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Surface interaction of different Cu precursors on oxidised Si(100)

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Two different model catalysts were prepared by means of spin-coating on an oxidised Si(100) surface using bis-salicyl-aldehydato-copper(II) and $Cu(NO_3)_2(H_2O)_{2.5}$, both solved in cyclohexanone, as precursors respectively. The prepared surfaces were examined by atomic force microscopy and Auger electron spectroscopy. Using bis-salicyl-aldehydato-copper(II) as a precursor resulted in a surface covered with highly disperse copper-oxide particles. The use of $Cu(NO_3)_2(H_2O)_{2.5}$ resulted in disperse copper-oxide clusters. We attribute this difference in surface morphology to a difference in surface interaction of the solutions used.

Keywords: Impregnation; model; catalyst; spin-coating; AFM; AES

1. Introduction

Recently Kuipers et al. [1] applied the method of spin-coating to impregnation of catalyst particles on flat oxidised silicon surfaces. Because the catalyst particles are deposited on top of a flat support they become readily accessible to most conventional surface science techniques, including atomic probe microscopies. Kuipers et al. investigated the effect of the rotation frequency and impregnation solution concentration on the particle size and density of the deposited precursors. They applied light- and scanning electron microscopies to observe the structure of the particles on top of the support surface. However, they did not investigate the influence of the precursor species on the surface morphology. We applied atomic force microscopy (AFM) to investigate the difference in surface morphology between samples impregnated with $Cu(NO_3)_2(H_2O)_{2.5}$ and samples using bis-salicyl-aldehydato-copper(II) precursors.

2. Experimental

2.1. SAMPLE PREPARATION

The Cu precursors were deposited by means of spin-coating [1] at the Koninklijke Shell Laboratory in Amsterdam. Single-crystalline Si(100) wafers were used as supports without further treatment, implying that the topmost atomic layers consist of amorphous silica. Two types of samples were prepared: 0.003 wt% bis-salicyl-aldehydato-copper(II) ($Cu(C_7H_5O_2)_2$) in cyclohexanone impregnated on the support at 5000 rpm, sample α and 0.11 wt%, $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone impregnated at 5600 rpm. The samples were dried and calcined in air by heating them to 323, 373 and 573 K for 15, 15 and 60 min consecutively. The wafers were cut into suitable pieces for the different analysis techniques used.

2.2. STRUCTURAL CHARACTERIZATION

Several techniques were used to investigate the structure of the prepared samples. Rutherford backscattering spectrometry (RBS) [2] was used to measure the

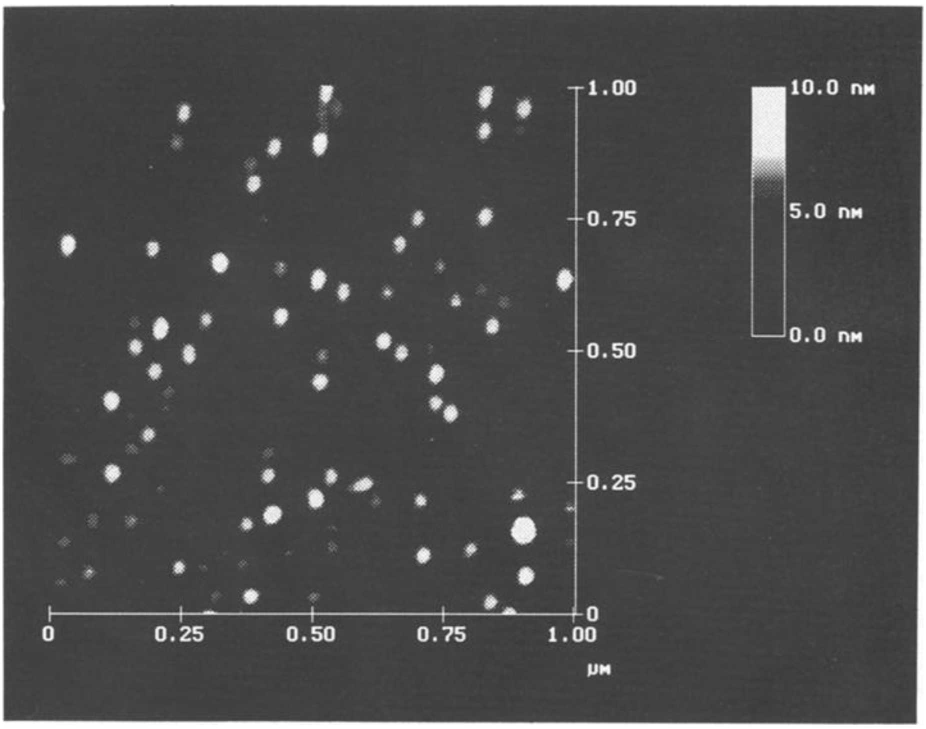

Fig. 1. AFM image of 0.003 wt% bis-salicyl-aldehydato-copper(II) in cyclohexanone impregnated on oxidised Si(100) at 5000 rpm, showing an area of 1 μm × 1 μm.

absolute copper coverage of the samples. RBS was performed using a 2 MeV He^+ beam. AFM was used to investigate the morphology of the sample surface. AFM was performed using a Nanoscope III [3] 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 5 lines s^{-1}. Samples could be mounted into an UHV chamber (background pressure $<3 \times 10^{-8}$ Pa) to investigate the chemical composition of the surface by Auger electron spectroscopy [2], using a Varian 981-2145/47 glancing incident electron gun in combination with a retarding field analyser.

3. Results

3.1. SAMPLE α

RBS showed that the Cu coverage of this sample was $(0.05 \pm 0.02) \times 10^{15}$ atoms cm^{-2}. AES showed no significant contaminations on the surface. No significant Cu peaks could be observed with AES. This was not surprising because the Cu cov-

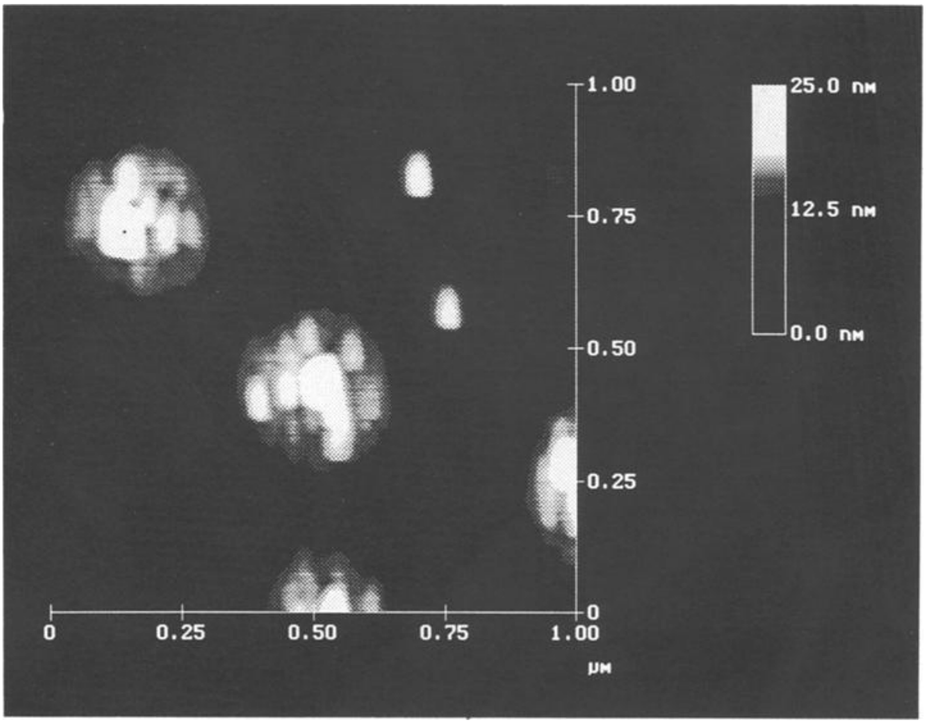

Fig. 2. AFM image of 0.11 wt% $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone impregnated on oxidised Si(100) at 5600 rpm showing an area of 1 μm × 1 μm.

erage was rather low. AFM showed disperse small copper-oxide particles, see fig. 1. The particles were typically 25 nm of width and 3 nm of height. The underlying surface was flat up to the atomic level.

3.2. SAMPLE β

The absolute Cu coverage of sample β was found to be $(1.68 \pm 0.07) \times 10^{15}$ atoms cm^{-2} by RBS, this number is much larger than the coverage of sample α. After mounting the sample in the UHV system AES showed a very large C KVV peak ($E = 271$ eV), corresponding to graphite. The Si $L_{23}VV$ peak at 92 eV had not broadened with respect to a standard oxidised Si(100) sample; indicating that no copper silicides had been formed during sample preparation [4]. Also no significant Cu peaks could be observed. AFM gained more insight into the morphology of the surface, see fig. 2. The AFM image showed vague clusters, composed of 5 nm particles, typically 300 nm of width and 10 nm of height. Some isolated particles were found (100 × 10) nm. Obviously the particles were not calcined properly and were covered with a thick layer of carbon. Probably this carbon layer shielded the

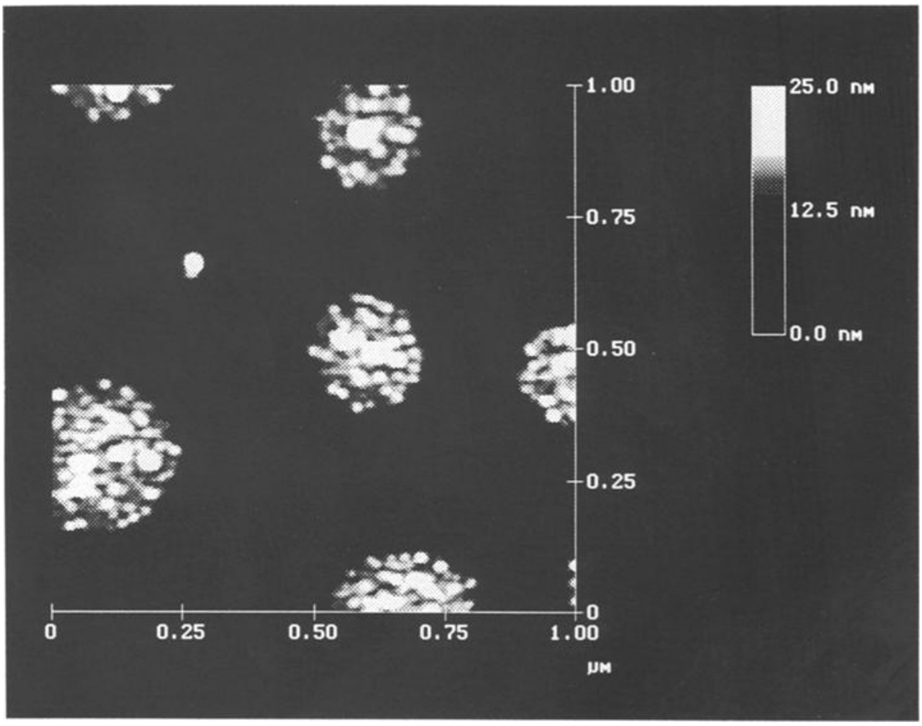

Fig. 3. AFM image of 0.11 wt% $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone impregnated on oxidised Si(100) at 5600 rpm and exposed to oxygen at 600 K and atmospheric pressure for 14 h, showing an area of 1 μm × 1 μm.

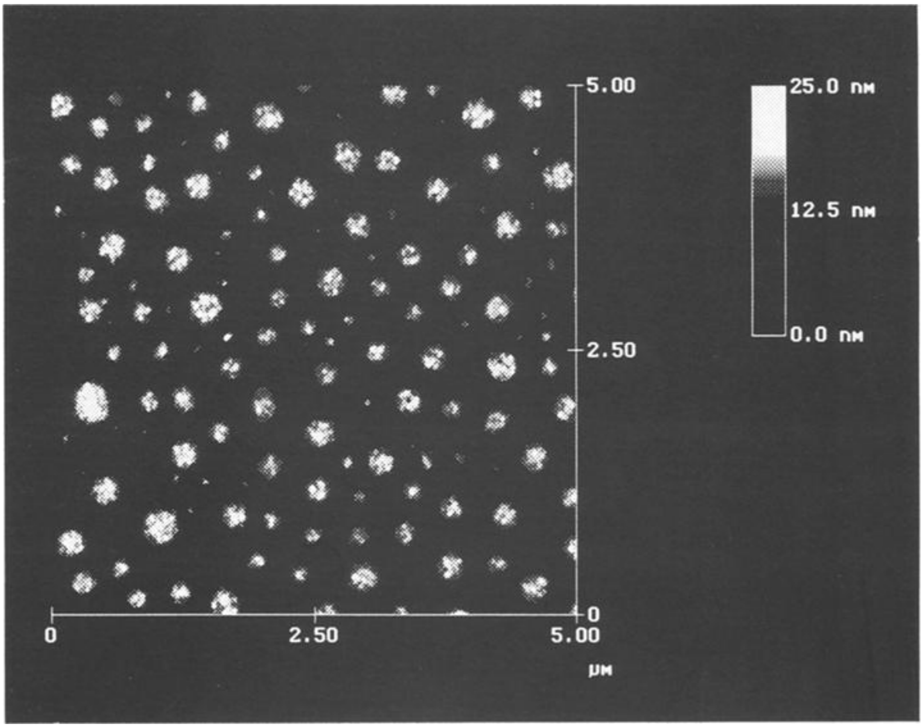

Fig. 4. AFM image of 0.11 wt% $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone impregnated on oxidised Si(100) at 5600 rpm and exposed to oxygen at 600 K and atmospheric pressure for 14 h, showing an area of 5 µm × 5 µm.

underlying copper so this could not be seen by AES. To remove the carbon we decided to perform an extra calcination by exposing sample β to oxygen at 600 K and atmospheric pressure of 14 h. After calcination RBS showed no difference in Cu coverage. AES indicated a dramatic decrease of the C KVV peak. Less than 10% remained of the original height; indicating that carbon was removed by calcination. AFM showed a dramatic change of the surface morphology, see fig. 3. The cluster size remained the same but the removal of carbon allowed AFM to probe the separate copper-oxide particles inside the clusters. The particles are typically 25 nm of width and 3 nm of height. Scanning a larger area, as shown in fig. 4, showed a large variety of cluster size: from single particles to large conglomerates. The cluster distribution was quite disperse.

4. Discussion

The difference in surface morphology between samples α and β can be explained by means of a difference in surface interaction of the two precursors used. Van den Brink et al. [5] showed that in the case of silica based iron-oxide catalysts impregnation of chelate iron complexes results in catalysts of a higher dispersion than in the case of simple iron salts. He stated that organic complexing ions exhibit a stronger interaction with the silica surface due to larger van der Waals interaction than simple salts. Bis-salicyl-aldehydato-copper(II) is an organic complexing ion with aldehyde groups which are able to establish hydrogen bonds with silanol groups [6] that are present at the silica surface. During spin-coating the bis-salicyl-aldehydato-copper(II) solution will be able to wet the support surface: the solution film will dry uniformly. $Cu(NO_3)_2(H_2O)_{2.5}$ is not able to form such hydrogen bonds. Once a $Cu(NO_3)_2(H_2O)_{2.5}$ crystallite is deposited on the support surface it is plausible that the surrounding $Cu(NO_3)_2(H_2O)_{2.5}$ solution will exhibit a stronger interaction with the $Cu(NO_3)_2(H_2O)_{2.5}$ crystallite than with the support surface. The film will redistribute and is not uniform anymore: new crystallites will be deposited in the neighbourhood of existing crystallites. Interaction between deposited material and solution may even be enhanced by capillary forces exerted by micropores that are formed during the growth of a $Cu(NO_3)_2(H_2O)_{2.5}$ cluster [7]. Impregnation with $Cu(NO_3)_2(H_2O)_{2.5}$ will therefore result in copper-oxide clusters after calcination.

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