In situ QEXAFS Study of the Thermal Decomposition of Anodically Grown Gold Oxide

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In recent years, the system oxygen/gold has received much attention through the discovery of highly active, oxide-supported gold catalysts for the low-temperature oxidation of carbon monoxide [1,2]. Mechanistically, this system is currently not very well understood. It has been suggested that the energetically most unfavourable elementary step of the reaction, namely dissociation of dioxygen (O2), leaves the gold particles covered by highly reactive atomic oxygen in a chemisorbed, oxidic or sub-surface state [1]. Unfortunately, however, very little is known about the chemical properties of such oxygen species in contact with gold.

The interfacial chemistry in the system oxygen/gold has previously not been the subject of many investigations because of the difficulties involved in preparing oxidised gold and chemisorbed layers of oxygen on gold under the ultra-high vacuum conditions required by the most common experimental techniques in surface and interface science. Similarly, the crystallographic properties of the only gold oxide known to be stable at ambient conditions, namely Au2O3, have only been elucidated in relatively recent times [3], as single-crystals of Au2O3 of sufficient quality and size were difficult to obtain. Almost nothing is known about the electronic structure of the compound, while its thermochemical behaviour has been the subject of only a few brief investigations [4]. An exception to the relative lack of interest in oxidised gold is the electrochemical literature, which contains several systematic studies of gold oxidation in aqueous solutions by voltammetric techniques [4-7]. These provide good indicators for the growth and decomposition kinetics of anodic oxide layers under control of the electrochemical potential. However, structural investigations or studies by spectroelectrochemical techniques probing their electronic structure have been rare (exceptions are two XPS studies [8,9]).

Figure 1: Gas-flow total electron-yield QEXAFS scan for the thermal decomposition of an anodically grown oxide layer on a polycrystalline gold foil. Only the near-edge region and part of the EXAFS are shown. Spectra were actually acquired over the photon energy region extending to 12580 eV. The duration of one such scan was 90 s. The thickness of the oxide layer was initially larger than the probing depth of TEY detection, i.e., > 1000 Å.
We have now prepared oxide layers on gold by galvanostatic oxidation at high current densities (> 10 mA/cm²), using 0.1 m HClO₄ as electrolyte solution. We followed the structural and electronic properties of these layers as a function of anodic oxidation time and current density by XAFS in the total electron-yield mode at station A1 of HASYLAB (see contribution in this Annual Report: N. Weiher & S.L.M. Schroeder: Anodic Oxide Growth on Gold: A Study of Emersed Gold-Electrodes by Gas-Flow Total Electron-Yield XAS). A central result of these studies is that the oxide films formed under the chosen conditions are, after emersion, essentially Au₂O₃ with a significant degree of disorder. We have now also followed the thermal decomposition of such layers by total electron-yield QEXAFS at station X1, during beamtime allocated in December 1999. Here we present selected results from these investigations. Qualitatively, we can already state from our preliminary inspection of the data that significant decomposition of the oxide layers begins at temperatures just above 100°C. The decomposition proceeds fast in the temperature region between 130°C and 170°C and reaches completion quickly at approximately 230°C. A full, quantitative analysis of the data body obtained during this beamtime is currently being performed in our laboratory.

Figure 2: Fourier-transformed EXAFS data (calculated using the GNXAS package) of one run of thermal decomposition of an anodic oxide layer grown on gold.

References