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# Study of Au multiple-twinned particle micelles by X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy (HeI) and metastable impact electron spectroscopy

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## Abstract

Multiple-twinned particle (MTP) micelles, comprised of Au MTP and self-assembled propionic-acid-thiolates, deposited onto highly oriented pyrolytic graphite and naturally oxidized Si(111) surfaces have been studied by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) (HeI) and metastable impact electron spectroscopy (MIES). Strong emission from the ionization of the molecular orbitals of the carboxyl (COOH) functional group is identified in the MIES and UPS spectra of the MTP-micelle on both substrates. The results suggest that the outermost functional group of the MTP-micelle is the carboxyl group, and that the Au MTPs are covered with propionic-acid-thiolates. By joint application of XPS, UPS (HeI) and MIES it is demonstrated that the thiolates desorb completely from the substrate (when heating to  $\sim 400^\circ\text{C}$ ) while Au remains there. In the case of the silica substrate the  $\alpha\text{-}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-Au}$  structure is observed with low energy electron diffraction after annealing to  $1000^\circ\text{C}$ . © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Alkanethiol; Gold; HOPG; Metastable impact electron spectroscopy; Multiple-twinned particle; Photoelectron spectroscopy [UPS (HeI) and XPS]; Self-assembled monolayer; Si(111)( $\sqrt{3} \times \sqrt{3}$ )R30°-Au; SiO<sub>2</sub>

## 1. Introduction

More than 30 years ago Ino discovered multiple-twinned particles (MTP) when he deposited Au onto the NaCl surface [1–4]. MTPs have icosahedron or pentagonal decahedron structures; the icosahedron structure is close to that of C<sub>60</sub> (truncated icosahedron). Since MTP is not formed when depositing Au onto KCl [5], its formation is closely related to epitaxial growth. Alternatively, as

reported by Lu et al. [6, 7]. MTPs can be produced in an electrochemical process. From total energy calculations it is concluded that the MTP is stable up to a particle size below  $\sim 90 \text{ \AA}$  [3, 8]. Exciting new properties can be expected from the MTP structure because it has only 111 faces whereas fcc Au particle has 100 and 111 faces; as an example the authors mention their potential application as catalyzers. However, MTPs are easily sintered when they meet, even at room temperature. Thus, for the application of this fascinating particle it is important to prevent sintering. This is possible by using the colloidal technique introduced by

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Faraday [9] and/or by self-assembling techniques with alkanethiols [10–15].

As far as Au fcc nano-particles are concerned, many researchers have studied strategies for their isolation: Schmid et al. synthesized  $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$  clusters [16], while Brust et al. produced nanometer-sized Au fcc particles by using two-liquid-phase colloidal technique and coating with dodecanethiols [17]. Whetten et al. selected the size of the Au particles and produced two- and three-dimensional crystals consisting of Au structures covered with dodecanethiols [18]. Andres et al. linked the Au particles with aryl dithiols or aryl di-isonitriles in order to verify nonlinear Coulomb charging behavior [19]. However, to the authors' knowledge there is so far no report of MTPs being isolated by organic molecules.

Recently, Takami and Ino created MTP-micelles comprised of an Au MTP and self-assembled thiolates. As verified by X-ray spectroscopy, proton nuclear magnetic resonance (NMR) and scanning electron microscopy, the micelle involves the propionic-acid molecules with the functional group X ( $\text{X}=\text{COOH}$ ) as schematically shown in Fig. 1 [20–23]. However, it is still not clear to which degree the thiolates cover the Au MTP: the chemical shift on the reported proton NMR spectrum [20,22] indicates that mercaptopropionic acids form disulfides. Therefore it is difficult to conclude that:

- (1) a chemical bond between the Au MTP and the thiolates is formed; and
- (2) whether and to which extent the MTP is covered with the thiolates.

In principle, whether the Au MTP is covered with thiolates can be determined by the joint application of metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS) (He I): photons can penetrate into the bulk and the spectra obtained give information on the near-surface bulk electronic structure. On the other hand, metastable atoms cannot penetrate into the surface, and, consequently, unique information on the electronic structure of the outermost layer can be obtained [24]. Hence MIES is a powerful technique for the investigation of the outermost surface electronic structure of, in particular, organic layers and films [25]. Thus it

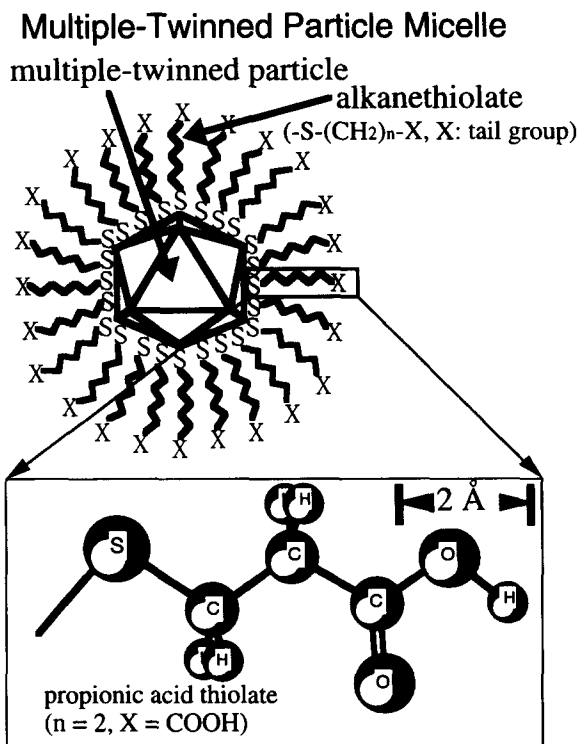


Fig. 1. Schematic view of MTP micelle comprised of Au MTP and alkanethiolates (propionic-acid-thiolates in this study).

appears promising to apply MIES to the study of the outermost chemical functional group of micelle surface.

In this paper, the combination of MIES and UPS (He I) is applied to the study of the electronic structure of MTP micelles and it is investigated whether and in which particular manner an Au MTP is covered with thiolates. It is also demonstrated by X-ray photoelectron spectroscopy (XPS) and UPS (He I) that by heating the thiolates can be desorbed from the Au MTP while Au still remains on the substrates. On the silica substrate, in particular, the reconstructed  $\alpha\text{-Si}(111)(\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{-Au}$  structure forms at a sufficiently high annealing temperature as confirmed by low energy electron diffraction (LEED).

## 2. Experimental

The method for producing MTP micelles has already been reported elsewhere [20,21]. Thus, this

paper comments on the procedure only briefly. A Pyrex glass beaker was introduced into a vacuum chamber, and NaCl was evaporated from an  $\text{Al}_2\text{O}_3$  basket, onto the beaker at room temperature with a thickness of 1500 Å. After the deposition the beaker was heated up to 300°C, and Au was deposited with a thickness of 100 Å in order to make Au MTPs by the method reported by Ino [1–3]. After the Au deposition, a NaCl film of 1500 Å thickness was deposited, again at 300°C, in order to bury the Au particles. Alternate evaporations of Au and NaCl follow in order to produce plenty of Au particles buried into the NaCl film. After cooling to room temperature, the beaker was exposed to air and  $10^{-3} \text{ mol l}^{-1}$   $\alpha$ -mercaptopropionic acid ( $\text{HSCH}_2\text{CH}_2\text{COOH}$ ) water solution was poured into the beaker so that the NaCl dissolved and the thiols adsorbed onto the surface of the Au particles producing the MTP-micelle.

The S and Au content in the MTP-micelle was checked by total-reflection-angle X-ray spectroscopy (TRAXS) focusing on the S  $K\alpha$ , Au  $M\alpha, \beta$  and Au  $L\alpha, \beta$  lines [20]. A proton NMR spectrum in  $\text{D}_2\text{O}$  solution was also measured in order to establish that the peaks at  $\delta H = 2.77$  (t,  $J = 6.8$  Hz, 4H) ppm are attributed to  $(\text{SCH}_2\text{-CH}_2\text{-COOH})_2$  and the peaks at  $\delta H = 2.95$  (t,  $J = 6.8$  Hz, 4H) ppm can be attributed to  $(\text{S-CH}_2\text{-CH}_2\text{COOH})_2$  adsorbed on Au MTP [22]. The internal structure of MTP-micelle was checked by transmission electron microscopy (TEM); the TEM image indicated that most of the particles have MTP structures, and that the average size of the particles is 70 Å [23].

Two substrates were employed for the present study: highly oriented pyrolytic graphite (HOPG) and a  $\text{SiO}_2$  surface naturally formed on Si(111) (As doped, 0.001–0.005  $\Omega\text{cm}$ ). A droplet of Au MTP-micelle or mercaptopropionic acid water solution ( $10^{-3} \text{ mol l}^{-1}$ ) was put onto the sample, dried with a heater at 100°C and finally introduced into the ultrahigh vacuum (UHV) analysis chamber.

The apparatus, equipped with XPS, UPS, MIES and LEED, has been described in detail previously [26,27]. Briefly, it features a cold-cathode gas discharge source for the production of metastable  $\text{He}^*(2^3\text{S}/2^1\text{S})$  (excitation energy 19.8/20.6 eV) atoms with thermal kinetic energies and He I pho-

tons ( $h\nu = 21.2$  eV) as a source for UPS. The triplet to singlet ratio in the metastable beam has been measured by  $\text{He}^*\text{-Ar}$  impact as 7:1.  $\text{He}^*(2^1\text{S})$  atoms are known to be converted into  $\text{He}^*(2^3\text{S})$  atoms in front of metallic and semiconducting surfaces efficiently [28–30]; also in the present study no spectral features were found which could be attributed to ionization by singlet helium. The contributions to the electron spectra from metastables and photons within the beam are separated by means of a time of flight technique combined with a double counter system allowing to measure MIES and UPS simultaneously. The angle of incidence of the probe beams is 45°; electrons emitted in the direction normal to the surface are analyzed. The simultaneous collection of a MIES/UPS spectrum requires  $\sim 1$  min. MIES, UPS and XPS measurements are performed using a hemispherical analyzer (VSW HA100) with an energy resolution of 250 meV for MIES/UPS and 2.5 eV for XPS. In all figures the spectra are presented as a function of the electron binding energy (abbreviated by  $E_B$  in the text) with respect to the Fermi level; its position is determined from measurements on a metallic substrate at the same position as those employed in the present studies. For differently prepared systems the spectral intensities shown in the same graph cannot be compared. The low-energy onset of the electron spectra directly reflects the surface work function; its change with exposure gives the adsorbate-induced change of the work function. XPS spectra are displayed as a function of the binding energy. MIES and UPS experiments were performed biasing the target by 50 eV, which has been shown to have almost no influence on the spectral features.

The surface cleanliness was monitored by MIES and XPS. All measurements are performed at room temperature. For annealing of the sample, a tungsten filament was heated behind the target, and a suitable voltage was applied between the filament and target.

### 3. Results

#### 3.1. General remarks

In order to get information on the formation and properties of the Au MTP-micelles from

electron spectroscopy results, the following strategy was pursued.

### 3.1.1. Electronic structure of thiolate molecules at surfaces and attached to Au MTPs

The thiolate-induced electron emission is studied by joint application of UPS and MIES to the following two situations, namely:

- (1) thiolate adsorbed on HOPG and silica substrates (without Au MTPs); and
- (2) Au MTP-micelles adsorbed on the same substrates as in (1).

The identification of the spectral features arising from the organic molecules is based on the comparison with an *ab initio* molecular orbital (MO) calculation carried out on an isolated mercaptopropionic acid by Yokoi and Ohno [31] using Gaussian 94 [32]. Particular emphasis is given to the identification of the emission which stems from the functional group X (COOH). It is anticipated that thiolates adsorbed on the substrates (without MTP) do not possess a high degree of spatial ordering, but rather form an amorphous layer. On the other hand, the micelle formation is expected to lead to a self-assembling structure of thiolate molecules surrounding the Au MTPs. For chemical reasons it can be expected that the adsorption takes place preferentially in such a manner that the functional group X points away from the MTP surface. Thus, features from the ionization of X, from the C=O and OH groups in particular, should appear considerably more pronounced than for thiolate molecules directly adsorbed to the substrates. Therefore, the enhancement of the emission from the functional group can serve as an indication for micelle formation on the Au MTP.

### 3.1.2. Micelle formation

As already pointed out under Section 3.1.1, the micelle formation should manifest itself in an enhancement of emission from the ionization of the functional group X. Moreover, as will be discussed in detail in Section 4, the electron emission induced by thiolate molecules sets in at about  $E_B=5$  eV. Any intensity observed at smaller binding energies must therefore be attributed to Au or substrate ionization. In particular, an appreciable

part of the spectrum from Au ionization is located between 2 and 5 eV binding energy with respect to the Fermi level [33]. Thus, emission seen at these binding energies in the UPS spectra can be used for the determination of the degree of coverage of the Au MTP by the organic molecules. More precisely, this intensity relative to that from thiolate molecules gives an upper limit for the fraction of the MTPs which is NOT covered by the thiolates. MIES is probably not very sensitive for this because the interaction of the He metastable atom with Au MTPs may be due to Auger neutralization [34] and therefore produces a smooth contribution to the spectra which cannot be analyzed easily.

### 3.2. MIES, UPS, XPS and LEED results

Fig. 2 shows UPS (Fig. 2a) and MIES (Fig. 2b) spectra obtained after the deposition of Au MTP-micelles on HOPG and naturally oxidized Si(111); the corresponding spectra obtained when only the mercaptopropionic acid molecules are adsorbed onto the substrates (without the Au particles) are also shown for comparison.  $E_B=0$  eV applies to electrons emitted from the Fermi level.

The UPS and MIES spectra recorded for the clean graphite substrate and those after heating off the MTP on HOPG are very similar to the spectra reported by Masuda et al. [34] and Harada et al. [35] and are therefore not shown here. The sharp peak seen in all results with the HOPG substrate (around a binding energy of  $\sim 13.7$  eV in UPS and 12.5 eV in MIES) appears to be a final state effect due to the accumulation of inelastically scattered electrons in the  $\sigma^*$  conduction bands of graphite above  $E_F$  [34]. The MIES and UPS spectra of the naturally oxidized silicon substrate correspond to those reported by Ishii et al. [36] and are therefore also not shown here. For both substrates the MIES spectra are caused by the Auger de-excitation process as the comparison with the UPS spectra shows.

As shown below, in the MIES and UPS spectra thiolate-induced structures appear at about the same binding energies. This indicates that the MIES spectra from MTP-micelles are, as those from the substrates, due to Auger de-excitation (surface Penning ionization) [34]. Other than the

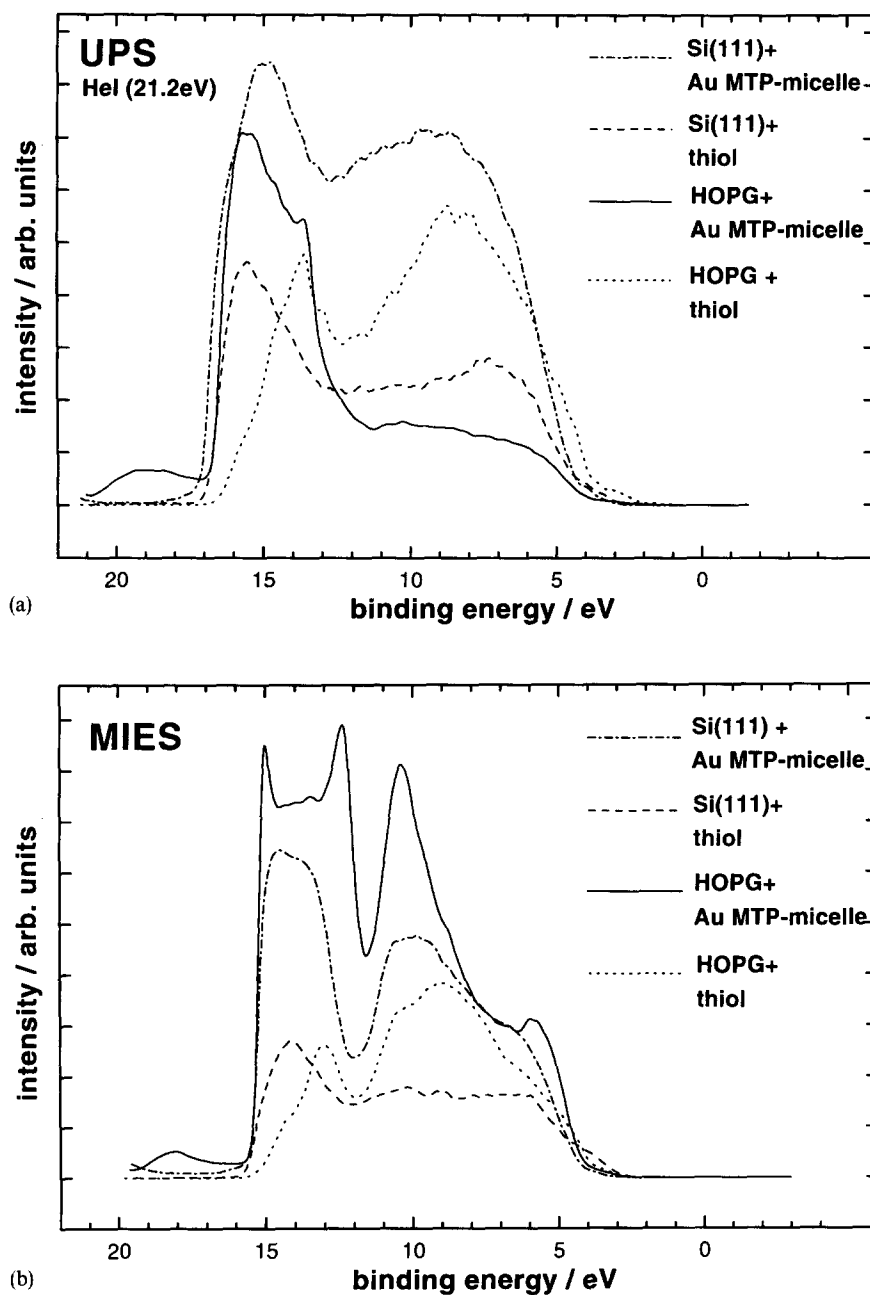


Fig. 2. (a) He I photoelectron spectra (UPS) and (b) metastable impact electron spectra (MIES) of MTP-micelles on HOPG and naturally oxidized Si(111) substrates. Also shown are the spectra obtained from propionic-acid-thiolates adsorbed on the same substrates.

substrate spectra, the thiolate spectra display two groups of spectral features:

(1) emission between 5 and ~11 eV; and

(2) between 12.5 and 14 eV, separated by a characteristic “gap” between ~11 and 12.5 eV.

The intensities in Fig. 2 cannot be compared

directly. The short escape depth of electrons in the film of organic molecules suppresses the emission from the Au and the substrate. Consequently, for a given substrate the UPS emission, coming mainly from the organic molecules both with and without Au particles, should display roughly the same energy dependence and intensity at least in the energy region from  $\sim 4$  to 12 eV. With MIES even the shape of the spectra must not necessarily be similar with and without the Au particles because an oriented film of organic molecules may form around the Au particles. MIES will then mainly detect electrons emitted from the part of the molecule that is oriented towards the vacuum. Indeed, as compared to the thiolate spectra, the emission about 6 and 10.5 eV in the MTP-micelles spectra is enhanced. This is particularly obvious for the MTP-micelles results on HOPG.

Fig. 3 shows the comparison of the thiolate-induced emission in the UPS (Fig. 3a) and MIES (Fig. 3b) spectra with an *ab initio* MO calculation performed on an isolated mercaptopropionic acid molecule by Yokoi and Ohno [31] using Gaussian 94 [32]. This comparison will be used for a partial identification of the observed emission. The notation of the character of each MO is as follows: nonbonding orbitals ( $n$ ),  $\sigma$  bonding orbitals ( $\sigma$ ) and  $\pi$  bonding orbitals ( $\pi$ ). The character of each MO is determined from the coefficients of the atomic orbitals of which each MO is a linear combination. The MO character noted at the first position has the largest contribution; the following ones have increasingly smaller contributions. The calculated MO energies are shifted by  $\sim 6$  eV; by this energy shift the emission seen in the UPS spectra at the lowest binding energies ( $\sim 3$  eV) corresponds to the ionization of  $n(S)$  and, in addition reasonable overall agreement between experiment and calculation can be obtained in the sense that the intensity in the MIES spectra is low at energies where the MO density is low.

Fig. 4 shows the UPS spectra obtained during heating the MTP-micelle film on naturally oxidized Si(111). Fig. 4a is for the as-prepared MTP-micelle film. Fig. 4b indicates that the thiolate molecules have been slashed to desorb; this finding is in qualitative agreement with that of alkanethiolates on Au(111) reported by Nishida et al. [37]. In

Fig. 4c no thiolates can be seen anymore. The spectrum displays features typical for a  $SiO_2$  surface, at  $E_B = 8$  eV, corresponding to non-bonding O 2p [36] and at  $E_B = 12$  eV, corresponding to  $\sigma$ -type Si–O bonding orbital [36]. In Figs. 4d and e the  $SiO_2$  features are shifted to lower binding energy, and two additional features, labeled Au 5d, appear at  $E_B = 4.5$  and 6.5 eV. In Fig. 4f they have developed into two pronounced peaks. Comparing Fig. 4f and g with those reported by Houzay et al. [38] and Karlsson et al. [39] it is concluded that the two pronounced peaks are due to Au 5d ionization, featuring the correct splitting of  $\sim 2.3$  eV. The emission seen at binding energies below  $\sim 4$  eV may come from the Si(111) substrate or could represent emission from Au–Si interface states. Finally, after annealing the sample at  $\sim 1000^\circ C$ , Fig. 4g is obtained, and the features at  $E_B = 4.5$  and 6.5 eV are in good agreement with the UPS spectrum of a Si(111)( $\sqrt{3} \times \sqrt{3}$ )R30°–Au surface as reported by Houzay et al. [38].

Fig. 5a displays the XPS spectrum of an MTP film on naturally oxidized Si(111) collected before starting the heating cycle. Upon heating the Au features start to become more pronounced; under the same conditions the UPS spectra start to display features typical for a  $SiO_2$  surface. Fig. 5b shows the XPS spectrum corresponding to the UPS results in Fig. 4g. The XPS results signal that the oxide layer has been removed practically completely although the Au is still present at the surface.

The LEED pattern taken under the conditions of Figs. 4g and 5b shows the  $\alpha$ -( $\sqrt{3} \times \sqrt{3}$ )R30° structure [39–44] with diffuse three spots [43,44] indicating the Au induced reconstruction of the Si(111) surface.

## 4. Discussion

### 4.1. Identification of the thiolate-induced spectral features

In order to arrive at an identification of the thiolate-induced emission seen both in the MIES and UPS spectra, namely the shoulder at  $\sim 3.5$  eV,

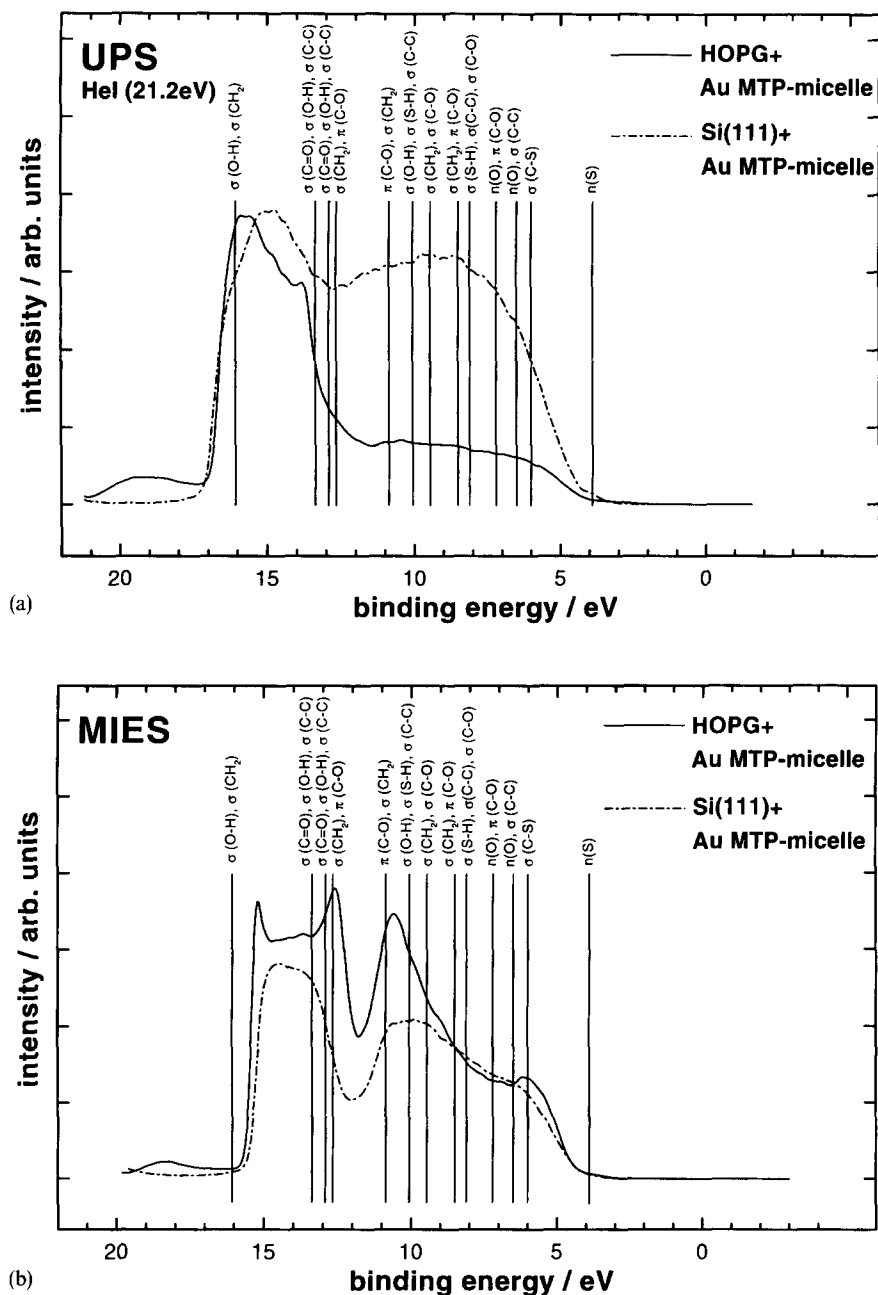


Fig. 3. Comparison of (a) UPS and (b) MIES on graphite (HOPG) and naturally oxidized Si(111) substrates with MO energies of mercaptopropionic acid calculated by Yokoi and Ohno [31]. The calculated values are shifted by 6 eV for comparison with experiment (see text).

the pronounced structure between  $\sim 5$  and 10.5 eV, the strong emission between 13 and 14 eV, and the gap separating the latter two pronounced struc-

tures, the following experimental and theoretical results will be taken into account:

(1) the UPS measurements for methanethiol

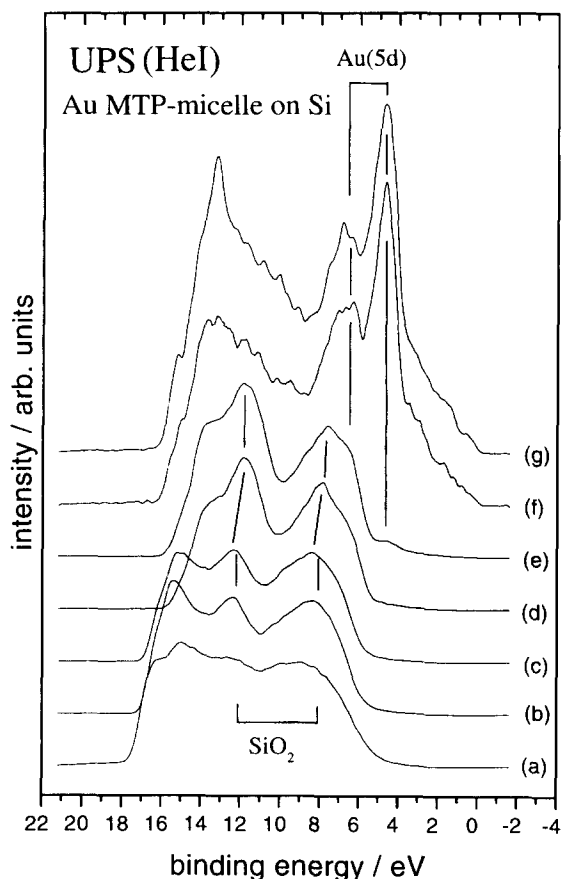


Fig. 4. UPS data for MTP-micelles on Si(111) substrate after annealing the substrate at (a) room temperature, (b) 300°C, (c) 400°C, (d) ca 600°C, (e) 800°C, (f) ca 900°C and (g) ca 1000°C. All spectra were registered at room temperature. The LEED pattern of the surface, recorded together with spectrum (g), was  $\alpha\text{-}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ .

adsorption on an aluminium surface as reported by Shen and Nyberg [45];

- (2) the gas-phase UPS measurements on propionic acid and thiol molecules presented by Kimura et al. [46];
- (3) the gas-phase UPS and MIES measurements carried out on propionic acid and thiol molecules by Ohno et al. [47,48]; and
- (4) the ab initio MO calculation on mercaptopropionic acid performed by Yokoi and Ohno [31].

The comparison with Shen and Nyberg [45] and the gas phase UPS measurements by Kimura et al.

[46] and Ohno et al. [48] suggest that the emission at the lowest binding energies should come from the ionization of the nonbonding sulfur [n(S)] orbital seen at ionization energies of 9–10 eV in the gas phase results [46,48]. The emission is expected to be shifted to a binding energy of  $\sim 4.5$  eV for surface-adsorbed thiolate molecules [45]. Moreover, as already pointed out in Section 3.1, reasonable overall agreement between the experimental spectra and the calculations of Ref. [31] (see Fig. 3) is achieved when the small shoulder at 3.5 eV is identified with emission from n(S). As compared to the gas phase calculations an additional bonding shift of the emission from the formation of an Au–S bond is expected.

The comparison with the calculations of Ref. [31] suggests the following assignment of the thiolate-induced emission:

- (1) the MOs from  $\sigma(\text{C-S})$  to  $\pi(\text{C-O})$ ,  $\sigma(\text{CH}_2)$  (between  $\sim 6$  and 9 eV in Fig. 3) contribute to the broad emission seen between  $\sim 5$  and 11 eV;
- (2) the gap observed between  $\sim 11$  and 13 eV is caused by the gap between  $\pi(\text{C-O})$ ,  $\sigma(\text{CH}_2)$  and  $\sigma(\text{CH}_2)$ ,  $\pi(\text{C-O})$  found in the calculation;
- (3) the strong emission above  $\sim 13$  eV originates, at least partly, from the carboxylic group (C=O) [ionization of  $\sigma(\text{C=O})$ ] [31].

However, it should be kept in mind that there is a large overlap with the substrate emission in the case of the HOPG substrate in this region (see the sharp feature) [34].

The UPS and MIES spectra of thiol/silica differ in details from those for thiol/HOPG: they display less structure and an apparently larger contribution of secondary electrons (between 14 and 15 eV). This may be due to a different degree of disordering of the surface structure for the two studied cases. As compared to the emission from thiolates adsorbed on the substrates directly, the emission from the Au MTP exposed to thiolates shows the following characteristic differences: the emission  $\sim 6$  eV and that between about 9 and 11 eV is considerably more pronounced, in particular in the MIES spectra. Following the assignment of the spectral features it is concluded that this enhancement is caused by the more efficient ionization of the components (O–H) ( $\sim 10$  eV) and



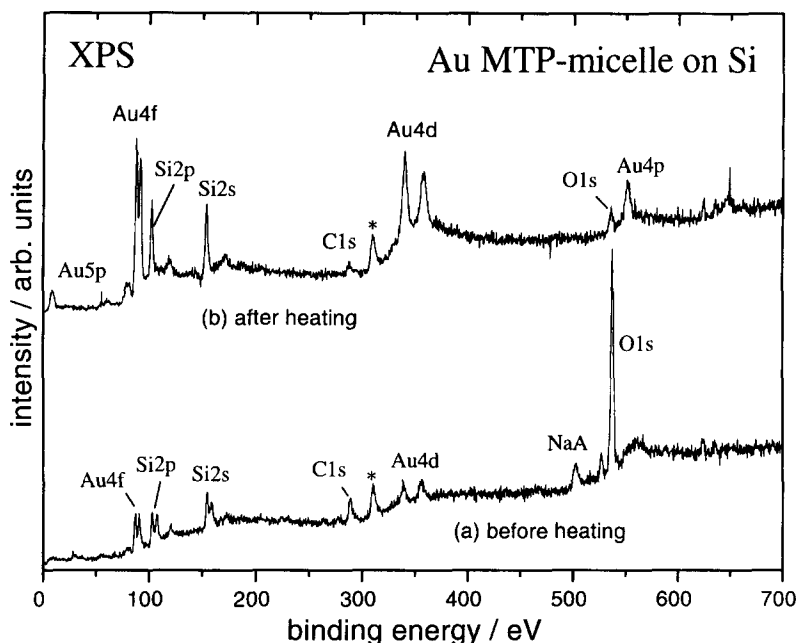


Fig. 5. XPS spectra of MTP micelles on Si(111) (a) at room temperature (corresponding to Fig. 4a), and (b) after annealing at  $\sim 1000^\circ\text{C}$  (corresponding to Fig. 4g). Peak \* is caused by a Mg contamination of the target chamber.

(C=O) ( $\sim 13$  eV) and of the nonbonding oxygen orbital [n(O)] ( $\sim 6.5$  eV) of the functional group X. Because the enhancement of the feature attributed to the functional group is particularly obvious in the MIES spectra it is concluded that the functional group is more exposed to the He\* probe atoms when the thiolates are coadsorbed with the Au MTPs.

#### 4.2. MTP-micelle formation

In order to get information on the formation of Au MTP-micelles the thiolate-induced emission with and without Au MTPs present on the surface is discussed on the basis of the MIES spectra. The observed enhancement of the emission from components of group X (relative to that from other groups in the thiolates) suggests the following picture:

- the thiolate molecules form an Au–S interface;
- the functional group X points away from the MTP surface, thus exposing itself more efficiently to the He\* probe atoms and, conse-

quently, being more likely subject to Auger de-excitation; and

- micelle formation occurs, and the structure originating from the thiolate–MTP interaction resembles closely to the pictorial representation of Fig. 1, that is, to that of a self-assembled structure.

Information on the degree of the coverage of the MTPs by the organic molecules can be derived from the UPS data. For only partial coverage of the Au structures by the thiolates emission attributable to Au ionization should be seen. Both with and without Au MTPs present on the substrates the spectra are very similar in the region from 4 to 6 eV where the characteristic double peak structure due to Au 5d ionization should show up (see Fig. 4f and g). Actually, there is no indication of such a structure present in the spectra. Therefore, it is concluded that the short escape depth of the electrons in the organic part of the Au MTP particle suppresses the emission from the Au core. This strongly suggests that indeed a micelle structure corresponding to a self-assembled monolayer

is formed by the preparation procedure as described in Section 2.

#### 4.3. Annealing MTP-micelles on silica: Au/Si(111) reconstructed surface structure

The results presented in Figs. 4 and 5 indicate that the organic molecules can be removed completely by heating the Au MTP micelle above 800°C while Au remains on the surface. The LEED results indicate that in the case of Si(111) this gives rise to epitaxial reconstruction. Thus, in principle, an epitaxial Au–Si interface can be produced without using evaporation techniques, simply by controlling the concentration of the MTP-micelle solution. This suggests the following method of producing metal nanostructures without using vacuum evaporation. Firstly, a resist pattern, eventually using self-assembling monolayer techniques, is drawn on the substrate. Secondly, metal micelles are offered to the surface in a solution and will adsorb to the sticky regions only. Finally, the organic part is removed by heating (or photochemical processes) and only a metallic nanostructure remains on the substrate [23,49].

The fact that the  $\alpha\text{-(}\sqrt{3}\times\sqrt{3}\text{)R}30^\circ\text{-Au}$  structure is formed on the Si(111) surface allows a crude estimate of the number of micelles on the silica substrate and of the concentration of Au MTP-micelles in the water solution: it is assumed that the Au coverage of  $\alpha\text{-(}\sqrt{3}\times\sqrt{3}\text{)R}30^\circ\text{-Au}$  is two-thirds of a monolayer [41,42,44,50]. The number density would then be  $5.24\times 10^{14}$  atoms  $\text{cm}^{-2}$ . From the average size of an Au MTP-micelle (70 Å [23]), and from the number and the size of the droplets deposited during the preparation of the film, it is then possible to estimate that the number of the Au MTP-micelles deposited onto the silica surface is of the order of  $3\times 10^9$  particles and that the concentration of Au MTP-micelles in the water solution is  $4.3\times 10^{-11}$  mol  $\text{l}^{-1}$ . This estimate, however, is rather crude since the surface is not well ordered and some Au islands may remain after annealing the surface. A more precise treatment of the solution is also needed. Nevertheless, it is believed that this is the first time that the  $\alpha\text{-(}\sqrt{3}\times\sqrt{3}\text{)-Au}$  structure

was produced without using evaporation techniques. Of course, this structure is presently obtained by just dropping large Au particles on naturally oxidized Si(111) substrates under air and subsequently anneal the system in vacuum. However, the advantage of this method is that the amount of Au can be controlled precisely by changing the concentration or the volume of the MTP solution. Hence, it is possible to control the amount of Au deposition in a very convenient and attractive way.

## 5. Summary

A procedure is described for the production of a thermally stable film of micelles formed from Au MTP embedded in thiolate molecules with carboxyl acid as a functional group. Both naturally grown silica and graphite (HOPG) served as substrates. The characterization of the micelle film was made by joint application of the MIES and photoelectron spectroscopies [UPS (He I) and XPS] together with LEED. The observations made can be summarized as follows:

- (1) The absence of the Au 5d features in the UPS spectra suggests that the Au MTPs are fully covered with thiolate molecules (functional group: carboxyl acid) using the preparation technique described. Both the MIES and UPS spectra show very similar structures which suggests that the MIES spectra are due to Auger de-excitation (surface Penning ionization). The spectra are dominated by emission from the ionization of thiolate molecules. This conclusion was made possible by the availability of ab initio MO orbital calculations for free mercaptopropionic acid molecule by Yokoi and Ohno [31]. The characteristic difference seen, in particular, in the thiolate-induced MIES spectra with and without Au MTPs present on the substrates forms a comparison with the mentioned ab initio calculations; the comparison suggests that the propionic acid points away from the Au surface. This explains the enhanced emission seen with MIES as caused by the large probability for Auger de-excitation involving the non-

bonding oxygen orbital and the MOs of the (C=O) and (O–H) components of the carboxyl acid functional group. This in turn implies that the thiolate molecules form a S–Au interface.

- (2) The MTP-micelle film comprised of Au MTP and self-assembled propionic-acid-thiolates desorbs gradually at temperatures above  $\sim 300^\circ\text{C}$  until (above  $\sim 800^\circ\text{C}$ ) only Au remains on the substrate. In the case of a naturally oxidized Si(111) substrate, the Au/Si interface leads to epitaxial reconstruction, and the Si(111)– $(\sqrt{3} \times \sqrt{3})R30^\circ$ –Au structure is observed with LEED. This result is noteworthy since it indicates the possibility of changing the amount of Au atoms on the substrate without using evaporation techniques, simply by changing the concentration or the amount of the MTP-micelle solution; this fact may be of importance for future technical applications.

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