The preparation and characterisation of nanometre platinum colloids on silicon wafers as model catalysts

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Platinum particles of 2 nm diameter have been immobilised on oxidised silicon wafers by spin coating with colloidal solutions and characterised by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The coverage and dispersion of the Pt colloids on the Si wafer are controlled by varying the concentration and the spin speed. Under optimal conditions mono-dispersed Pt colloids on silicon wafers are prepared. For the Pt colloids immobilised on the Si wafer, the majority of the stabilising ligands are removed through a reduction (with H_2 at 200°C) or an oxidation (in air at 300°C) procedure. AFM showed that particle sizes are retained after the reduction procedure, while significant sintering occurs after oxidation. The mechanism of ligand removal was studied using an in situ XPS reaction cell.

Keywords: model catalysts, spin coating, Pt colloid, AFM, XPS, Si wafer, particle size, oxidation, reduction

1. Introduction

Progress in the basic understanding of catalytic processes depends, to an extent, on meaningful characterisation of model systems by surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS). Catalytic systems on realistic supports are frequently difficult to analyse by XPS as they are irregular, making quantitative data interpretation uncertain. Further, they are inhomogeneous and non-conducting, giving rise to differential charging and its associated peak broadening. The use of planar model substrates allows these disadvantages to be overcome [1–3]. In particular, a layer of approximately 5 nm SiO_2 on a Si wafer forms a good structural analogue to commercial silica supports whilst retaining sufficient conductivity to avoid differential charging in XPS.

It is important to use model systems that mimic the real catalyst as closely as possible. Various preparation routes are possible, including evaporation (possibly using mass-selected clusters [4]), chemical vapour deposition [5], atomic layer epitaxy [6], spin-coating [7], lithography [8] and colloid deposition from solution [9]. The dispersion of metal colloids on oxidised silicon wafers by spin-coating is an attractive alternative for the preparation of realistic model catalysts. Metal colloids are small (nanometre-sized) metal particles consisting of several hundreds or thousands of atoms. The mono-dispersed particle sizes and the homogeneous composition of these materials makes them ideal precursors for the controlled preparation of metal catalysts [10]. Metal colloids are usually stabilised with ligands, often surfactants or polymers, which usually need to be removed before their use in catalytic reactions.

Here, we report on the immobilisation of Pt colloids on silicon wafers for the preparation of $Pt/SiO_2/Si(100)$ model systems. Key to success in using these systems as model catalysts is the removal of the stabilising ligands from the surfaces of the Pt particles prior to catalyst testing. This has been performed using either a reduction or an oxidation process. The influence on the catalyst structure and composition by ex situ reduction and oxidation treatments is reported. Further, we report on the use of an in situ XPS reaction cell to follow the chemical changes during reduction in some detail. Atomic force microscopy (AFM) measurements (ex situ) were also made before and after reduction.

2. Experimental

2.1. Analysis techniques

The dispersion of the colloidal Pt on the surface was studied by taking atomic force microscope (AFM) images using a Nanoscope-III instrument (Digital Instruments) with commercial silicon cantilevers operated in the tapping mode. The advantage of AFM over scanning electron microscopy is that calibrated height information on surface features is obtained. The accuracy of the calibration is typically around 20%. Information on the surface composition and chemistry of the colloidal dispersions was obtained by X-ray photoelectron spectroscopy (XPS) using a VG Scientific

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Escalab 220i-XL spectrometer with Al Kα radiation. The binding energy scale of the instrument is calibrated using known reference binding energies for Cu, Ag and Au photoelectron and Auger peaks [11]. It is equipped with a preparation chamber containing a high pressure gas cell from which samples can be rapidly transferred to the analysis chamber without exposure to ambient air. Spectra are quantified using calculated cross-sections [12] corrected for the instrument transmission and the energy dependence of the electron inelastic mean free paths.

2.2. Sample preparation

Silicon wafers ($2''$ diameter) were pre-oxidised in air at 800°C for 5 h to obtain an amorphous SiO_2 layer on the surface. This treatment is expected to result in the formation a SiO_2 layer of ca. 5 nm [13]. The nanometre Pt colloids, which are highly soluble in water and ethanol, consist of 26.3 wt% platinum. The remainder is stabilising ligand $(n\text{-}C_{12}H_{25})(CH_3)_2N(CH_2)_3SO_3$, with an elemental composition ratio $C:S:N:O$ of $17:1:1:3$. The average Pt particle size is 2 nm. The immobilisation of these Pt colloids on the silicon wafers was performed by spin-coating the wafer with a solution of the colloids in ethanol. The effect of spin speed and solution concentration on the dispersion was studied.

The prepared Pt colloid dispersions were subject to various treatments. A reduction treatment was applied using H_2 at a pressure of 1 bar and a flow rate of 30 ml/min for 2 h at 200°C, with an initial heating rate of 10°C/min. Using separate samples, an oxidation treatment was applied by heating in air at 300°C for 3 h with an initial heating rate of 85°C/min. An in situ treatment in the high pressure gas cell of the XPS instrument was performed for samples prepared using a solution concentration of 0.36 mg Pt colloids/ml in ethanol and a spin speed of 5000 rpm. Separate specimens were reduced in the XPS gas cell for 30 min at each of 200, 300, 400 and 500°C under 2 bar of H_2 at a flow rate of 5 ml/min.

3. Results and discussion

3.1. Effect of concentration and spin speed

We first studied the effect of the concentration of the coating solution (Pt colloids in ethanol) and the spin speed on the coverage and dispersion of the platinum colloids on the oxidised silicon wafers. Solutions with a concentration of 2.5 and 0.25 mg Pt colloids/ml, and spin speeds of 2000 and 6000 rpm were used. The results are summarised in table 1.

For sample C, which was prepared at 6000 rpm with a coating solution of 2.5 mg Pt colloids/ml, a non-continuous thin layer of Pt colloids on the silicon wafer was observed by AFM (figure 1a). The thickness of the layer is ca. 3 nm, corresponding approximately to the size of the platinum particles plus the ligand. For samples prepared with a lower concentration (0.25 mg/ml) and a spin speed of 2000 or 6000 rpm, the coverage of Pt colloids was much lower, and individual Pt colloidal particles were observed by AFM. Figure 1b shows a typical AFM image of such a sample (B).

XPS spectra of the as-prepared samples showed Pt, Si, O, and a significant amount of C, together with some N, S and Cl. This result indicates that a considerable amount of ligand material was present on the as-prepared samples. The N and S elements found in the XPS measurements originate from the ligand. Cl was only found on the as-prepared sample with the highest Pt concentration, and is likely to be due to chlorine from the $PtCl_2$ precursor used for the colloid preparation. The quantitative XPS results of the as-prepared samples and those after the ex situ oxidation or reduction treatments described in section 2 are listed in table 2. It is clear that increasing the Pt concentration increases the amount deposited, as expected, whereas a change in spin speed over the range 2000–600 rpm does not have a large effect on the amount deposited.

Table 1
Immobilisation of Pt colloids on silicon wafers – preparation conditions and AFM observation

Sample code	Pt conc. (mg/ml)	Spin speed (rpm)	Sample history [a]	AFM observation
A	0.25	6000	as-prepared	individual particles 3 nm
			reduced	individual particles ca. 2 nm
			oxidised	6–10 nm particles
B	0.25	2000	as-prepared	individual particles 3 nm
			reduced	individual particles, mostly around 2 nm
			oxidised	8–15 nm particles
C	2.5	6000	as-prepared	non-continuous thin layer with a thickness of 3 nm ±0.3 nm
			reduced	some large particles (height ca. 15 nm) on a background of 2–3 nm particles
			oxidised	large particles (15–25 nm) on a background of 2–3 nm particles

[a] Conditions for reduction: 1 bar H_2, 30 ml/min, 200°C for 2 h; for oxidation: in air, 300°C for 3 h; heating rate: both at 85°C/h.

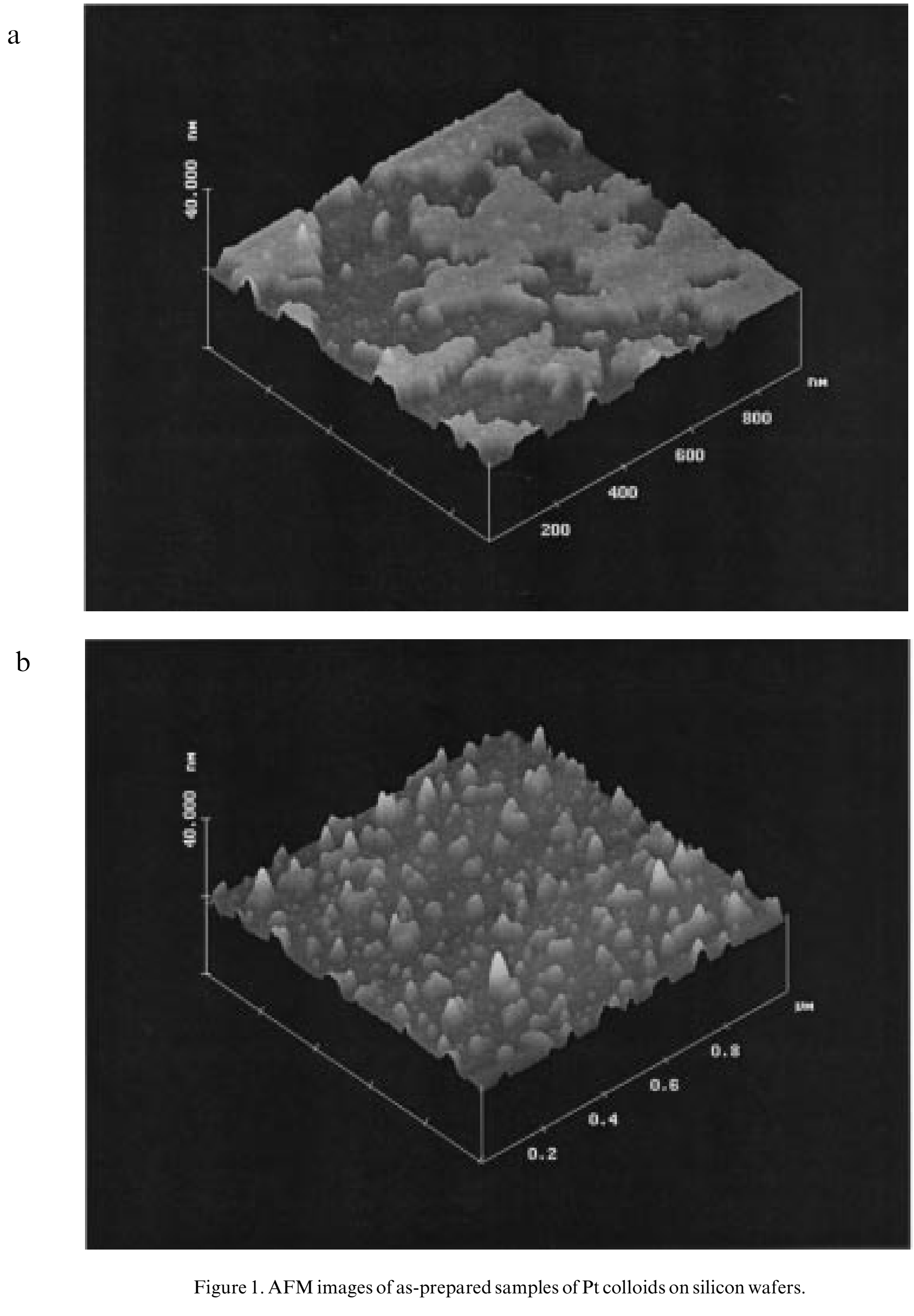

Figure 1. AFM images of as-prepared samples of Pt colloids on silicon wafers.

3.2. *Ex situ treatments*

The as-prepared samples were subjected to oxidation in air or reduction in H_2, followed by transport in air to the XPS spectrometer, as described in section 2. The aim of these treatments was removal of the ligands from the colloidal Pt particles. XPS measurements (table 2) showed that a significant amount of ligand was removed after either the reduction or the oxidation procedure. For the cases where a solution concentration of 0.25 mg/ml Pt was used, the sulphur was entirely removed by both processes. The continued presence of nitrogen may be due to contamination from the air during transport to the XPS instrument after the oxidation or reduction treatment. The removal of the ligands appeared to be incomplete since the amount of carbon on the surface was still rather high after these treatments. The binding energy of the C 1s peak in XPS and the shape of the X-

Table 2
Surface compositions of Pt colloids on silicon wafer

Sample code	atom%						
	Pt	C	S	N	Si	O	Cl
A	0.2	21.0	0.7	1.4	48.7	28.0	
A, red.	0.2	10.7		0.5	46.1	30.6	
A, oxi.	0.2	9.3		0.4	58.5	31.7	
B	0.1	21.2	0.6	0.1	50.5	26.6	
B, red.	0.3	10.8		0.5	58.3	30.1	
B, oxi.	0.2	10.1		0.5	57.2	31.9	
C	1.6	59.6	3.3	4.5	13.9	13.9	3.3
C, red.	1.6	30.9	1.6	0.5	41.5	24.0	
C, oxi.	3.0	15.3	1.2	1.5	44.0	35.0	

ray excited C KVV Auger peak [14] indicated that these carbons were still hydrocarbon species. It is possible that the temperature applied in these treatments was not high enough for the complete removal of all ligands. However, in these experiments the samples were in contact with air during transfer to the XPS instrument, making it difficult to exclude the possibility of contamination by atmospheric hydrocarbons. To overcome this ambiguity, in situ studies were also carried out using the high pressure gas reaction cell built into the XPS apparatus. The results are described in the following section.

Observations with AFM on the ex situ treated samples showed that the Pt particles retain their particle size (2 nm) after the reduction procedure, while significant sintering occurred for samples after the oxidation procedure. This difference can be clearly seen from figures 2a and 2b, which show the AFM images of sample B after a reduction or an oxidation treatment, respectively. For other samples (table 1) this effect was also very evident. Though the temperature used for the reduction was lower than that used for the oxidation procedure, in the following section it is shown that the Pt particles also retain their small particle sizes after being reduced at 300, 400 and 500°C.

It is interesting to observe that after a reduction treatment, the sample C no longer showed a "non-continuous thin layer" structure (figure 1a). Instead, individual small (2–3 nm) Pt particles with occasional large ones were observed (figure 3). This probably indicates that in the as-prepared samples the space between colloidal Pt particles was filled by ligands. If so, this would be consistent with observations of Pt colloid dispersions prepared on sapphire single crystals by deposition from solution [9].

3.3. *In situ treatments*

For the in situ treatment experiments samples were prepared using a solution concentration of 0.36 mg Pt colloids/ml in ethanol and a spin speed of 5000 rpm.

XPS data were acquired from the as-prepared surface and after reduction treatments in the XPS reaction cell for 30 min at each of 200, 300, 400 and 500°C under 2 bar of H_2 at a flow rate of 5 ml/min. Separate specimens were used for each reduction. To aid interpretation of the data, XPS spectra for comparison were also acquired from specimens of the ligand alone, the Pt–ligand colloid in the solid state, and the ligand dispersed on a Si wafer under the same spin-coating conditions.

The results of the XPS analysis of the reference samples and of the Pt colloid on Si wafer are summarised in table 3. The expected stoichiometry of the ligand is approximately reflected in the XPS analysis for both the ligand alone and the Pt colloid, although there is some evidence for a slight excess of S. On the Si wafer surfaces the C level was slightly higher than expected from the stoichiometry. This is probably a result of bonding of the ligand to either the Pt or Si surfaces through the N, resulting in attenuation of the XPS N 1s signal by the outermost hydrocarbon chains.

High signal to noise ratio scans over the individual photoelectron lines were made to aid identification of the chemical states of the species present. S, where detected, was always found at an energy corresponding to sulphone, SO_3^-. Two states of N were found, except for the ligand-only data, at 1s binding energies of approximately 399.8 and 402.5 eV. These correspond respectively to neutral and ionic nitrogen. On the Pt colloid sample, the neutral N contributed 10% of the total N 1s intensity. For the ligand on Si, the neutral contribution was 26%, and for the colloid on Si it was 52%. The N 1s scans are shown in figure 4. The neutral N corresponds to ligand bonded through the N to either the Pt or Si wafer surface, and the ionic N corresponds to ligand physically trapped but not chemically bonded to the surface. XPS measurements of similarly-prepared Pt dispersions on graphite and sapphire surfaces also show ligand material on the support as well as on the Pt particles [9].

The changes in surface composition after treatment of the Pt colloid on Si wafer samples in the XPS reaction cell are summarised in table 4. All analyses showed Si and O from the substrate together with Pt from the dispersed particles. At the lower reduction temperatures substantial amounts of C were found, declining rapidly above 300°C. The lower temperature results showed higher levels of N and S, originating from the ligand of the colloidal dispersion. The Cl seen in the as-prepared result is probably a residue from the $PtCl_2$ precursor used in the colloid production process. The level of Pt declined slightly after each reduction treatment, possibly as a result of slight sintering of the particles. Figure 5 shows the AFM images of the samples before and after the reduction treatment at 300, 400 and 500°C. No significant large-scale structural changes could be observed for the samples reduced at different temperatures, except the one reduced at 400°C where some larger Pt particles were observed.

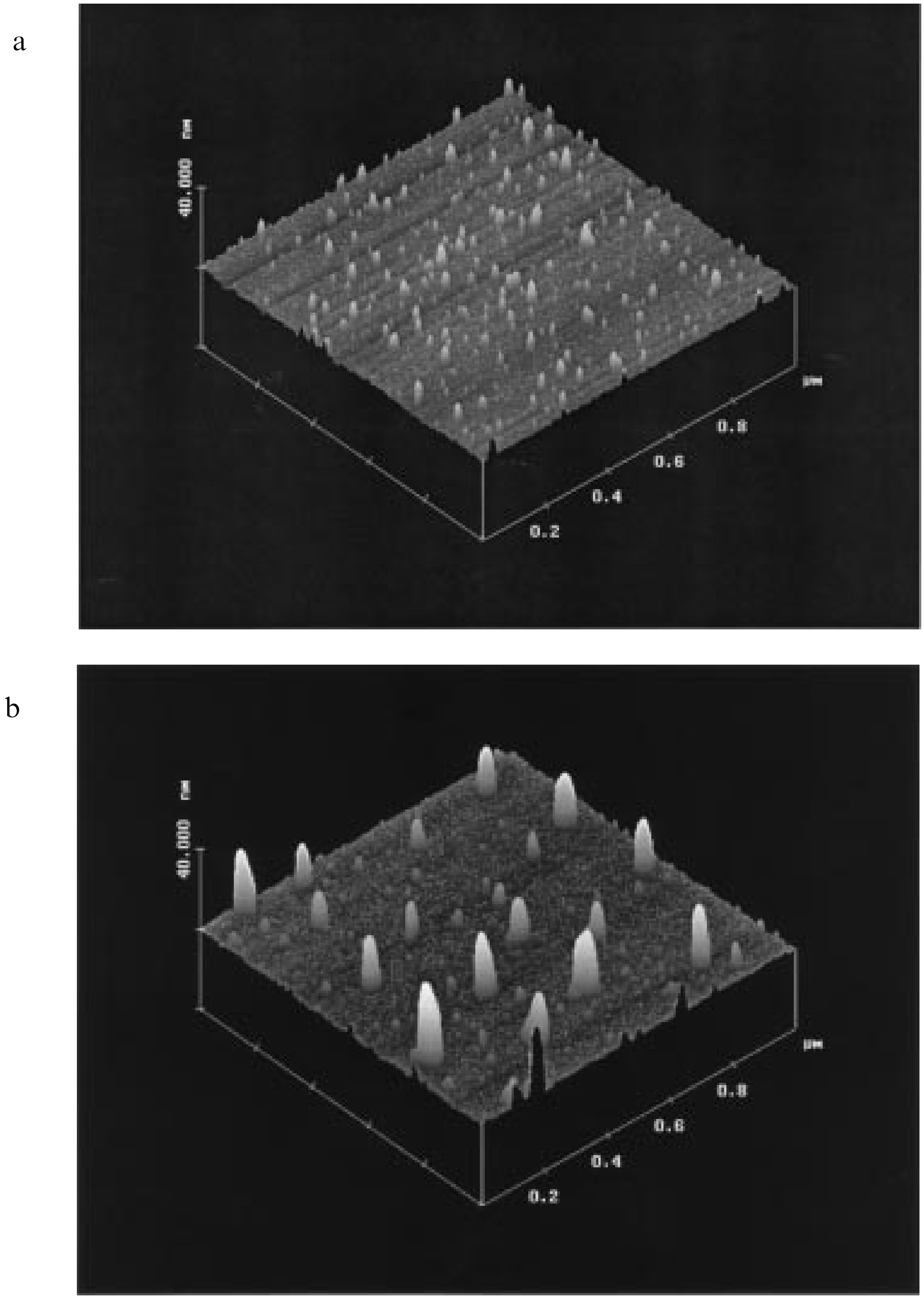

Figure 2. AFM images of samples 960124B after (a) reduction and (b) oxidation.

Examination of the individual line-shapes showed that on heating in H_2, the ionic nitrogen and the sulphone groups were rapidly removed, whereas the bound (neutralised) nitrogen was more persistent. For comparison, the N 1s spectrum recorded after the 300°C treatment is included in figure 4. After this treatment, only 15% of the nitrogen detected was in the ionic state. This is consistent with the interpretation that the ionic nitrogen is from trapped ligand molecules that are entrained within the hydrocarbon tails of the bound ligand molecules, and consequently are more readily removed in the reduction treatment.

4. Conclusions

The immobilisation of nanometre Pt colloids on silicon wafers by the spin-coating technique is a feasible

Table 3
Summary of surface composition by XPS of the reference samples and the as-prepared Pt colloid on Si wafer

Element	Ligand (solid state)	Pt colloid (solid state)	Ligand on Si wafer	Pt colloid on Si wafer
C (atom%)	78.1	70.1	14.5	14.8
N	4.2	4.9	0.6	0.8
S	5.4	5.5	0.6	0.6
O	12.4	13.9	52.3	49.4
Pt		0.80		0.15
Si			32.0	34.0
Cl		4.0		0.2

Table 4
Summary of XPS surface compositions in atom% after H_2 reduction in the in situ reaction cell at the temperatures shown

Element	As-prepared	200°C	300°C	400°C	500°C
C	14.8	13.3	8.7	0.8	1.3
N	0.8	0.2	0.2		
S	0.6	0.4		0.1	
O	49.4	51.0	54.3	59.6	59.0
Pt	0.15	0.15	0.14	0.13	0.12
Si	34.0	34.9	36.7	39.3	39.5
Cl	0.2				

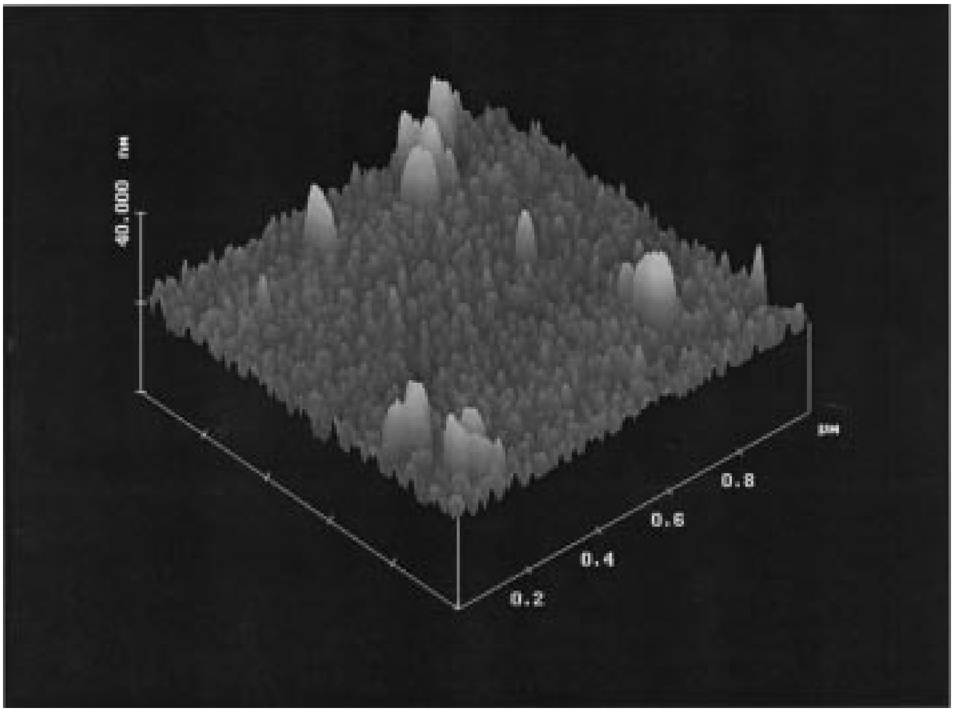

Figure 3. AFM image of sample 960116C after reduction treatment.

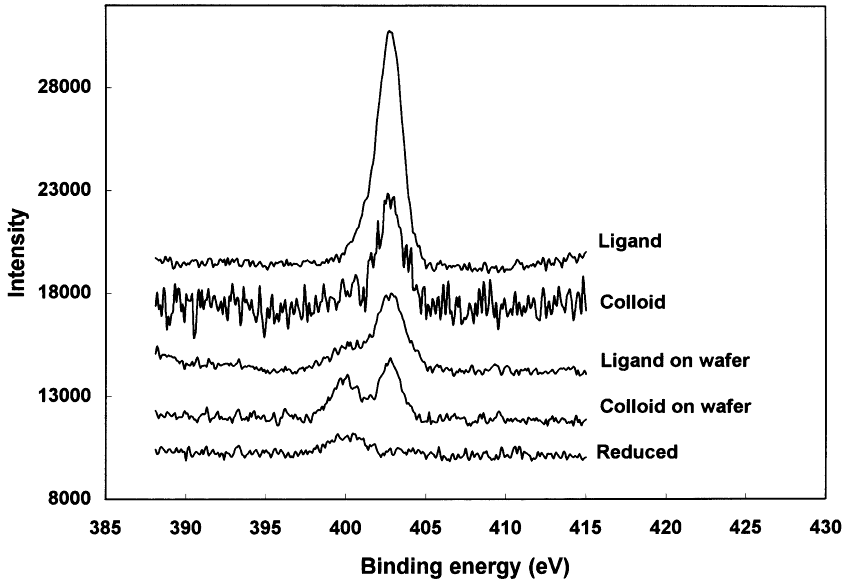

Figure 4. XPS N 1s photoelectron peaks for the reference samples, the as-prepared Pt colloids on Si sample and that after the 300°C reduction treatment.

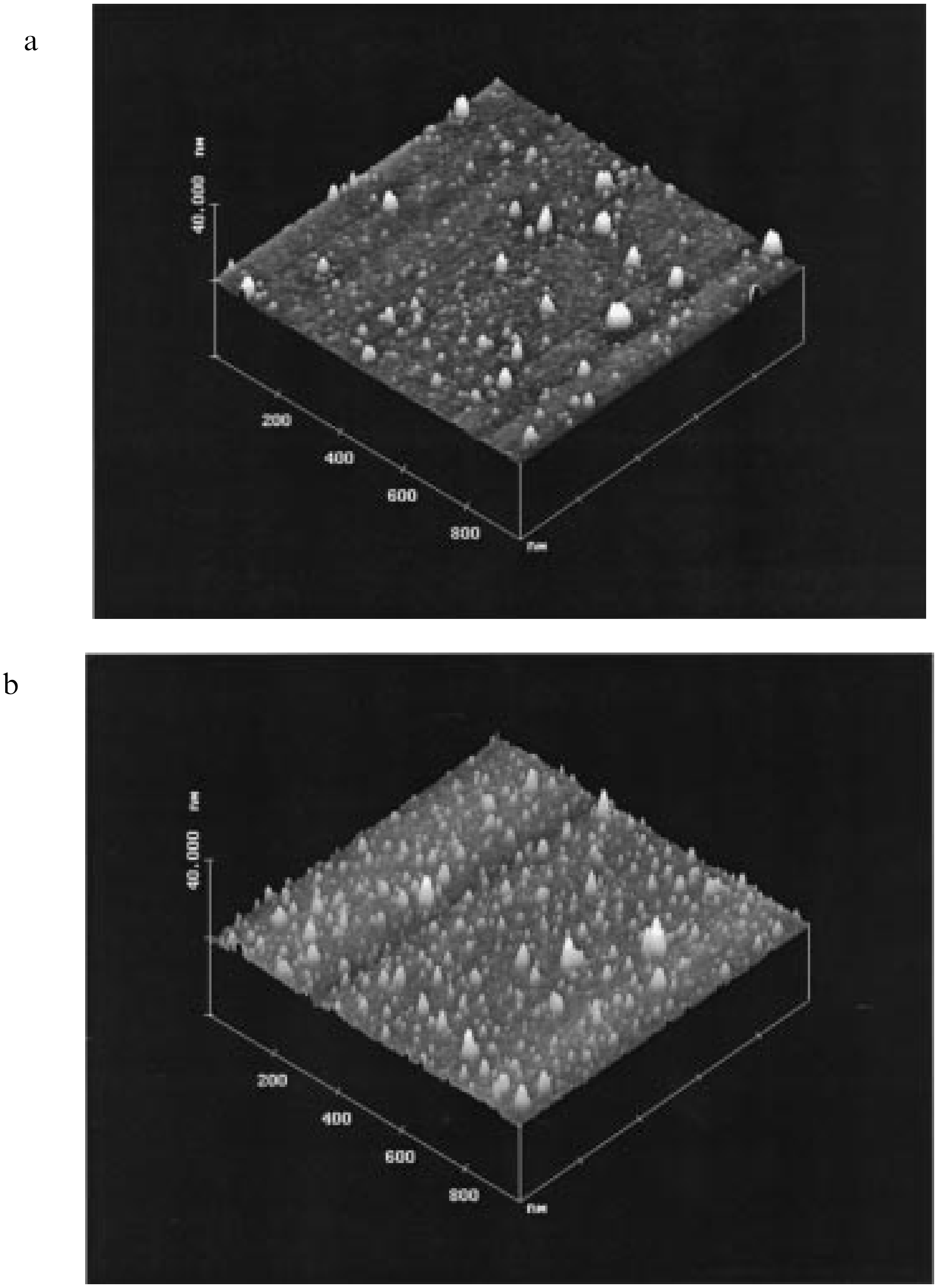

Figure 5. AFM images of Pt colloids on silicon wafers (a) as-prepared, and after a reduction treatment with H_2 at (b) 300°C, (c) 400°C and (d) 500°C.

method of controlled preparation of model catalysts. The coverage of Pt colloids and the dispersion are controlled by varying the concentration of the coating solution and the spin speed. Under optimal conditions samples consisting of mono-dispersed Pt particles on silicon wafers may be prepared.

XPS measurements have shown that, as-prepared, the surface has a covering of ligand molecules which may be either bound to the surface of the Pt particles through neutralisation of the nitrogen group, or trapped in the overlayer as intact molecules. On reduction, the trapped molecules are rapidly lost but the neutralised ligand species are only fully removed after reduction at 400°C. This information is important in the definition of optimal process conditions for the removal of the ligands from the Pt particles.

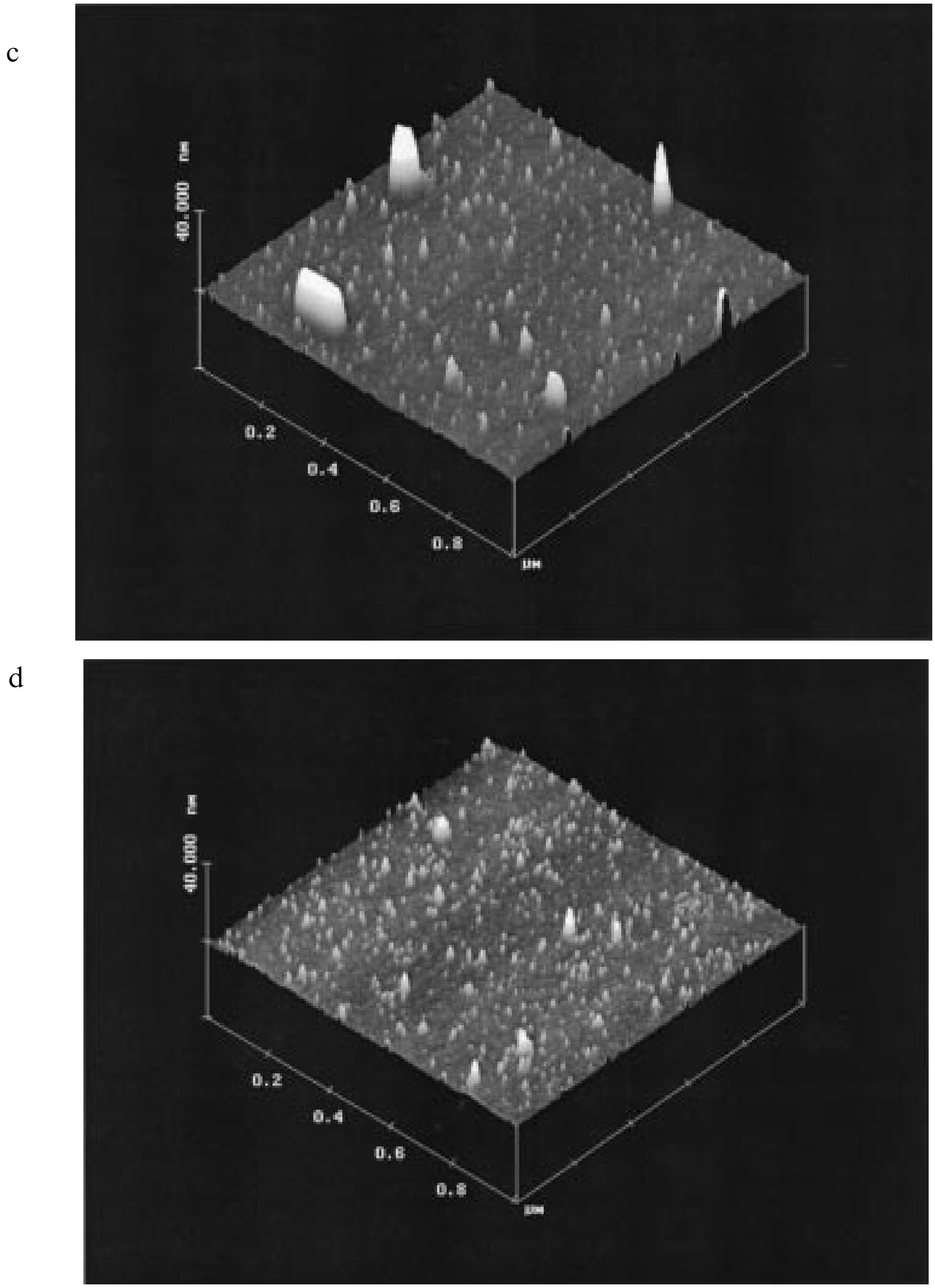

Figure 5. Continued.

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