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Deposition of nanocrystals on flat supports by spin-coating

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Monodisperse particles can be evenly distributed over flat supports by "spin-impregnation". In this way Cu precursors have been deposited onto Si wafers. The effects of the rotation frequency and the concentration of the "impregnation" solution have been investigated. The mean diameter of the deposited particles can be varied from several nanometers upto several micrometers as is shown by microscopy images. "Spin-impregnation" appears a useful tool to prepare well-defined flat model catalysts, which are readily accessible both to quantitative characterisation and to catalytic testing.

Keywords: Impregnation; model; catalyst; preparation; spin-coating; microscopy

1. Introduction

Most heterogeneous catalysts are made by impregnation of porous supports, such as silica, alumina and active carbon [1]. In this way a high surface area of the active material(s) can be obtained. However, quantitative analysis of the structure and composition of these catalysts is difficult. Therefore in studies aimed at unravelling the factors governing the performance of catalyst systems, flat model systems are an attractive alternative to porous ones.

The first advantage is the direct accessibility of the catalyst particles to analysis when they are deposited on a flat support. In contrast, porous supports have to be crushed prior to analysis, which frequently poses sampling problems, since the distribution of active material(s) through the catalyst particles need not to be homogeneous. The flat supports can be left intact.

Secondly, flat surfaces of, e.g., Si or Al covered with a few nanometers of oxide give much less rise to charging than silica and alumina during surface analysis [2].

A third advantage of flat supports is that if they are well polished (like commercially available Si-wafers), their surface is absolutely flat and featureless.

Therefore the recognition of deposited particles by light or scanning electron microscopy is straightforward. Porous supports hinder the discrimination between deposited particles and the texture of the support itself. This problem is even more pronounced in atomic force microscopy (AFM) and scanning tunnelling microscopy (STM), which techniques are hardly able, if at all, to discriminate between small catalytic particles and the support, if the latter is not extremely flat. Because of the above, the use of a flat model support is often beneficial in studies aimed at pinpointing the factors governing catalytic behaviour of surfaces.

The deposition of catalytic precursors on a support is mostly effected by impregnation. During drying the impregnation solution will be kept inside the pores by capillary forces. Thus a fairly homogeneous deposition of small active particles throughout the support can be obtained. On a flat support, however, the impregnation solution is not kept stationary by capillary forces. In the first instance, the impregnation solution will form a single puddle. The size and shape of this puddle will change upon evaporation of the solvent. Depending on the wettability of the surface by the solvent the puddle may end up as a ring or break up in many separate droplets. Eventually this results in supported particles which differ widely in size and are unevenly distributed over the support.

In this study it will be shown that by spinning the support during impregnation a homogeneous deposition of monodisperse particles can be achieved. Spinning the support is a commonly used technique for the preparation of coatings of homogeneous thickness on flat supports [3,4]. Especially in the electronic industry spin-coating is commonly used for the coating of wafers with a thin layer of photo resist. With this in mind we have investigated whether spin-coating can also be used to evenly "impregnate" flat supports with particles of active material or their precursors in a controllable fashion.

2. Experimental

In this study polished single-crystalline Si-wafers (Si(100) and Si(111)) of 2 and 3 inches diameter served as supports. They were used without further treatment, which means that the outermost atomic layers consisted of amorphous silica [5,6]. To enable the wafers to be spun during impregnation, they were held by suction on a chuck, placed on the axis of the spin coater. Two different spin coaters were used. The first prototype version consisted of a stirring motor placed upside down. Its rotation frequency could be varied between 0 and 2000 rpm. The second version was a commercially available spin-coater for the deposition of photo resists (Headway Research Inc.); its rotation frequency could be varied between 0 and 10000 rpm. This spin-coater sits inside a closed volume, which is continuously purged with N_2. In a preliminary feasibility study we "impregnated" the Si wafers with Cu precursors, namely $Cu(NO_3)_2$ and bis-salicyl-aldehydato-copper(II) ($Cu(C_7H_5O_2)_2$). To this end 1 ml of the solution was squirted through a 0.2 μm pore filter (Millipore) onto the centre of the wafer prior to spinning. The impregnated supports were analysed before and after calcination using optical dark field microscopy (DFM) (Zeiss Axioscope), scanning electron microscopy (SEM) (Jeol JSM 840A) and high resolution scanning electron microscopy (HRSEM) (Jeol HRSEM). The samples were dried and calcined in air by heating them to 323, 373 and 573 K for 15, 15 and 60 min, respectively. The samples have not been reduced to Cu-metal.

3. Results and discussion

Prior to spinning the impregnation solution forms a puddle in the centre of the wafer. When spinning is started the droplet spreads quickly over the wafer in a liquid film due to the centrifugal force. Hence most of the solution is flung from the wafer. Since the shear force increases very strongly with decreasing film thickness, the amount of liquid leaving the support at the edges decreases very quickly [3,7]. At a certain point in time the solvent flux leaving the support via evaporation will be the dominant one. At this point, which is reached within a fraction of a second, the thickness of the film is circa 1 μm. Newton interferences start to give rise to colours. These colours change homogeneously, all over the wafer, with diminishing layer thickness. This shows that during evaporation the thickness of the film remains more or less constant over the entire wafer. Because of this, the deposition of precursors during evaporation of the solvent is extremely homogeneous all over the support, yielding an even distribution of particles. But this is not the only advantage. Figs. 1 and 2 show two typical results for samples prepared in this way. Fig. 1a shows the DFM image from a $Cu(NO_3)_2$ deposition experiment, which was obtained by spinning a 0.62 wt% solution of $Cu(NO_3)_2(H_2O)_{2.5}$ in *n*-butanol at 2000 rpm. Fig. 1b shows the number-based diameter distribution obtained from fig. 1a using automated image analysis. Fig. 2a shows a HRSEM image of a calcined sample obtained by spinning a 0.1 wt% solution of bis-salicyl-aldehydato-copper(II) in propanol at 500 rpm. Again, fig. 2b shows the diameter distribution obtained from fig. 2a using image analysis. In figs. 1 and 2 we see not only, that the particles are evenly distributed, but also that the size distribution of the particles is very narrow. This holds for the entire wafer surface. Only at the very edge of the wafer are commonly larger particles found. Note that both particle size distributions have about the same standard deviation, despite the fact that their means differ by almost three orders of magnitude.

After having established that spin-impregnation can yield evenly distributed monodisperse deposits, we set out to investigate more closely the role of rotation frequency. To this end Si wafers were "impregnated" with a solution of

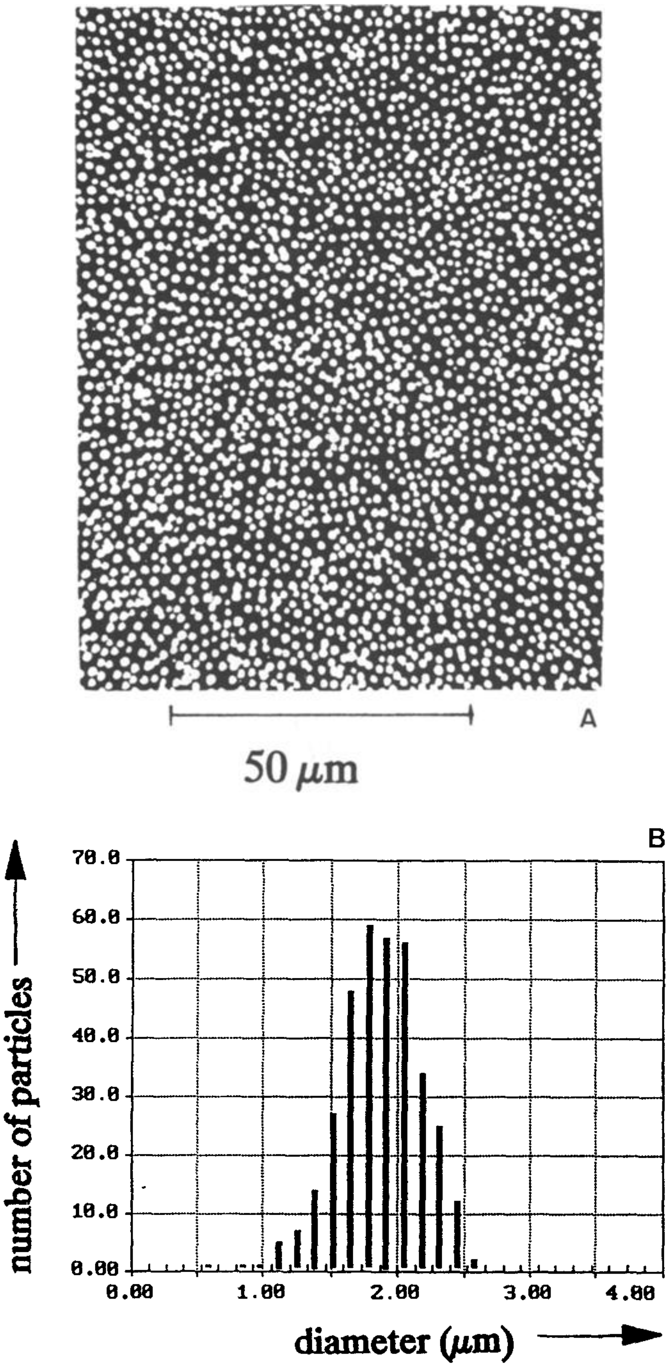

Fig. 1. (A) Optical dark field microscopy image of $Cu(NO_3)_2$ particles deposited on Si by "spin-impregnation" with a 0.62 wt% solution of $Cu(NO_3)_2(H_2O)_{2.5}$ in *n*-butanol at 2000 rpm spinning frequency. (B) The diameter distribution obtained from (A) using image analysis.

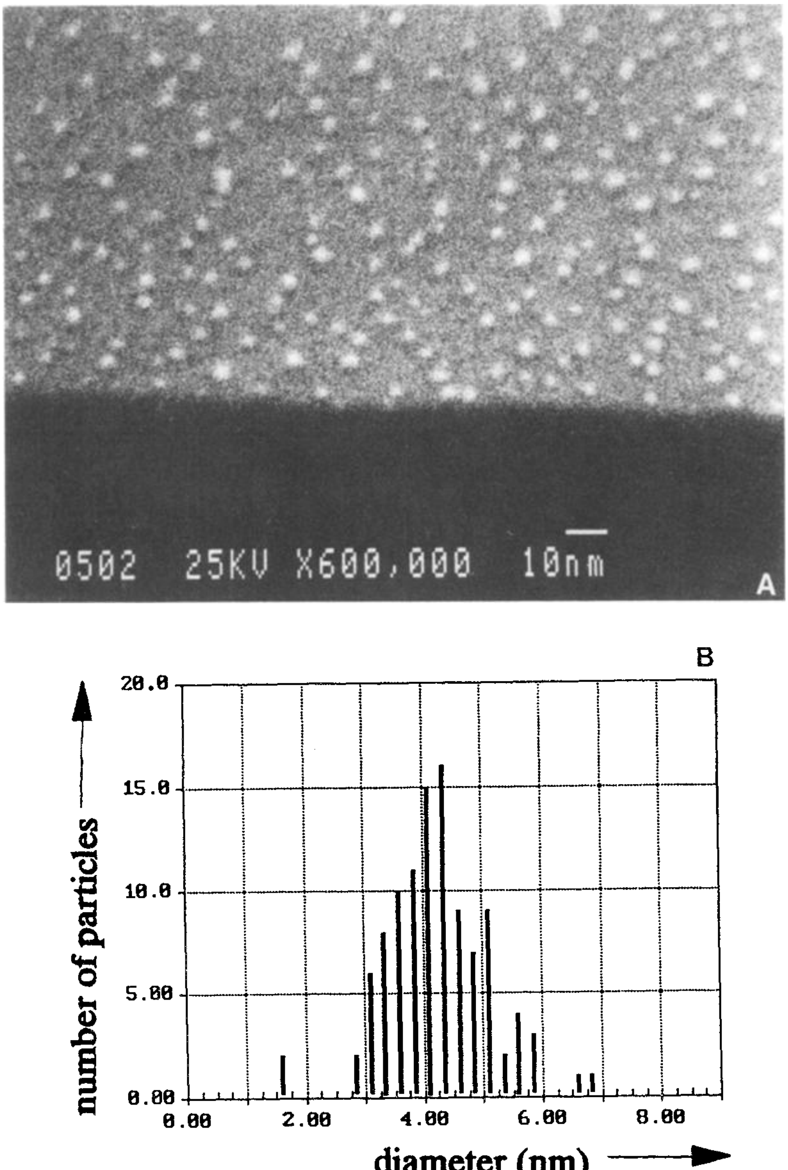

Fig. 2. (A) High resolution scanning electron microscope image of a calcined sample obtained by spinning a 0.1 wt% solution of bis-salicyl-aldehydato-copper(II) in propanol at 500 rpm on Si. (B) The diameter distribution obtained from (A) using image analysis.

0.053 wt% $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone at different rotation frequencies. In fig. 3a the average diameter of the resulting $Cu(NO_3)_2$ particles is plotted as a function of the rotation frequency. Fig. 3b shows the average number density of particles (100 μm^{-2}) versus the rotation frequency. From fig. 3 we see that the particle diameter decreases and the number density increases

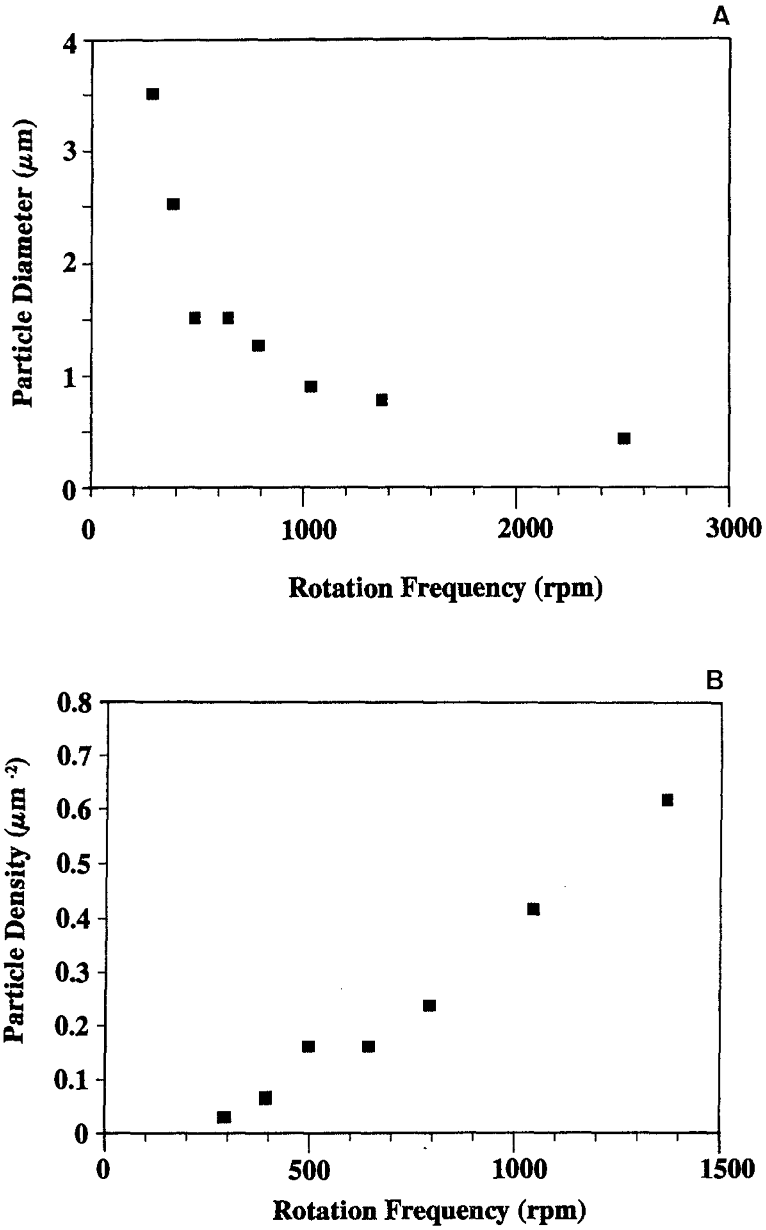

Fig. 3. (A) The average diameter of $Cu(NO_3)_2$ particles deposited on a Si wafer by "spin-impregnation" with a 0.053 wt% solution of $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone as a function of the rotation frequency. (B) The number density of $Cu(NO_3)_2$ particles deposited on a Si wafer by "spin-impregnation" with a 0.053 wt% solution of $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone as a function of the rotation frequency.

with rotation frequency. This can be understood qualitatively. During spin-coating the radial flow is proportional to $\Omega^2 h^3$, in which h is the thickness of the film and Ω the rotation frequency [3]. The flux of solvent leaving the wafer by evaporation, Φ, depends only on the surface area and not on h. Thus at the point where $h^3 < (\Phi/\Omega^2)$, evaporation will be the dominant way in which the solvent leaves the wafer. As mentioned above, this situation is reached at within a fraction of a second. Therefore to a first approximation, we may assume that up to that point evaporation was negligible and thus the concentration of the solution on the wafer remained constant. However, from that point onwards, i.e. the point at which evaporation takes over, the concentration of the dissolved material will increase until sufficient supersaturation is reached and the solute will nucleate and grow to separate crystals. Therefore to a first approximation the amount of material deposited on the substrate, m, is expected to depend on Ω as

$$m = k\frac{c_0}{\Omega^{2/3}}, \tag{1}$$

in which k is a constant and c_0 is the initial concentration of the solution.

According to the literature, the rate of nucleation increases with a 4–10th power of the concentration above the nucleation threshold. The rate of growth obeys a first or second order law of the concentration above the growth threshold [8]. The threshold for growth is lower than the threshold for nucleation. Thus, the faster the rate of concentration increase will be at the threshold for nucleation, the more the rate of nucleation will be favoured with respect to growth.

It can be deduced that at the threshold concentration for nucleation, c_n, the concentration increase is given by [9]

$$(\mathrm{d}c/\mathrm{d}t)_{c=c_\text{n}} = \frac{\Phi c_\text{n}^2 \Omega^{2/3}}{c_0 k}, \tag{2}$$

in which c is the concentration of the solution of the wafer, and t is the time. From eq. (2) we see, that the rate of concentration increase at the threshold for nucleation increases as $\Omega^{2/3}$. This qualitatively explains the experimentally observed dependence of number density on Ω.

The total amount of deposited material decreases as $1/\Omega^{2/3}$. Thus the final particle diameter will decrease, as observed experimentally. So we can qualitatively understand the dependence of number density and particle size on Ω.

For the preparation of model catalysts one would like to independently control the number density and particle size. As shown above, particle size and number density can be varied by changing Ω. Another way to change both quantities is by varying the initial concentration of the solution, c_0. An independent control would be possible, if the relation between number density and particle size would respond differently to variations of Ω and initial

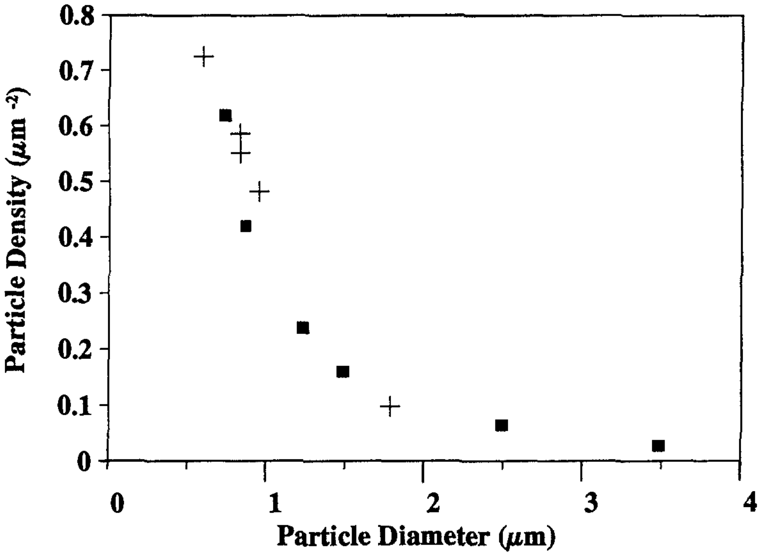

Fig. 4. Plot of the number density versus the observed particle size for a Si wafer "spin-impregnated" with a 0.053 wt% solution of $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone at various rotation frequencies (■). For comparison the results of "spin-impregnation" at 2000 rpm with various concentrations of $Cu(NO_3)_2(H_2O)_{2.5}$ in cyclohexanone are shown as well (+).

concentration. As described above, number density and particle diameter are governed by m and $(\mathrm{d}c/\mathrm{d}t)_{c=c_n}$. Eqs. (1) and (2) show that the dependence of these two factors on Ω and c_0 is not decoupled. Therefore, we do not expect an independent control of particle size and number density by varying both Ω and c_0 to be feasible. To verify this expectation experimentally we have spin-impregnated a Si wafer with cyclohexanone solutions containing various concentrations of $Cu(NO_3)_2$ at 2000 rpm (fig. 4). Indeed, within the error bars the relation between number density and particle diameter is the same for both the change of Ω and c_0. Thus independent control of number density and particle diameter requires the change of parameters other than Ω and c_0. Examples of such parameters include variation of the solvent, addition of other components to the solution and pretreatment of the wafer [9].

4. Conclusions

"Spin-impregnation" allows the preparation of customised model catalysts on flat supports. Active material(s) can be deposited in particles which are characterised by

- an even distribution all over the surface,
- a very narrow particle size distribution,

– a mean particle diameter that can be controlled over at least three orders of magnitude by changing, e.g., the spinning frequency.

"Spin-impregnation" is expected to facilitate the establishment of quantitative structure/performance relationships in catalytic studies. Moreover, it allows the study of factors relevant to the chemistry of catalyst preparation.

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