

## Electronic supplementary information -

### Observation of a novel double layer surface oxide phase on Ni<sub>3</sub>Al(111) at low temperature

Xinzhou Ma<sup>1,2</sup>, Tim Kratky<sup>1</sup>, and Sebastian Günther<sup>1</sup>

1: Technische Universität München, Zentralinstitut für Katalyseforschung, Chemie Department, Physikalische Chemie mit Schwerpunkt Katalyse, Lichtenbergstr. 4 D-85748 Garching, Germany,

E-mail sebastian.guenther@tum.de

2: Current address: Foshan University, College of Materials Science and Energy Engineering, Foshan, 528000 Guangdong, P.R.China

#### a) STM-Movie on the formation of the (7 × 7) single layer oxide phase

The Ni<sub>3</sub>Al(111) surface was imaged by *in situ* STM during O<sub>2</sub> exposure at T = 740 K and  $p(O_2)=3.7 \times 10^{-8}$  mbar and shows the almost entire coverage of the imaged area with the (7 × 7) single layer oxide phase. The moiré results from the registry of 6 O-O distances on 7 next - nearest -neighbor substrate atom distances and appears in the STM image with a characteristic vertical corrugation. The growth fronts of the growing oxide phase proceed along straight lines that are mainly aligned to the moiré. The growth proceeds always at emerging kinks followed by fast growth along the aligned lattice direction of the substrate. The effect of kinks on surface reaction kinetics was observed and discussed during etching reactions on Si surfaces,[47] but note that the observed kinks in Fig. 1 and in the respective movie in the supporting information do not refer to atomic kinks but rather to whole units of the moiré cell of the surface oxide. Similar growth kinetics with kinks consisting of a whole units cell were observed during the growth of graphene on Rh(111).[48] The movie was acquired at U = 0.85 V and I = 0.4 nA. The displayed dosage indicated in each frame of the movie translates to a time at the applied O<sub>2</sub> pressure of  $3.7 \times 10^{-8}$  mbar which amounts to about 30 sec per frame.

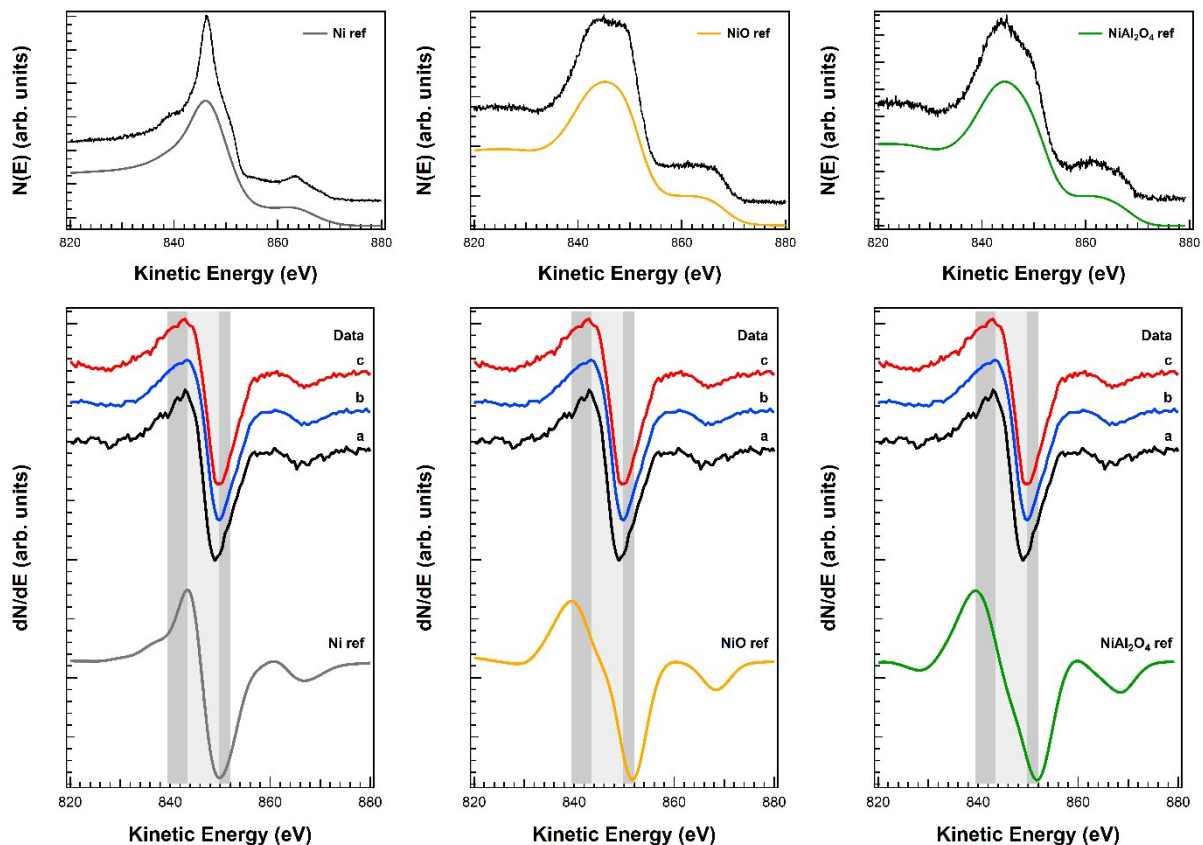
#### b) STM-Movie on the formation of the ( $\sqrt{67} \times \sqrt{67}$ )R12.2° double layer oxide phase

The formation of a defective ( $\sqrt{67} \times \sqrt{67}$ )R12.2° double layer oxide on the Ni<sub>3</sub>Al(111) surface was monitored by *in situ* STM during O<sub>2</sub> exposure at 800 K and  $p(O_2)=3.5 \times 10^{-8}$  mbar. The typical appearance of the ( $\sqrt{67} \times \sqrt{67}$ )R12.2° unit cell with dark protrusions surrounded by bright flower like features is observed. The surface oxide grows in islands with kinked edges. The movie was acquired at U = 0.85 V and I = 0.4 nA. The displayed dosage indicated in each frame of the movie translates to a time at the applied O<sub>2</sub> pressure of  $3.5 \times 10^{-8}$  mbar which amounts to about 30 sec per frame.

### c) STM-Movie on the formation of the novel $(4\sqrt{3} \times 4\sqrt{3})R30^\circ$ double layer oxide phase

The  $\text{Ni}_3\text{Al}(111)$  surface was imaged by *in situ* STM during oxygen exposure at 720 K and  $p(\text{O}_2)=3.0 \times 10^{-8}$  mbar. At first, the  $(7 \times 7)$  single layer oxide phase is formed which appears as dark, triangular islands with the characteristic corrugation of the moiré. Temporarily, after having dosed 46-66 L bright dots appear on top of the  $(7 \times 7)$  single layer oxide patches. The bright dots disappear after the 2nd layer oxide growth on top of the single layer oxide proceeds at higher speed. The movie was acquired at  $U = 0.85$  V and  $I = 0.5$  nA. The displayed dosage indicated in each frame of the movie translates to a time at the applied  $\text{O}_2$  pressure of  $3.0 \times 10^{-8}$  mbar which amounts to about 30 sec per frame.

### d) AES analysis of the $(4\sqrt{3} \times 4\sqrt{3})R30^\circ$ double layer oxide in comparison with the $(7 \times 7)$ single layer oxide phase - proving the metallic state of the Ni atoms:



The formation of NiO and the formation of a potential spinel phase with a  $\text{NiAl}_2\text{O}_4$  stoichiometry during the oxidation of  $\text{Ni}_3\text{Al}(111)$  at 740 K and at 720 K can be excluded with the help of XPS data of reference substances. For this purpose the  $N(E)$  spectra of the Ni(LMM) transition from three different reference substances were recorded in an XPS experiment (\*):

- the  $N(E)$  spectrum acquired from a clean Ni metal foil,
- from a commercial NiO powder after hydroxide has been removed by a temperature treatment in oxygen and
- from a separately synthesized  $\text{NiAl}_2\text{O}_4$  spinel powder.

After adjusting the energy resolution of the acquired N(E) XPS spectra to the one of the CMA spectra displayed in Fig. 4 of the manuscript main text and after taking the derivative, the reference spectra can be compared with the displayed Ni(LMM) dN/dE spectra:

a - clean Ni<sub>3</sub>Al(111),

b - Ni<sub>3</sub>Al(111) after O<sub>2</sub> exposure of 134 L at 740 K and

c - after exposure of 170 L O<sub>2</sub> at 720 K.

We can clearly show that the auger spectra acquired from the clean Ni<sub>3</sub>Al(111) surface before and after exposure of oxygen at 740 K and 720 K match the reference spectrum of metallic Ni, while the formation of NiO and of NiAl<sub>2</sub>O<sub>4</sub> can be readily excluded, since the respective dN/dE reference spectra do not match the experimental data of Fig. 4.

(\*) The metallic Ni foil was sputter cleaned prior to the measurements, commercial NiO powder was purchased from Sigma Aldrich. The adventitious hydroxides were removed from the NiO powder by a high temperature anneal at 1000°C in O<sub>2</sub> at p = 10<sup>-6</sup> mbar for 30 min prior to the XPS data acquisition. The NiAl<sub>2</sub>O<sub>4</sub> spinel phase was synthesized by Stefan Ewald and Moritz Wolf which is gratefully acknowledged.

### **e) AES analysis of the (4√3 × 4√3)R30° double layer oxide in comparison with the (7 × 7) single layer oxide phase**

In the main text of the paper we state that the relative O<sub>KLL</sub>/Ni<sub>LMM</sub> peak intensities acquired from the (7x7) single layer surface oxide and from the (4√3 × 4√3)R30° low temperature oxide prove that the latter structure is a double layer surface oxide, i.e. that the Ni<sub>3</sub>Al(111) surface is covered by two Al-O layers.

For the estimation of the expected numbers, we approximate the effective attenuation length by the inelastic mean free path for electrons with a kinetic energy of 510 eV (the O<sub>KLL</sub> auger electrons) and with a kinetic energy of 848 eV (the Ni<sub>LMM</sub> auger electrons) in Al<sub>2</sub>O<sub>3</sub> as 12.0 Å and 17.9 Å according to the calculation of Ackermann et al. in Ref. [1]. These numbers agree well with the calibration performed by Mom et al. in Ref. [2].

As outlined in the main text of the manuscript, the (4√3 × 4√3)R30° surface layer oxide consists of two Al-O layers stacked one on another where each layer contains the same amount of Al and O atoms as the (7x7) single layer oxide. The average layer distance between the outermost Al-O layer and the first Al-O layer is assumed to amount 2.23 Å, similar to the value calculated by DFT for the (√67 × √67)R12.2° double layer oxide in Ref.[3].

The acceptance angle of the used cylindrical mirror analyzer amounts 42.3 ° and is taken into account in the estimation below. In order to remove alignment errors during subsequent measurements of auger spectra, we consider the O<sub>KLL</sub>/Ni<sub>LMM</sub> intensity ratio of the (7x7) single layer oxide and compare it to the acquired one of the (4√3 × 4√3)R30° double layer oxide which is larger by a factor of 1.89 as stated in the main text.

The expected relative signal increase can be estimated as follows:

$$\begin{aligned} & \frac{O_{KLL}}{Ni_{LMM}}(4\sqrt{3} \times 4\sqrt{3}R30^\circ) \div \frac{O_{KLL}}{Ni_{LMM}}(7 \times 7) \\ &= \frac{O_{KLL}(4\sqrt{3} \times 4\sqrt{3}R30^\circ)}{O_{KLL}(7 \times 7)} \cdot \frac{Ni_{LMM}(7 \times 7)}{Ni_{LMM}(4\sqrt{3} \times 4\sqrt{3}R30^\circ)} \\ &= \left[ 1 + \exp\left(-\frac{2,23\text{\AA}}{\cos(42,3^\circ) \cdot 12,0\text{\AA}}\right) \right] \exp\left(\frac{2,23\text{\AA}}{\cos(42,3^\circ) \cdot 17,9\text{\AA}}\right) \end{aligned}$$

The result of the estimation amounts 2.11 which is only about 11% larger than the experimental value of 1.89 and thus identifies the  $(4\sqrt{3} \times 4\sqrt{3})R30^\circ$  surface oxide phase as a bilayer oxide.

#### References:

- [1] Akkerman A, Boutboul T, Breskin A, Chechik R, Gibrekhterman A, Lifshitz Y, Inelastic Electron Interactions in the Energy Range 50 eV to 10 keV in Insulators: Alkali Halides and Metal Oxides. *Physica Status Solidi (b)* 1996; 198(2): 769-784.
- [2] Mom R V, Vermeer J, Frenken J W M, Groot I M N, Structural Dynamics of  $Al_2O_3/NiAl(110)$  During Film Growth in  $NO_2$ , *J. Phys. Chem B* 2018, 122(2) 788-793.
- [3] Schmidt M, Kresse G, Buchsbaum A, Napetschnig, E, Gritschneider S, Reichling M, Varga P, Nanotemplate with Holes: Ultrathin Alumina on  $Ni_3Al(111)$ , *Phys. Rev. Lett.* 2007, 99(19) 196104.