

On the Substrate-Driven Oxidation of Ni/NiO(001) by X-ray Photoelectron Spectroscopy and Molecular Dynamics Simulations

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The reactivity of the substrate plays a critical role in the formation of metallic particles and thin films on oxide substrates, which are related to technological applications, such as gas sensors, metal-oxide contacts, microelectronic and photovoltaic devices, anticorrosion coatings, and oxide supported transition metal catalysts. Certain oxides can oxidize deposited metals at elevated temperatures via oxygen diffusing to their surface from the bulk. This has been reported for Ni and Cr of the order of a few monolayers deposited under UHV on single crystals of yttria-stabilized-zirconia (YSZ), the oxidative capacity of which is due to the known presence of a small bulk concentration of excess non-stoichiometric oxygen [1-3]. This behaviour is not exhibited by α -Al₂O₃ (0001) [1], while Ni deposits on NiO (001) have been also found to oxidize upon annealing in UHV above ~ 750 K [4]. The present work aims in investigating the capacity of NiO (001) single crystal to oxidize deposited Ni in excess of a monolayer, as well as in revealing the origin of the oxygen species involved. The experimental study was done by means of X-ray photoelectron spectroscopy (XPS), while the obtained results were further interpreted with the help of Molecular Dynamics simulations.

Three series of depositions were carried out, resulting in final metallic Ni coverages of 1.6 ML, 3.8 ML and 7.5 ML, as obtained by XPS. Each series was followed by annealing at temperatures ranging from 810K to 940K. When the oxidation of a deposit was completed, the next deposition series took place, whereby only the 7.5 ML deposit could not be fully oxidized within the available experimental time. Figure 1 shows the O1s/Ni2p area ratio, plotted versus the equivalent monolayers of metallic Ni on the surface for the 7.5 ML deposition. The solid line in fig.1 corresponds to the prediction of a model of continuous, amorphous and homogeneous Ni⁰ film completely covering the NiO (001) substrate. The good agreement between the experimental results and the model supports the layer-like character of the deposit even at 550 K, where the XP spectra were taken, meaning that any Ni⁰ clusters formed cover fully the substrate. It also demonstrates the absence of any oxygen that could have been adsorbed on the Ni from the gas phase following deposition.

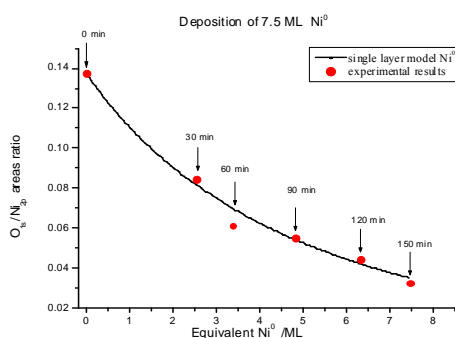


Fig.1 Intensity ratio O1s/Ni2p vs. equivalent ML of deposited Ni⁰ (experimental points) and prediction of a Ni⁰/NiO (100) layer model (solid line) for deposition up to 7.5 ML of Ni⁰.

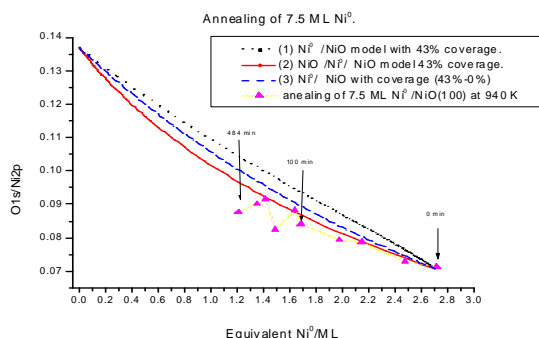


Fig.2 Intensity ratio O1s/Ni2p vs. equivalent ML of remaining Ni⁰ and predictions of three oxidation models upon annealing at 940K of 7.5 ML initially deposited Ni⁰, sintered to a substrate surface coverage of 43%.

Annealing above 550 K, up to a maximum of 940 K, results first in a fast, within a few minutes, decrease of the equivalent monolayers of metallic Ni, which is attributed to deposit sintering and secondly to a further gradual decrease of the equivalent monolayers of Ni⁰ which signifies oxidation. The evolution of the interface for sintered Ni⁰ particles partly covering the substrate is described using three limiting models. In model 1 the Ni⁰ particles are oxidized only from the bottom up, in model 2 from the top down and in model 3 from the side only. Figure 2 shows the predictions of the three models for an initial 43% substrate coverage by sintered particles, as derived from the initial fast decrease of the equivalent XPS monolayers upon annealing of the

deposited 7.5 ML. As shown in fig.2, the second model, which predicts oxidation from the top, matches best the experimental results. Furthermore, the plot (not shown) of the remaining quantity of Ni, as deduced from the XPS results in accordance with the model, versus $(\text{time})^{1/2}$ yields a straight line, suggesting that the slow step of the oxidation is the diffusion of oxygen from the bulk towards the Ni particles. The final conclusion is that the metallic Ni particles that are formed after the sintering are covered by NiO, via an oxidation process that proceeds towards their metallic core with oxygen supplied by the substrate. Taking into account the three series of depositions and annealing, at least 6 ML of metallic Ni could be oxidized by the NiO substrate.

The molecular dynamics simulations were carried out in the constant temperature canonical ensemble using the Nose scheme. Slab geometry was used, in which the simulation cell consisted of 1728 ions arranged in 12 planes, each plane containing 72 cations and 72 anions, while in the [001] direction, there was an empty space of four times the length of the slab along the z-direction. The use of periodic boundary conditions resulted in a system with two free surfaces perpendicular to the [001] direction. The equations of motion were integrated by means of Verlet's algorithm and a time step of 10^{-15} s. For the atomic interactions, we adopted a rigid ion potential developed for NiO [5], while the Coulombic contributions were evaluated with the use of the Ewald summation. The system was initially equilibrated for 20 ps, while the simultaneous deposition of Ni ions at adcation positions and the same number of O ions on the other surface of the slab maintained the charge neutrality of the system. These O ions remain at adlayer position over the surface during the simulations. It should be noted at this point that in the simulations the Ni adatoms were let to carry their formal charges (+2). Initial deposits of 8 Ni (0.06ML), 16 Ni (0.11ML) and 32 Ni adocations (0.22ML) were performed and the evolution of the system was followed for 100000 or 300000 time steps at temperatures corresponding to $0.37T_m$ and $0.57T_m$. The local density distribution function was recorded every 2000 time steps in order to monitor the evolution of the oxygen ions distribution of the slab during each simulation run. By integration of each of the peaks that correspond to each lattice layer the average number of oxygen ions by layer during each simulation can be obtained. Fig. 3 shows the local density distribution function for a simulation of 200000 time steps, whereby 32 Ni ions were placed near the surface at the positive side of the slab and fig. 4 shows the evolution of the average number of anions by layer down to the fourth (layer 5) for 300 000 time steps, expressed as percentage deviation from the perfect lattice, while the solid line displays the deviation from the 32 anions of the fully oxidized adlayer. The deposited Ni ions are initially forming diffusing Ni_xO_y chains, which eventually collide to form non-diffusing NiO ad-islands. The increase of the anions on the surface that occurred between 80000 and 100000 steps coincides with the coalescence of several chains into ad-islands.

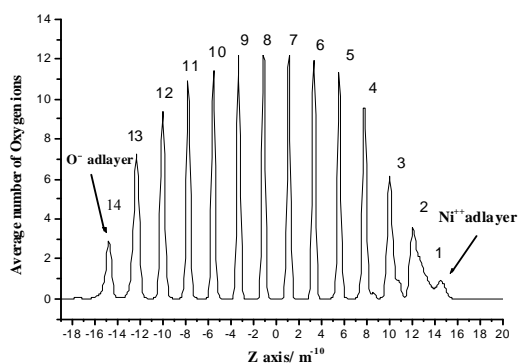


Fig.3 Local density distribution function on the Z axis of the slab, of oxygen ions for deposition of 32 Ni^{++} and 32 O^- ions and after 200 000 simulation steps, (numbers are used to identify lattice layers).

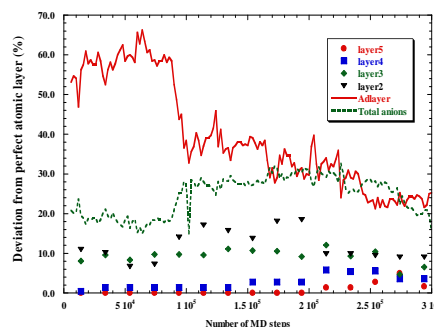


Fig.4 Deviation (%) from the perfect lattice of the average number of oxygen ions per layer (for four layers), after the deposition of 32 Ni^{++} ions during 300 000 simulation steps, total anions line refers to layers 2, 3, 4 and 5.

The simulations demonstrated the capability of the NiO (100) perfect crystal to provide large number of oxygen ions that are bonded to the deposited Ni ions on the surface, with concomitant formation of vacancies in the near-surface layers. This is a possible explanation for the origin and the quantities of the oxygen that is needed for the oxidation of the 6 ML of Ni^0 that was oxidized during the experiment.

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