FORMATION OF CATALYST MODEL DISPERSED FOR THE SYSTEM Pd/MgO(100)

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Abstract

We performed calculations and recounts of various parameters related to the first quantitative study on the nucleation and growth of a catalyst model dispersed Pd/thin MgO(100) which was deposited at substrate temperatures ranging from 573 K - 1073 K. This simulation was performed by developing a new programs using Fortran. The nucleation kinetics are interpreted according to the theory of random nucleation. It follows that the general scheme is consisting of three stages: nucleation, growth and coalescence. It is shown that the saturation density of clusters decreases when the substrate temperature increases in following Arrhenius law. This behavior is in agreement with a recent AFM study for Ag/MgO and Au/MgO. The phenomena of coalescence can be explained by the process of island migration. The coalescence occurs at high substrate temperature more rapidly than at lower substrate temperature.

Keywords: Model catalyst, palladium, nucleation, growth, coalescence

1.   INTRODUCTION

Nowadays nano-objects provide a promising research path for implementing identification of new fundamental properties of the material, for their potential technological applications. Much effort is devoted to understanding of the physical and chemical properties of material which can serve as model catalyst systems. Consequently, fundamental studies have been carried out on a range of heterogeneous catalyst, e.g., thin metal films [1-3] and well-defined metal islands [4-9] grown on single-crystal or over thin film substrates. Perhaps, palladium deposits on the MgO(100) surface have become one of the most widely used model systems, and have given rise to many detailed experimental studies [10]. Although the main microscopic steps governing nucleation and growth of the films are now understood, detailed characterization of these processes has proven difficult. Earlier, more recent empirical and theoretical studies of Pd over single crystal MgO(100), investigated defect nucleation [11, 12] when only a minority of sites are nucleation centres. On the other hand, the results of nucleation kinetics over the thin layer governed by random nucleation (each atomic site is potentially a nucleation centre). Here we build upon the many experimental and theoretical studies [13-15] that have been dedicated to understanding these processes. The aim of this work is to connect the microscopic mechanisms, which can calculate various parameters related to the quantitative study on the nucleation, growth and coalescence of Pd/thin MgO(100) with using Fortran.

2.   THEORY

2.1   Transmission electron microscopy experiments

In the goal of the understanding the first quantitative study of nucleation and growth of Pd on thin layers of MgO(100) was made in the experimental work of C. Henry et al., who used transmission electron microscopy and electron diffraction at high energy to measure the Pd island density as a function of time at given temperature and a constant flux. The experiments start with the preparation of the composite layer of MgO(100)/LiF(100)/NaCl(100) which serves as support then. Immediately it is condensed with a palladium flux

$1 \cdot 10^{13}$ atoms cm^{-2}·s^{-1}, with exposure time of 10 to 240 s at substrate temperatures between 573 and 673 K. After deposition, the Pd islands are viewed with in situ transmission electron microscopy (TEM) to determine the island density. The results are interpreted according to the theory of random nucleation. From this theory, the experimenters get the energy of adsorption and diffusion of palladium on MgO(100). In this study, we were able to vary the average size D of particles 0.8 - 3.5 nm, the density n of 0.6 to $3 \cdot 10^{12}$ cm^{-2} and the covered area A of the substrate surface of 0.4 to 15 percent.

2.2   Overview of nucleation and growth theories

Nucleation on a surface has been discussed in both classical thermodynamic and in atomistic terms, and both have a long history. Classical nucleation theory was developed by Volmer [16]. From this theory, the critical nucleus is only one atom, which means that the dimer is already stable. In that case, the classical nucleation theory is no longer applicable. The growth process occurs by accretion of adatoms. It is described by the atomistic nucleation theory which has been developed by Zinsmeister [17]. In this case, the critical nucleus composites of two atoms and the supercritical nuclei do not dissociate. The probability of adsorption is equal to one and that only single atom can return in the phase steam. The frequency of nucleation is then determined by the frequency of meeting of adsorbed atoms.
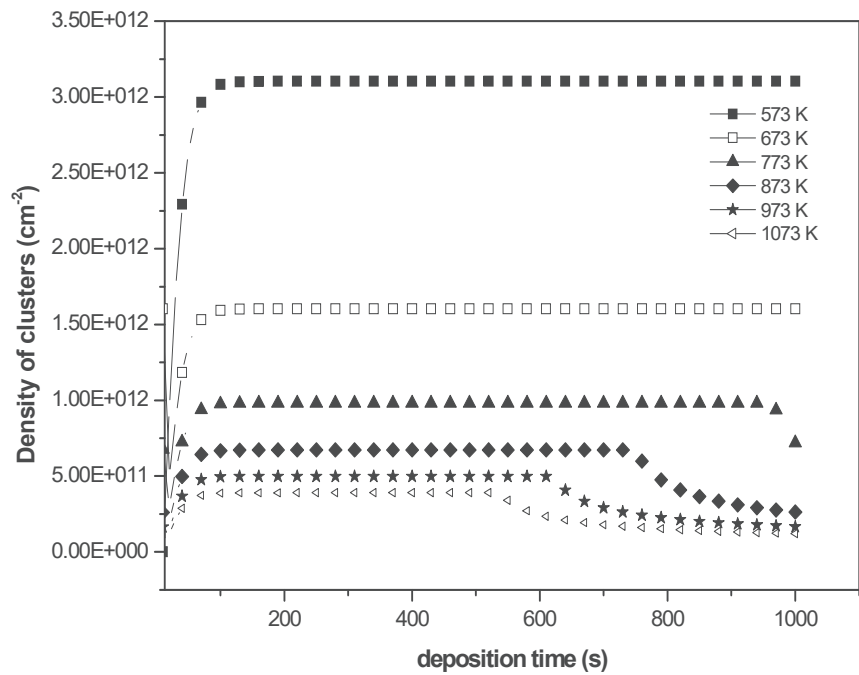

Fig. 1 Variation of cluster density as a function of exposure time for different substrates temperatures and a constant flux 1x10^{13} atoms cm^{-2}·s^{-1}

2.2.1 Nucleation kinetics

The rate equations given by Zinsmeister express the variation with time of the number of clusters of size i:

$$dn_i/dt = \omega_{i-1}\, n_{i-1} - \omega_i\, n_i \quad \text{for } i = 2,3 \ldots \infty \tag{1}$$

ω_i is the attachment frequency of an adatom to a cluster containing i atoms which is expressed by:

$$\omega_i = \sigma_i\, D\, n_i \tag{2}$$

Where σ_i is the capture number for a cluster of size i. We are obliged to integrate the system of differential equations in order to calculate the number of nuclei present on the substrate. Forsake of simplicity Zinsmeister assumes that it is a constant between 1 and 4. From this scheme the nucleation frequency is:

$$J = 2\,\omega_1\, n_1 \tag{3}$$

Supposing that the growth is negligible, the density of adatoms is equal to the stationary value:

$$n_1 = F\,\tau \tag{4}$$

where F is the flux of atoms impinging on the substrate and τ the life time of an adatom before desorption. Then combining Eqs. (2) and (4) the nucleation rate becomes:

$$J = 2\,\sigma_1\,D\,F^2\,\tau^2 \tag{5}$$

The nucleation rate is proportional to the square of the impinging flux for a homogeneous substrate without defects.

2.2.2 Growth Kinetics

Zinsmeister solved the system of differential equation assuming a constant value for the attachment frequency (w_i) [18]. However by this treatment several characteristics of the growth of clusters are not taken into explanation. Several researches have tried to treat more precisely the calculation of the attachment frequencies [19-24]. In the typical growth, the diffusion of adatoms is limited by desorption and the diffusion length X_s of an adatom is:

$$X_s=(D_s\,\tau)^{1/2}\,, \tag{6}$$

where D_s is the surface diffusion coefficient which is expressed by:

$$D_s = (a_0^2\,\nu_d)\,\exp\,(-E_d\,/k\,T_s\,) \tag{7}$$

Then the mean life time τ of a physisorbed molecule as explain by:

$$\tau = (1/\,\nu_a)\,\exp(\,E_a\,/k\,T_s\,) \tag{8}$$

where E_a and E_d is the adsorption and the diffusion energy, and a_0 the jump distance, of the order of the surface repeat distance, say 0.2-0.5 nm, ν_d and ν_a the frequency factors for the diffusion and the adsorption process, k the Boltzmann constant and T_s the substrate temperature.

In a general case, the growth rate of a cluster can be expressed by a power law of the deposition time.

$$R = R_0\,t^p \tag{9}$$

The exponent for any experimental has been calculated in the case of the lattice approximation for 3D clusters.
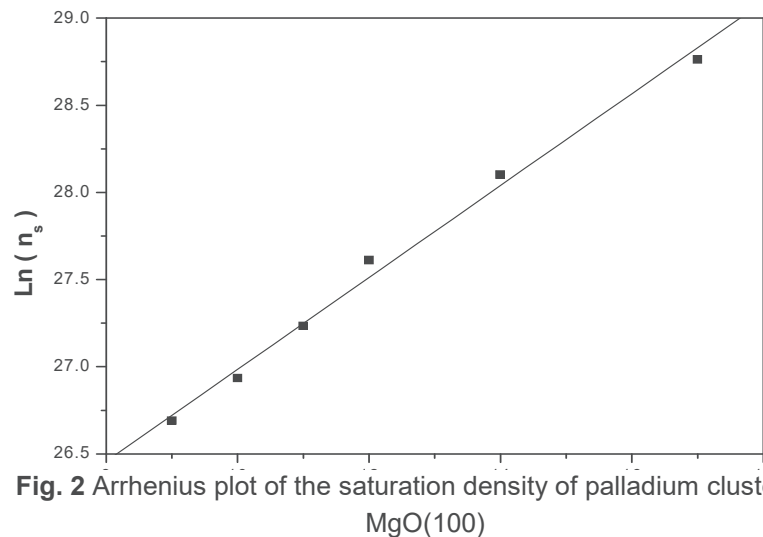

Fig. 2 Arrhenius plot of the saturation density of palladium clusters on MgO(100)

2.2.3 Coalescence

The transformation of two touching nuclei into one nucleus can be described by a time constant shown by Nichols and Mullins [25]:

$$\tau_c = 0.2\,(R^4\,/\,B)\ \text{with}\ B = \gamma\,\Omega^{4/3}\,D_s/k\,T_s \tag{10}$$

where R is the radius of the coalescing spheres, γ the surface free energy, and Ω the atomic volume of Pd.

2.2.4 Algorithm

We have been developed many programs using "Fortran". The following list details of given in this simulation:
1.   Pd deposition over the thin MgO(100) is at a rate flux $1.13\cdot10^{13}$ atoms $cm^{-2}\cdot s^{-1}$.

2.   Pd atoms are deposited randomly onto the surface with an activation energy about 0.22 eV.
3.   The substrate temperatures are tested over a 573 - 1073 K temperature range and exposure time of 1000 s.
4.   Pd islands are estimated in the case of the lattice for 3D clusters.
5.   The parameters to entry are: the velocity of nucleation, velocity of growth, the average mean life time, the surface repeat distance, the diffusion length, the surface free energy, the atomic volume of Pd, the activation and the diffusion energies.

3.   RESULTS

Fig. 1 shows the variation of cluster density as a function of exposure time at different substrate temperatures in the range of 573 - 1073 K with step of 100 K and a constant palladium flux $1 \cdot 10^{13}$ atoms cm$^{-2} \cdot$s^{-1}.

For T_s = 573 K and 673 K, we see that the density n of germs growing rapidly after 10 to 70 s (nucleation stage), up to a plateau (saturation density) corresponding to n_s = $3 \cdot 10^{12}$ cm^{-2}, $1.6 \cdot 10^{12}$ cm^{-2}

Fig. 3 Variations of the covered area as a function of temperature with deposition time 1000 s

respectively. Similar behavior for remaining substrate temperatures unto the coalescence occur, it decreases rapidly by an order of ten. It is important to note that the cluster density decreases when the temperature increases.

In **Fig. 2**, the saturation density is plotted in an Arrhenius diagram. It represented by the equation**:** n_s = B$_0$ · exp(E/k T$_s$). When the activation energy E is equal to 0.22 ± 0.05 eV and B$_0$ is pre-exponential term equal $3.63.10^{10}$ cm^{-2}. We show that it increases when the substrate temperature decreases. This behavior is in agreement with a recent AFM study for Ag/MgO [26], Au/MgO(100) [27] and our previous studies by TEM [13] on the same system.

Figs. 3 and **4** show the variations of the covered area (A) and the coalescence parameter (B) as a function of temperature, obtained under the same conditions. We see that the fraction of covered area decreases when deposition temperature rises, opposite behavior is observed as depicted in the coalescence parameter.

4.   DISCUSSION

The work reported here was initiated on the basis of some interesting observations made during studies on the formation of Pd over thin film MgO. From our recent experiential result in this system, the curves of the initial nucleation rate indicated a random nucleation mechanism. The theory of this nucleation process is represented by the kinetic equations of Zinsmeister [17]. Robinson and Robins [14] have given analytical solutions in two limit cases, low and high temperatures. In this letter, we focus the light at high substrate temperatures (regime of incomplete condensation), where the particle number density is expressed by:

n = n$_s$. tanh (t/τ)   (11)

The calculated curves in the first stage with the random nucleation model have given a good agreement with the experimentally measured time dependencies of island density (nucleation regime **Fig. 1**) [13], then the curves have shown the plateau such as the maximum particle density that is reached at the end of the
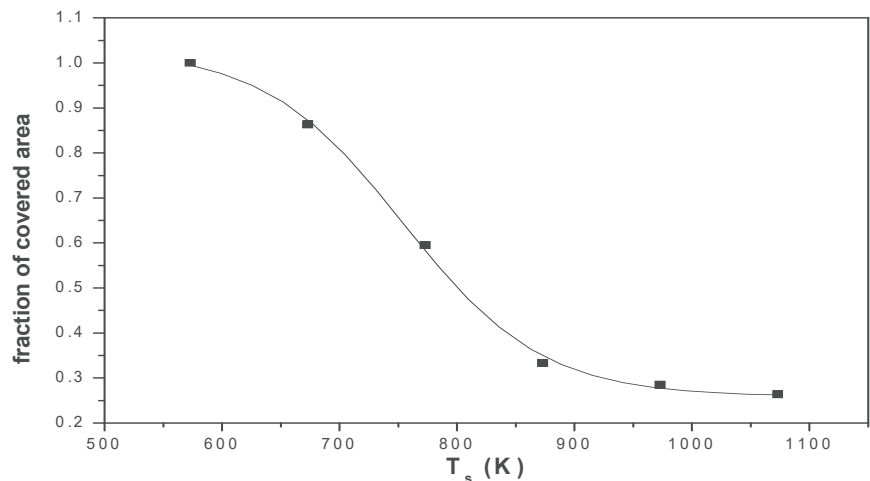
nucleation regime which characterize the Volmer-Weber growth. The value of saturation of island density is one of the important parameters determining the mode of thin film growth which may have a perceptible influence on the physicochemical properties of the thin films obtained [28]. The linear behavior of the Arrhenius plot observed for the temperature dependence of the saturation density of clusters has been also found in the case of Ag on Ar-cleaved MgO(100) [26], Au on MgO(100) [27] and Pd on UHV-cleaved MgO(100) [29, 30] .

In the stage of coalescence, the density decrease can be fitted by a simple power law:

$$n = n_s \ (1 + t/\tau)^{-3/m} \qquad \text{with } m = 7 \tag{12}$$

The coalescence curves were better fitted by the Cluster diffusion model [15] than with the Ostwald ripening model.

We now return to consider each parameter used in the simulation in order to discuss the availability of a quantitative analysis. The most crucial parameter in our results is the coalescence time. It is defined as the mean time for two clusters that come into contact to coalesce. From equation (10) we observe two parameters (R and B) that are important to determine the duration of the coalescence stage. One can also observe the influence of the deposition temperature which modifies the coalescence time of clusters. At high temperature, clusters coalesce more rapidly [31]. This phenomena can be explained by the process of island migration.
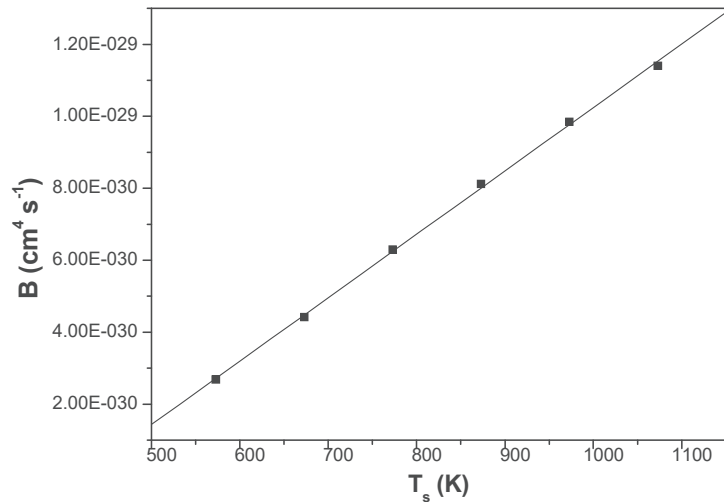
The process of island migration in the

Fig. 4 Variation of the coalescence parameter B as a function of temperature with deposition time 1000 s

presented calculation is described by the parameter B. For explanation of results (see **Fig. 4**) it needs to take into account that values of B are not high enough means that the process of island density coalescence cannot be ignored even at the initial stages of deposition [32]. The mechanism of coalescence which can be expected at such a low value of surface coverage is the migration of islands on the surface, prior to the mechanism of immobile islands in which the coalescence occurs at high values of surface coverage when the islands touch each other [33].

The surface coverage does not depend on parameters B, but it strongly depends on the number of cluster density and the shape of the particles. The fraction of the substrate covered by the clusters, which is considered as the contact surface of the half sphere is a circle can be written as:

$$A = n \ \pi \ D^2 \ / \ 4 \tag{13}$$

In this range of temperature the diameter D of the clusters follows a power law: $D_o \ t^p$ with $0.33 < P < 0.55$. At 673 K, our recent experimental work obtained $D_o = 3.72$ and $p = 0.4$ with diffusion length $X_s = 1.6$ nm. In this simulation, we used the mean value of the range ($p = 0.45$) and we determined the value of D_s by combination of equations (6) and (7). As indicated in the last section the cluster density decreased when the substrate temperature increased due to the increased ad-atom mobility [34] and we assumed that D relatively constant in this range of temperature with lower error 10 % as a result the fraction of the substrate covered by the particles decreases and more decreases when the coalescence occurs.

CONCLUSION

In the present study, we have simulated the microscopic mechanisms, which can calculate various parameters related to quantitative study on the formation of Pd/thin MgO(100) with using Fortran. The formation kinetics follows the general scheme consisting of three stages: nucleation, growth and coalescence. The saturation density observed an Arrhenius law with an activation energy of 0.22 eV. The phenomena, that island density with time reaches saturation or immediately decreases after maximum value, are explained by the processes of migration of islands. The coalescence time and the fraction of the substrate covered by the clusters are decreased when the temperature increased and the clusters coalesce more rapidly.

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