

## Oxidation process of Ag(110) and chemical reactivity of the oxygen-covered surface studied by time-resolved high-resolution photoemission and scanning tunneling microscopy

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The dissociative adsorption of O<sub>2</sub> on Ag(110) results in the quasi-one dimensional -Ag-O-Ag-O- chains running along the [001] direction. The interval between the chains is changed in self-organized manner depending on the surface coverage of adsorbed oxygen atoms. At low coverage, (7x1)-O structure is formed and the distance between the chains decrease with the increase of the coverage, and finally the surface is covered with the (2x1)-O structure. The chemical reactivity of these structures is not fully understood as demonstrated by our recent STM work where the CO oxidation reaction is accelerated by the fluctuation of the chains [1].

In the present work, we have investigated the oxidation process of the Ag(110) surface by using photoemission combined with supersonic molecular beams (SSMB's). The monochromatic synchrotron radiation of 768 eV was used for Ag 3d and O1s photoemission measurements. The O<sub>2</sub> SSMB's are continuously generated by the

adiabatic expansion of O<sub>2</sub>, He and/or Ar mixture. The nozzle can be heated up to about 1400 K so that the upper limit of the O<sub>2</sub> translational energy is 2.26 eV. A Ag(110) crystal was cleaned by the repeating of a cycle of Ar ion sputtering, annealing at 750 K, oxidation and annealing at 750 K. The oxygen coverage was measured by the intensity ratio of O1s and Ag3d photoemission peaks.

The uptake curves of O were measured as a function of translational energy of O<sub>2</sub> SSMB's. We found that the adsorption process follows the Langmuir kinetics, and that the initial sticking probability depends on the O<sub>2</sub> SSMB translational energy such that the initial sticking probability at 2.26 eV is much lower than those measured at lower translational energies.

[1] O. Nakagoe, K. Watanabe, N. Takagi, Y. Matsumoto, Phys. Rev. Lett. 90 (2003) 226105.

## Properties of ultra-thin Al<sub>2</sub>O<sub>3</sub> films on NiAl(100) formed by oxidation with O<sub>2</sub> and H<sub>2</sub>O

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The oxidation of NiAl(100) to Al<sub>2</sub>O<sub>3</sub> by H<sub>2</sub>O opposed to O<sub>2</sub> was investigated in order to clarify whether hydroxyl (OH) groups, known to be stable on Al<sub>2</sub>O<sub>3</sub>/NiAl(100) surfaces below 700 K, might influence the oxidation process.

The in-situ cleaned NiAl(100) surface was exposed to molecular beams of the oxidants (O<sub>2</sub>, H<sub>2</sub>O) while monitoring the oxidation process via the O1s, Al2p and Ni3p emission signals with photoelectron spectroscopy in real time. The photon energy was chosen as 688.0 eV to probe the O1s emission from the entire oxide film up to its saturation thickness of 1.0 nm in normal emission.

As a reference, oxidation in O<sub>2</sub> was performed at 800 K, where epitaxial growth of crystalline  $\theta$ -Al<sub>2</sub>O<sub>3</sub> occurs, characterized by a (2x1;1x2) LEED pattern. The XPS spectra of the Al<sub>2</sub>O<sub>3</sub> film show a symmetric O1s emission of O<sup>2-</sup> and oxidized Al<sup>3+</sup> in addition to metallic Al<sup>0</sup> and Ni signals of the underlying alloy substrate. At no stage of the film growth is oxidation of Ni observed, consistent with the larger thermal stability of Al<sub>2</sub>O<sub>3</sub> vs. NiO and Ni diffusion into NiAl.

Oxidation at 500 K in O<sub>2</sub> produces amorphous Al<sub>2</sub>O<sub>3</sub> exhibiting a diffuse LEED pattern and an asymmetrically broadened O1s emission line in XPS (Fig. 1), which is shifted by 0.5 eV towards lower BE against the O1s spectrum of crystalline Al<sub>2</sub>O<sub>3</sub>. Intermediate Al<sup>III</sup> oxidation states observed in the Al2p spectra suggest that the low BE shift of the O1s line is induced by defects in the oxide with reduced coordination numbers of O<sup>2-</sup> anions and Al<sup>3+</sup> ions. Ordering of the oxide during high temperature (>973 K) annealing removes these defects, as indicated by the disappearance of the Al<sup>III</sup> states and converts

the O1s line into a symmetric shape at 156.16 eV KE (Fig. 1) as for the crystalline  $\theta$ -Al<sub>2</sub>O<sub>3</sub>.

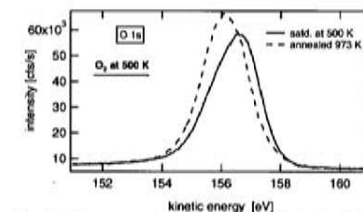


Fig. 1: O1s spectra of Al<sub>2</sub>O<sub>3</sub>/NiAl(100) obtained by O<sub>2</sub> oxidation at 500 K and after annealing at 973 K.

In contrast to O<sub>2</sub>, oxidation in H<sub>2</sub>O at 500 K yields Al<sub>2</sub>O<sub>3</sub> of almost crystalline-like ion coordination, as seen in Fig. 2 by a much smaller number of defect states and the absence of Al<sup>III</sup>. Yet the LEED pattern is without structure, indicating that the oxide has no long-range order; only the nearest-neighbor coordination of the O/Al ions seems to be improved. There is no evidence of remaining hydroxylation. We tentatively attribute the effect of H<sub>2</sub>O to a slower O-uptake in the initial oxidation stage, which may allow for better ordering of the interface thus providing improved epitaxial conditions for the growth of subsequent oxide layers.

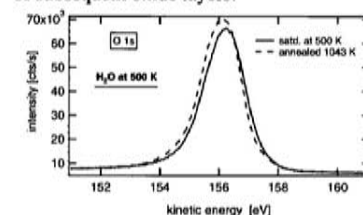


Fig. 2: O1s spectra of Al<sub>2</sub>O<sub>3</sub>/NiAl(100) grown by H<sub>2</sub>O oxidation at 500 K and after annealing at 1043 K.