Shaping Ag clusters on Titania

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Abstract. We present a study of the growth of silver clusters on a TiO$_2$(110) substrate in ultra-high vacuum. The growth is monitored in situ by Low Energy Ion Scattering (LEIS) using He$^+$ scattering and X-ray Photoelectron Spectroscopy (XPS) and ex situ by scanning electron microscopy (SEM). Experimental results show that the deposition rate, the substrate temperature and the annealing temperature are key parameters for controlling the size and morphology of the Ag clusters. By changing the deposition rate, the mean cluster diameter can vary from 5 to 20 nm. The growth of Ag at low substrate temperature shows a transition from quasi 2D flat islands to a 3D growth mode at submonolayer coverage. The substrate was annealed at different temperatures and the clusters shape controlled from a quasi 2D flat island to 3D sharp islands with a maximum substrate exposure, prior to cluster desorption.

1. Introduction
The deposition of noble metals on oxides has important applications on heterogeneous catalysis. These metals on such surfaces produce clusters in the nanometer range. The resulting nanostructured surfaces behave neither as oxides nor as chemically inert noble metals, since adatoms or molecules “see” simultaneously both surface species. The active sites of Au/TiO$_2$ surfaces has been discussed by Campbell [1].

The size of the clusters is an essential parameter which concerns the surface reactivity. Several authors found a clear relationship between the cluster size and the catalytic activity in specific reactions [2, 3].

The growth of Ag clusters was unequivocally determined as 3D island growth on TiO$_2$(110) surfaces at room temperature [4-13]. A 2D island growth was inferred for deposition of Ag at low temperature based on LEIS [11] measurements as well as on our recent results. The islands nucleate along step edges rather than at flat terrace defect sites indicating rapid diffusion of Ag on TiO$_2$.

Despite the large number of studies reported in the literature on the growth of metal overlayers on TiO$_2$(110), not many researchers focused on the effect of deposition rate and temperature on the growth mode for the Ag/TiO$_2$ system. Nonetheless, the stability of the clusters size or morphology at different temperatures can be a critical issue, since it indirectly determines the catalytic activity of the system. It is also known that the growth mode of a metal overlayer is not uniquely determined by thermodynamic considerations [14]. In this system, growth is a non–equilibrium kinetic phenomenon. The degree to which growth proceeds away from equilibrium influences the morphology which in turn is governed by thermodynamic quantities, such as surface and interface free energies, or by the growth kinetics.
In this study, the kinetic parameters that can influence the clusters growth mode has been investigated. The influence of deposition rate, substrate temperature and annealing temperature on the cluster size has been characterized in situ by Low Energy Ion Scattering (LEIS) and X-ray Photoelectron Spectroscopy (XPS) and ex situ by scanning electron microscopy (SEM).

2. Experimental Methods

The experiments were performed in the Andromeda and in the Multitechnique system, both ultra-high vacuum (UHV) systems, described in detail elsewhere [15, 16]. Several surface analysis techniques were available like AES, SIMS, LEIS and XPS. For LEIS, a Hiden IG20 ion gun was operated at 1 keV with a typical current of He⁺ of 20 nA. The ion beam path makes a 45° incident angle with the surface normal and the energy analyzer was normal to the surface (135° scattering angle). XPS measurements were performed with a VSW X-ray source using the Mg anode at a current of 10 mA. The hemispherical energy analyzer, VSW Class 100, was set in a fixed transmission mode with pass energy of 90 eV for both ISS and XPS.

In order to get the size of the Ag clusters the Andromeda’s samples were imaged using SEM (Phillips, Model XL 30S) with a resolution of about 3 nm. Growth of Ag was monitored in-situ by LEIS and the sample was then imaged ex-situ on the SEM.

The TiO₂ crystal was cylinder shaped with a diameter of 10 mm and 5 mm height. It was mounted on a molybdenum sample holder that could be cooled down with liquid nitrogen and indirectly heated by means of electron bombardment. The crystal surface was submitted to cycles of 2 keV Ar⁻ ion sputtering at grazing angles less than 10° and subsequent annealing to ~850K for 10 minutes. The procedure was repeated until only oxygen and titanium peaks were present in the LEIS analysis. After annealing, the presence of a clear 2p Ti doublet in XPS spectrum indicated that no Ti₂O₃ or TiO were present and the crystal was in good stoichiometric agreement with (1×1) surface reconstruction.

A high purity Ag wire (99.99%) wrapped around a tungsten filament was used for vapor deposition. The thickness was measured by a quartz crystal microbalance. The arrangement of the apparatus is such that only 1/10th of the silver deposited on the quartz crystal reaches the sample surface. A mechanical shutter provided an accurate vapor blanking to the surface.

In earlier experiments we found that the He beam did modified the surface during acquisition time. We think that islands growth can be stimulated by the radiating beam. The impact of fast He projectiles on the surface may supply the energy needed by the adatoms to overcome the low energy barrier that keep those atoms stuck to the surface. Therefore, we decided not to follow the overlayer growth with LEIS since the results achieved were different from those when followed only by XPS. Moreover, the acquisition time for LEIS scan after annealing was reduced from the typical 4 min to 40 s. The beam was scanned over a 2 mm² area to decrease the current density on the surface and keep the LEIS technique as gentle as possible just to probe the surface without introducing much perturbation [17].

3. Results

Firstly, the effect of coverage at a fixed deposition rate on the cluster’s size distribution. For increased deposition times of 0.6, 1.2 and 2.4 eqML of Ag at a rate of 0.02 eqML/min the clusters with a mean diameter rising from 11 to 15 nm was measured. This showed that the total flux is not a crucial parameter on the cluster size, providing enough atoms are available to feed the cluster growth.

Secondly, the effect of evaporation rates was observed using SEM images obtained for 2 rates as shown in Figure 1. Very large and isolated Ag clusters were obtained at the lowest evaporation rate while smaller cluster size of the order of 6 nm were observed at higher evaporation rate of 0.05 eqML/min. Note that the finite resolution of the SEM, due to the size of the electron beam spot (around 3 nm), will slightly overestimate the clusters’ sizes. This size agrees with that reported by Lai et al. [6] who used similar high evaporation rates.
Figure 1. Effect of the deposition rate on the clusters size. Lower rates lead to larger clusters.

The growth of silver clusters was studied by LEIS and XPS during deposition at different surface temperatures—at room temperature and LN₂ temperature. Figure 2 shows the LEIS intensities as function of the coverage at both temperatures. For the purpose of comparison, the signals were normalized to the peak areas sum. Therefore, the intensity scale shows the fractions of the signal coming from the substrate (Ti+O) and from the overlayer (Ag) in relation to the total signal. It is clear the differences— at low temperature the coverage of the substrate is much higher than at room temperature for the same overall thickness. This points to a different cluster shape when deposited at low temperature— clusters lower in height and wider in diameter, covering much more the substrate.

Figure 2. Overlay and substrate normalized intensities acquired by LEIS at room temperature (a) and at LN₂ temperature (b). At low temperature, the substrate is much more covered by the overlayer.

Further experiments were carried out to investigate the stability of the structures grown at LN₂. The aim was to determine at what temperature the shape would become the same as if it would be grown at room temperature. Starting with about 1 eqML deposited on the surface the substrate was annealed for 5 minutes and cooled down again to LN₂ temperature. Sufficient time was allowed to the temperature
properly stabilize. This time increased with the annealing temperature, from 10 minutes in the early stages to 1 hour in the final stages. XPS and LEIS spectra were obtained after each annealing temperature. Fig. 3 shows the results obtained.

![LEIS peak areas](image1)

![XPS peak areas](image2)

**Figure 3.** LEIS (a) and XPS (b) data obtained during annealing after a deposition at LN$_2$ temperature. When annealed above 0°C is noticeable a change in the cluster’s shape.

Close to the annealing temperature of 0°C the LEIS data shows a clear change— the hidden substrate becomes more exposed and the Ag signal less evident. Cluster desorption was not the case since the XPS data shows the some amount of silver. Only at higher (~200°C) desorption may be present, since both signals visibly decrease. The slight and constant negative slope observed in LEIS and XPS signals should be attributed to the overlayer erosion induced by the He$^+$ beam used for LEIS.

**4. Discussions**

The different average sizes observed (Fig.1) at the various evaporation rates may be due to the interplay between Ag flux and diffusion kinetics on the surface. It is the trade off between the mobility of the adatoms or mobile clusters and the deposition flux that will determine the density and the size distribution of clusters formed by vapor deposition on the surface.

If the vapor flux is very low, the probability of the Ag atom being captured by an existing cluster is higher than that of forming a new nucleus, as a result of the lower mean density of mobile clusters on the surface. Very large clusters can thus be formed. At a higher deposition rate, the density of mobile clusters on the surface will increase, leading to a larger number of nucleation sites and a lower mean cluster size. This is consistent with the scaling law of nucleation theory [14]. According to this theory, the density of stable clusters will be proportional to the ratio between the incident particle flux and the diffusion coefficient raised to an exponent $\chi$ given by $\chi = i/(i+2)$, where $i$ is the critical cluster size. For a fixed temperature, the diffusion rate is constant, therefore the cluster density will be larger for a higher deposition rate. This is also consistent with recent results by Benz et al. [8], that point to a critical cluster size $i$ of 2 at room temperature, i.e. that the trimer is the smallest stable cluster.

At low temperatures it may be energetically more favorable for new adatoms to keep stuck to the surface than to nucleate in a 3D manner. If such 2D growth takes place, islands will enlarge with further metal deposition until a critical coverage is reached, as defined by Campbell [18]. After this critical coverage, a second layer starts to grow over the previous 2D islands. This growth mode was called pseudo-layer-by-layer or 2D island growth. This mode is very similar to the monolayer-by-monolayer mode observed in most metals on metals, with the main difference that the surface is not completely covered. This was the growth observed at low temperatures shown in Fig.2.

The 2D structures are not thermodynamically stable. Their structures may be reshaped if there is adequate energy. This happens when the substrate is annealed at increasingly higher temperatures. 3D island growth is then triggered with Ag atoms stepwise from islands edges to upper layers.
5. Conclusions

Cluster size is mostly controlled by the deposition rate and deposition time, slower rates and prolonged times will lead to bigger clusters. Cluster shape may be also determined from the mobility of the silver atoms on the TiO$_2$ surface. When at room temperature silver is highly mobile and will from 3D structures, but at lower temperatures mobility is reduced and the favoured structures are of only two dimensions at submonolayer coverage.

Cluster shape may also be made to switch from 2D to 3D structures by depositing at low temperature with subsequent annealing. Comparisons between LEIS and XPS data obtained during annealing the sample, from liquid nitrogen temperature up to 200ºC, show that the added kinetic energy promotes mobility of the silver atoms. Being more mobile these atoms will prefer the thermodynamically most stable arrangement which is a 3D structure.

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