Surface interaction of $Cu(NO_3)_2(H_2O)_{2.5}$ with oxidised Si(100)

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Model catalysts were prepared by spin-coating untreated and hydrated silicon wafers using $Cu(NO_3)_2(H_2O)_{2.5}$ solved in cyclohexanone as precursor. The prepared surfaces were examined by atomic force microscopy and Rutherford backscattering spectrometry. Spin-coating untreated silicon wafers resulted in clusters composed of small particles. The use of hydrated silicon wafers as substrate resulted in highly disperse small particles. We attribute the difference in surface morphology to the presence of more silanol groups on the surface of the hydrated wafers.

Keywords: AFM; catalyst; copper; impregnation; model; spin-coating

1. Introduction

The method of spin-coating was first applied by Kuipers et al. [1] to the impregnation of small particles on flat oxidised silicon surfaces. Kuipers investigated the influence of the spinning frequency and the initial concentration of different Cu precursors on the resulting particle size and density. Particle sizes ranged from a few nanometers to several microns. Van Wijk et al. investigated the dependence of the resulting particle size and distribution on the precursor species. They showed that large particles resulting from impregnation with $Cu(NO_3)_2(H_2O)_{2.5}$

appeared to be clusters of smaller particles [2]. By comparing the particle distribution of a $Cu(NO_3)_2(H_2O)_{2.5}$ precursor with a bis-salicyl-aldehydato-copper(II) ($Cu(C_7H_5O_2)_2$) precursor, which is an organic complexing ion, they attributed the cluster formation in the case of $Cu(NO_3)_2(H_2O)_{2.5}$ to less surface interaction of this precursor compared to bis-salicyl-aldehydato-copper(II). In this paper we investigate the influence of surface pretreatment on the interaction of the $Cu(NO_3)_2(H_2O)_{2.5}$ precursor with the oxidised silicon surface. We pretreated the surface with a basic solution, thereby hydrating the surface and increasing surface interaction. Hydrated oxidised surface silicon wafers are better models for catalytic SiO_2 surfaces as they contain a large number of OH groups.

2. Experimental

2.1. HYDRATION OF THE SILICA SURFACE

The surface layer of untreated single-crystalline Si(100) wafers consists of amorphous silica [1]. Under normal atmospheric conditions these silica surfaces are not fully hydrated. To hydrate the surface, the wafers were boiled in a H_2O_2/NH_4OH/H_2O solution [3]. A mixture of 25% ammonium hydroxide and 35% hydrogen peroxide (60 : 40 v/v) was used. The initial pH of this mixture was 11.2. After boiling for 1 h the pH had dropped to 7.6. Silanol bonds are best formed from siloxane bonds in an environment with pH 10.5–10.6. They remain on the surface if the pH remains higher than 9 [4]. The maximum OH-group coverage of the surface (5 OH/nm^2 [4,5]) was therefore obtained after boiling for 20 min.

2.2. PREPARATION

Single crystalline Si(100) wafers were used as supports. Without pretreatment the surface of these wafers is flat. After treatment with the $H_2O_2/NH_4OH/H_2O$ solution no increase in surface roughness was observed by atomic force microscopy (AFM). Spin-coating was done with a home-built spin-coater. The rotation frequency could be varied between 0 and 10000 rpm. The spin-coater was located in a closed volume which could be purged continuously with nitrogen. For most experiments we used the same solution: 3.5 g ℓ^{-1} $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexane, one sample was prepared using 2.0 g ℓ^{-1} $CuAc_2{\cdot}H_2O$ in ethanol. Prior to spin-coating the solution was filtered. Spin-coating was done by pouring 0.75 ml of the solution by means of a micropipet on top of a wafer that was spun at 4000 rpm. After spin-coating the wafers were calcined in air at 600 K for 2 h. Some of the resulting model catalysts were also reduced in hydrogen at 700 K.

2.3. CHARACTERIZATION

Several analysis techniques were used for the characterization of the initial solution and the prepared samples. Dynamic light scattering (DLS) [6] measurements were performed on the solution prior to spin-coating to investigate whether particles were present in the solution. DLS results were obtained using an argon laser. Autocorrelation functions were measured with a Malvern Multibit K 7025 128 points correlator. AFM was used to investigate the morphology of the sample surface. Measurements were performed using a Nanoscope III [7] under atmospheric conditions. Microfabricated cantilevers (length 100 μm, spring constant 0.6 N m^{-1}) with an integrated pyramidal tip were used. All images were acquired without filtering in constant force mode with a scan speed of 2 lines s^{-1}. Because AFM images represent the interaction of the tip with the real sample topography they must be interpreted carefully. Especially lateral dimensions of small particles will be larger than the real size. This effect is not significant when imaging larger particles ($d > 50$ nm). Particle heights can be determined reliably [8]. Rutherford backscattering spectrometry (RBS) [9] was used to measure the absolute copper coverage of the samples. RBS was performed using a 2 MeV He^+ beam. X-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation state of the copper atoms at the surface of the particles. XPS was performed in a standard Vacuum Generators MT 500/CLAM-2 two-chamber UHV system. Inside the analytical chamber (base pressure $< 1 \times 10^{-8}$ Pa) XPS was performed at a fixed angle using non-monochromatic Al Kα radiation. The sample could be transferred to a preparation chamber (base pressure $< 1 \times 10^{-5}$ Pa) in which it could be heated, $298 < T < 873$ K, and exposed to H_2 (99.90%) and O_2 (9.998%) at pressures up to 1 atm.

3. Results

No particles could be detected in the solution by DLS. This indicates that all $Cu(NO_3)_2(H_2O)_{2.5}$ was dissolved properly. Spin-coating untreated wafers proceeds similar to Kuipers' work [1]. The liquid film that is formed on the surface starts to evaporate and while the film thickness diminishes Newton interferences start to give rise to homogeneously changing colours. At this stage the $Cu(NO_3)_2(H_2O)_{2.5}$ particles were loosely bound to the surface: in all cases, also in the case of pretreated surfaces, the $Cu(NO_3)_2(H_2O)_{2.5}$ dissolved when the wafers were immersed in water. AFM shows that spin-coating the solution described above results in large clusters, evenly distributed on the surface (fig. 1). The diameter distribution of the clusters is depicted in fig. 2: the average diameter of the clusters is 350 nm, their height is 10 nm. These clusters appear to consist of small particles (fig. 3). The particles inside the clusters are typically 5 nm in height. Some of these particles are also deposited separately (fig. 3). RBS showed that the Cu coverage of this sample was $(1.12 \pm 0.06) \times 10^{15}$ atoms cm^{-2}.

Though spin-coating hydrated wafers seems to proceed visually in a manner similar to untreated wafers, the result is dramatically different. AFM shows a highly disperse distribution of particles that are typically 5 nm in height (fig. 4).

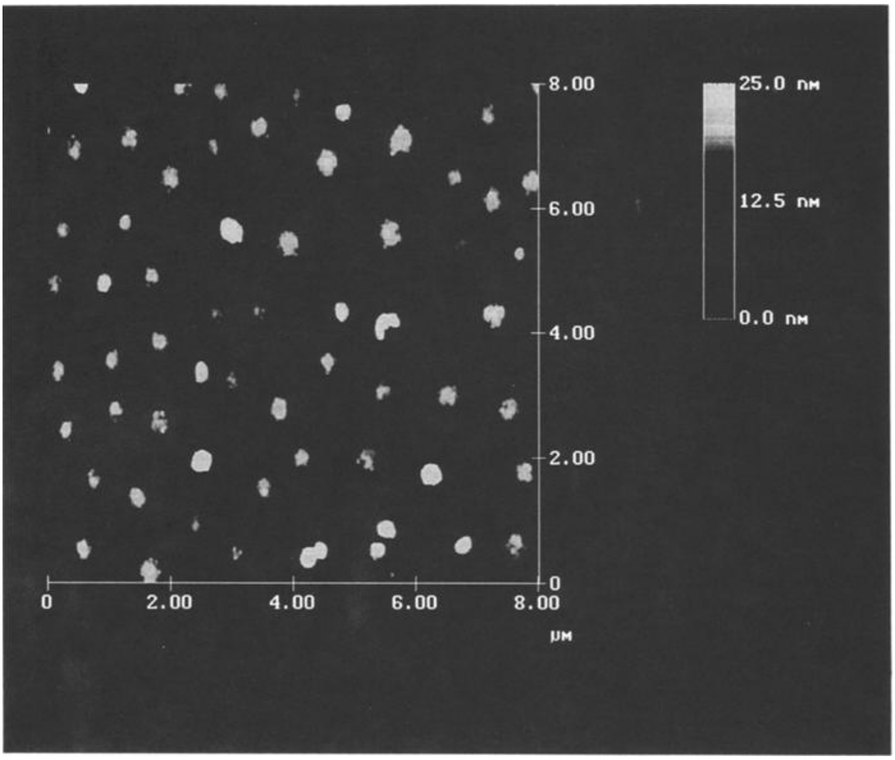

Fig. 1. AFM image of 3.5 g ℓ^{-1} $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone impregnated on an untreated Si(100) surface at 4000 rpm, showing an area of 8 μm × 8 μm.

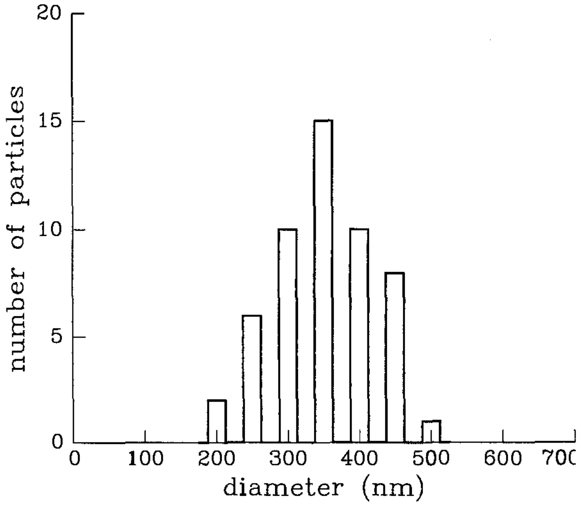

Fig. 2. Diameter distribution of particles shown in fig. 1.

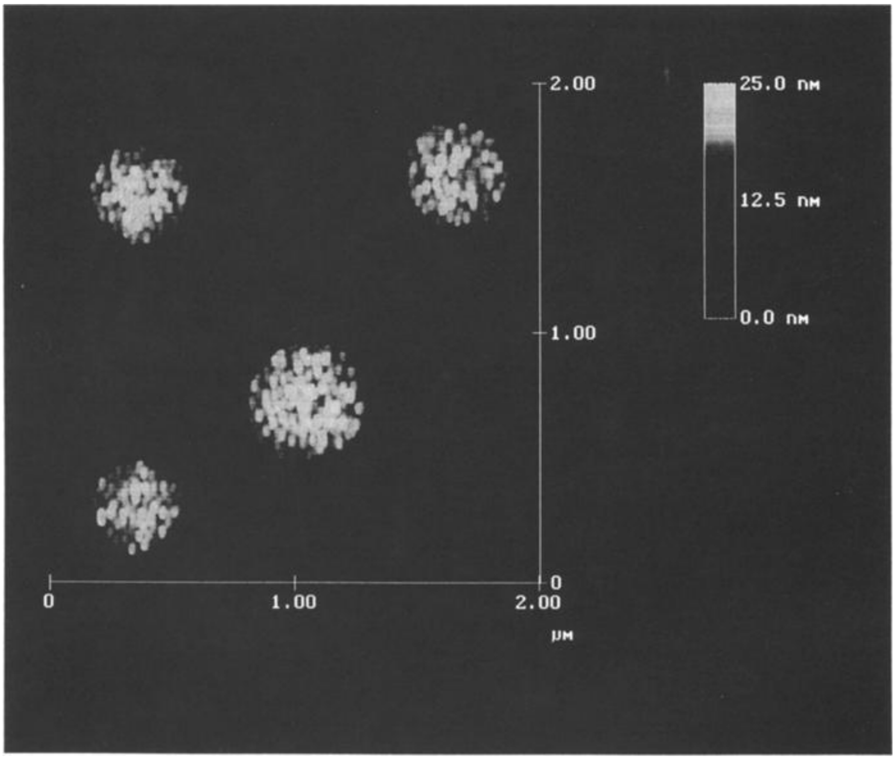

Fig. 3. AFM image of 3.5 gℓ^{-1} $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone impregnated on an untreated Si(100) surface at 4000 rpm, showing an area of 2 µm × 2 µm.

The height distribution of these particles is shown in fig. 5. Their diameter, as measured by AFM, is 25 nm. Clearly no clustering has occurred. According to RBS the coverage of this sample is $(1.6 \pm 0.2) \times 10^{15}$ atoms cm^{-2}. The higher Cu coverage is probably due to a better wetting of the fully hydrated wafers by the solution.

Spin-coating partially hydrated wafers results in an intermediate between hydrated and untreated surfaces. A typical image of such a surface is shown in fig. 6. Small particles and large clusters are deposited on the surface. The average diameter of the small particles is 90 nm, their average height is 5 nm. Large clusters are typically 350 nm in diameter and 30 nm in height. A striking feature of this sample is the empty area around the large clusters. It appears as if all particles that could have been present in this area were incorporated in the clusters.

XPS showed that exposing the samples to 1 atm H_2 at 673 K leads to the disappearance of the characteristic Cu^{2+} satellites: the particles are reduced, see fig. 7. The sample used for XPS was the sample prepared with $CuAc_2 \cdot H_2O$. XPS data from this sample also apply to the other samples though the Cu coverage is higher. Reduction of the copper-oxide particles did not change the morphology of all

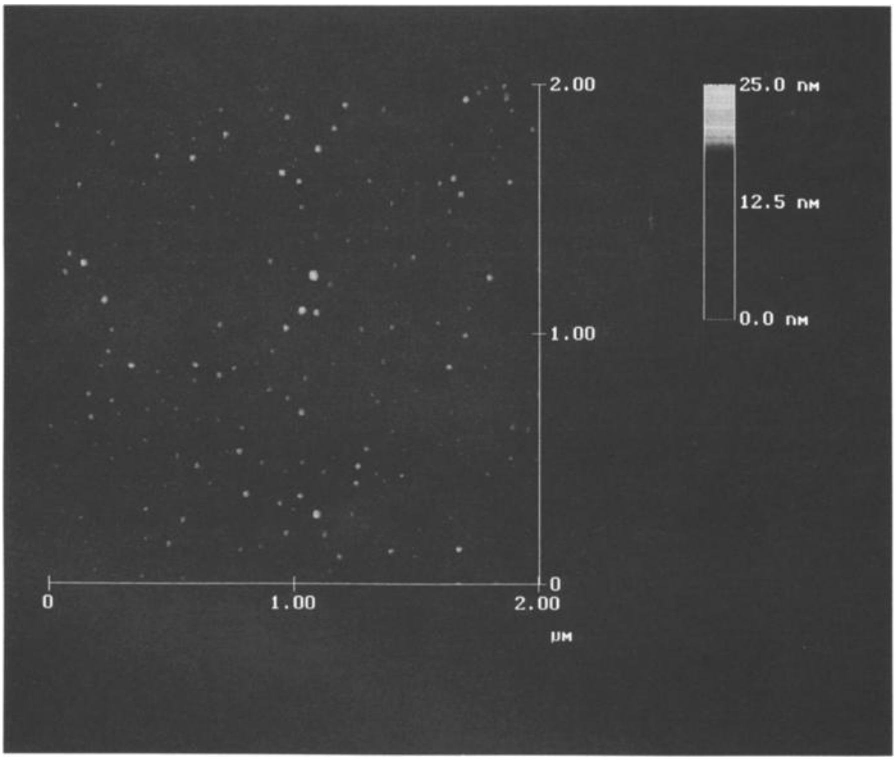

Fig. 4. AFM image of 3.5 gℓ^{-1} $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone impregnated on an hydrated Si(100) surface at 4000 rpm, showing an area of 2 μm × 2 μm.

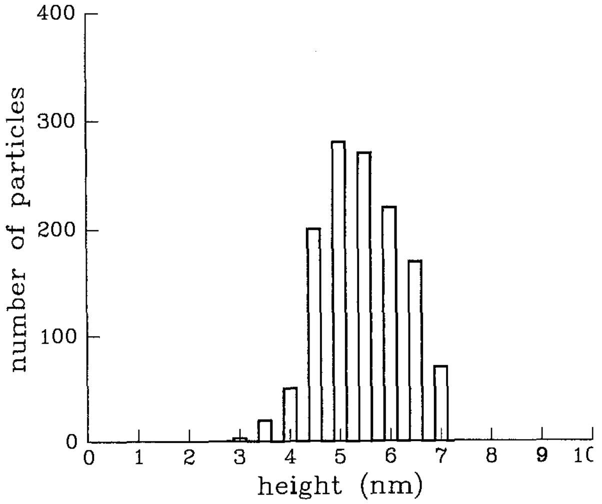

Fig. 5. Height distribution of particles shown in fig. 4.

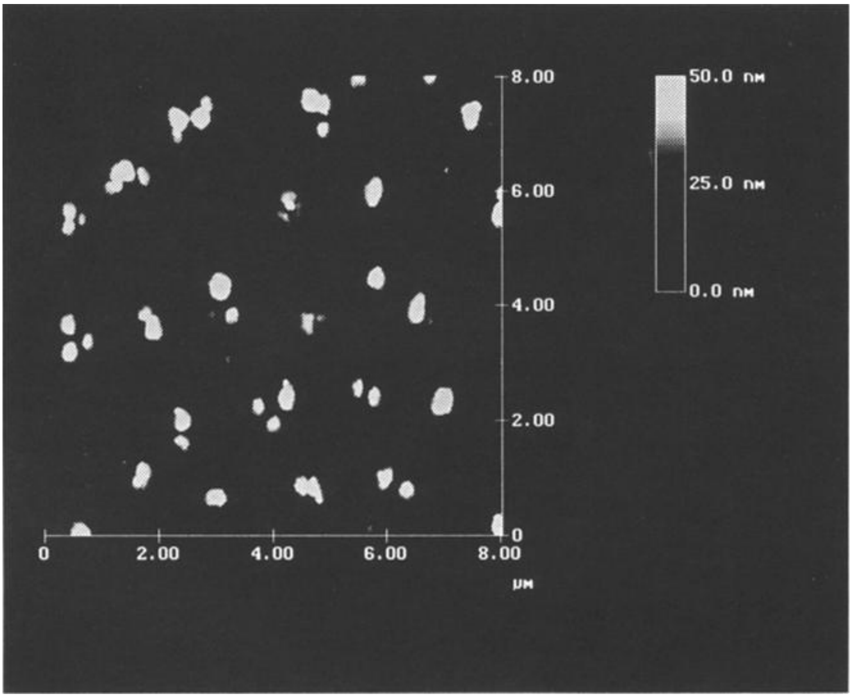

Fig. 6. AFM image of 3.5 g ℓ^{-1} $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone impregnated on an partially hydrated Si(100) surface at 4000 rpm, showing an area of 8 µm × 8 µm.

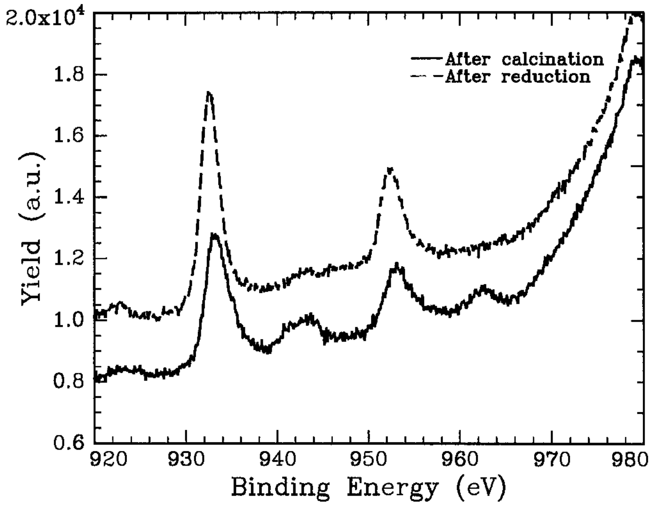

Fig. 7. XPS Cu(2p) peaks before and after reduction in 1 atm H_2 at 673 K of the sample spin-coated with 2.0 g ℓ^{-1} $CuAc_2{\cdot}H_2O$ in ethanol at 4000 rpm.

samples in this investigation as observed by AFM. Therefore, they must exhibit strong surface interaction. If this would not be the case sintering would occur.

4. Discussion

There is a large difference between the samples investigated in this study. Large clusters of particles were formed on untreated wafers. Small particles were formed on hydrated wafers. The formation of large clusters was explained by a lack of surface interaction of the $Cu(NO_3)_2(H_2O)_{2.5}$ precursor with untreated wafers [2]. It was stated that, once a crystallite was deposited on the support surface, the surrounding solution will exhibit a stronger interaction with the crystallite than with the support surface. The interaction between deposited material and solution may even be enhanced by capillary forces exerted by micropores that are formed during the growth of the $Cu(NO_3)_2(H_2O)_{2.5}$ clusters [10]. The clusters were compared with particles deposited from a solution of bis-salicyl-aldehydato-copper(II) in cyclohexanone, an organic complexing ion. The latter precursor is able to establish hydrogen bonds with the surface. Van den Brink [11] stated that organic complexing ions exhibit a stronger interaction with a silica surface. By creating more silanol groups on the surface, interaction of $Cu(NO_3)_2(H_2O)_{2.5}$ with the silica surface could be increased. Spin-coating hydrated wafers therefore results in highly dispersed small particles. Obviously, surface interaction has become large enough to prevent individual particles from clustering. The clustering effect became visible by spin-coating partially hydrated wafers: on the non-hydrated part of the surface clustering occurred while the hydrated part was covered with a disperse distribution of small particles. The non-hydrated part of the surface has been depleted and particles were incorporated in the clusters.

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References

[1] E.W. Kuipers, C. Laszlo and W. Wieldraaijer, Catal. Lett. 17 (1993) 71.
[2] R. van Wijk, O.L.J. Gijzeman, J.W. Geus, E. ten Grotenhuis and J.C. van Miltenburg, Catal. Lett. 24 (1994) 171.
[3] W. Kern, J. Electrochem. Soc. 137 (1990) 1887.
[4] H.P. Boehm, Adv. Catal. 16 (1966) 225.

[5] J.D.L. Grange, J.L. Markham and C.R. Kurkjian, Langmuir 9 (1993) 1749.
[6] R. Pecora, ed., *Dynamic Light Scattering: Applications of Photon Correlation Spectroscopy* (Plenum Press, New York, 1985).
[7] ©Digital Instruments Inc., 520 E. Montecito St., Santa Barbara, CA 93103, USA.
[8] R. Wurster and B. Ocker, Scanning 15 (1993) 130.
[9] L.C. Feldman and J.W. Mayer, *Fundamentals of Surface and Thin Film Analysis* (North-Holland, Amsterdam, 1986).
[10] A.Q.M. Boon, PhD Thesis, Utrecht University, The Netherlands (1990).
[11] P.J. van den Brink, PhD Thesis, Utrecht University, The Netherlands (1992).