Sulphur overlayers on the Au(110) surface: LEED and TPD study.

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Abstract

The adsorption and desorption of sulphur on the clean reconstructed Au(110)–(1×2) surface has been studied by low energy electron diffraction, Auger electron spectroscopy and temperature programmed desorption. The results obtained show a complex behaviour of the S/Au(110) system during sulphur desorption at different temperatures. Two structures of the stable ordered sulphur overlayer on the Au(110) surface, p(4×2) and c(4×4), were found after annealing the S/Au(110) system at 630 K and 463 K, respectively. The corresponding sulphur coverage for these overlayers was estimated by AES signal intensity analysis of the Au NOO and S LMM Auger lines to be equal to 0.13 ML and 0.2 ML, respectively. Both sulphur structures appear after removing an excess of sulphur, which mainly desorbs at 358 K as determined from TPD spectra. Furthermore, it was not possible to produce the lower coverage p(4×2) sulphur structure by annealing the c(4×4) surface. In the case of the p(4×2) S overlayer on the Au(110)–(1×2) surface it is proposed that the sulphur is attached to "missing row" sites only. The c(4×4) S overlayer arises via desorption of S_2 molecules that are formed on the surface due to mobility of sulphur atoms after a prolonged anneal.

Introduction

The adsorption and desorption of sulphur or sulphur containing compounds on metal surfaces has been an area of intense experimental and theoretical investigation for several decades, because the bonding of such compounds to metal surfaces is an important topic in catalysis (catalyst poisoning and hydrodesulphurisation processes), interfacial physics, electrochemistry and material science [1-11]. The nature of the sulphur-metal interaction is believed to influence the self-assembly mechanism of ordered overlayers, thus affecting the functionality of the surface for practical applications in catalysis, lubrication, adhesion, sensor devices and anchoring large sulphur-containing biomolecules. The possibility of several different ordered sulphur overlayers forming on a given metal surface suggests a complicated balance of forces between the adsorbed sulphur atoms or molecules and between these sulphur species and the metal surface. Low energy electron diffraction (LEED) and temperature programmed desorption (TPD) provide information about structure and bonding interaction, respectively, within the chosen sulphur-metal system which can help elucidate the sulphur adsorption process.

The present work is aimed at investigating the adsorption and desorption of sulphur atoms on the clean reconstructed Au(110)–(1×2) surface by means of LEED, Auger electron spectroscopy (AES) and TPD. The results of this work provide important information about the possible types of the ordered sulphur overlayers on the Au(110) surface that could shed light on sulphur adsorption processes and give a starting point to develop an understanding of the mechanism for anchoring large sulphur-modified organic molecules on gold surfaces.

Experiment

All experiments were performed in an ultrahigh vacuum chamber of base pressure 1×10^{-10} mbar. The chamber was equipped with LEED, AES and mass spectrometry facilities. The temperature of the single crystal Au(110) sample (Surface Preparation Laboratory) was monitored by a chromel-alumel thermocouple inserted in a hole at the side of the crystal. The Au(110) crystal was cleaned *in situ* by repeated cycles of argon ion sputtering ($U = 1$ kV) and annealing at 820 K until a (1×2) LEED pattern with sharp diffraction spots was obtained. A sulphur molecular beam was generated from decomposition of silver sulphide in a solid-state electrochemical cell Pt/Ag/AgI/Ag_2S/Pt [12] and adsorbed at room temperature on the clean reconstructed Au(110)–(1×2) surface. The total pressure during sulphur deposition was in the 10^{-8} mbar range. The sulphur coverage on the Au(110) surface was determined by comparing the intensities of the Au NOO and S LMM Auger emission lines. The AES spectra were recorded using a retarding field analyser with a 3 keV incident electron beam. TPD experiments were performed using a Vacuum Generators VGQ residual gas analyser. The intensities of mass 32 (S) and mass 64 (S_2) species were monitored simultaneously during the desorption process. The heating rate during all TPD measurements was 2 K per second.

Results

The clean Au(110) surface exhibits a (1×2) reconstruction described by the "missing row" model [13, 14]. In this model every second row of closed packed atoms in the [1$\bar{1}$0] direction is omitted and the unit cell is doubled in the [001] direction. Fig. 1(a) shows typical LEED pattern obtained from the clean Au(110)–(1×2) reconstructed surface. This

atomically clean surface was the starting point for all the experiments reported in this paper.

Sulphur was deposited onto the clean Au(110)–(1×2) surface at room temperature from the electrochemical cell. After an exposure of approximately 6 L of S_2, the thickness of the sulphur layer on the Au(110) surface reaches a saturation coverage which is equal to approximately 0.75 monolayer (ML). This value was obtained from an AES signal intensity analysis of the Au NOO and S LMM Auger lines taking into account the corresponding sensitivity factors [15] and photoelectron mean-free path data [16, 17]. The thickness of the first 3.5 ML of the Au(110)–(1×2) surface is equal to 3.85 Å [14]. The inelastic mean free path of an electron having energy of 70 eV (intensity maximum of the Au NOO Auger line) in gold is approximately equal to 5 Å [17]. Taking into account the ratio between sensitivity factors for S and Au which is equal to 2.1 [15] and that the relative intensity ratio between Au NOO and S LMM AES signals is equal to 2.2 for the saturated sulphur layer, the thickness of the latter is estimated to be 0.75 ± 0.05 ML. Approximately the same thickness for the saturated sulphur layer was reported in previous studies of sulphur or sulphur containing compounds on Au(110) [1], Au(111) [3] and Au(100) [4]. Further exposure to 50 L S_2 did not change the relative intensity of the Au NOO and S LMM AES signals. The saturated sulphur layer on Au(110) produced no well defined LEED pattern.

Fig. 1 (b-d) shows the LEED patterns from two sulphur overlayer structures on the Au(110)–(1×2) surface obtained by applying different annealing procedures to the saturated sulphur layer. After annealing the initially deposited saturated sulphur layer at 630 K for one hour, a sharp LEED pattern (Fig. 1(b)) was obtained corresponding to the p(4×2) sulphur structure. Annealing the initially deposited saturated sulphur layer at lower temperature (463 K) produces a different sulphur structure, namely c(4×4), having the

corresponding LEED patterns presented in Fig. 1, (c) and (d). For this type of sulphur overlayer the annealing time plays a significant role in increasing the definition of the LEED pattern. Indeed, the initial stage of c(4×4) sulphur overlayer was formed after 3 hours of annealing at 463 K. Further annealing of up to 10 hours at the same temperature greatly improved the quality of the corresponding LEED pattern (Fig. 1 (d)) which is attributed to the removal of a small quantity of the adsorbed sulphur which is seen from an AES spectra analysis. It should be noted that even after a 10 hour anneal there is still evidence of disorder in the c(4×4) LEED pattern as seen by the "streaking" along the [001] direction (× 2 direction of the clean Au surface). Furthermore, it was not possible to produce the p(4×2) sulphur structure by annealing the c(4×4) surface at 600 K. A complicated intermediate LEED pattern (not presented here) having contributions from both structures was obtained in this case. No effects due to electron beam induced damage were observed during acquisition of the LEED images and spectra from the sulphur overlayer structures.

Fig. 2 shows a comparison of the IV-LEED spectra measured for some of the bulk and fractional order beams in the case of the clean Au(110)–(1×2) surface (top curves) and the p(4×2) sulphur overlayer structure (bottom curves). It is clear that there is a good correlation between the peak positions and intensities in the spectra for all diffraction spots. This fact allows us to conclude that the Au surface remains (1×2) reconstructed underneath the sulphur overlayer. Although small changes in the IV spectra for some diffraction beams are observed in Fig. 2 between the Au(110)–(1×2) surface and the p(4×2)-S-Au(110) surface, this may be attributed to small displacements of the Au atoms participating in adsorption sites.

The corresponding AES spectra measured from the clean Au(110)–(1×2) surface, the ordered sulphur layers and at some intermediate stages are presented in Fig. 3. The spectra

are normalized to the intensity of the Au NOO main line. The Auger spectrum obtained from the p(4×2) sulphur overlayer (Fig. 3, curve f) shows a significant reduction of the S LMM signal intensity in comparison with the saturated sulphur layer (Fig. 3, curve b). The ratio of the intensities of the main lines in the S LMM and Au NOO Auger spectra (I_S/I_{Au}) decreases from 1/2.2 for the saturated sulphur layer to 1/8.3 for the p(4×2) S overlayer on the Au(110) surface. The surface coverage of this sulphur layer was estimated to be approximately 0.13 ML according to AES signal intensity analysis. The ratio of intensities of the main lines in the S LMM and Au NOO Auger spectra (I_S/I_{Au}) decreases to 1/7.4 in the case of the well defined c(4×4) structure (Fig. 3, curve e) compared to 1/7 obtained for the initial stage of the c(4×4) structure (Fig. 3, curve d). This fact indicates a further removal of a small quantity of the adsorbed sulphur which leads to the improved quality of the corresponding LEED pattern (Fig. 1 (d)). The sulphur coverage corresponding to a well defined c(4×4) S overlayer on the Au(110) surface was estimated to be approximately equal to 0.2 ML according to AES signal intensity analysis. The TPD spectra of the S and S_2 signals taken from the saturated sulphur layer on Au(110) surface (Fig. 4, curves (a)) show four main features labelled A to D at 358 K, 520 K, 584 K and 635 K, respectively. It is interesting to note that 54% of S and S_2 species desorb from the saturated sulphur layer in the temperature range between 295 K and 450 K, producing the strong TPD peak (A) at 358 K. These species are weakly bonded on the surface forming the saturated sulphur layer and show no significant ordering (no well defined LEED pattern). For the c(4×4) surface obtained after a long anneal, the TPD spectrum (Fig. 4, curve c) shows two desorption peaks C and D of approximately equal intensity, at 584 K and 635 K. The TPD spectrum for the p(4×2) surface (Fig. 4, curve d) shows a single desorption peak at a temperature of 650 K.

Discussion

It is well known that adsorbed sulphur prefers high coordination sites [7], and that the (1×2) "missing row" reconstruction of the clean Au(110) surface provides binding sites which make this surface reactive towards adsorbates. It is proposed that at a low sulphur coverage of 0.13 ML in the case of the p(4×2) sulphur overlayer, the sulphur atoms occupy "missing row" sites. Referring to the comparison of the IV-LEED spectra presented in Fig. 2, we conclude that the Au(110)–(1×2) surface undergoes no significant restructuring in the case of such a thin sulphur overlayer. Also a high temperature anneal of the p(4×2) sulphur overlayer at 900 K removes all sulphur species from the surface according to AES data and restores a (1×2) LEED pattern of good quality, providing evidence for a return to the Au(110)–(1×2) reconstruction.

During previous studies of sulphur adsorption on metal surfaces that exhibit a (1×2) "missing row" reconstruction several ordered sulphur overlayers were observed: c(4×2) on the Au(110) [1], c(2×4) and c(2×6) on the Pt(110) [18], p(2×2) and c(2×4) on the Ir(110) [6, 19]. In all cases H_2S gas was used as a sulphur source and the surface was maintained below [1] or above room temperature [18] during deposition. For Au(110) and Pt(110) no structural model or adsorption sites were proposed. In the case of the Ir(110) surface it was found that sulphur atoms occupy top row adsorption sites. This is due to the faceted reconstruction of the clean Ir(110) surface which is stabilised via (331) minifacets [20] and has a "streaked" (1×3) LEED pattern. The stable (1×2) "missing row" reconstruction of this surface was obtained only after deposition of small amount of sulphur [6].

On other (110) metal surfaces possessing no (1×2) "missing row" reconstruction several similar ordered sulphur overlayers were observed at low sulphur coverage: c(2×2) on the

Ni(110) [21-23] and Cu(110) [24], c(3×1) and p(2×2) on the Fe(110) [25, 26]. It was found that in all these cases the sulphur atoms occupy high coordination sites (four-fold or three-fold hollow sites) available on the surface. No significant surface restructuring during the deposition of such small amounts of sulphur (0.1 – 0.4 ML) was found for these surfaces. The same site preference was reported for sulphur adsorbed on the Au(111) surface at low sulphur coverage [2, 7]. Furthermore, it was reported that adsorption energies for four-fold sites are slightly larger than for three-fold sites, which in turn are larger than for low coordinated sites such as atop or bridge sites [2, 7, 26].

The analysis of the TPD spectra (Fig. 4) taken from the two ordered sulphur overlayers obtained on the Au(110) surface as well as from the saturated sulphur layer help to elucidate the processes arising during annealing and to obtain information about possible adsorption sites. The most probable adsorption sites for this sulphur species, desorbing at 358 K (TPD peak A), are low coordinated positions along the top layer rows of Au atoms. Indeed, annealing this system for one hour at a rather low temperature (423 K) helps to remove these weakly bonded species producing a significant reduction of the S LMM Auger signal intensity in comparison with initial saturated sulphur layer (Fig. 3, curves c and b, respectively). For the p(4×2) sulphur overlayer a single desorption peak is observed at a temperature of 650 K (Fig. 4, curve d) that can be described by a simple model where the sulphur species are only bonded to the high coordinated missing row sites (four-fold hollow adsorption sites).

The situation is more complicated in the case of the c(4×4) sulphur overlayer where two desorption peaks (C and D) were observed. Even after a 10 hour anneal there is still evidence of disorder in the c(4×4) LEED pattern as seen by the "streaking" along the [001] direction (× 2 direction of the clean Au surface). This indicates that a fraction of the sulphur species is bonded not in the missing row position but slightly displaced towards

top layer atoms of the gold surface. In this case peak C is attributed to desorption of sulphur species that are bonded to Au atoms in the first and second layers (i.e. three-fold hollow adsorption sites situated at the "missing row" walls having (111) surface structure). In turn, peak D is attributed to sulphur atoms adsorbed in the higher coordinated missing row sites (four-fold hollow adsorption sites).

Using a simple model [27] the adsorption energies associated with the features in the TPD spectrum are calculated as 1.60 eV for peak C, 1.75 and 1.8 eV for peak D in the case of the c(4×4) and p(4×2) surfaces respectively. These values were calculated using a heating rate of 2.0 K per second and a pre-exponential factor of 10^{13} Hz and compare favourably with those reported for the desorption of sulphur from the Ag(111) surface [28]. These adsorption energies also agree well with theoretical values for sulphur on Au(111) surface calculated using pseudopotential density functional theory [2, 7].

Desorption spectra presented in Fig. 4 were integrated to yield a measure of the total amount of desorbing S and S_2 species in the TPD. The integrated TPD signals were then plotted as a function of sulphur coverage as shown in Fig. 5. From Fig. 5 it is clearly seen that the S_2/S desorption yield ratio is smaller in the case of the c(4×4) sulphur overlayer (equal to ~1.6) in comparison with the p(4×2) overlayer (~2.0) and the saturated sulphur layer (~2.0). Taking into account that all ordered sulphur overlayers on the Au(110)–(1×2) surface were obtained by annealing of the saturated sulphur layer, it is reasonable to suppose that c(4×4) sulphur overlayer arises by means of additional desorption of S_2 species which are formed on the surface due to the mobility of sulphur atoms. In this case the annealing time plays a significant role, since the longer the annealing takes – more S_2 molecules can be formed on the surface and can be desorbed after migrating to desorption centres giving a more well defined c(4×4) sulphur overlayer as a function of annealing time.

Conclusion

A study of the sulphur overlayers on the clean Au(110)–(1×2) surface has been carried out by means of low energy electron diffraction, Auger electron spectroscopy and temperature programmed desorption. Two ordered sulphur overlayers on the Au(110) surface at low sulphur coverage, p(4×2) and c(4×4), were found after annealing the S/Au(110) system at 630 K and 463 K, respectively. It is proposed that in the case of the p(4×2) sulphur overlayer on the Au(110) surface, the remaining sulphur species are bonded to the "missing row" sites (four-fold hollow adsorption sites) leading to many possible structural models. In turn, the c(4×4) sulphur overlayer on the Au(110) surface was produced by desorption of the S_2 molecules that form on the surface due to mobility of the sulphur atoms.

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List of Graphics Captions

Fig. 1. LEED patterns of the clean Au(110)–(1×2) substrate (a), p(4×2) sulphur overlayer (b), and c(4×4) sulphur overlayer on the Au(110) surface obtained after different annealing times (c and d). All patterns are acquired at a kinetic energy of 80 eV.

Fig. 2. IV-LEED spectra taken from the clean Au(110)–(1×2) surface (top spectra on each graph) and from the p(4×2) sulphur overlayer on the Au(110) surface.

Fig. 3. Auger electron spectra of the clean Au(110)–(1×2) substrate (a) and the deposited sulphur layer on the Au(110) surface taken after different annealing procedures (b-f). The dN(E)/dE signals are shown. Primary electron beam energy was 3 keV. The spectra are normalized to the intensity of the Au NOO main line.

Fig. 4. TPD spectra (m/e is equal to 32 (S) and 64 (S_2)) taken from the as-deposited sulphur layer (a) and from possible ordered sulphur overlayers on the Au(110) surface (b-d). The heating rate was 2 K per second.

Fig. 5. Integrated area of the TPD spectra in Fig. 3 as a function of sulphur coverage.

a) clean Au(110) – (1×2)   b) (4×2) S on Au(110); 1h @ 630 K

c) c(4×4) S on Au(110); 3h @ 463 K   d) c(4×4) S on Au(110); 10h @ 463 K

(0,1/2) (0,3/2) (1,1/2) (1,3/2)

(1x2)-Au(110)
(4x2)-S-Au(110)

(0,1) (0,2) (1,1) (1,2)

energy, eV

Au NOO S LMM

f)
e)
d)
c)
b)
a)

intensity (dN(E)/dE)

I_S/I_{Au}
f) (4x2) S on Au (1h @ 630 K) 1/8.3
e) c(4x4) S on Au (10h @ 463 K) 1/7.4
d) c(4x4) S on Au (3h @ 463 K) 1/7
c) S on Au (1h @ 423 K) 1/6
b) S on Au (as deposited) 1/2.2
a) Au(110) clean

60 80 100 120 140 160 180

kinetic energy, eV