Nucleation and growth kinetics of palladium nanoparticles on thin films of MgO (100)

Cinétique de nucléation et de croissance de nanoparticules de palladium sur des couches minces de MgO (100)

Fatma Baara[1] & Abdelbaki Chemam[2*]

[1]Laboratory of surfaces and interfaces of solids studies - (LESIMS) –Department of Physics, Faculty of Sciences-Badji Mokhtar University-Annaba-Algeria.
[2]Preparatory School for Science and Technology of Annaba, Annaba 23000, Algeria.

Soumis le 05/04/2016 *Révisé le 27/01/2017* *Accepté le 21/02/2017*

ملخص:

محاكاة حركية التنوي و النمو عن (100) Pd/MgO من خلال تطوير العديد من البرامج باستخدام برنامج فورتران . ويستند هذا الحساب على المعايير درست بالميكروسكوب الالكتروني(MET) ، تتعلق بالدراسة الكمية الأولى لتنوي ونمو الجزيئات النانوية (100) Pd / MgO. اختبرت الجزيئات النانوية البلاديوم إيداعها في نطاق درجة حرارة K 1073-573 وترسب الوقت s 1000. يتم تفسير حركية التنوي وفقا لنظرية التنوي العشوائي. يشير المخطط العام إلي ثلاث مراحل وهي التنوي والنمو والتحام. كثافة تشبع مجموعات تنخفض عند ارتفاع درجة الحرارة وفقا لقانون أرينيوس. يعتبر هذا السلوك في اتفاق مع دراسة AFM في Au/MgO و Ag/MgO. يفسر ظاهرة التحام عبر عملية الهجرة. وتبين أن التحام يحدث بسرعة أكبر عند درجة حرارة عالية.

الكلمات المفتاحية :التنوي- النمو- محاكاة – بلا د يوم المانيزوم اكسيد - (100).MgO .

Résumé :
La cinétique de nucléation et de croissance de nanoparticules de Pd sur des couches minces de MgO (100) sont simulées en développant de nombreux programmes utilisant le logiciel Fortran. Ce calcul est basé sur les paramètres étudiés in situ par microscopie électronique à transmission (MET), liée à la première étude quantitative sur la nucléation et la croissance de Pd / MgO (100). Les nanoparticules de palladium déposées sont testées dans la gamme de température 573-1073 K et le dépôt du temps de 1000 s. La cinétique de nucléation est interprétée en fonction de la théorie de la nucléation aléatoire. Le régime général est constitué de trois étapes à savoir, nucléation, croissance et coalescence. La densité de saturation des pôles diminue lorsque la température du substrat augmente d'après la loi d'Arrhenius. Ce comportement est en accord avec une étude récente par AFM pour Ag / MgO et Au / MgO. Le phénomène de coalescence est expliqué par le processus de migration d'ilots. Il est montré que la coalescence se produit plus rapidement lorsque la température du substrat est élevée.

Mots-clés: Nucléation, Croissance, Simulation, Palladium, MgO (100).

Abstract:
The Nucleation and growth kinetics of Pd nanoparticles on thin films of MgO (100) are simulated by developing numerous programs using Fortran software. This calculation is based upon parameters studied in situ by transmission electron microscopy (TEM), related to the first quantitative study on the nucleation and the growth of Pd/ MgO(100). The deposited Palladium nanoparticles are tested in the temperature range 573–1073 K and deposition time of 1000 s. The nucleation kinetics is interpreted according to the theory of random nucleation. The general scheme is consisting of three stages namely, nucleation, growth and coalescence. The saturation density of clusters decreases when the substrate temperature increases following Arrhenius law. This behavior is in agreement with a recent AFM study for Ag/MgO and Au/MgO. The phenomenon of coalescence is explained via island migration process. It is shown that the coalescence occurs more rapidly when the substrate temperature is high.

Keywords: Nucleation, Growth, Simulation, Palladium, MgO (100).

[*] Corresponding author : a.chemam@epst-annaba.dz

I. INTRODUCTION

Nowadays, nano-objects provide a promising research for the identification of new fundamental properties of the materials and their potential technological applications. Much effort is devoted to understand the physical and chemical properties of materials, which can serve as model catalyst systems. Consequently, fundamental studies have been carried out on a range of heterogeneous catalyst, for example, metal islands grown on thin films [1-4] or on single-crystals surfaces [5, 6]. Palladiums 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 [7-9]. Although the main microscopic steps governing nucleation and growth of the films are now understood, detailed characterization of these processes has proven difficult. Earlier, empirical and theoretical studies of Pd over single crystals MgO, investigated defect nucleation [10, 11] when nucleation centers occupy minority of sites. On the other hand, the results of nucleation kinetics over thin films governed by random nucleation [1, 12], each atomic site is potentially a nucleation centre. In this study, we build upon many experimental and theoretical studies [1, 13] have been carried out to understand these processes. The aim of this work is to investigate the microscopic mechanisms focusing on the nucleation, growth and coalescence of Pd / thin MgO (100) using Fortran software.

2. THEORY AND CALCULATION

2.1. Overview of nucleation and growth theories

In the goal of the understanding the nucleation processes on surface, two theories have been developed in two terms classical thermodynamics and atomistic. The classical theory has been developed by Volmer and Weber [29]. The critical nucleus is assumed only one atom, meaning that the dimmer is already stable. In this reason, the classical nucleation theory is unavailable. The growth process occurs by accretion of adatoms. It is described by the atomistic nucleation theory which has been developed by Zinsmeister [15]. The rate equations given by Zinsmeister expressed by:

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

Where n_i is the number of clusters of size i and ω_i is the attachment frequency of an adatom to a cluster containing i atoms which is expressed by:

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

σ_i is the capture number for a cluster of size i and D is the diffusion coefficient .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 mean life time of an adatom before desorption. Then, combining equations (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. Zinsmeister has solved the system of differential equation assuming a constant value for the attachment frequency ω_i [28]. 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 [16–18]. In the typical growth, the diffusion of adatoms is limited by desorption and the diffusion length X_s of an adatom is:

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

Where D_s is the surface diffusion coefficient. It is expressed by:

$$D_s = (a_0^2\, \nu_d)\ exp\left(-\frac{E_d}{KT_s}\right) \tag{7}$$

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

$$\tau = (1/\nu_a)\ exp\left(\frac{E_a}{KT_s}\right) \tag{8}$$

where E_a and E_d is the adsorption and the diffusion energy, and a_0 the jump distance , 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. The transformation of two touching nuclei into one nucleus can be described by a time constant shown by Nichols and Mullins [19]:

$$\tau_c = 0.2\left(\frac{R^4}{B}\right) \qquad \text{with } B = \frac{\gamma\ \Omega^{4/3} D_s}{K\, T_s} \tag{9}$$

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

2.2. Algorithm

To understand the first quantitative study of nucleation and growth of Pd on thin layer of MgO(100), we exploited the experimental work of C.R. Henry and al [1], who used transmission electron microscopy and electron diffraction at high energy to measure the Pd island density as a function of time a given temperature and a constant flux . Firstly, the MgO (100) / LiF (100) / NaCl (100) composite layer is achieved which serves as support. Palladium is then deposited with a flux of $1x1O^{13}$ atoms cm^{-2}. s^{-1} and exposure time of 10 to 240 s on a substrate heated at temperatures between 573 and 673 K. After deposition, the Pd islands are in situ characterized with a transmission electron microscopy (TEM) to determine the island density. The results are interpreted according to the theory of random nucleation. The energy of adsorption and diffusion of palladium on MgO (100) are derived from the latter theory. It was possible to vary the average size of particles in the range 0. 8 - 3.5 nm.

3. RESULTS

Our theoretical results are based by developing numerous programs exploiting Fortran software. The following list details this mapping.

1. Pd deposition flux rate on MgO (100) is $1.13x1O^{13}$ atoms cm^{-2}. s^{-1}.
2. Pd atoms are deposited randomly onto the surface with activation energy of about 0.22 eV.
3. Pd nanoparticles deposited on thin MgO are tested in the temperature range 573 - 1073 K and deposition time of 1000 s, table 1.
4. Pd islands are approximated to be three-dimensional clusters.
5. The diffusion of adatoms is limited by desorption. Hence, the values of the surface diffusion are calculated by combination of Eqs (6) and (7).
6. The entry parameters are: the velocity of nucleation, velocity of growth, the average means life time, the surface repeat distance, the diffusion length, the surface free energy, the atomic volume of Pd, the activation and the diffusion energies.

Table 1. Calculated of the cluster density (cm^{-2}) at different substrate temperatures (K) and deposition times (s).

Ts (K)	10 (s)	70 (s)	τ_c (s)	1000 (s)
573	9.39305E11	3.02867E12	No coalescence	3.10299E12
673	4.85012E11	1.56386E12	No coalescence	1.60223E12
773	2.97145E11	9.58107E11	9.80843E11	6.77174E11
873	2.03673E11	6.56717E11	6.71283E11	2.59969E11
973	1.50874E11	4.86474E11	4.98060E11	1.64566E11
1073	1.18191E11	3.81093E11	3.90260E11	1.19319E11

Figure 1 shows the variation of cluster density as a function of exposure time at different substrate temperatures ranging from 573 K to 1073 K and a constant palladium flux $1x10^{13}$ atoms cm^{-2}. s^{-1}. For Ts = 573 K and 673 K, we can see that the density of clusters is increasing rapidly after 10 to 70 s (see table 1) due to the large adsorption energy for the Pd adatom confirming the nucleation stage, up to a plateau (saturation density) corresponding to $n_s = 3.10^{12}$ cm^{-2} and $1.6x10^{12}$ cm^{-2} respectively.
A similar behavior is observed for the remaining substrate temperatures till the coalescence occurrence, were the cluster density decreases. It is worth to note that the cluster density decreases when the temperature increases.

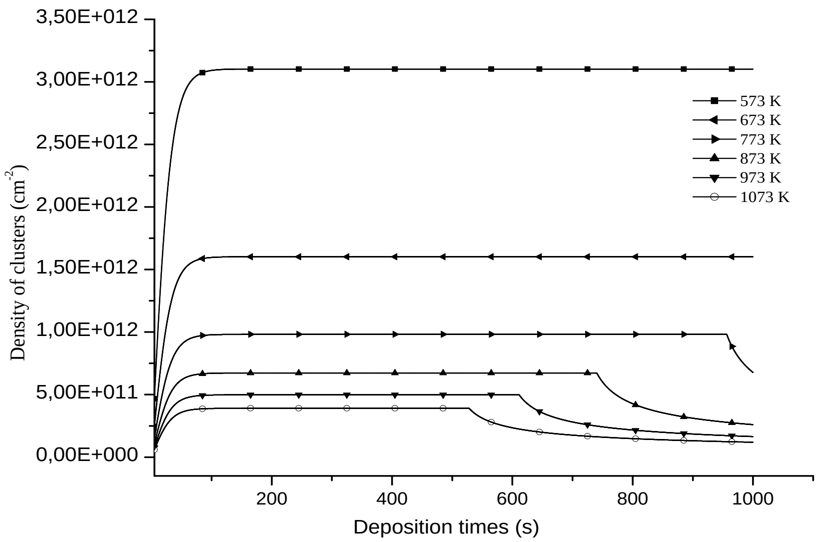

Figure .1 Nucleation kinetics of Pd on MgO (100) for a Pd flux $1x1O^{13}$ atoms cm^{-2}. s^{-1}.

In Figure 2, the saturation density is plotted in an Arrhenius diagram. It is represented by the equation**:**

$$n_s = B_0 . \exp^{E/KT_s} \qquad (10)$$

When the activation energy E is equal to 0.22 ± 0.05 eV, B_0 (preexponential factor) is $3.63x10^{10}$ cm^{-2}. We show that n_s increases when the substrate temperature decreases. This behavior is in agreement with a recent AFM study for Ag/MgO [20], Au/MgO (100) [21] and our previous studies by TEM [1] on the same system.

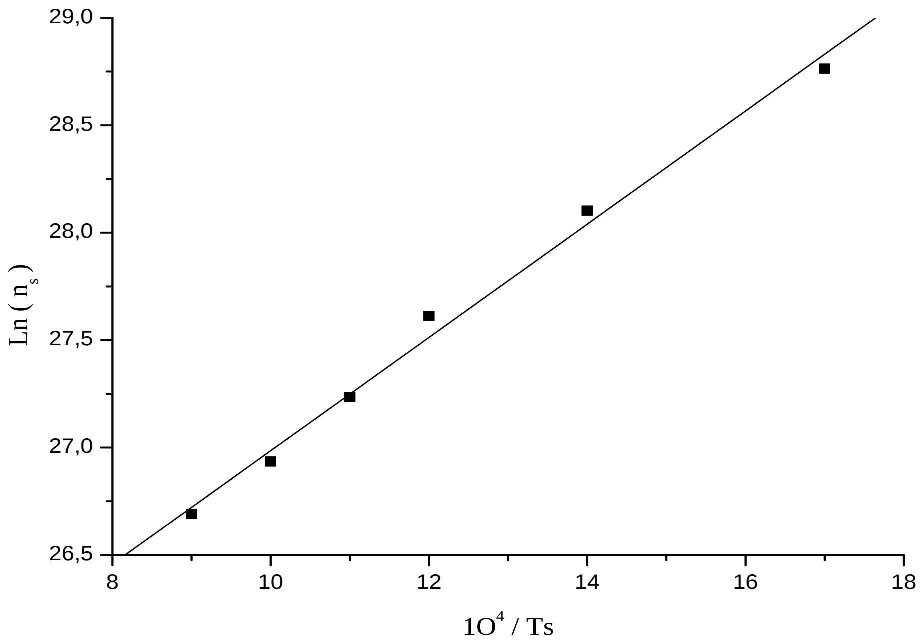

Figure. 2 Arrhenius plot of the saturation density of palladium clusters on MgO (100).

Figures 3 and 4 show the variations of the covered area (A) and the coalescence parameter (B) as a function of substrate temperatures obtained under the same conditions. We see that the fraction of covered area decreases when deposition temperature increases. An opposite behavior is observed for the coalescence parameter.

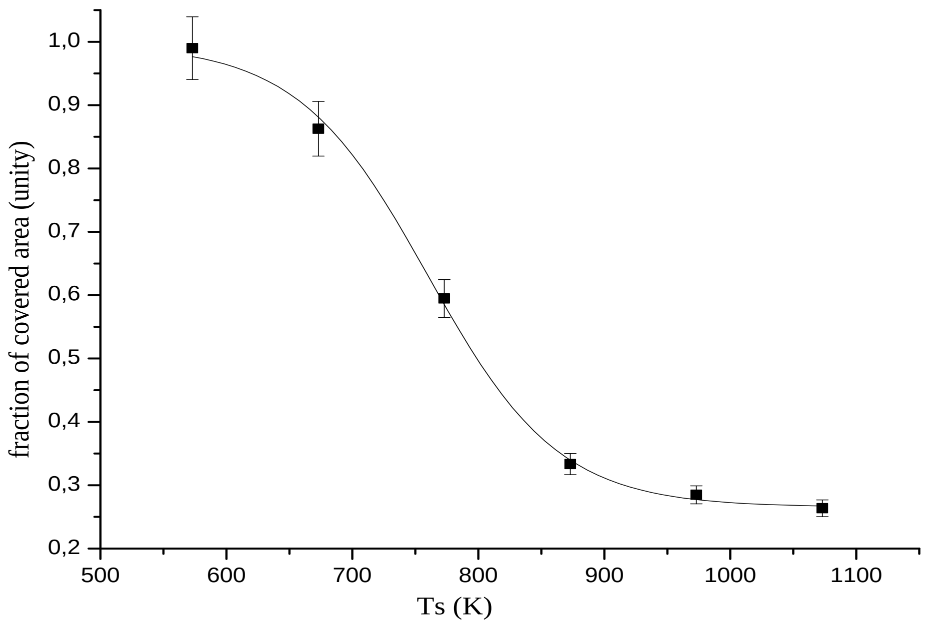

Figure 3: The temperature dependence of the fraction of the covered surface.

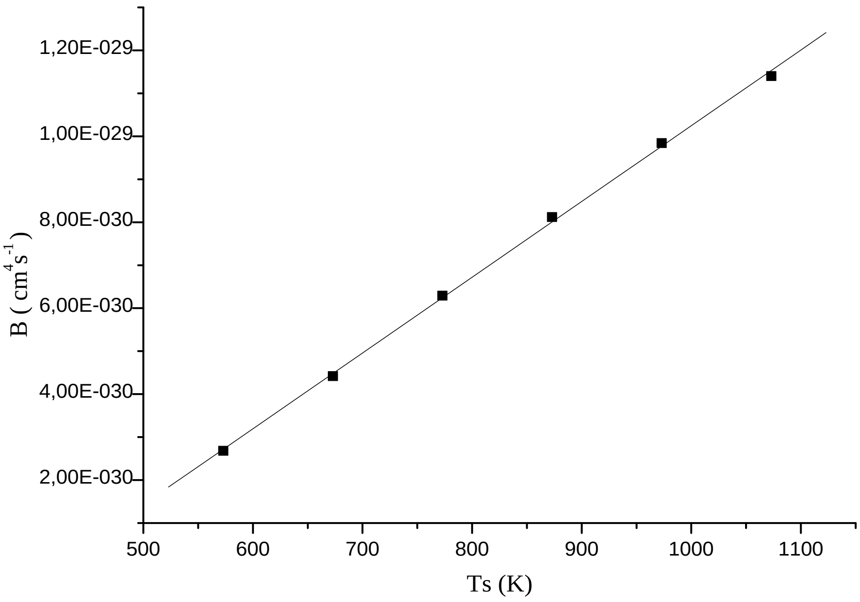

Figure .4 Variation of the coalescence parameter (B) as a function of substrate temperatures.

4. DISCUSSION

From our previous empirical result for Pd/MgO thin film, the initial nucleation curves suggest the occurrence of a random nucleation mechanism. The theory of this nucleation process is expressed by the kinetic equations of Zinsmeister [15]. Robinson and Robins [13] have given analytical solutions in two limit cases, namely at low and high temperature. In this work, we focus on the high substrate temperatures (regime of incomplete condensation), where the particle number density is given by:

$$n = n_s \tanh\left({}^{t}/_{\tau_s}\right) \qquad (11)$$

When the random nucleation model is used, the calculated curves in the first stage agree well with the experimentally measured time dependencies of island density (see nucleation regime in figure 1) [1]. Hence, the curves show a plateau as a maximum particle density reached at the end of the nucleation regime characterizing the Volmer-Weber model.

The value of saturation island density is important parameters which determine the mode of thin film growth. 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 / Ar-cleaved MgO(100) [20], Au /MgO(100) [21] and Pd/ UHV-cleaved MgO(100) [22,23].

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

$$n = n_s \left(\frac{1+t}{\tau_s}\right)^{-\frac{3}{m}} \quad \text{with} \quad m = 7 \qquad (12)$$

The coalescence curves were better fitted with a Cluster diffusion model [14] rather than Ostwald ripening model. 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 (9), we can note that two parameters are important to determine the duration of the coalescence stage, which are R and B. One can also notice the influence of the deposition temperature, that modifies the clusters coalescence time. It is clearly seen that clusters coalesce more rapidly at high temperature [24]. This phenomenon is

explained by the process of island migration. The process of island migration in this calculation is essentially described by the parameter B. The derived B values from Figure 4 are not high enough meaning that the process of island density coalescence is not ignored even at the initial stages of deposition [25]. 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 [26]. The surface coverage does not depend on B parameter, but it strongly depends on the 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:

$$A = n \frac{\pi D^2}{4} \qquad (13)$$

In this range of temperatures, the diameter D of the clusters follows a power law: $D_o t^p$ with 0.33 <P<0.55. At 573 K and 673 K, our previous experimental work yielded values of D_o to 0.024 nm, D equal to 0.80 nm and 0.37 to 0.39 nm respectively [1]. The obtained values are used for the calculated curves of the covered area of the substrate surface. As indicated in the last section the cluster density decreases when the substrate temperature increases due to the increased ad-atom mobility [16]. In addition, we assumed that D is relatively constant with a low error ($\Delta D/D = 11\%$). Accordingly, the fraction of the substrate covered by the particles decreases and the decrease is more pronounced when the coalescence occurs. This behavior is in good agreement with growth rate of the particles in the case of the random nucleation theory [27].

5. CONCLUSION

In the present study, we have simulated the microscopic mechanisms, which can calculate various parameters related to the formation of Pd / thin MgO (100) using Fortran software. The formation kinetics follows a general scheme consisting of three stages: nucleation, growth and coalescence. It is determined that saturation density obeys an Arrhenius law with activation energy of 0.22 eV as a fit parameter. It is observed that the variation of island density upon time reaches the saturation. In some cases the cluster density decreases slowly after a saturation regime. The latter decrease is interpreted via the processes of islands migration .It is shown that the coalescence time and the fraction of the substrate covered by the clusters decrease when the temperature increases. Furthermore, the clusters coalesce more rapidly when the temperature increases.

REFERENCES

[1] Chapon.C, Henry.C.R & Chemam.A, 1985, Formation and characterization of small Pd particles deposited on MgO as a model catalyst ,Vol 162, Surface Sci, 747-754.

[2] Stiehler.C, Pan.Y, Schneider.W-D, Koskinen.P, Hakkinen.P.H, Nilius.N and Freund.H.J, 2013, N° 11-15, Vol 88, Phys. Rev, 115-415.

[3] Shao.X, Cui.Y,. Schneider.W-D, Nilius.N & Freund.H-J, 2012, Growth of Two-dimensional Lithium Islands on CaO (001) Thin Films, N° 33, Vol 116, Phys. Chem, 17980-17984.

[4] Wang.H-F, Ariga.H, Dowler.R, Sterrer.M &Freund.H-J, 2012, Surface Science Approach to Catalyst Preparation—Pd Deposition onto Tin $Fe_3O_4^{111}$ Films from $PdCl_2$ Precursor, Vol 286, Journal of Catalysis, 1-5 .

[5] Nolte.P, Stierle.A, Kasper.N, Jin-Phillipp.N-Y, Jeutter.N& Dosch.H, 2011, Reversible Shape Changes of Pd Nanoparticles on MgO(100) , N° 11, Vol 11, Nano Lett, 4697- 4700.

[6] Nolte.P, Stierle.A, Kasper.N, Jin-Phillipp.N-Y, Reichert.R, Rühm.A, Okasinski.J, Dosch.H& Schöder.S, 2008, Combinatorial high-energy x-ray microbeam study of the size-dependent oxidation of Pd nanoparticles on MgO(100), N° 11-15, Vol 77, , Phys. Rev, 11-15.

[7] Xu.C, Oh.W-S, Liu.G, Kima.D-Y & Goodman.D-W, 1997, Characterization of Metal Clusters (Pd and Au) Supported on Various Metal Oxide Surfaces (MgO and TiO2, N° 3, Vol 15, J.Vac. Sci. Technol, 1261-1268.

[8] Henry.C.R, Chapon.C, Duriez.C & Giorgio.S,1991 , Growth and morphology of palladium particles epitaxially deposited on a MgO(100) surface ,N° 1-3, Vol 253, Surface Science, 177-189.

[9] Fornander.H, Hultman.L, Birch.J& Sundgren.J-E, 1998, Initial growth of Pd on MgO(0 0 1) , N° 1-2, Vol 186, Journal of Crystal Growth, 189-202.

[10] Xu.L, Campbell.C-T, Jonsson.H, Henkelman.G, 2007, Kinetic Monte Carlo simulations of Pd deposition and island growth on MgO (100) , N° 14, Vol 601, Surface Science, 3133-3142.

[11] Venables.J-A & Harding.J-H, 2000, Nucleation and growth of supported metal clusters at defect sites on oxide and halide (001) surfaces, N° 1-4, Vol 211, Journal of Crystal Growth,27-33.

[12] Renaud.G, 2005 , Real-Time Monitoring of Growing Nanoparticles by in situ Small Angle Grazing Incidence X-Ray Scattering, N° 63, Vol 748, American Institute of Physics, 63-71.

[13] Robinson.V-N-E & Robins.J-L, 1974, Nucleation kinetics of gold deposited onto UHV cleaved surfaces of NaCl and KBr, N° 1, Vol 20, Thin Solid Films , 155-175.

[14] Kashchiev.D, 1976, Kinetics of thin film coalescence due to crystallite surface migration, N° 2, Vol 55, Surf. Sci, 477-493.

[15] Zinsmeister. G, 1966, A contribution to Frenkel's theory of condensation, N° 10, Vol 16, J. Vacuum, 529-535.

[16] Halpern. V-I, 1969, Cluster Growth and Saturation Island Densities in Thin-Film Growth, N° 11, Vol 40, J. Appl. Phys, 4627- 4632.

[17] Venables. J-A, 1973, Rate equation approaches to thin film nucleation kinetics, N° 3, Vol 27, *Phil. Mag,* 697-738.

[18] Lewis. B, 1974, Adatom migration, capture and decay among competing nuclei on a substrate, N° 6, Vol 29, Phil. Mag, 1253-1276.

[19] Nichols. F-A & Mullins. W-W, 1965, Morphological Changes of a Surface of Revolution due to Capillarity-Induced Surface Diffusion, N° 6, vol 36, J. Appl. Phys, 1826-1835.

[20] Menck. A, 1998, Defects and growth processes at ionic and oxide crystal surfaces studied by atomic force microscopy, Ph. D. thesis, EPLF-Lausanne.

[21] Hansen. K-H, Ferrero. S &Henry. C-R, 2004, Nucleation and growth kinetics of gold nanoparticles on MgO (1 0 0) studied by UHV-AFM, N° 1-3, Vol 226, Applied Surface Science, 167-172.

[22] Meunier. M, 1995, Nucleation and growth of metallic clusters on MgO (100) by helium diffraction, Ph.D. thesis, Marseille-France.

[23] Henry. C-R, 1998, Surface studies of supported model catalysts, N° 7-8, Vol 31, Surf. Sci. Rep, 231-325.

[24] Carrey. J, Maurice. J-L, Petro. F &Vaurès. A, 2002, Growth of Aux clusters on amorphous Al2 O3, N° 1-2, Vol 504, Surface Science, 75-82.

[25] Carrey. J &Maurice. J-L, 2002, Scaling laws near percolation during three-dimensional cluster growth: A Monte Carlo study, N° 20, Vol 65, physical review B, 205401:1-10.

[26] Bartelt. M-C& Evans. J-W, 1994, Dendritic islands in metal-on-metal epitaxy I. Shape transitions and diffusion at island edges, N° 1, Vol 314, Surf. Sci, L817-L865.

[27] Harsdorff. M, 1982, Heterogeneous nucleation and growth of thin films, N° 1, Vol 90, Thin Solid Films, 1-14.

[28] Henry. C-R &Poppa. H, 1988, Effect of substrate preparation on the structure and chemisorption properties of Pd/MgO model catalyst, Vol 6, J. Vac. Sci. Technol, 1113-1117.

[29] Volmer. M &Weber. A, 1926, Keimbildung in übersättigten Gebilden (Nucleation of supersaturated structures), Vol 119, Phys. Chem, 277-301.