ESRF	**Experiment title:** Very first stages of adsorption and growth of Pd on MgO(00 1): structure and morphology by in situ 3D surface diffraction.	**Experiment number:** SI 232
Beamline: ID32	**Date of experiment:** from: 06/08/96 to: 13/08/96	**Date of report:** 26 / 02 / 97
Shifts: 18	**Local contact(s):** Andreas Stierle	*Received at ESRF:* - 3 MAR. 1997

Names and affiliations of applicants (* indicates experimentalists):

Gilles RENAUD, Antoine BARBIER

Report:

Metal-oxide interfaces are used in various technological areas. such as microelectronics. catalysis and glass industry. The structure, as well as the nature and strength of the bonding at these interfaces strongly influence their mechanical. electrical and optical properties. Despite the numerous recent experimental and theoretical studies, the nature of bonding between such dissimilar materials is still poorly understood. The Pd/MgO(00l) interface is a model catalyst. as well as a model metal/oxide system for theoreticians. If numerous experimental investigations dealt with the nucleation of clusters at different temperature for extremely low equivalent deposits (< 1 ML), nothing was known of the growth of Pd over MgO(001) at room temperature (RT), from the submonolayer to the thick deposits ranges.

The questions raised in this study were : (1) is there epitaxy at RT, and if yes, what are the epitaxial relationships and the structure of the growing film, given the 7.68 lattice parameter misfit with MgO ? ; (2) how is the misfit relaxed ? is a part of the film pseudomorphic (on-site) ? : (3) if there is on-site Pd, what is the epitaxial site (0 or Pd or in between), knowing that the Mg site was found by SEXELFS, which contradicts recent unpublished theoretical calculations ? ; (4) what is the growth mode and the morphology of the film during growth, and its correlation with structural relaxation ? (5) for thick films, how is the misfit accomodated ? Is their an ordered network of interfacial dislocations. and if yes, what is its structure and evolution upon annealing ?

The GIXS study was performed in UHV, in situ, during Pd deposition onto MgO(001) .The results were presented in detail at the ESRF User's meeting. We only recall here the main points.

Fig. 1 illustrates the evolution of Pd scattering along an in-plane radial scan crossing the MgO and Pd rods, close to in-plane Bragg peaks. It shows that, for all deposit. Pd in in cube on cube epitaxy, and their is relaxed Pd. with an in-plane lattice parameter close to the bulk Pd one. For thick deposits, a satellite appears, which arises from an interfacial network of misfit dislocations. Between 0 and 1 ML, the MgO CTR is strongly affected by Pd deposition, which indicates that some Pd deposited is pseudomorphic, i.e. on-site : it has the same in-plane lattice parameter as the substrate.

This « pseudomorphic part » can be analyzed in more detail along crystal truncation rods (Fig. 2 and 3), where there are strong interferences between MgO CTRs and the rods of scattering by the thin pseudomorphic Pd layer. A qualitative inspection of the (201) (Fig. 2) and (311) (Fig. 3) CTRs allows an unambiguous determination of the epitaxial site : Pd atoms are above 0

ions of the substrate. A quantitative tit of the (201) CTR also allows to deduce the interfacial distance between the last .MgO plane and the first Pd one : d = 2.216 A (for 1 ML) , as well as the roughness of the Pd film. Fig. 4 shows the same measurement as Fig. 1. on the final 356 A thick film grown in situ, after annealing at 700°C. The annealing clearly recrystallizes the Pd film, mainly by a decrease of its mosaic spread. and induces a pronounced ordering of the interfacial dislocation network as evidenced by much narrower and new satellites diffraction peaks from the interfacial network. The reflectivity (Figure 5) shows the very low roughnesses of both the surface and the interface.

A detailed study of the results is under way, and the results will be compared to very similar ones obtained on the Ag/MgO(00l) interface in the recent years. An interesting comparison relates to the interfacial network ordering and to the amount of strain remaining in the film. in the Ag/MgO system, the expansion coefficients are such that the misfit decreases with increasing temperature, while the opposite is true for Pd. Hence, when heating, less interfacial dislocations are required than at room temperature to relax the misfit in the Ag/MgO system. while more are required in the Pd/MgO system. This explain why, after cooling back to room temperature, the remaining strain is larger than before annealing in the Ag/MgO system, while the opposite is true for the Pd/MgO system : in the former case. some dislocations are eliminated during annealing, and not enough dislocation nucleate during cooling. thus leaving a residual strain, while in the latter, new dislocations nucleate at high temperature, that help completely releasing the misfit strains after cooling.

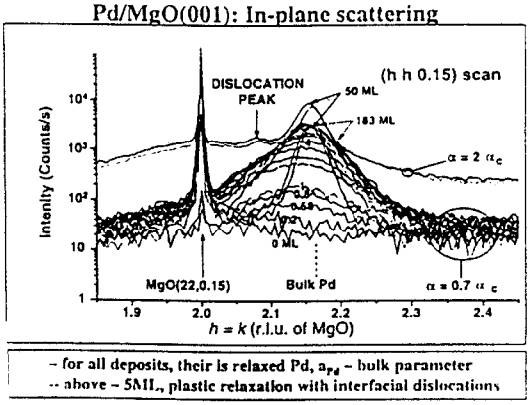

Fig. 1

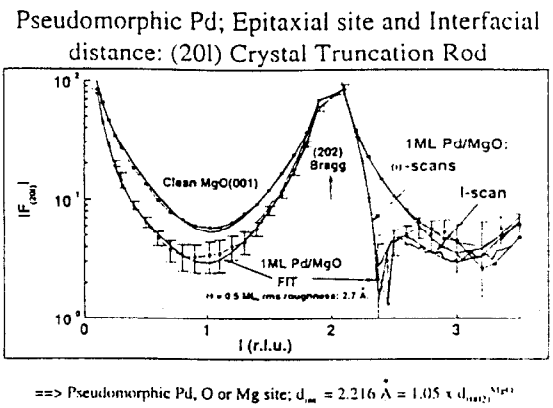

Fig. 2

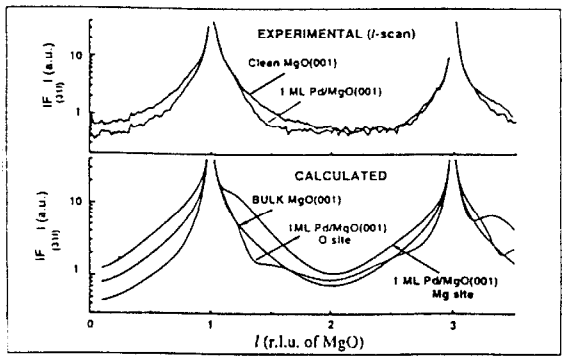

Fig. 3

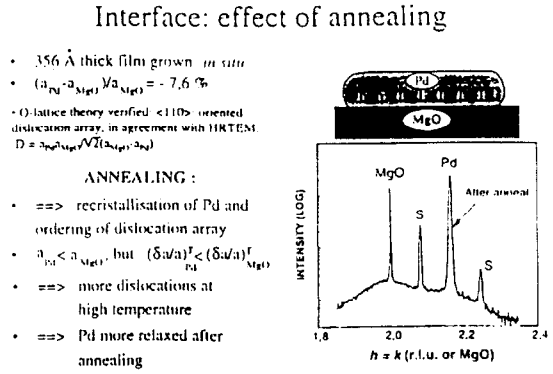

Fig. 4

Fig. 5 :