Real time observation of ultrathin epitaxial oxide growth during alloy oxidation*

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Abstract. We have studied the thermal oxidation of the intermetallic alloy CoGa in situ, in real time on the atomic scale, during the growth of an ultrathin, epitaxial Ga oxide layer. On the basis of an extended set of surface x-ray diffraction data, density functional theory calculations and core level spectroscopy data, we find that the oxide film consists of an oxygen ion double layer, which contains the basic building block of bulk β-Ga₂O₃. The oxide formation takes place via the nucleation of two-dimensional, anisotropic oxide islands which laterally grow and coalesce. A dramatic increase of the oxide island size is observed for low O₂ pressures in the 10⁻⁸ mbar regime, which we interpret as the onset of a step flow like growth mode. This allows us to conclude that thermal oxidation can be considered as a hetero-epitaxial growth process, that follows similar atomistic growth principles to molecular beam epitaxy. As a consequence, the structural perfection of the oxide layer can be tailored by the appropriate choice of oxygen pressure and temperature.

* We write this paper in memorial to René Franchy [1].
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The oxidation of technologically relevant alloys like, e.g. steel, is a rather destructive and undesired process, leaving behind a more or less destroyed surface, which loses its optical and mechanical properties. In contrast, by the selective oxidation of alloys under controlled conditions the formation of very well ordered, epitaxial oxide films with a thickness in the sub-nanometre regime can be observed [2]. These oxide films are atomically flat and possess a homogeneous chemical composition in addition to an abrupt interface to the alloy substrate. These properties make them attractive as insulating barriers for organic field effect transistors [3] or as tunnel barriers in tunnelling magneto-resistance (TMR) devices [4]. In addition, they serve as non-charging substrates for the investigation of nano-systems on oxide surfaces, like metal particles or big organic molecules, by electron based surface science techniques [5]. As a prerequisite for all applications, a precise structural and chemical analysis of the oxide films is mandatory, as well as an *in situ* characterization of the oxide growth process, which is still poorly understood. This is frequently hampered by the complexity of the evolving oxide structures and their unknown chemical composition.

To shed light on the very initial oxide growth stage, we have studied the oxidation of a CoGa(100) single crystal surface; Ga oxide films are discussed as promising candidates for TMR barriers and as gas sensors [2]. Previous studies gave insight into Cu–Au and Co–Ni alloy oxidation on the sub-micrometre level [6, 7]. Here, we present a combined high resolution *in situ* surface x-ray diffraction (SXRD), density functional theory (DFT) and core level spectroscopy (CLS) study of the atomic scale oxide growth mechanism and the atomistic structure of the oxide layer during growth. In addition, the chemical composition of the metal/oxide interface is investigated.

We find that the oxide film consists of an oxygen ion double layer (O$_4^-$), which is the thinnest conceivable oxide film structure (see figure 1(b)). The two Ga ions are located in truncated octahedral and tetrahedral sites of the fcc oxygen ion sublattice. At the interface, two more Ga ions occupy sites of the corresponding stacking sequence of bulk $\beta$-Ga$_2$O$_3$ [8] (we will therefore use the notion Ga$_4$O$_4$ throughout the manuscript).

We followed the nanoscopic oxide layer growth *in situ* by spot profile analysis of an oxide x-ray reflection. From the time-dependent diffraction signal, a simple growth mechanism via two-dimensional (2D) island nucleation, lateral growth and coalescence was identified, which is exponentially slowed down when the layer is nearly completed. The average oxide island width and the time for the completion of one full layer depend strongly on the oxygen partial pressure, which is controlling the incoming oxygen particle flux. For oxygen pressures $>10^{-7}$ mbar, the mean island width does not depend on the oxygen pressure but on the sample temperature only. For pressures $\leq 10^{-8}$ mbar, a strong increase of the mean oxide island width is observed along with a decrease in the initial nucleation rate by a factor of 50. We interpret this as evidence for a transition from a predominantly on terrace nucleation of oxide islands at elevated pressures to a nucleation of oxide islands at step edges for pressures in the $10^{-8}$ mbar regime. Thus, we conclude that thermal oxidation can be considered as a hetero-epitaxial growth process that follows similar atomistic growth principles to molecular beam epitaxy (MBE). As a consequence, the structural perfection of the oxide layer can be tailored by the appropriate choice of oxygen pressure and temperature.

The x-ray experiment was performed in an *in situ* SXRD chamber on beamline ID32 at the European Synchrotron Radiation Facility (ESRF) at a photon energy of 20 keV. A complete structural analysis of the oxide film at different stages of the growth process was performed by the measurement of 16 symmetry inequivalent surface rods of the (2 × 1) superstructure and
Figure 1. (a) $\beta$-$\text{Ga}_2\text{O}_3$ bulk unit cell. The slab used for the refinement of the x-ray data is highlighted in the box. (b) View of the refined structure of the Ga$_4$O$_4$ layer on CoGa(100) along the (010) axis; the unit cell used for the x-ray refinement is indicated as a rectangle. (c) View of the oxide structure along the (100) axis. (d) Ga 3d and O 1s core level spectra after growth of a full $(2 \times 1)$ Ga$_4$O$_4$ layer. The experimental spectra are decomposed and the theoretical energy positions for the atoms a–j from (b) are indicated.

Four independent crystal truncation rods, which contain information on the registry and distance of the overlayer with respect to the substrate (in total 850 independent structure factors). The $(2 \times 1)$ superstructure forms after exposure to oxygen at temperatures above 500 K at $10^{-7}$ mbar O$_2$ [2, 9]. The time-resolved in situ experiments were performed on the MPI-MF beamline at the Angstrom Quelle Karlsruhe (ANKA) [10] at a photon energy of 10 keV using a mobile ultra high vacuum (UHV) SXRD chamber. Core level experiments were performed at beamline i311 at MAXLAB [11].

For the DFT calculations, we have used the Vienna ab initio simulation package (VASP) [12], employing the projector augmented wave method [13] and the local density approximation of Ceperley and Alder [14, 15]. The valence wave functions were expanded in a plane wave basis set with a kinetic energy cut-off of 400 eV. Brillouin zone integration was performed using grids of $(5 \times 9 \times 1)$ $k$-points in the $(2 \times 1)$ surface cell for all calculations. With this set-up we obtain a CoGa bulk lattice constant of $a_0 = 2.82$ Å (experiment: $a_0 = 2.87$ Å) and the bulk $\beta$-$\text{Ga}_2\text{O}_3$ lattice parameters $a = 12.15$ Å, $b = 3.02$ Å, $c = 5.76$ Å, and $\beta = 103.8^\circ$ (experiment: $a = 12.23$ Å, $b = 3.04$ Å, $c = 5.80$ Å, and $\beta = 103.7^\circ$). The CoGa (100) substrate was modelled by a slab of four Co and four Ga $(2 \times 1)$ layers. The bottom four layers were kept fixed, whereas the top four layers were allowed to relax. The oxide layers were placed on top of the relaxed side of the slab (asymmetric set-up). Periodic images were separated by at least 10 Å of vacuum.
Figure 2. Experimental x-ray diffraction structure factors (open circles) as a function of the reciprocal lattice coordinate $L$ perpendicular to the surface for different in-plane momentum transfers $(H,K)$ ($H \parallel (100)$ and $K \parallel (010)$, $a$ is the CoGa layer spacing$^6$). DFT model (green) and best fit structure (red) are also shown. Error bars are given by combined systematic and statistical errors.

The CoGa single crystal was oriented along the (001) direction better than 0.05°. Prior to oxidation, the sample was sputtered, annealed at 850 K and cleaned by oxidation at 700 K and $10^{-6}$ mbar $O_2$, until the clean surface exhibited the characteristic $c(4 \times 2)$ reconstruction and terrace sizes larger than 1000 Å [16]. For the surface structure determination, an oxide layer was prepared at 750 K and $5 \times 10^{-7}$ mbar $O_2$, which produces an oxide film with an average in-plane domain size of $\sim$100 Å. The oxide layer desorbs in UHV at 800 K. Figure 2 shows the set of x-ray structure factors together with the best fit (red curves) and the structure factor based on the most stable DFT model (green curves).

To find a starting model for the structure refinement, different slabs cut out of a Ga$_2$O$_3$ bulk unit cell, as depicted in figure 1(a), were considered and their calculated structure factor was compared to the x-ray data plotted in figure 2. $\beta$-Ga$_2$O$_3$ exhibits a monoclinic structure and it is the only known thermodynamically stable bulk phase of Ga oxide. In addition, it has a very small mismatch to the CoGa surface and is therefore a natural candidate for structural refinement [9]. First, the thickness of the oxide layer was determined by cutting slabs with different height out of the bulk Ga$_2$O$_3$ crystal, such that the calculated structure factor matches the finite film thickness oscillation period on the surface rods.

In the second step, all possible, differently terminated slabs with the same thickness were considered in the x-ray and DFT refinement. The best fit to the data was achieved by the slab highlighted in the bulk unit cell in figure 1(a), yielding a $\chi^2$ value of 1.05 (red curves in figure 2).

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$^6$ $H$, $K$ and $L$ are given in units of $2\pi/2.878$ Å.

New Journal of Physics 9 (2007) 331 (http://www.njp.org/)
Figure 3. (a) Inset: typical 2D diffraction pattern with lines of constant (H, K, L). H-scan (data points) and Lorentzian fit (red line). (b) (0.5,0) rod for different coverages, together with the calculated structure factor (red line) based on the structure given in figure 1. (c) Coverage as a function of oxidation time (upper part) and island width $W_0$ as a function of oxide coverage (lower part). Triangles correspond to data taken at 790 K, circles to data taken at 650 K. Data points plotted in red were taken at $10^{-8}$ mbar, in blue at $10^{-7}$ mbar and in green at $10^{-6}$ mbar. Solid lines represent fits to the corresponding data.

For the fit, an equal distribution of $(2 \times 1)$ and $(1 \times 2)$ domains, as well as mirror domains due to the monoclinic structure were included. The structural model (figures 1(b) and (c)) consists of an fcc-like oxygen ion double layer ($O_4$) with Ga ions occupying octahedral and tetrahedral sites, which is the key structural element of $\beta$-Ga$_2$O$_3$. The Ga ions at the interface occupy sites that follow the Ga$_2$O$_3$ bulk sequence [8]. Because of the low x-ray scattering contrast between Co and Ga, it is not possible to distinguish between Co and Ga termination at the interface from the fit of the x-ray data. However, the structure factors for a DFT relaxed structure with Co termination at the interface disagree significantly with the experimental structure factors. The structure factor for the most stable DFT model is plotted in figure 2 (green curves), exhibiting a remarkably good agreement between the theory and the experiment. The average deviation between the x-ray and DFT positions within the oxide film is 0.04 Å.

Furthermore, the calculated Ga 3d and O 1s core level shifts (including final state effects) for a fully relaxed structure with Ga interfacial termination are in good agreement with the experimental core level spectra, as plotted in figure 1(d). The Ga atoms ‘a’ and ‘b’ exhibit an interfacial core level shift of 0.15 eV to lower binding energies; for atoms ‘c’ and ‘d’ (‘e’ and ‘f’) a chemical shift of 0.54 eV (1.53 eV) to higher binding energies is observed. For oxygen, atoms ‘g’, ‘i’ and ‘j’ have a similar binding energy, whereas atom ‘h’ possesses a lower binding energy ($-0.6$ eV), giving rise to the experimentally observed two component lineshape of the O 1s level.
Having established the structural model for the ultrathin Ga$_4$O$_4$ layer on CoGa(100), we can now address a quantitative description of the growth mechanism of such a layer by SXRD. Using a 2D wired detector, we have characterized the line profile and intensity of the (0.5,1,0.4) oxide reflection in situ, during oxidation, in real time. The wired detector allows one to record an integral signal of the whole spot simultaneously to the 2D diffraction images. The integral signal is proportional to the oxide surface coverage $\theta$, as plotted for different oxidation conditions as a function of the oxidation time $t$ in the upper part of figure 3(c). The temporal evolution of $\theta$ can be described by the simple equation

$$\frac{d\theta}{dt} = \frac{1}{\tau}(1 - \theta) \Rightarrow \theta(t) = 1 - e^{-t/\tau},$$

representing an exponentially slowed down growth close to $\theta = 1$ (see figure 3(c)). This indicates that the rate limiting step is most likely oxygen dissociation taking place only on the clean surface and not the surface oxide. The initial growth rate $1/\tau$ decreases strongly with oxygen pressure, but it exhibits only a weak temperature dependence. Evidence for a change in the growth mechanism comes from the detailed oxide peak profile analysis. A typical 2D diffraction pattern is plotted in figure 3(a) in the inset. Figure 3(a) represents a bar scan along the H direction, obtained after transformation of the detector image to reciprocal space [18]. These scans show a Lorentzian lineshape, which is characteristic for an exponential island width distribution $P(W) = \frac{1}{W_0}e^{-W/W_0}$ [19]. $W_0$ represents the mean island width parallel to (100) and H, which is the statistical quantity measured in our experiment. The island length (typically few 1000 Å [20]) is beyond the resolution in the K-direction, because of the horizontal focusing of the x-ray beam.

The analysis of the temporal evolution of the oxide peak profile is possible, because the structure and thickness of the oxide islands do not change during the oxide film growth. This is confirmed by a comparison of the rods after partial oxidation of the surface as exemplified for the (0.5,0) rod (figure 3(b)) and by the evolution of the O 1s core level spectra as a function of oxygen coverage (not shown). Figure 3(c) shows the average island width $W_0$ as a function of the oxygen coverage $\theta$. For both temperatures, we can now observe an $O_2$ pressure dependent splitting into two linear branches: at $10^{-6}$ mbar and $10^{-7}$ mbar $O_2$ pressure, the increase of $W_0$ as a function of $\theta$ is very similar, whereas for $10^{-8}$ mbar three times wider oxide islands are formed. The linear dependence of $W_0$ on $\theta$ corresponds to a constant island density, in-line with a classical nucleation and growth mechanism [21]. This points to similar nucleation mechanism for $10^{-6}$ mbar and $10^{-7}$ mbar $O_2$ pressure: the initial island density is set by the temperature dependent heterogeneous nucleation probability. In this pressure regime, the density of diffusing oxygen atoms is high enough to form critical oxide nuclei on the CoGa terraces and at step edges, growing laterally in size to cover the whole surface and giving rise to the monolayer growth mode. STM data suggest that nucleation takes place only at the step edges at low pressure, similar to a step flow like growth [9], inline with our observation of a lower island density at $p_{O_2} = 10^{-8}$ mbar and a concomitant larger island width $W_0$. In the limit $\theta \rightarrow 0$, $W_0$ yields a finite value of 10–20 Å, in agreement with 2–3 unit cell wide oxide stripes. Such a formation of critical nuclei was also observed by STM after low oxygen exposure [20].

An atomistic view of the scenario of the strongly anisotropic oxide growth is presented in figure 4. Oxygen is very likely supplied by dissociative chemisorption on the metal surface. The oxide grows much faster along the oxide (010) direction probably via the formation of parallel
Figure 4. Scenario for anisotropic Ga oxide growth on CoGa(100). Dissociatively chemisorbed oxygen and Ga adatoms are incorporated at the (010) island facets. The slow growth in the (100) direction takes place by the attachment of rows that, once added, extend rapidly along the (010) direction.

Ga–O–Ga chains, shifted relative to each other by half a substrate unit cell along the (010) direction. We exclude here an autocatalytic oxidation process, in which oxide islands serve as the main dissociation centers for oxygen, as was proposed for Pb particles [22], because in the pressure regime above $10^{-7}$ mbar, our data are inline with a statistical nucleation of oxide islands on the substrate terraces.

In conclusion, we have investigated the onset of oxidation in alloys in real-time on an atomic length scale. During the very initial oxidation of CoGa(100), an ultrathin Ga$_4$O$_4$ surface oxide layer is formed, which we also expect for different Co/Ga alloy compositions, because of the predominant heat of formation of Ga oxide [20]. We find that the growth evolves via well-known epitaxial growth modes, i.e. by 2D nucleation and growth. We observe an oxygen pressure dependent transition in the growth behavior accompanied by a strong increase of the mean oxide island and a strong decrease in the initial nucleation rate, which we interpret as a transition from heterogeneous oxide island nucleation on terraces to step edge nucleation. This is important for many applications involving ultrathin oxide films, which can be prepared by a very simple thermal oxidation treatment under controlled conditions, prevailing layers of extremely high degree of crystallinity and thickness uniformity, with tuneable thickness and structural perfection.

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