



Experiment title: O₂ pressure and temperature dependent stability of the ultra-thin aluminum oxide layers on NiAl(110)	Experiment number: SI-1109	Beamline: ID 32	Date of experiment: from: 26.10.2004 to: 02.11.2004	Date of report: 01.09.2005
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Report:

The goal of this experiment was to study the stability of the ultra-thin aluminum oxide layer grown on NiAl(110) as a function of the partial oxygen pressure and oxidation temperature using surface x-ray diffraction as an in-situ tool. The measurements were performed at ID 32 beamline using a photon energy of 12.5 keV.

Prior to the experiment, the NiAl(110) surface was prepared in an UHV chamber by repeated cycles of Ar⁺ sputtering, annealing and oxidation until the surface contaminants were removed. The cleanliness of the sample was checked by AES and LEED. An ultra-thin oxide layer was grown by thermal oxidation using the well-established recipe: oxidation at 270°C with 5·10⁻⁶ mbar O₂ for 15 minutes and annealing at 800°C for 5 minutes [1]. The sample was then transferred in a portable UHV diffraction chamber equipped with a cylindrical beryllium window, which allows performing oxidation experiments in a wide range of temperatures and partial oxygen pressures.

As a first step, we checked the interface and the ultra-thin oxide film structure by measuring several CTR's (Fig. 1 – black symbols), surface rods (Fig. 2 – black symbols), as well as a set of in-plane data.

It was reported in the literature that the thickness of the aluminum oxide film can be increased by performing multiple-oxidation cycles [2]. We have repeated the above mentioned oxidation treatment, while monitoring the intensity of the (0 1 0.8) peak. After 15 minutes of oxidation, there was no change of the intensity at this position. Since this is a very sensitive test for changes of the interfacial structure, it proves that there was no additional mass transport through the interface, therefore no thickening of the oxide layer was observed.

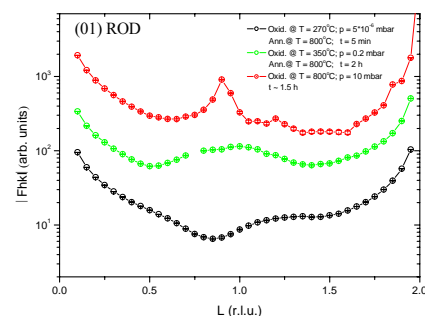


Fig.1: Structure factor amplitude of (01) superstructure rod for different oxidation conditions

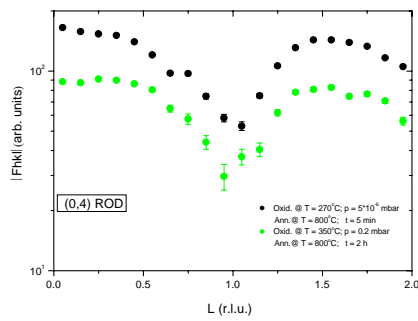


Fig.2: Structure factor amplitude of (04) surface rod for different oxidation conditions

The next step was to test the stability of the oxide grown at higher temperatures and partial oxygen pressures ranging from 10^{-7} – 10 mbar. At 350°C the ultra-thin oxide layer was found to be stable up to 0.01 mbar O_2 . At this pressure we observed a change in the (01) truncation rod shape, as well as a decrease in the (0 4 0.03) peak intensity. In Fig. 3 the in-plane rocking scans on the (0 4 0.03) surface oxide peak are plotted for different oxidation conditions. After the oxidation at 350°C and 0.2 mbar O_2 followed by annealing at 800°C in addition to the surface oxide, a spinel-like bulk oxide has been found. Quantitative information was obtained by measuring several CTR's and surface rods. A change in the (01) superstructure rod shape takes place, which indicates a different interfacial structure (Fig. 1 - green symbols). Anyway, no thickening of the surface oxide was observed since there was no change of the surface rods profile (Fig. 2 - green symbols). The decrease in the structure factor amplitude is just a consequence of both surface oxide and bulk oxide islands being present.

The bulk oxide structure was probed by performing out-of-plane measurements along the rods, for which an additional momentum transfer is provided perpendicular to the surface. The oxide was identified to be $\gamma\text{-Al}_2\text{O}_3$, a metastable phase of $\alpha\text{-Al}_2\text{O}_3$. Fig. 4 (green symbols) shows the diffracted intensity as a function of the azimuthal angle θ (rotation of the sample around its surface normal) for the in-plane momentum transfer $Q = 4.56 \text{ \AA}^{-1}$. The four peaks correspond to (4-40)-type reflections of $\gamma\text{-Al}_2\text{O}_3$. The epitaxial relationship at $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$ interface is Kurdjumov-Sachs (KS) [3] orientation, where two equivalent domains appear to be rotated by $\sim 10^\circ$ with respect to each other.

The increase in both the oxidation temperature to 800°C and in the partial oxygen pressure to 10 mbar leads to the bulk oxide formation which shows a coexistence of two epitaxial relationships: the Ni-shiyama-Wassermann (NW) [4,5] and $R30^\circ$ orientation. In Fig. 4 an in-plane rocking scan through the (4-40)-type reflection of the oxide (red symbols) is shown. The NW peaks appear at 170° and 230° , while the peak at $\theta = 200^\circ$ is attributed to $R30^\circ$ orientation. The transition from KS to NW orientation relationship was previously observed [6] in the case of fcc(111)/bcc(110) systems and it implies a coalescence of the two KS domains which may be related with the increase in the oxide thickness as a function of increasing pressure and oxidation temperature. The peak which is present at $L = 0.9$ on (01) superstructure rod (Fig. 1 – red symbols) might be an indication of a new phase formation, which will be determined in a quantitative manner in a future detailed analysis.

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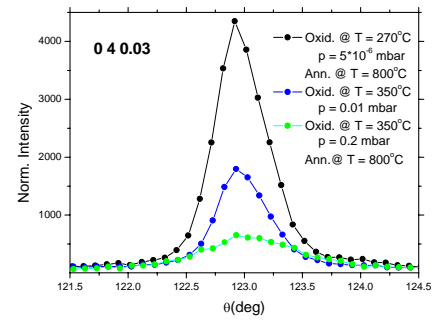


Fig.3: In-plane rocking scans on (0 4 0.03) peak of the surface oxide after different oxidation conditions

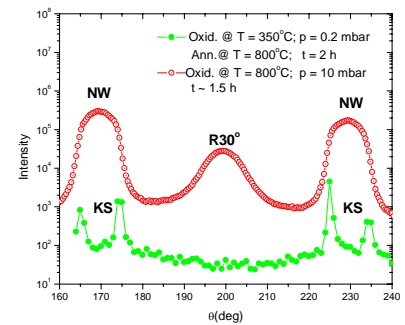


Fig.4: In-plane rocking scans showing KS (green) and NW + $R30^\circ$ (red) orientation of the Al_2O_3 oxide layer with respect to the substrate