

Nucleation and growth of transition metals on a thin alumina film

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Abstract

We have studied the growth of various metals (Pd, Rh, Co and Ir) on a thin well-ordered alumina film in order to elucidate the influence of film structure and deposition conditions on nucleation and growth behaviour. All metals exhibit a three-dimensional growth mode in agreement with thermodynamic considerations. The nucleation is, however, dominated by the defects of the substrate. At a deposition temperature of 90 K, point defects are the primary nucleation centres. At 300 K, the situation is different for some metals (such as Pd and Rh) since decoration of steps and film domain boundaries is favoured under these conditions. This temperature dependence points to a stronger interaction of the diffusing metal atoms with the line defects which, however, can only play a role if the thermal energy is sufficiently high to reach them. Metals which are expected to interact more strongly with the support (such as Ir and Co) do not show such a diversity with respect to their nucleation behaviour. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal ceramic interfaces play an important part in a large number of technological fields such as thin film technology, fibre optics, microelectronics and heterogeneous catalysis. In many of these applications, the performance depends crucially on the physical or chemical interaction between the metal and the oxide [1]. Nevertheless, there is still very limited knowledge at the microscopic level about the factors which determine the structure and thus the mechanical, electronic or chemical properties of these systems. This has stimulated

many fundamental studies regarding, for instance, the growth behaviour of metals on oxide surfaces [2,3]. Most of them have been carried out on oxide single crystals such as MgO, ZnO and, to a smaller extent, Al₂O₃ (see Refs. [2,3] and references therein). This approach sometimes meets with experimental difficulties, though. These are related to sample mounting and cleaning, or arise from poor electrical and thermal conductivity. An alternative, in this context, is the use of thin oxide films supported on a metal substrate as has occasionally been proposed in the literature [4–7]. This has the obvious advantage that scanning tunneling microscopy (STM) and electron spectroscopic techniques can be applied without charging problems.

For this reason, we have employed a thin well-

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ordered alumina film grown on NiAl(110) for our investigations. The structure and electronic properties of this 5 Å thick film have previously been characterized in detail [6,8]. In the past, we have already investigated the growth of various transition metals, including Rh and Pd, on this support [6,18,19]. Recently we have extended this work to more reactive metals such as Co and Ir. In this paper, we will give an overview with respect to nucleation and growth on this support, considering Pd, Rh, Co and Ir as examples.

Our study demonstrates that the defect structure of the support dominates the nucleation and growth behaviour but that the different defect sites can play varying roles depending on deposition temperature.

2. Experimental

The experiments were performed in two different ultra-high vacuum (UHV) systems, both equipped with Omicron STM instruments (variable temperature STM (VT-STM), and atomic force/scanning tunneling microscopy system (AFM/STM) respectively) and X-ray photoelectron spectroscopy (XPS) facilities. In both cases, the samples were mounted on small carrier plates which could be transferred between the microscopes and the main chambers containing low energy electron diffraction (LEED) optics and all instruments necessary for the preparation of the surface. In order to control the crystal temperature, NiCr/Ni thermocouples stuck or spot welded to the sample were used. The electrical contacts were realised by plug–socket connectors between sample holder and carrier plate.

The ordered Al₂O₃ film used as a substrate in this study was obtained by oxidation of an NiAl(110) single crystal surface and subsequent annealing [8,9]. The quality of the oxide film could be checked by STM and its characteristic LEED pattern.

The metals (>99.9% purity) were evaporated from a rod with commercial evaporators (Focus, EFM 3 and EFM3T) based on electron bombardment. Their flux was calibrated by a quartz microbalance prior to use and checked by STM

(deposition of submonolayer amounts of the metals on the clean NiAl crystal, where a layer-by-layer growth is observed). The usual deposition rates varied between 0.25 and 1.5 Å min⁻¹ (about 0.1–0.6 ML min⁻¹). During deposition, the crystal was biased with a retarding voltage in order to prevent ions from being accelerated towards the sample (point defect creation). The deposition temperature was either 90 or 300 K. Due to experimental limitations, however, the characterisation of the deposits by STM was always performed at 300 K.

3. Results and discussion

Before turning to the deposition experiments, it is important to recall a few details regarding the structure of the thin alumina film which are of relevance for the following discussion. As described in detail elsewhere, the film exhibits a characteristic defect structure which is dominated by a network of antiphase and reflection domain boundaries [6,8]. While the first type is the consequence of a lateral displacement between two adjacent oxide areas, the latter separates domains with two different azimuthal orientations (the result of the twofold symmetry of the NiAl support). The domains themselves have long range order but contain a certain concentration of point defects. Although it has not been possible to observe them with STM, their existence has been inferred from electron spin resonance [10] and cathodo-luminescence experiments [11].

Fig. 1 contains a series of STM images, taken (at 300 K) after deposition of Pd, Rh, Co and Ir onto the thin alumina film at 90 and 300 K. Accordingly, all metals prefer a three-dimensional growth mode, irrespective of the deposition temperature. This is not too surprising since such a result is usually expected on the basis of the surface free energies involved [2].

Considering the 90 K deposits first, it is conspicuous that a relatively isotropic arrangement of particles on the surface is found in all cases. Neither the domain boundaries, which are visible as protruding lines in the pictures, nor the steps play a dominant role. In fact, a quantitative evalua-

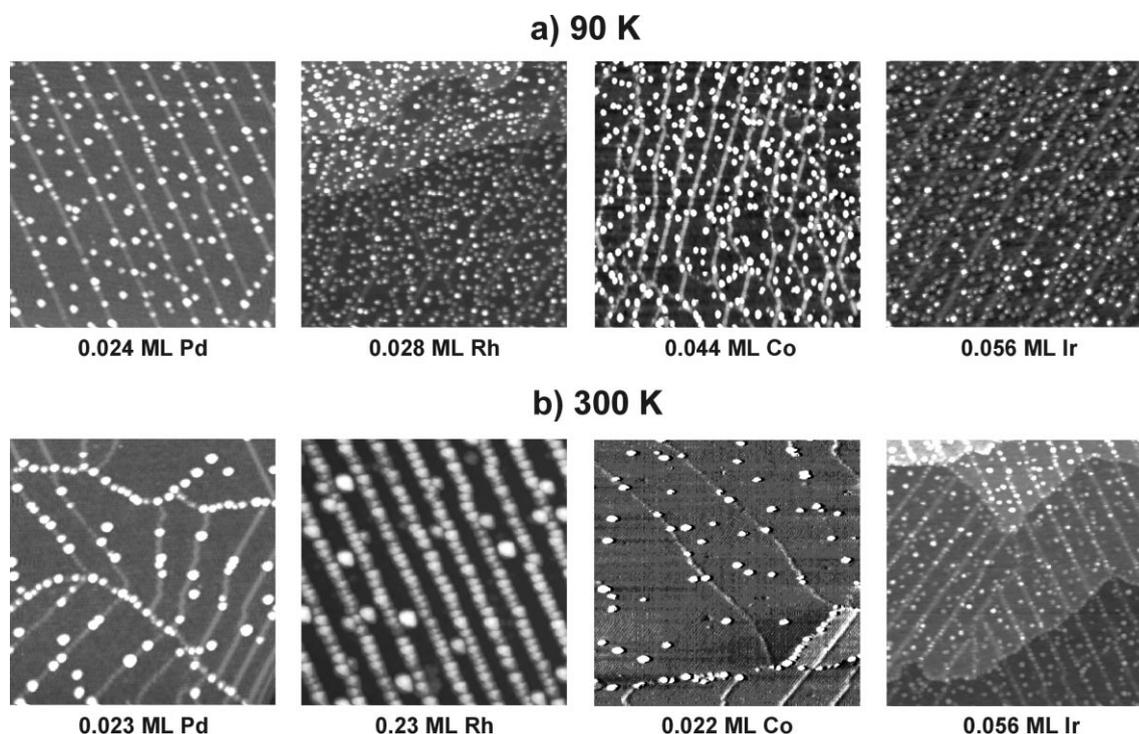


Fig. 1. Series of STM images (constant current topographies, all pictures $1000 \times 1000 \text{ \AA}$) taken after deposition of small amounts of Pd, Rh, Co and Ir on the thin alumina film at: (a) 90 K and (b) 300 K (evaporation flux $\sim 0.1\text{--}0.6 \text{ ML min}^{-1}$, data acquisition at 300 K).

tion of the island densities corroborates that the nucleation behaviour is essentially independent of the specific metal under investigation. As shown in Fig. 2 for Ir and Rh, the evolution of the

densities as a function of coverage, as well as the saturation densities, are almost identical ($\sim 1.2 \times 10^{13}\text{--}1.3 \times 10^{13} \text{ cm}^{-2}$ at a coverage of about 0.2 ML). Palladium deposition gives rise to

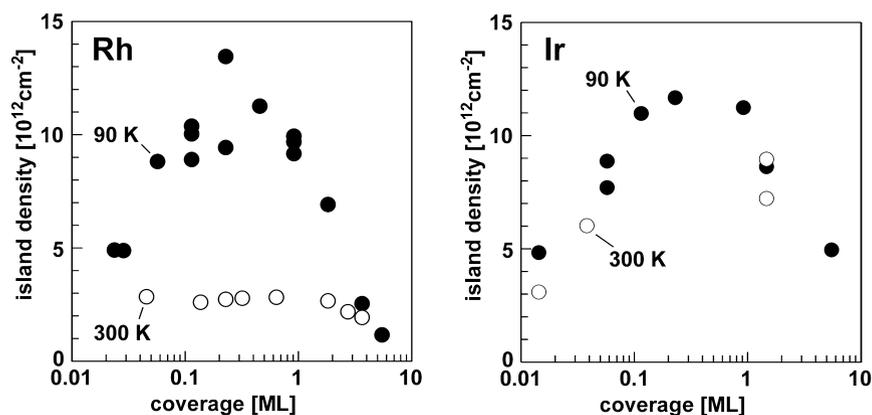


Fig. 2. Densities of Rh and Ir particles on the thin alumina film as a function of coverage (full circles = deposition at 90 K, open circles = deposition at 300 K; evaporation flux $\approx 0.1\text{--}0.25 \text{ ML min}^{-1}$).

lower densities and, thus, larger particles in the regime of very low coverages (see Fig. 1). Nevertheless, the saturating density is again similar to the one found for Ir and Rh. Other metals, including Co, have not been studied systematically in this respect, but the results obtained at selected coverages fit very well into the general trend [6].

In order to get more information about the nucleation mechanism, which is obviously dominant for all metals, experiments at different evaporation fluxes have been conducted using Rh as an example. The corresponding STM images are displayed in Fig. 3. Although the flux has been changed by two orders of magnitude, no significant difference can be noted in the two pictures (the island density in both cases is $3.5 \times 10^{12} \text{ cm}^{-2}$). In this way, a homogeneous nucleation mechanism can be ruled out since the island densities should vary with the flux in this case [2]. This leads to the conclusion that the *point defects* of the film act as nucleation centres under these conditions.

Note, however, that the observed nucleation behaviour results from the combined effects of growth at 90 K and possible changes taking place on warming up the particle ensemble to 300 K. Therefore, an attempt has been made to assess the influence of the thermal treatment on the basis of an IR spectroscopic study (with CO as a probe molecule) which will be discussed in detail else-

where [12]. These experiments have indeed revealed differences between the metals. Ir, for instance, initially seems to form smaller aggregates (by homogeneous nucleation?) which are unstable and diffuse to the point defects at higher temperatures. In the case of Rh and Pd, on the other hand, the measurements provided no indications that the particle sizes or their distribution on the surface change on raising the temperature to 300 K. For Rh, only the disappearance of single atoms trapped at point defects of the film at 90 K has been detected [13]. Apparently, these atoms are captured by existing islands if they start to diffuse.

Comparing the STM images of the 90 K to the 300 K deposits (see Fig. 1), it turns out that some metals largely reproduce their behaviour at 90 K, while others apparently prefer different nucleation sites at 300 K. Examples of the latter type are Rh and Pd, for which an almost exclusive decoration of the domain boundaries, especially of the curved boundaries, and steps is observed. So, heterogeneous nucleation still governs the growth, but the *line defects* are the primary nucleation centres under these conditions. Evidently, they offer sites with a higher adsorption energy which, however, only come into play if the thermal energy is sufficiently high to escape from the point defects. This change in the nucleation behaviour is also

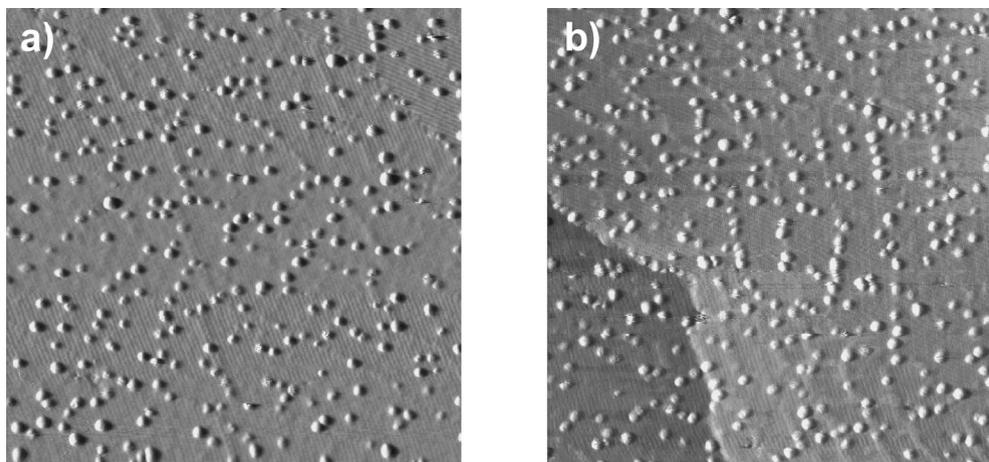


Fig. 3. STM images (CCT, 4.1 V, 0.5 nA, $1000 \times 1000 \text{ \AA}$) taken after deposition of 0.023 ML Rh onto $\text{Al}_2\text{O}_3/\text{NiAl}(100)$ at 90 K (data acquisition at 300 K). Evaporation flux: (a) 0.3 ML min^{-1} ; (b) $0.003 \text{ ML min}^{-1}$.

connected with a noticeable reduction of island densities as seen in Fig. 2. On the contrary, a clearly weaker preference of the line defects can be discerned for Ir and Co. Consequently, the particle densities here are higher and resemble those determined after deposition at 90 K (see Fig. 2).

In principle, two factors could be responsible for the different behaviour of the metals. On the one hand, it cannot be excluded that the interaction with the line defects (especially with the different types of line defects) is not the same for all metals. On the other hand, the trends are consistent with a decreasing metal support interaction in the series $\text{Ir} \sim \text{Co} > \text{Rh} > \text{Pd}$ resulting in an increasing overall mobility of the metal atoms on the surface. In fact, this sequence is in agreement with the enthalpies of formation of the corresponding oxides [2] which have been found to correlate with the interaction strength in a number of other UHV studies as well [14,15]. This interpretation also provides an explanation for the slight differences detected at 90 K. Since Ir is the metal with the strongest interactions, it is quite conceivable that the diffusion length is too short to reach the point defects already at 90 K. This would result in the growth of smaller aggregates as compared to the other metals, which eventually diffuse to the defect sites if the temperature is increased to 300 K. Moreover, Pd being the metal with the weakest interaction, is likely to form the largest aggregates, as indeed is observed.

4. Summary and conclusions

According to our studies, the defects of a thin alumina film play a dominant role in the nucleation of metals on this support. This fits nicely to a number of other investigations which likewise suggest that heterogeneous nucleation is the prevailing mechanism on many oxide supports, such as films, ex situ cleaved or polished single crystals, i.e. substrates which are expected to contain a relatively high concentration of defects as compared to vacuum cleaved samples [16,17].

Moreover, the results demonstrate that the preferred nucleation site can change as a function of

temperature. The most prominent examples in this respect are Rh and Pd. While at 90 K point defects are the primary nucleation centres, line defects come to the fore at 300 K. Obviously, the point defects represent energetically less favourable sites which lose significance as the thermal energy increases. For other metals, such as Ir and Co, no such diversity has been detected. Here, the point defects also determine the growth at 300 K. The trends can be explained by an increasing metal support interaction resulting in a decreasing overall mobility of the adatoms in the series $\text{Pd} < \text{Rh} < \text{Co} \sim \text{Ir}$.

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