Oxidation of epitaxial Y(0 0 0 1) films

M. Ay\textsuperscript{a}, O. Hellwig\textsuperscript{b}, H.W. Becker\textsuperscript{c},
B. Hjörvarsson\textsuperscript{d}, H. Zabel\textsuperscript{e,}\textsuperscript{*}

\textsuperscript{a}Laboratory for Neutron Scattering ETH & PSI, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
\textsuperscript{b}San Jose Research Center, Hitachi Global Storage Technologies, San Jose, CA 95135, USA
\textsuperscript{c}Ruhr-Universität Bochum, Fakultät für Physik und Astronomie, Institut für Ionenstrahlphysik, 44780 Bochum, Germany
\textsuperscript{d}Department of Physics, Uppsala University, S-751 21 Uppsala, Sweden
\textsuperscript{e}Ruhr-Universität Bochum, Fakultät für Physik und Astronomie, Institut für experimentelle Festkörperphysik, 44780 Bochum, Germany

Received 12 September 2007; received in revised form 28 October 2007; accepted 29 October 2007

Abstract

We have investigated the oxidation behavior of MBE grown epitaxial Y(0 0 0 1)/Nb(1 1 0) films on sapphire (1 1 2 0) substrates at elevated temperatures under atmospheric conditions with a combination of experimental methods. At room temperature X-ray diffraction (XRD) reveals the formation of a 25 Å thick YO\textsubscript{x}H\textsubscript{y} layer at the surface, while simultaneously oxide growth proceeds along defect lines normal to the film plane, resulting in the formation of a single crystalline cubic Y\textsubscript{2}O\textsubscript{3} (2 2 2) phase. Furthermore, nuclear resonance analysis (NRA) reveals that hydrogen penetrates into the sample and transforms the entire Y film into the hydride YH\textsubscript{2} phase. Additional annealing in air leads to further oxidation radially out from the already existing oxide channels. Finally material transport during oxidation results in the formation of conically shaped oxide precipitations at the surface above the oxide channels as observed by atomic force microscopy (AFM).

© 2007 Elsevier B.V. All rights reserved.

Keywords: Oxidation; X-ray scattering; Nuclear resonance analysis

1. Introduction

The oxidation and corrosion behavior of metals on an atomic scale is of general interest in order to understand and to control oxidation processes and oxide structures [1,2]. Especially important is the use of various metal oxides as protective layers against further oxidation or corrosion [3,4]. For the protection of metals a variety of capping mechanisms have been established, such as the chemical vapor deposition of coatings [5] or thick laser coatings [6]. However, the natural growth of thin oxide layers on metals, preventing further oxidation due to its passivating character, such as in the case of Al, Cr, Ni, and Zn, is the most effective form of protection [7,8]. For magneto-electronic devices with ultra thin oxide tunneling barriers it is of utmost importance to control the oxidation process on the atomic scale [9,10]. Metal oxides are also of great importance in the area of heterogeneous catalysis [11–13]. Moreover, oxide layers have been used as diffusion barriers in X-ray multilayer mirrors for very high thermal stability [14–16]. Finally, surface oxidized yttrium films have been used as an indicator layer for hydrogen uptake [17].

Yttrium is a metal, which shows rare earth (RE) like structural properties, although the 4f-shell is empty. Therefore, Y is non-magnetic, which is the main difference compared to the rare earth metals. The crystalline growth of Y in hcp-structure with lattice parameters of $a = 3.6474$ Å and $c = 5.7306$ Å [18] resembles that of RE metals. Therefore, Y has often been used as a spacer layer in RE superlattices for the investigation of long-range interlayer exchange or RKKY coupling [19–22]. Yttrium is also well known to dissolve hydrogen in its lattice structure [23]. Usually one observes three different possible hydrogen phases depending on the surrounding hydrogen pressure. Changing the external hydrogen pressure, a reversible transition in band structure and optical properties from a reflecting metallic conductor YH\textsubscript{2} to a transparent insulator YH\textsubscript{3} is observed. This behavior and its possible applications are currently subject of intense research [24–27]. In connection with these research efforts the corrosion...
behavior of Y cannot be ignored. The utilization of these effects are not possible until the growth of Y layers can be controlled on an atomic scale and the reaction with atmospheric gases and/or oxygen is fully understood.

Only few studies have been reported in the literature exploring the growth of thin Y films [28,29] and their oxidation behavior [30,31]. Huiberts et al. [30] have investigated the oxidation of polycrystalline Y films at room temperature (RT) conditions. Using RBS two different kinds of oxide formation could be identified. At the surface a continuous oxide layer (presumably Y2O3) of about 50 Å thickness forms and in addition oxide channels of more than 1750 Å deep into the Y layer were observed.

Van der Molen et al [31] have also studied the oxidation behavior of polycrystalline Y films at RT, however this time with Y films that were capped with Pd layers of varying thickness. For a 200 Å thick Pd overlay no oxygen but only hydrogen could penetrate through the capping layer and reach the Y film beneath. For thinner Pd cap layers of less than 50 Å thickness Pd islands are formed on the Y surface, which no longer protect Y from oxidation. RBS studies indicated an oxidation depth of up to 1500 Å in channels along Y grain boundaries.

Wildes et al. [32] studied epitaxial Y(0 0 0 1) layers (thickness 1000 Å) at RT, which were capped with a Au layer of varying thickness between 0 Å and 60 Å. For the uncovered Y film the pure Y(0 0 0 1) Bragg peak could be detected with X-ray diffraction (XRD). In addition, a roughly 50 Å thick oxide layer was determined with RBS methods. However, preferential diffusion of oxygen along grain boundaries, as reported for polycrystalline films, was not observed. With increasing thickness Au-islands form on the Y surface that promote a thicker oxide layer and an increased hydrogen concentration in the Y film. Finally at 60 Å Au thickness a coexistence of the dilute lattice gas α-phase YH4 and the hydride phase YH2 was observed by X-ray scattering. RBS measurements revealed an oxide layer thickness of about 600 Å at the surface. But no oxide related Bragg reflections could be detected by XRD. The authors have therefore assumed that the oxide layer is in an amorphous state.

In the present study we report on the oxidation of thin single crystalline epitaxially Y(0 0 0 1) films grown on Al2O3 (1 1 2 0) substrates with a Nb(1 1 0) buffer layer. The choice of substrate and buffer is the same as in the study of Kwo et al. [33]. The oxidation was carried out in air from RT up to 600 °C. Thus we report here the first studies of the oxidation kinetics of Y(0 0 0 1) films at elevated temperatures.

2. Experimental

We deposited Y(0 0 0 1) films via molecular beam epitaxy (MBE) on epi-polished Al2O3 (1 1 2 0) substrates using Nb(1 1 0) as a buffer layer. The Al2O3 (1 1 2 0) substrates have a typical surface roughness of less than 3 Å determined by AFM, a miscut angle below 1°, and a mosaicity between 0.003° and 0.006°. The substrates were cleaned ultrasonically in acetone and ethanol and transferred into the MBE chamber with a base pressure of 1 × 10−10 mbar. Prior to the deposition the substrates were annealed at 1100 °C for 20 min. To optimize the quality of the Y films, a Nb(1 1 0) buffer layer was deposited at 900 °C with a rate of 0.3–0.5 Å/s and annealed for 20 min at 950 °C [34,35]. Subsequently, after cooling the sample down to 500 °C, the Y film was deposited likewise at a rate of 0.3–0.5 Å/s. In situ reflectivity high-energy electron diffraction (E = 30 keV), low-energy electron diffraction, and ex situ XRD measurements are used to monitor the structure and crystal quality of the layers. The nominal thicknesses of the deposited Y films were in the range of 30–2000 Å.

After taking the Y-films out of the MBE chamber, an oxide layer forms at the surface immediately. This condition is referred to as the initial oxidation state at RT. After that the samples were heated in ambient air at elevated temperature for a defined time to reinitiate the oxidation process. Subsequent studies were carried out at RT, where the oxidation processes is kinetically limited, thus keeping the sample in a well-defined state during its characterization.

X-ray reflectivity (XRR), XRD, AFM, and nuclear resonance analysis (NRa) were performed at RT. XRR measurements provide information about the film thickness, the interfacial roughness and the electron density profile perpendicular to the film plane irrespective of the crystallinity of the sample via radial (θ–2θ) scans in the small-angle regime. High-angle radial scans at a reciprocal-lattice point (Bragg scans) provide information about the crystal structure and orientation of the films. Additionally transverse scans through the Bragg peak (rocking curves) reveal the out-of-plane mosaicity of the film. In thin film studies it is beneficial to compare the total thickness by thin film oscillations at low angle XRR scans (also called Kiessig fringes [36]) with the coherent film thickness expressed by Laue oscillations around high angle Bragg peaks. Any difference is due to a loss of crystallinity in the film structure [37]. If Laue oscillations cannot be resolved in XRD scans, the structural coherence length can also be determined from the FWHM using the Debye-Scherrer formula [38]:

\[ L_{coh} = \left( \frac{\ln 2}{\pi} \right)^{1/2} \frac{2\lambda}{\Delta(2\theta) \cos \theta} \]  

The X-ray measurements were carried out with the use of synchrotron radiation at the W1.1 beamline at HASYLAB (λ = 1.3937 Å) and with a rotating anode generator at the Ruhr-University in Bochum (Cu Kα radiation, λ = 1.542 Å).

For topographic properties AFM images were obtained in contact mode using an AFM from Park Scientific Instruments.

The depth dependent chemical properties have been studied via RBS and resonant backscattering (BS) methods. The principle of recording a depth-profile for hydrogen or oxygen is based on resonant nuclear reactions. For hydrogen profiling we used the nuclear resonance reaction \(^{15}\text{N} + ^{1}\text{H} \rightarrow ^{12}\text{C} + ^{1}\alpha + ^{\gamma}\text{gamma}\) with a proton resonance energy of \(E(1^{15}\text{N}) = 6.385\text{ MeV}\). For oxygen the resonant backscattering of alpha particles \((^{16}\text{O} + \text{energy} \rightarrow ^{16}\text{O} + ^{3}\alpha + ^{3}\text{He} + \text{energy})\) at a resonance energy of 3.045 MeV is employed. In both cases of NRA the ion beam
is first tuned to the resonance energy at the surface and scatters resonantly at surface atoms. By increasing the ion energy, ions loose surplus energy to match the resonance energy in deeper regions. The stopping-power is a measure for the loss of energy/unit length and depends on ion energy, ion mass, and target material. Thus with increasing energy the ions scatter resonantly in different regions below the surface with the reflection intensity being proportional to the corresponding atom concentration [39].

3. Results and discussion

3.1. Virgin Y(0 0 0 1) film

In Fig. 1 we show a XRR scan of an as-prepared Y(0 0 0 1)/Nb(1 1 0) film grown on a Al2O3 (1 1 2 0) substrate. Data were taken at room temperature under normal atmospheric conditions using synchrotron radiation with wavelength $\lambda = 1.3937$ Å. We find easily separable finite layer thickness oscillations (Kiessig fringes) due to the 60 Å Nb buffer layer as well as the 300 Å Y film. Bragg-scans (Fig. 2b) along the growth direction show the sapphire substrate (1 1 2 0) and the Nb (1 1 0) reflection from the buffer layer. In addition, we observe the Y(0 0 0 2) peak accompanied by Laue oscillations corresponding to a coherent layer thickness of 300 Å, which is identical to the total Y layer thickness as obtained from the Kiessig fringes in the XRR scan. Furthermore, we observe a sharp bcc Y2O3 (2 2 2) Bragg reflection and a broad Y(OH)3 component (see Fig. 2a). The Gaussian fits to the line profiles confirm two different thicknesses for Y2O3 and Y(OH)3. The peak positions are in accordance with the published crystal structures [40]. The broad component is shifted slightly to higher $q_z$-values, indicating a depletion of the Y(OH)3 lattice. The Laue oscillations, which can be recognized around the Y(OH)3 peak, correspond to a layer thickness of 25 Å (see Fig. 2c). Using Eq. (1) the coherence length normal to the Y2O3 film (sharp component) could be determined to 300 Å (Fig. 2a), revealing that the thicknesses of the Y2O3 and the Y-films are roughly the same. Because of the depletion in the Y(OH)3 layer, we will refer to it as YOxHx. From the X-ray measurements follows that Y-oxide domains locally penetrate through the entire film thickness (oxide channels), while additionally a uniform 25 Å YOxHx layer develops on top. AFM measurements on the Y(0 0 0 1) surface reveal a roughness of about 7 ± 3 Å in agreement with previous results by Krause et al. [41]. A simplified structural model for this film is shown schematically in Fig. 8a. In air and at RT this state is apparently stable. However, the oxidation rate may be just extremely slow. Burnham and Jameson described the oxidation kinetics of yttrium by a direct logarithmic rate law with an initial growth rate of 2.5 nm/month [42].

3.2. Oxidation of Y(0 0 0 1) at high temperatures

3.2.1. X-ray measurements

To continue the oxidation process, the samples were post-annealed in air at 300 °C. The subsequent X-ray characterization was performed at RT. Fig. 3 shows a sequence of Bragg-scans taken after successive oxidation steps during time intervals as indicated in the figure. Fig. 3a displays the Bragg-scan of the virgin sample after exposing it to air. This scan is identical to the one shown in
In the first oxidation step at 300°C for 5 min (Fig. 3b) the Y(0 0 0 2) peak shifts to a position corresponding to the YH_x alpha-phase (hydrogen lattice gas) and a new peak occurs corresponding to the YH_2 beta-phase in fcc (1 1 1) direction. Despite increasing scattering intensity no well-defined and coherent oxide thickness can be recognized, which is explained later via ion scattering. The original Bragg reflections of the two oxides (Y_2O_3/YO_xH_x) are no longer visible. After the second oxidation step at 300°C for 0.5 h (Fig. 3c) the YH_x alpha-phase peak has vanished and the YH_2 beta-phase peak intensity has increased further indicating that the transformation from Y into YH_2 via the intermediate YH_x alpha-phase is completed. In addition new YOOH_x and Y_2O_3(2 2 2) reflections appear. Moreover we find that the hydrogen continues to diffuse into the Nb buffer layer thus causing a lattice expansion as indicated by the shift of the Nb(1 1 0) reflection to smaller scattering vectors. The penetration of hydrogen into Y and Nb is also confirmed by NRA measurements. The YOOH_x compound originates from H_2O, which reacts with the Y at the sample surface. Probably due to the size, OH^- ions cannot penetrate into the sample. Therefore, a crystalline YOOH_x compound forms at the surface, and its increasing thickness can be followed by the respective Bragg reflection. Further annealing (scan d.~f. Fig. 3) triggers additional oxidation of YH_2 and YOOH_x into Y_2O_3. The YH_2 peak vanishes and the YOOH_x peak decreases, while the intensity of the Y_2O_3 reflection increases.

Fig. 4 shows a Bragg scan of a 400 Å Y(0 0 0 1)/200 Å Nb(1 1 0)/Al_2O_3(1 1 2 0) film oxidized at 400°C for 6 h (completely oxidized). Due to the hydrogen lattice gas formation the Y_2O_3 and Nb lattices are expanded in out-of-plane direction by about 0.45% and 4%, respectively.

3.2.2. Ion scattering
NRA methods were used to confirm the hydrogen diffusion as the origin of the lattice expansion in the Y_2O_3 and Nb after the final oxidation step as seen in Fig. 4. In Fig. 5 we show the hydrogen-depth-profile obtained from the 15N resonance method. Starting from 6.34 MeV the intensity increases over the total Y_2O_3 film continuously until point (a) is reached. This point is equivalent to the Y_2O_3/Nb interface. Between the Y_2O_3/Nb and the Nb/Al_2O_3 interface (point (b)), the scan shows a maximum hydrogen concentration in the Nb lattice. At (b) the...
ion beam starts to penetrate into the substrate but the scattered hydrogen ion intensity is not instantly absent. Because of energy straggling, the ion beam reaches an energy distribution of $\pm 0.04$ MeV at the Nb/Al$_2$O$_3$ interface (between point (b) and (c)), which has to be very sharp due to the smooth interface. A fit to the RBS measurements (not shown here) indicates a relative proportion of Y:O:H of 2:3:1 and the hydrogen-depth-profile verifies an increasing hydrogen concentration in the Y$_2$O$_3$ until the interface to the Nb is reached. In the Nb film the hydrogen concentration stays constant on a high level. The proportion of oxygen in Nb measured with RBS is 1:100, strongly indicating that the shift of the Nb Bragg reflection is not induced by oxygen but by hydrogen, which confirms earlier work on the oxidation of Nb [43–45].

In order to gain further information on the oxygen distribution during oxidation we performed an oxygen depth profile analysis using the oxygen resonance BS method for a 2300 Å Y(0 0 0 1)/400 Å Nb(1 1 0)/Al$_2$O$_3$ (1 1 2 0) sample that was oxidized for 5 min at 400 °C. The corresponding depth profile is shown in Fig. 6. Because of the energy distribution of the incoming ion beam and because of surface oxide precipitates forming on the surface (see below) an increase of the scattered intensity is observed around the resonance energy of 3045 keV in the range from 3020 keV up to 3060 keV. Between 3060 keV and 3085 keV (up to line (a)) the constant intensity corresponds to the Y$_2$O$_3$ that forms the surface layer. The energy at point (a) corresponds to the surface oxide/Y interface. If the sample only had a surface oxide layer, the intensity would rapidly decrease with increasing energy. Instead a gradual decrease between 3085 keV (point (a)) and 3165 keV (point (c)) is observed. At point (b) the Y/Nb interface is reached and point (c) can be identified with the Nb/Al$_2$O$_3$ interface. At (c) the ion beam with an energy distribution of $\pm 17.5$ keV starts to penetrate into the substrate and therefore the intensity increases again until all ions reach the resonance energy in the Al$_2$O$_3$ substrate at point (d). The gradual decrease of the oxygen concentration from the surface oxide to the bottom layer is a strong indication for the formation of a laterally heterogeneous network of oxide channels that develops along defect lines in the Y.

3.2.3. Surface morphology

AFM measurements supply information about surface morphology and surface roughness (rms). The as prepared Y(0 0 0 1)/Nb(1 1 0)/Al$_2$O$_3$ (1 1 2 0) samples exhibit a surface roughness of about 7 ± 3 Å [26,41].

After heating the Y(0 0 0 1)/Nb(1 1 0)/Al$_2$O$_3$ (1 1 2 0) samples with Y film thicknesses of 300 Å, 500 Å, and 2000 Å at 400 °C for 15 h, a completely oxidized quasi-equilibrium state has been reached. Fig. 7 shows the AFM images of these three completely oxidized Y samples. In the AFM image of the nominally 300 Å thick Y film (Fig. 7a) we recognize conical shaped oxide precipitates of about 200 Å height with a lateral base diameter of about 1500 Å. In Fig. 7b a nominally 500 Å thick Y layer features 280 Å high precipitates with a base diameter of about 4000 Å. For the nominally 2000 Å thick Y film shown in Fig. 7c the precipitates overlap, whereby isolated peaks with well-defined height and diameter are hardly recognizable. The form and shape of the conical peaks, which form upon oxidization of the Y films, clearly depends on the initial Y-film thickness. Thin films lead to small
and isolated precipitate peaks, whereas in thicker films the peaks coalesce and pile up. The oxidation of Y films along grain boundaries requires perpendicular material transport, which is seen as overgrowth in form of conical shaped precipitations. The opening angle of the conical precipitates increases until the oxide growth front reaches the Y/Nb interface and the oxidation of the Y is complete. Thin films require less material transport than thicker films and therefore the precipitates are smaller in diameter, more uniform in size and shape, and separated from each other.

4. Discussion and conclusion

From X-ray reflectivity and Bragg-scans it can be concluded that after exposure to atmospheric conditions at RT, Y(0 0 0 1) forms lateral oxide precipitates that pierce through the entire Y-film thickness (oxide channels) and that coexists with a 25 Å thick laterally uniform YOxHx surface layer.

Continued oxidation at elevated temperature occurs at the interface between Y/Y-oxide. Lateral oxide growth proceeds faster at the surface than in deeper regions due to the increased diffusion length of oxygen at the surface. Due to this mechanism oxide channels develop a conical form that result in an oxygen gradient normal to the film plane. First Y2O3 forms along deep channels and expands laterally (Fig. 8a), resulting in randomly distributed conical shaped oxygen precipitates. The oxygen depth profile of a partly oxidized sample confirms a gradual decrease of the oxygen intensity with increasing penetration depth. At the same time hydrogen penetrates into the sample and transforms the entire Y film into the hydride YH2 phase.

Hydrogen continues diffusing into the Nb film, thus causing a lattice expansion of up to 4% in the Nb buffer layer. After hydrogen-saturation is reached in the Y layer, oxidation advances at the YH2/Y2O3 interface (Fig. 8b). Small arrows indicate the oxide growth direction at the boundary of the conical channels. The large arrow indicates that previously formed oxide is now pushed to the surface, where it forms oxide precipitates on top of the oxide layer. Hydrogen and oxygen depth profiles reveal that hydrogen diffuses through the Y-oxide layer into the Nb buffer, while oxygen transport stops at the Y/Nb interface.

In closing, we would like to remark that the role of hydrogen and its interaction with metal oxides in general and more specifically with yttrium oxides is of high relevance for the heterogeneous catalysis [46,47] and for hydrogen storage [48]. In this context it is interesting to note that surface oxidized yttrium is capable of splitting water.

Acknowledgements

We would like to thank W. Caliebe and O. Seeck (HASYLAB, Hamburg) for their assistance during measurements at the
HASYLAB and K. Westerholt and K. Theis-Brohl for valuable discussions.

References