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Growth Kinetics of Cu Clusters on a α -Al₂O₃ Surface Studied by SEXAFS

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Abstract

We show that SEXAFS can be used to determine the growth law of subnanometric particles. In the case of copper deposited on alumina, the dynamic scaling of the mean cluster size distribution, in the radius range 2-10 Å, is demonstrated. This scaling is explained by the coalescence of copper clusters, as in breath figures due to the condensation of liquid droplets. This growth law can be fitted by a power law with an exponent 1.2 and is fairly well reproduced by a purely stochastic coalescence model.

1. Introduction

Metal/oxide interactions play essential roles in many applications, such as thin film technology, semi-conductor devices, and heterogeneous catalysis. The copper/alumina interface is important in catalysis and microelectronics, and the growth of Cu on α -Al₂O₃ has received renewed attention in the last years [1]. A very weak chemical interaction between copper atoms and the alumina substrate has been evidenced. Very recently, Madey and co-workers [2] have studied the initial stages of Cu growth on ordered ultrathin Al₂O₃ films deposited at 80 K and 300 K. Their LEIS (low-energy ion scattering) results show unambiguously that Cu grows via the Volmer-Weber (VW) mode. In addition, their XPS and AES experiments clearly indicate that Cu is not oxidised at the interface. In our previous papers [3-5], we have evidenced a similar behaviour for the Cu/alumina interface by means of XAS, whatever the state of the monocrystalline alumina surface (oxygen-rich or reduced, reconstructed or not). Indeed, EXAFS is useful for studying specific properties of small metallic clusters, like the contraction of the nearest neighbour (NN) bond distances and the reduction of the NN coordination numbers [6-8]. This latter effect is caused by the increase of the fraction of atoms at the cluster surface when the cluster size decreases and it permits to estimate the mean Cu cluster size by comparing the coordination numbers obtained by EXAFS and those calculated for a given cluster size [4-7]. For doing that, we assume that the clusters had the fcc structure, which seems to be a very reasonable hypothesis in view of previous results [2-5].

As concerns the mechanisms of the VW growth, which is common to an important number of metal / oxide interfaces, an analogy with the formation of breath figures, as observed when water is condensed on glass, has been proved for Ag particles with mean radius between 20 and 200 Å deposited on SiO₂. Self-similar cluster distributions, due to coalescence phenomena, have been observed by electron microscopy [9]. But in the case of subnanometric particles (with radius R ranging from 2 to 10 Å), to our knowledge, no study of dynamical scaling for VW growth has been published. This is likely due to experimental difficulties in imaging in situ subnanometric clusters (R < 10 Å) deposited on insulating surfaces by the microscopy techniques widely used in most nucleation-growth studies.

In this paper, we show how EXAFS can be successfully used for following the kinetics of subnanometric Cu cluster growth on a monocrystalline α -Al₂O₃ surface. We find that the mean cluster size increases with deposition time, following a scaling law characteristic of a coalescence process, enhanced by the mobility of the small clusters. This result is discussed in the framework of a simple stochastic growth model, in which copper clusters coalesce upon contact like liquid droplets.

2. Experimental

The substrates were thin slabs of monocrystalline (0001) α -Al₂O₃ reconstructed $(\sqrt{3} \times \sqrt{3})R \pm 9^\circ$. This surface structure and its preparation mode are extensively described in refs. [10,11]. Referring to ideal layer by layer deposition, the deposited thicknesses measured with a quartz microbalance were 1.7, 2.3 and 4.0 Å, which are equivalent measurements of the deposition time. Taking into account the corrections due to the different balance-evaporator and sample-evaporator distances, and assuming a sticking coefficient equal to 1, they correspond to about 0.5, 0.6 and 1 equivalent monolayer (eq. ML) deposited on the sample. The Cu K edge SEXAFS measurements were carried out in ultra high vacuum (1 10⁻¹⁰ Torr) at room temperature, using the Si(311) double crystal monochromator of the wiggler DW21 beamline of the storage ring DCI at the LURE facility (Orsay, France). The Cu K edge SEXAFS spectra [8950-9650 eV] were recorded at normal incidence in the fluorescence mode.

3. Results

Data processing for extracting the EXAFS curve $\chi(k)$ from the raw data was done following standard procedures described elsewhere [12]. The Fourier transform amplitude of $[k\chi(k)]$, also called radial distribution function (RDF), were calculated between $2.55 \text{ \AA}^{-1}$ and $12.75 \text{ \AA}^{-1}$ using a Kaiser window. For studying the local structure of the Cu clusters, we have isolated the main peak of the RDF using a window between 1.47 and $3.0 \text{ \AA}$. Our fitting procedure is extensively detailed in ref. 4 and 5. For ensuring the correctness of our results, the obtained Fourier backtransformed spectra have been fitted following two independent procedures: we have used the amplitude and the phase shifts computed by Mc Kale *et al.* and also we have used those extracted from a reference copper sample. We have obtained high quality fits for similar structural parameters from both procedures. The results are summarised in table 1. For the thinner deposit, we needed to add 6 Cu-Al bonds in average at $3.24 \text{ \AA}$ to the expected Cu-Cu ones for obtaining a good fit of our EXAFS signal [5]. These Cu-Al bonds may be interpreted as bonds between the Cu clusters and the reconstructed alumina surface, which is oxygen depleted and terminated by two aluminium planes [10,11]. In addition, incorporation of some copper atoms can also take place in vacancies or substitution sites of the $(\sqrt{31} \times \sqrt{31})R \pm 9^\circ$ reconstruction.

Deposited thickness	bond type	d (Å) ($\pm 0.02 \text{ \AA}$)	N ($\pm 10\%$)	$\Delta\sigma^2(\text{\AA}^2)$ ($\pm 0.5 \times 10^{-3}$)
1.7 Å	Cu-Cu	2.42	4.7	0.012
	Cu-Al	3.24	5.7	0.012
2.3 Å	Cu-Cu	2.52	7	0.010
4 Å	Cu-Cu	2.52	9	0.010

Table 1 : Structural parameters of the Cu NN shell giving the best least-squares fits corresponding to the three deposits 0.5, 0.6 and 1 eq. ML. d represents the mean distance, N the average number of atoms and $\Delta\sigma^2$ the mean square relative displacement of each shell. The error bars in the determination of each parameter are also given.

Figure 1 : Evolution of the cluster radius as a function of deposition time (measured as the equivalent deposited thickness). The error bars are also given.

In order to deduce from the experimental Cu NN numbers a mean cluster size, the mean coordination number was calculated as a function of cluster radius, assuming that the Cu clusters had the same fcc structure as bulk Cu [4]. The mean cluster radius R obtained for the three deposits 0.5, 0.6 and 1 eq. ML are respectively 2.5, 4 and $7 \text{ \AA}$. The mean cluster densities N , derived by the mass conservation law, assuming a monomodal distribution of clusters are respectively 12 , 4 and $1.3 \times 10^{13} \text{ clusters/cm}^2$. Note that in the case of the thinner deposit, the cluster density may be overestimated due to the fact that some copper atoms are incorporated to the alumina surface.

4. Discussion

The increase of the mean cluster radius, and the related decrease of the cluster density with deposition time, strongly suggest a coalescence mechanism, where adjacent clusters coalesce upon contact, as do liquid droplets in breath figures. In the condensation of droplets, different stages of growth have been identified. First, the droplets grow individually, without interaction between them. When the surface coverage typically exceeds 30%, the droplets interact by coalescence [9]. The evolution of the radius with deposition time can be fitted by a power law t^α with an exponent $\alpha \approx 1.2$ (figure 1). In the coalescence of droplets, the evolution of radius with deposition time t is a power law t^x ($x=1/3$ or $1/4$) in the stage where droplets grow individually, and t^x in the coalescence stage [9]. From our results, a power law with an exponent smaller than 1, corresponding to individual growth, can be completely discarded. We find an exponent characteristic of the coalescence regime, slightly larger than 1. This could be due to the mobility of the copper clusters on the alumina surface, favoured by the weak interaction of the clusters with the substrate. As theoretically predicted by Jensen *et al* [13], the diffusion of the clusters on the surface may lead to an enhancement of the cluster size growth with deposition time.

In order to simulate this evolution of the cluster distribution with deposition time, we have built a simple stochastic coalescence model, assuming an heterogeneous nucleation where clusters form and grow at certain nucleation centers which are initially chosen at random. First, we consider a two-dimensional random monomodal cluster distribution at the surface with mean radius R , and density N . In a first approximation, we assume a spherical cluster shape, in view of the 130° wetting angle of copper on alumina [14]. We associate to each cluster an interaction area (πR_c^2) defined as follows : if the interaction area of a given cluster intersects the interaction areas of $(i-1)$ other clusters, then the i clusters coalesce in a resulting spherical cluster ('multiple cluster' of multiplicity i) with a radius given by mass conservation. As the deposition time increases, the clusters grow, leading to an increase of their interaction radius R_c . When twice the interaction radius becomes of the same order than the mean distance between clusters, coalescence may occur, and a new cluster distribution is obtained. Both its density N' and mean cluster multiplicity $\langle i \rangle$ depend on the value of the interaction radius R_c , itself depending on the

deposition time. In order to calculate N' and $\langle i \rangle$, we use a Poisson law. For a given cluster, the probability P_i that there is no overlap of its interaction area with that of any other cluster is $P_i = \exp(-N \cdot 4\pi R_c^2)$, and the number of 'single clusters' writes : $N_1 = NP_1$. The probability P_i that there is overlap with exactly $(i-1)$ other interaction areas, and the number of 'multiple clusters' of multiplicity i write:

$$P_i = \frac{(N \cdot 4\pi R_c^2)^{i-1}}{(i-1)!} \exp(-N \cdot 4\pi R_c^2) ; N_i = \frac{N}{i} P_i$$

The cluster density N' is equal to $\sum_i N_i$, and the mean cluster multiplicity is $\langle i \rangle = (\sum_i i N_i) / (\sum_i N_i)$.

This purely statistical model fairly well accounts for the experimentally observed growth kinetics. Indeed, considering the experimental density N of 0.5 eq. ML, the density N' of 0.6 eq. ML can be obtained with a R_c parameter of 4 Å (figure 2a). In the same way, the density N' of the 1 eq. ML can be deduced from the experimental density N of the 0.6 eq. ML with a R_c parameter of 7.5 Å (figure 2b). In both cases, the calculated mean multiplicity is the same : $\langle i \rangle = 3$, which is exactly what is observed from the experimental N'/N ratios. From the mean radius of the 0.6 and 1 eq. ML deposit, this would give a mean radius of the individual clusters before coalescence of about 3 Å and 5 Å respectively. These values are equal to the radius expected from a $t^{1/3}$ individual growth of the clusters of 0.5 eq. ML and 0.6 eq. ML respectively. The agreement of this stochastic model with the experimental results would indicate that the growth and coalescence of the small clusters formed onto the alumina surface in the submonolayer range proceeds in a purely random manner, with no preferential growth directions like step edges or extended defects. This is the reason why the observed evolution of the cluster distribution appears to follow the universal laws of formation of breath figures. It seems that slight deviations of the ideal spherical shape does not alters the mechanism of coalescence [9]. The fact that the obtained values of R_c are larger than the radius of the clusters before coalescence points out that the mobility of the small clusters plays an important role in the growth process. Density functional calculations about the mobility and adhesion of small clusters are in progress.

Figure 2 : Calculated cluster density N' , obtained from an initial density N , as a function of the interaction radius R_c (Å), in the case of (a) the 0.5 ML deposit ($N = 1.2 \times 10^{14}$ clusters/cm²), and (b) the 0.6 ML deposit ($N = 4 \times 10^{13}$ clusters/cm²).

5. Conclusion

To our knowledge, this is the first time that submonolayer scaling due to the coalescence of subnanometric metallic clusters ($R < 10$ Å) supported on an oxide surface is evidenced. We show that SEXAFS spectroscopy can be successfully used as an alternative method to electron microscopy for measuring the size of subnanometric particles, which permits to lower in an order of magnitude the size of the studied clusters.

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References

- [1] V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, Cambridge, 1994) ch. 7.
- [2] Y. Wu, E. Garfunkel and T. E. Madey, *J. Vac. Sci. Technol. A* **14**(3) (1996), 1662.
- [3] M. Gautier, J. P. Duraud and L. Pham Van, *Surf. Sci.* **249**, L327 (1991); *Europhys. Lett* **18**, 175 (1992).
- [4] S. Gota *et al.*, *Surf. Sci.* **323**, 163 (1995).
- [5] S. Gota *et al.*, *Surf. Sci.* **352-4**, 1016 (1996).
- [6] G. Apai *et al.*, *Phys. Rev. Lett.* **43**, 165 (1979).
- [7] P. A. Montano *et al.*, *Phys. Rev. Lett.* **56**, 2076 (1986).
- [8] A. Pinto *et al.*, *Phys. Rev. B* **51**, 5315 (1995).
- [9] D. Beysens, C. M. Knobler, H. Schaffar, *Phys. Rev. B* **41**, 9814 (1990).
- [10] M. Gautier *et al.*, *J. Am. Ceram. Soc.* **77**, 323 (1994).
- [11] G. Renaud *et al.*, *Phys. Rev. Lett* **73**, 1825 (1994).
- [12] B. K. Teo, in *"EXAFS: Basic principles and data analysis"* (Springer-Verlag, Berlin, 1984).
- [13] P. Jensen *et al.*, *Phys. Rev. B* **50**, 15316 (1994).
- [14] D. Chatain, I. Rivollet, N. Eustathopoulos, *Journ. Chim. Phys.* **83**, 561 (1986).