

リアルタイム XPS による NiAl 表面の酸化過程における 水素ビーム照射効果の解明

Real-time XPS study on the effect of hydrogen in the oxidation process of NiAl to nano-scale Al₂O₃ films

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NiAl(100)表面酸化過程に見られる水素の影響をリアルタイム XPS を用いて調べた。酸素分子線および水分子線を用いて表面を酸化し、膜厚が飽和した試料について酸化膜由来の Al³⁺ 信号強度と基板由来の Al⁰ 信号強度の取り出し角依存性を測定した。その結果、水分子線を用いて酸化した試料の方が Al³⁺ 信号強度が強く、飽和酸化膜厚が厚いことがわかった。このことは、表面に OH 基が形成されそれに基づく強い電場のために酸化が促進されるというモデルを支持すると考えられる。

Our previous real-time synchrotron X-ray photoelectron spectroscopy (XPS) investigations of the growth kinetics of ultra-thin Al₂O₃ films on NiAl(100) in O₂ have revealed a strong acceleration of the oxidation reaction by hydrogen and, in particular, by water. To clarify the role of hydrogen in the oxidation mechanism, the present study examines whether the growth rate acceleration by H₂O correlates with an increased oxide thickness, as would be expected within the Cabrera-Mott model at large surface hydroxyl (OH) coverages. We thus evaluate the saturation thickness of the Al₂O₃ films from the take-off angle dependence of Al_{2p} emission signals from the oxide overlayer (Al³⁺) and the metallic NiAl substrate (Al⁰). The results confirm our expectation that at temperatures where OH is stable on Al₂O₃, H₂O oxidation should yield slightly thicker Al₂O₃ films than those grown in O₂. This confirms our hypothesis that the rate acceleration by H₂O below 500 K is due to its ability to provide a higher stationary oxidant (OH) coverage than O₂. Consistent with the thermal stability of surface OH groups, the H₂O-related effects decrease at higher oxidation temperatures.

Introduction

Quality control of ultra-thin Al₂O₃ films is essential for their application as dielectrics in electronic devices such as metal-oxide-semiconductor

(MOS) structures or field emitters. Dense, defect-free and strongly adherent oxide films with smooth interfaces are pivotal requirements. Understanding of the oxidation mechanism may

provide the essential knowledge to achieve these goals.

By previous real-time synchrotron X-ray photoemission (XP) studies on the oxidation kinetics of NiAl alloy surfaces we have demonstrated that nano-scale (0.5-1 nm thin) Al_2O_3 films of reduced oxide defect densities and dramatically enhanced film growth rates result when the oxidation is performed with H_2O instead of O_2 (2004A0404-NSa-np-Na). Acceleration of the oxidation was also observed in mixtures of O_2 and hydrogen gas (both molecular H_2 and atomic H, 2004B0566-NSa-np-Na), but contributions from background H_2O impurities in the H_2 gas could not be excluded during earlier experiments.

Our hypothesis is that owing to the polarity of the H-OH bond H_2O adsorption to form surface OH-groups occurs with higher probability on the Al_2O_3 surface (containing both Al^{3+} and O^{2-} ions) than the dissociation of non-polar, double-bonded O_2 molecules. H_2O thus accelerates the reaction by providing a higher stationary coverage of surface oxidant (OH). In the Cabrera-Mott model [1] the oxidation rate is determined by the diffusion of Al^{3+} and O^{2-} ions, which is enhanced at low temperatures by an electric field through the oxide, created by negative O^{2-} (OH) ions on the surface and excess Al^{3+} ions forming at the metal-oxide interface. OH-coverages higher than the respective stationary O-adatom concentration can thus stabilize larger negative surface charge densities and generate stronger electric fields within the oxide. This should hence give rise to *faster* growth of *thicker* oxides, which we try to verify experimentally in the present study.

Experimental

As previously, the O-uptake kinetics on the UHV-prepared clean NiAl(100) surface under

well-controlled exposure to successive molecular beam doses of O_2 (flux $5.2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$) or H_2O (flux $6.2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$) were first monitored by O1s XPS until saturation. Oxidation temperatures were chosen within the range of 320-500 K, where according to our characterization of the H_2O adsorption behavior by H-sensitive ^{15}N nuclear reaction analysis OH groups are thermally stable on the Al_2O_3 surface [2]. Series of Al2p spectra were then collected from the respective O-saturated Al_2O_3 films at different electron detection angles by rotating the sample under the incident synchrotron X-ray beam (fixed light source/analyzer angle, photon energy $h\nu = 687.5 \text{ eV}$).

All spectra were taken with an Omicron EA125-5MCD analyzer at 10 eV pass energy. Due to the narrow bandwidth of the synchrotron radiation ($\Delta E/E < 10^{-4}$) the energy resolution of the Al2p spectra is very high despite fully open detector slits (setup optimized for fast kinetic data acquisition in 'real-time'), which easily discriminates emission signals from the oxide overlayer (Al^{3+}) at 612.6 eV and the metallic NiAl substrate (Al^0) at ~615 eV KE; even the small spin-orbit splitting of the $\text{Al}2p_{1/2}$ and $\text{Al}2p_{3/2}$ doublet (0.4 eV) is duly resolved (Figs.1+2).

Results and discussion

Figures 1 and 2 show the take-off angle series of the Al2p signals recorded after oxidizing the NiAl(100) surface to saturation with at 400 K with doses of $3.12 \times 10^{17} \text{ O}_2 \text{ molecules/cm}^2$ and $9.3 \times 10^{16} \text{ H}_2\text{O molecules/cm}^2$. The smaller molecular H_2O dosage to achieve saturation reflects the higher reactivity of H_2O versus O_2 that corresponds to the 'acceleration' of the oxidation as mentioned above.

Comparison of the spectra in Figs. 1 and 2 clearly shows that H_2O oxidation leads to a stronger attenuation of the substrate Al^0 peak and higher Al^{3+}

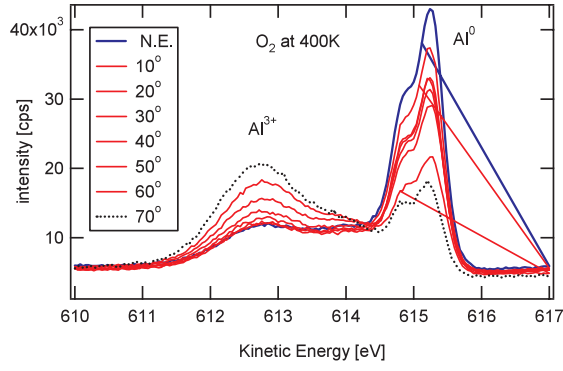


Fig.1 Take-off angle series of Al2p spectra recorded after O-saturating NiAl(100) at 400 K with O₂

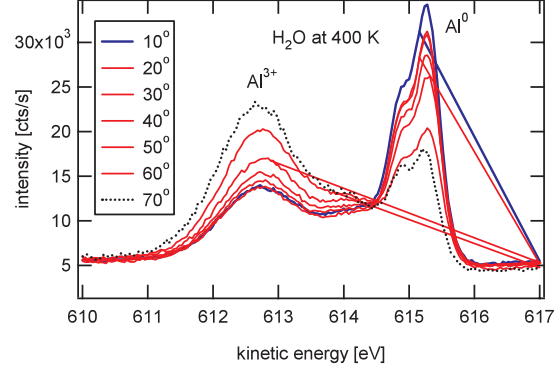


Fig.2 Take-off angle series of Al2p spectra recorded after O-saturating NiAl(100) at 400 K with H₂O.

intensities than O₂. We can thus conclude that the much faster oxidation by H₂O yields also slightly *thicker* oxides than O₂, in qualitative agreement with the expectations of the Cabrera-Mott oxidation mechanism outlined above. Consistent with the reduced thermal stability of surface OH groups (between 400 K and 500 K the OH coverage reduces by a factor of 2), this effect is smaller, yet noticeable, also at 500 K.

In both spectrum series the oxidic Al³⁺ signal increases and the substrate Al⁰ peak is attenuated as the take-off angle is varied from normal emission to grazing exit, which naturally results from the finite escape depth of the Al2p photoelectrons ($\lambda \sim 13$ Å at 615 eV) [3]. In a more quantitative analysis, the angular dependence of the Al⁰/Al³⁺ intensity ratio will be used to evaluate the oxide thickness d . At the present (preliminary) stage we simply note from Fig. 3 that the Al⁰/Al³⁺ intensity ratio is always larger for the O₂-grown oxide, which qualitatively indicates that this oxide is thinner than the Al₂O₃ film grown from H₂O. A quantitative analysis will follow.

We previously observed an accelerating effect of H₂ and atomic H on the O-uptake rate (2004B0566-NSa-np-Na). These measurements were performed at a comparatively low O₂ flux (5.2×10^{13} cm⁻²s⁻¹) and rather a high H₂ pressure of 1×10^{-4} Pa. However, under conditions of the present

experiments with a high O₂ flux (5.2×10^{14} cm⁻²s⁻¹) and H₂ pressures $\leq 1 \times 10^{-5}$ Pa, a heated W-filament near the sample surface to provide atomic H did influence neither the oxide properties nor the oxidation kinetics noticeably. Due to the different experimental conditions we cannot conclude decisively at the present stage, whether the previously observed catalytic hydrogen effect was simply not reproduced due to an insufficient flux of atomic H arriving at the growing Al₂O₃ surface in the present measurements, or if the H₂ gas may have been contaminated with highly reactive H₂O impurities in the former machine time.

The above experiments were performed with the aim to address the fundamentally interesting question whether OH groups on the Al₂O₃ surface would have a similar accelerating effect on the oxidation rate, if the hydrogen was supplied as atomic H rather than

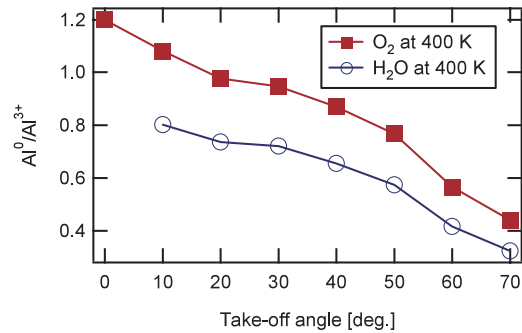


Fig.3 Take-off angle dependence of the Al⁰/Al³⁺ intensity ratio for NiAl(100) oxidized at 400 K with O₂ and H₂O, respectively.

from H_2O , hence whether the negative charge stabilization in the surface would differ between O adatoms and OH. Moreover, due to different electron affinities of O and OH, a different tunneling efficiency of electrons originating from the $\text{Al}^0 \rightarrow \text{Al}^{3+}$ oxidation at the interface may be expected. Provision of atomic H is the only experimental way to elucidate this problem, as equal coverages of O and OH are otherwise probably impossible to establish due to the unknown and apparently largely different sticking coefficients of O_2 and H_2O molecules. Only if any perturbations of the kinetic O-uptake measurements by traces of highly reactive H_2O impurities from the UHV background can successfully be suppressed, this fundamentally interesting aspect of the oxidation mechanism can be further investigated.

References

- [1] N. Cabrera, N.F. Mott, Rept. Progr. Phys. **12** (1948) 163.
- [2] M. Wilde, K. Fukutani, K. Moritani, Y. Teraoka, A. Yoshigoe, to be published.
- [3] M.P. Seah and W.A. Dench, Surf. Interface Anal. **1** (1979) 2.

Presentations at Conferences

M. Wilde et. al., IVC-16/ICSS-22/Nano-8, Venice, Italy, June 28-July 02, 2004.

M. Wilde et. al., ISSS-4, Omiya, Japan, November 14-17, 2005.