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Ultrathin alumina film on Cu–9at%Al(1 1 1)

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ABSTRACT

We have investigated the structure of the clean and the oxidized (1 1 1) surface of a Cu–Al alloy with 9 at% Al by scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), low energy ion scattering (LEIS) and low energy electron diffraction (LEED). Annealing of the clean crystal at 680 °C leads to segregation of Al to the surface. The Al concentration at the annealed surface is 23 ± 2% and domains with a $(\sqrt{3} \times \sqrt{3})R30°$ superstructure are visible, as well as small Cu(1 1 1) areas and disordered patches. Oxidation at 680 °C leads to the formation of a well-ordered flat alumina film with two very similar oxide structures. One oxide structure has a nearly commensurate rectangular cell rotated by 30° with respect to a close-packed row of the substrate and grows in three different domains. The second structure has a commensurate cell consisting of four equivalent building blocks and has a rectangular centered symmetry. This structure is rotated by 18° with respect to a close-packed row of the substrate and grows in six different domains. The rectangular building blocks of these two oxide structures have a similar thickness, the same surface termination and the same number and arrangement of the atoms as the oxide film on NiAl(1 1 0) [G. Kresse, M. Schmid, E. Napetschnig, M. Shishkin, L. Köhler, P. Varga, Science 308 (2005) 1448]. In contrast to the oxide on NiAl(1 1 0), alumina on the Cu–Al alloy crystal does not show stress-induced domain boundaries and grows in large defect-free domains. Thus, Pd deposited on this oxide nucleates not only on domain boundaries and steps but also on the unperturbed oxide, forming (1 1 1)-oriented clusters.

1. Introduction

Thin alumina films grown on various metal substrates are of interest for different technological applications. They are used in catalysis, for gas sensors, as coatings and in microelectronics. In research, a very common application is the use of thin alumina films on a metal substrate as a support for metal particles serving as model catalysts. Using such ultra thin oxide films eliminates charging problems when applying measurement methods involving charged particles. For well-defined and reproducible results, the alumina film has to be well ordered. Since more than two decades, many groups have attempted to find suitable substrates and recipes for growing such ultra-thin alumina films [1–7].

The Cu–Al(1 1 1) alloy with 9 at% of Al is one of the substrates where growth of a well ordered Al_2O_3 film was reported [8–10]. Concerning the clean (not oxidized) alloy, Auger electron spectroscopy (AES) measurements show an increase of the Al concentration at the surface when the crystal is annealed in ultrahigh vacuum (UHV) [11,12]. The different Al concentrations at the surface induce different superstructures, which are visible in low-energy electron diffraction (LEED) [11,12]. At low annealing temperatures the LEED pattern indicates a (1×1) structure which evolves to a diffuse $(\sqrt{3} \times \sqrt{3})R30°$ pattern at elevated temperatures. While the sample is at high temperatures, LEED shows a (1×1) pattern again. The temperature reported for the second reversible transition is between 227 °C [13] and 327 °C [11].

The high Al concentration at the surface, reported as 22% Al at the surface [12], should make it possible to grow a stoichiometric alumina layer. It was argued that the relatively small misfit of 6–8% between the close-packed O planes of α-Al_2O_3 or γ-Al_2O_3 and the Cu–9at%Al(1 1 1) lattice should facilitate epitaxial growth [8]. Recent studies [8–11] have reported the formation of 0.4–3.5 nm thick γ-Al_2O_3-like alumina films with a $(7/\sqrt{3} \times 7/\sqrt{3})R30°$ structure on Cu–9at%Al(1 1 1) after oxygen adsorption at temperatures between 577 and 725 °C, using rather high O_2 doses (1200–4000 L; $1\ L = 1.33 \times 10^{-6}$ mbar s). In these studies, AES, XPS (X-ray photoelectron spectroscopy), SEM (scanning electron microscopy), LEED and RHEED (reflection high energy electron diffraction) were used. As STM (scanning tunneling microscopy) measurements were missing for the clean surface as well as for the alumina-covered crystal, in our work we have focused on STM measurements.

We compare our findings on the alumina film grown on Cu–9at%Al(1 1 1) with the well-known thin alumina film on NiAl(1 1 0).

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For the alumina film on NiAl(1 1 0), the oxide film structure was determined recently by combining STM images and density functional theory calculations [14]. The alumina film on NiAl(1 1 0) has a structure and a stoichiometry that differs from all Al_2O_3 bulk phases. It has a nearly rectangular unit cell (a = 18.0 Å, b = 10.6 Å; bold lines in Fig. 1) in two reflection domains. The unit cell has twofold rotational symmetry with glide planes parallel to the two sides of the unit cell, i.e., $p2gg$ plane-group symmetry. The film consists of two aluminium and two oxygen layers and the surface is oxygen terminated. Fig. 1a shows the two topmost layers, named O_s and Al_s ("s" for surface). Both layers have been imaged by STM, O_s at room temperature and Al_s at low temperatures [14]. The O_s layer shows triangular and square atomic arrangements and consists of 28 atoms per unit cell. The Al_s layer is only 0.4 Å lower than the topmost layer and has 24 atoms per unit cell, which are all in the center of either a triangle or a square of the O_s atoms. The Al_s layer has a slightly distorted hexagonal structure. The O atoms of the third alumina layer, named O_i ("i" for "interface"), replicate the Al_s lattice; each O_i atom is located below an Al_s atom [14]. Fig. 1b shows the atomic structure of this layer together with the atomic positions of the interfacial Al_i layer. The 16 Al_i atoms are arranged in pentagon-heptagon pairs and can be probed by STM at larger tip sample distances [14]. The Al_i atoms are located preferentially above Ni rows of the substrate and avoid its Al rows. This row matching leads to a compressive stress and a slight distortion of the rectangular oxide cell.

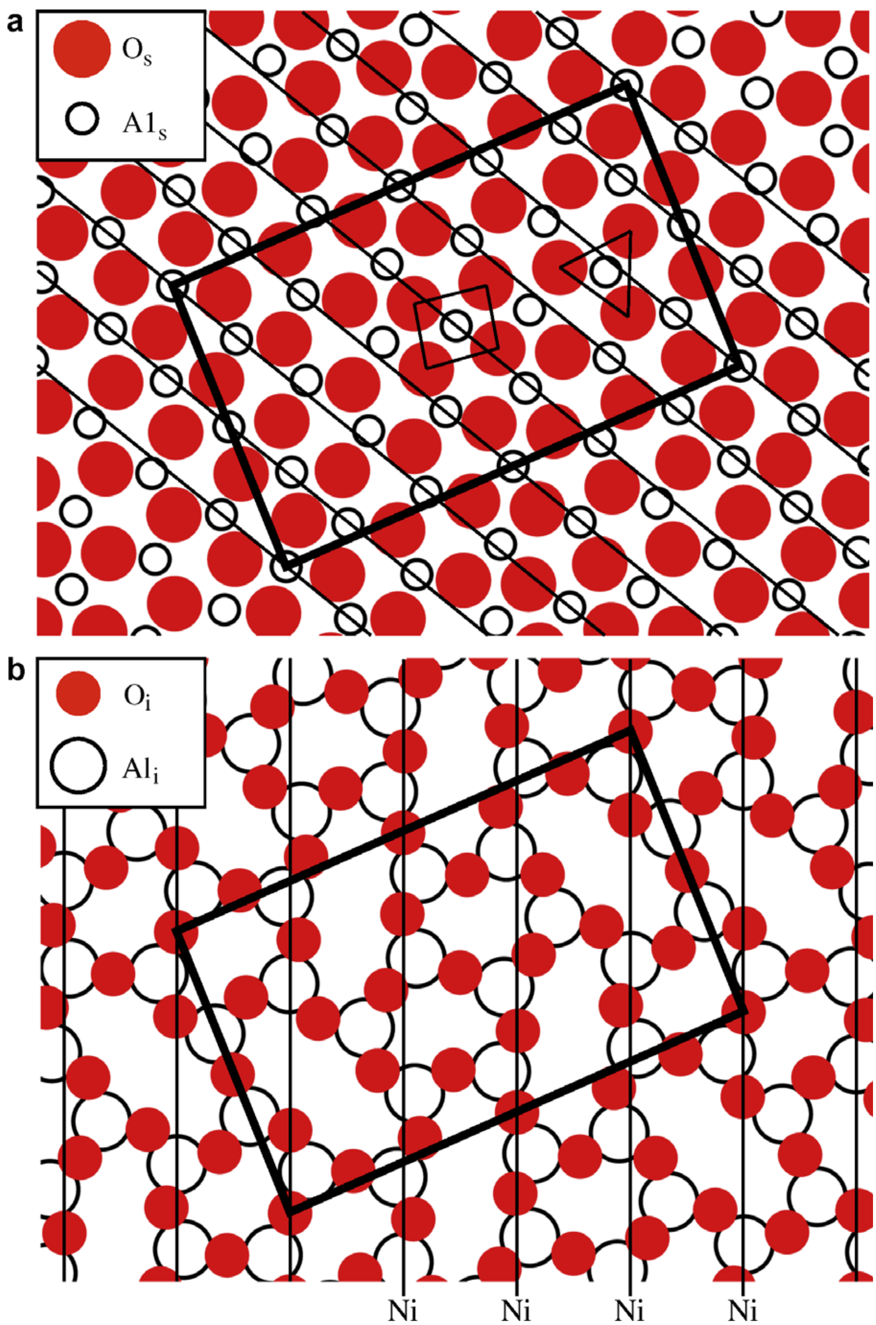

Fig. 1. The atomic arrangement of the alumina film on NiAl(1 1 0). (a) The surface – a square and triangular arrangement of oxygen atoms is marked, and the thin lines mark rows of Al_s atoms leading to a strong (6,2) LEED spot. (b) The third (oxygen) and fourth (aluminium) layer. Ni rows of the underlying NiAl(1 1 0) surface are indicated by vertical lines.