酸素と水を用いた NiAl(100)表面酸化による Al_2O_3 超薄膜形成のキネティクスと構造

Growth Kinetics and Properties of Ultra-Thin Al_2O_3 Films on NiAl(100) Obtained by O_2 and H_2O Oxidation

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酸素と水を用いた NiAl(100) 表面での Al_2O_3 超薄膜形成過程を，X 線光電子分光（XPS）により調べた．酸素分子で酸化した場合，試料温度 800K では良質のθ-Al_2O_3 が形成されるのに対して，500K 以下では欠陥が多く秩序性の低い Al_2O_3 が得られることがわかった．また成長速度と飽和膜厚は基板温度に依存しないことがわかった．これは界面からの Al 原子の供給が酸化膜成長の律速となっていることを示している．500K で水分子を用いて酸化した場合，酸素分子に比べて酸化速度は遅くなることがわかった．XPS の解析を行ったところ，Al と O の局所的な配位構造の観点からは欠陥密度の低い酸化膜が形成されていることがわかった．表面水酸基と酸化膜形成との関係について議論する．

The growth kinetics of ultra-thin Al_2O_3 films on NiAl(100) at 400-800 K were investigated by means of synchrotron X-ray photoelectron spectroscopy during exposure of the NiAl(100) alloy to molecular beams of O_2 or H_2O. A well-ordered, crystalline film of θ-Al_2O_3 results from oxidation at 800 K with O_2, while amorphous, defect-rich Al_2O_3 is obtained at 400-500 K. The nearly temperature-independent oxygen uptake kinetics and saturation thickness of the oxide layer are indicative of self-limiting growth driven by oxidation of Al at the oxide/alloy interface followed by field-enhanced diffusion of Al ions to the oxide surface. The same mechanism appears to be operative also for H_2O oxidation at 400 K, resulting in oxide films very similar in quality and thickness to the oxidation product of O_2. At an intermediate temperature of 500 K however, the rate of the oxygen uptake is found to be significantly reduced during H_2O oxidation. These H_2O-based Al_2O_3 films are characterized by a substantially lower defect density in terms of O/Al ion coordination. The retarding effect of H_2O on the oxidation kinetics at 500 K is discussed in relation to the strongly temperature-dependent concentration of surface hydroxyl (OH) groups on the oxide.

Introduction

The present study is motivated by a recent report that ordered Al_2O_3 films of equal thickness and comparable phonon spectra can be obtained by oxidation of NiAl(100) with O_2 as well as with H_2O as oxidant [1]. The only apparent difference is that the oxide surface is hydroxylated in the latter case, i.e. covered by OH groups as a result of H_2O dissociation. We therefore investigate the oxidation of NiAl(100) to Al_2O_3 by H_2O opposed to O_2 in order to clarify whether these surface hydroxyl groups might influence the oxidation process. The oxidation temperature will be the key parameter since vibrational spectroscopy [1] as well as our recent results from hydrogen-sensitive ^{15}N Nuclear Reaction Analysis (NRA) indicate that the surface OH concentration on Al_2O_3/NiAl(100) is strongly temperature-dependent in the 300-600 K range [2]. Consequently we studied first the temperature dependence of the oxidation kinetics with O_2 using fast high-resolution synchrotron X-ray photoelectron spectroscopy (XPS) to obtain insight into the oxidation mechanism and to assess the quality of the resulting oxide films. In a second step we compare these results to the oxidation in H_2O at 400-500 K, where significant surface hydroxylation can be expected [2].

Experimental

The in-situ cleaned NiAl(100) surface [1] was exposed to molecular beams of the oxidants (O_2, H_2O) while monitoring the progress of the oxidation reaction via the O1s, Al2p and Ni3p emissions with XPS after certain time intervals. The impingement rate of O_2 (H_2O) molecules on the sample surface was equivalent to pressures in the 10^{-7} mbar order (1.6×10^{14} $cm^{-2}s^{-1}$), while the background in the XPS chamber of the surface chemistry experimental station (Surface Reaction Analysis Apparatus:SUREAC2000) on BL23SU did not exceed 3×10^{-9} mbar with the beam on. The photon energy of 688.0 eV was chosen to probe the O1s emission from the entire oxide film up to its saturation thickness of 1.0 nm in normal emission.

Results and discussion

Oxidation of NiAl(100) in O_2 at 800 K produces well-ordered *crystalline* θ-Al_2O_3, characterized by a slightly streaky (2×1;1×2) LEED pattern [1,3]. XPS spectra of this Al_2O_3 film show a symmetric O1s emission line of O^{2-} and oxidized Al^{3+} in addition to attenuated metallic Al^0 and Ni signals of the underlying alloy substrate. At no stage of the film growth we observe oxidation of Ni, which is consistent with preferential oxidation of Al due to the much larger thermal stability of Al_2O_3 compared to NiO and diffusion of excess Ni into the NiAl substrate [3].

At the lower reaction temperatures of 400 K and 500 K the oxidation in O_2 yields *amorphous* Al_2O_3 exhibiting diffuse LEED illumination and an asymmetrically broadened O1s emission line in XPS (Fig. 1a), which is shifted by ~0.5 eV

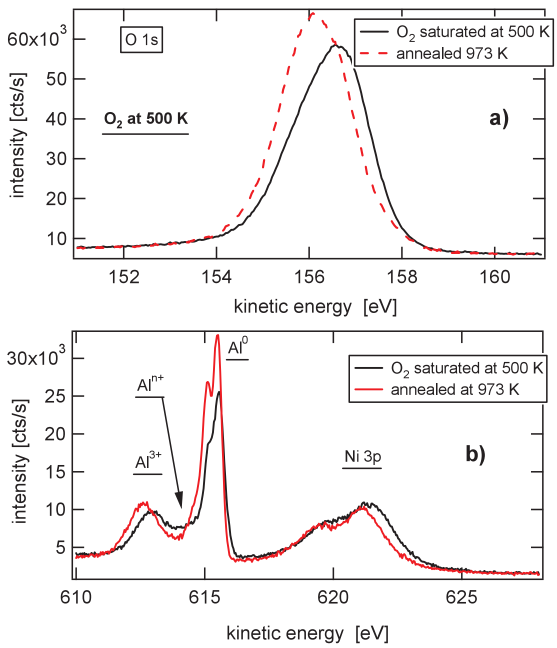

Fig. 1 a) O1s, b) Al2p/Ni3p photoemission spectra of Al_2O_3/NiAl(100) obtained by O_2 saturation at 500 K and after annealing at 973 K. hν=688 eV.

towards lower BE against the O1s spectrum of crystalline Al_2O_3. In the Al2p/Ni3p spectra of O_2-saturated NiAl(100) (Fig. 1b), intermediate Al^{n+} oxidation states appear in addition to similar low BE shifts of all signals, which suggest that the origin of the latter is due electrostatic effects caused e.g. by trapping of positive charge at oxide defects during photoemission. We also attribute the intermediate oxidation states of Al and the O1s BE shift to values below O^{2-} to defects of reduced O^{2-}/Al^{3+} ion coordination. As indicated by the disappearance of the Al^{n+} states and the conversion of the O1s line into a symmetric shape at 156.16 eV KE (as for crystalline θ-Al_2O_3), such defects are removed upon annealing the oxide to T≥973 K.

The Al_2O_3 growth kinetics were analyzed on the basis of O1s spectra series such as exemplary shown in Fig. 2a for O_2 oxidation at 500 K. Nearly *identical* O-uptake curves (Fig. 2b,

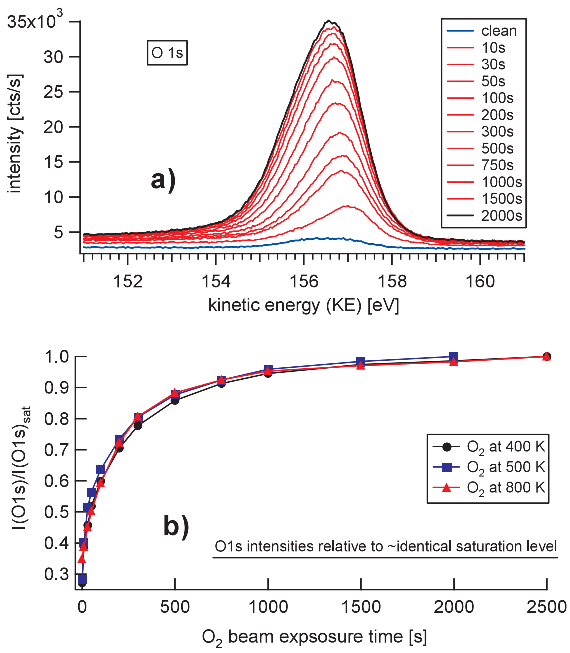

Fig.2 a) Uptake series of O1s spectra during oxidation at 500 K in O_2. Note the asymmetric line shape indicative of high defect densities in the growing Al_2O_3 film. b) O-uptake kinetics from O_2 at 400 K, 500 K and 800 K

obtained from O1s spectra integration) for the three oxidation temperatures (400 K, 500 K, 800 K) reveal that the oxide thickness at saturation and the uptake kinetics are *independent* of the oxidation temperature in the 400-800 K range.

These observations are compatible with an oxidation mechanism [4], in which Al is oxidized at the alloy/oxide interface by transferring its electron(s) to O adsorbed on the oxide surface, creating an electric field between O^{2-} and Al^{n+} that enhances the diffusion of the Al ion to the surface, where it can dissociate further O_2. Due to the field-(not concentration gradient-)driven Al^{n+} diffusion through the oxide layer the oxidation speed is temperature-independent. The growth then stops after a critical thickness of the insulating oxide prevents the electron tunneling.

In order to clarify which possible influence surface OH groups might take in this scenario, the oxidation was performed with H_2O at 400 K and 500 K, respectively, which according to our recent H-sensitive ^{15}N NRA study [2] changes the strongly T-dependent degree of hydroxylation of the Al_2O_3 film surface by a factor of ~2.

The O-uptake curves in Fig. 3 indicate that the oxide growth at 400 K in O_2 and H_2O proceeds by almost identical kinetics and leads to equivalent film thickness at saturation for both

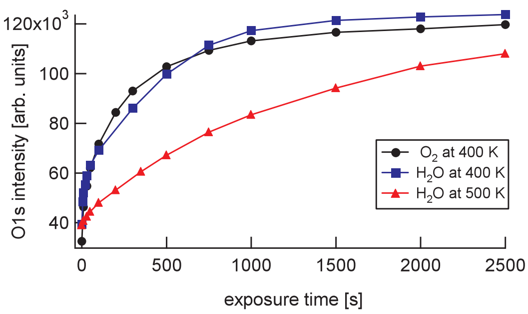

Fig.3 O-uptake kinetics during H_2O oxidation at 400 K and 500 K versus O_2 oxidation at 400 K.

oxidants, despite OH groups present on the Al_2O_3 surface during H_2O oxidation. In both cases defect-rich, amorphous Al_2O_3 is formed. This demonstrates that there seems to be no principal difference within the above Mott-Cabrera oxidation mechanism [4], as to whether the oxidant on the growing Al_2O_3 surface is present as dissociated oxygen or in the form of OH. We have verified with ^{15}N NRA that no H is built into the Al_2O_3 film during H_2O oxidation [2], which implies that the hydrogen contained in the surface OH groups is released - probably as H_2 - in the course of the oxidation reaction.

Oxidation in H_2O at 500 K, on the other hand, proceeds by a significantly slower O-uptake (Fig. 3) and yields Al_2O_3 of much improved ion coordination, as suggested by the symmetrical O1s line in Fig. 4, which even resembles the growth of *crystalline* θ-Al_2O_3 at 800 K in O_2, and by the absence of Al^{n+} in corresponding Al2p spectra. The LEED pattern however is without structure as for O_2 oxidation, showing that the oxide still lacks long-range order. Whether the improved nearest-neighbor coordination of the O/Al ions in the H_2O grown oxide at 500 K is simply a consequence of the slower O-uptake (Fig.3), providing more time for ordering, will be subject of further experimental investigation.

A possible explanation for the retarded oxidation may be the lower stationary OH coverage the on Al_2O_3 film during H_2O oxidation at 500 K, which will be reduced by ~50% as compared to 400 K [2]. Hence the tendency of OH to desorb as H_2O, which might be more likely than the recombination of adsorbed O atoms, may be regarded as a competitive reaction pathway that diminishes the surface oxidants and thus reduces the probability of Al oxidation by H_2O at 500 K.

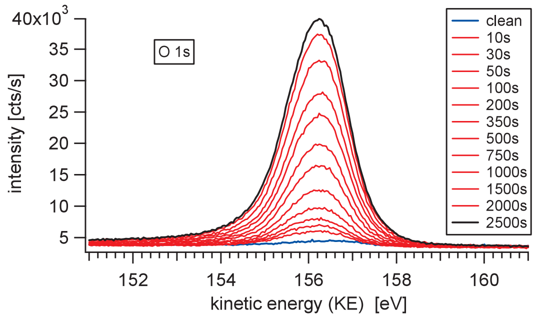

Fig.4 Uptake series of O1s spectra during oxidation at 500 K in H_2O. Note the symmetric line shape indicative of low defect densities in the Al_2O_3 film and that there is no indication of hydroxlation.

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Presentations at Conferences

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