As nearly all authors who investigated the oxidation of gold under UHV conditions with different methods (see above) find evidence for the existence of a more or less significant amount of oxidised species on the surface (either with XPS or TPD measurements), it appears to say that all methods yield a compound similar to gold(III) oxide. The differences in the oxidation methods manifest themselves in different efficiencies of oxidation and - in the case of electrochemical oxidation - also the degree of hydration of the samples.

#### 4.5 XPS Results

Despite the fact that the combination of electrochemical experiments with UHV methods is achievable, only few publications deal with the investigation of electrochemically prepared samples. Most XPS data is available from experiments with oxidising compounds as  $O_3$ ,  $NO_x$  or  $O_2$  RF plasma discharges. Absolute binding energies reported in these studies vary significantly. Table 4.3 summarises the literature up to now. In this table, only the peak positions are given, FWHM, Gauss/Lorentz distribution and area are not listed. The data obtained in this study have already been given in table 3.6. A closer look at the XPS interpretation found in the publications given above reveal that most authors did not apply the strict fitting procedures followed in this work. Concerning the work on UHV oxidation methods ( $O_3$ , UV, plasma oxidation) one can state the following:

- Saliba *et al.* [65] only showed the O 1s region but performed no fit routines. They find a slight peak shift, which could also be understood by applying a fit with two Gaussian functions of which one grows only at higher coverages. If one compares their data with those presented here, similarities can be seen. Therefore, the interpretation given here (two oxygen states formed due to  $O_2$  plasma oxidation procedures) appears reasonable.
- The data presented by King *et al.* [41] is more consistent and shows two O 1s signals after UV/ $O_3$  oxidation of a gold surface. The authors claim that the peak widths varied only slightly, but a look at the fit reveals visible differences. The difference between the two peak positions in their case is 1.8 eV, while in this work, a value of 1.5 eV is reported. This could be due to the fact that not the same FWHM values have been applied in King's studies.
- Krozer *et al.* [47] explicitly report differences in the FWHM values, which are attributed (in the case of the Au 4f lines) to Au atoms which lie near  $AuO_x$  species.
- Studies by Koslowski *et al.* [46] have to be treated with caution because they applied two peaks with a very large FWHM value and one with a smaller one and attribute the two side peaks to contaminations by water or hydroxyl groups. However, the Au 4f spectra presented in

Table 4.3: Summary of XPS data provided in the literature.

Experiment	Line	BE Value(s) [eV]	Reference
UV/O <sub>3</sub> exposure 1h	Au 4f	84.0	King <i>et al.</i> [41]
	Au 4f	85.4	
	O 1s	529.6	
	O 1s	531.4	
UV/O <sub>3</sub> exposure 1h	Au 4f	84.0	Krozer <i>et al.</i> [47]
	Au 4f	84.85	
	O 1s	529.0	
	O 1s	530.1	
O <sub>3</sub> exposure (1 ML)	Au 4f	84.0	Saliba <i>et al.</i> [65]
	O 1s	529.8 - 530.1	
O <sub>2</sub> plasma exposure p=1-3 mbar, P=50-100 W	Au 4f	84.0	Koslowski <i>et al.</i> [46]
	Au 4f	85.8	
	O 1s	529.1	
	O 1s	530.2	
	O 1s	532.0	
electrochemical oxidation (0.5 M H <sub>2</sub> SO <sub>4</sub> )	Au 4f	84.0 - 84.1	Peuckert <i>et al.</i> [60]
	Au 4f	85.7 - 86.1	
	O 1s	530.7 - 532.4	
electrochemical oxidation (0.5 M H <sub>2</sub> SO <sub>4</sub> )	Au 4f	83.8	Juodkazis <i>et al.</i> [38]
	Au 4f	85.9	
	O 1s	530.0	
	O 1s	532.0	
electrochemical oxidation (0.5 M H <sub>2</sub> SO <sub>4</sub> )	Au 4f	84.0	Dickinson <i>et al.</i> [11]
	Au 4f	85.9	
	O 1s	531.5	
	O 1s	532.8	

this study show the same feature as has been observed here - i.e. that the lines for the oxidic species are broader than the metallic ones. This fact is not discussed in the publication by Koslowski *et al.*

The data published on electrochemically prepared materials can be summarised as follows:

- Peuckert *et al.* [60] interpret the O 1s data as a superposition of two oxygen states - an oxidic and one hydroxidic peak. In this study, by a careful XPS data analysis, three species of oxygen could be detected on the surface.
- Juodkazis *et al.* [38] did not perform peak fitting but also observe a shift of the peak maximum towards lower BE values if the oxidation potential is increased. This is also found in this thesis.

For a more precise interpretation of the XPS data obtained in this thesis, the peak intensity ratios O 1s / Au 4f have been computed for the sum of all intensities as well as for the different oxidic compounds. For the oxygen phases obtained *via* the oxygen plasma, a peak form analysis of the 60 s / 250 eV spectra shows one O 1s signal (529.3 eV,  $O_{sp}$  1 in table 3.6) and two Au 4f components (84.0 eV - Au<sup>0</sup> and 85.6 eV - Au<sup>3+</sup>). The addition of CO to a surface exposed to a plasma discharge of oxygen leads to an immediate decrease (about 50%) of the O/Au ratio in the XP spectra. The surface states furthermore vanish at lower temperatures. This suggests a highly reactive O species on the Au surface. However, after CO addition, a signal remains in the XP spectrum. This can be attributed to the fact that CO only titrates the topmost layers of oxygen (i.e. the atoms not incorporated in the metal). The second O 1s signal which is detectable at high exposure times, could be a hint on the population of the bulk oxygen states available in the material. For some selected electrochemically prepared oxide samples, the peak intensity ratios are given in fig. 4.1 and 4.2. The interesting points are (i) the existence of three distinguishable states with BE values corresponding to an oxidic, an hydroxidic and an aqueous surface state and (ii) the drastic change in the relative intensities of these three states. The intensity changes show a conversion of the sample from an oxidic character at the beginning of the heat up to a hydrous one at the end. The high temperature stability which has already been mentioned in the previous chapter is remarkable.

