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Epitaxial growth of cobalt clusters on the bare and the oxide film grown on NiAl(1 0 0) surfaces

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Abstract

The structure of the nano-sized cobalt clusters on bare NiAl(1 0 0) and an oxidized NiAl(1 0 0) surfaces have been investigated by AES, LEED and RHEED. The deposition of Co onto bare NiAl(1 0 0) at room temperature led to small crystalline Co grains and surface asperities of substrate. The latter is likely induced by replacement of surface Al, Ni atoms by Co deposit. At 800 K Co particles aggregate to form clusters, but incorporation of Co into bulk NiAl(1 0 0) could occur upon annealing at 900 K. On the other hand, pure face-centered cubic (fcc) phase of Co crystallites of ≈1 nm in diameter with inclusion of smaller-sized particles ($D < 1$ nm) are observed on Θ-Al_2O_3 after Co deposition at room temperature. After annealing the Co nano-clusters grow larger at expense of small particles ($D \approx 3$ nm), where the [1 1 0] and [−1 1 0] axis of the Co(0 0 1) facets are parallel to the [1 0 0] and [0 1 0] directions of (0 0 1)oxide, respectively. The in-plane lattice constant of Co clusters is ca. 4% larger than that of bulk Co, yielding less strain at the Co/oxide interface. A 15° ± 10% random orientation of the normal to (0 0 1) facet of Co clusters with respect to (0 0 1)oxide surface was deduced from the "arc"-shape reflection spots in RHEED. These results suggest that both orientation and phase of Co clusters are strongly affected by the nature and structure of oxide surface.

Keywords: Reflection high-energy electron diffraction (RHEED); Auger electron spectroscopy; Cobalt; Aluminum oxide; Clusters

1. Introduction

There is considerable experimental and theoretical interest in the study of metal clusters for a number of reasons. Since they constitute intermediates between molecules and condensed matter [1]. Clusters with a dimension can exhibit a finite size effects to affect electronic, magnetic [2,3] and structural properties that are quite different from those of small molecules or condensed matter [4]. Physics/chemistry of the metal–oxide interface has been extensive investigated [5–7]. Though the morphology of cobalt clusters as well as the oxide film on NiAl(1 0 0) substrate have been studied by STM [8–10], attempts to elucidate the phase and orientation dependent of Co clusters on the oxide substrates have so far not been successful. A cubic phase (fcc, β-phase) of Co clusters of 2.5 nm in diameter embedded in sandwich of amorphous alumina has been recently observed, while those larger than 3 nm are hcp [11]. Co has been often found in the form of an intimate two-phase mixture of fcc and hcp forms, while it forms β-phase at room temperature under the stress of epitaxy [12]. The origin of such an unusual behavior found in Co still remains ambiguous. Therefore the structural analysis of the nano-sized cobalt clusters grown on an ordered Θ-Al_2O_3 film on NiAl(1 0 0) are of considerable interest in comparison with those obtained by other conditions [11–13]. We show how a detailed crystalline structure of Co nano-crystals can be obtained by means of RHEED. In order to explain the Co clusters (fcc) growing in (0 0 1)-orientation with respect to the (0 0 1)oxide surface, we compare the lattice mismatch between the (0 0 1)oxide and the facets of the hcp- and fcc-Co clusters, respectively.

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2. Experimental

Experiments were performed with an apparatus consisting of an UHV chamber equipped with LEED, RHEED and AES [14]. The NiAl(100) sample was cleaned by repeated cycles of Ar^+ ion sputtering (5×10^{-5} mbar, 2 keV, 4–5 μA cm^{-2}) and subsequent annealing for ca. 10 min at 1000 K. The NiAl(100) crystal was exposed to 1000 L O_2 at ca. 1000 K to induce oxidation followed by annealing at ca. 1000 K for 30 min under UHV conditions. The Θ-Al_2O_3 film was ca. 0.5–1 nm thick [15]. The Θ-Al_2O_3 film on NiAl(100) has been characterized previously [16]. Cobalt was deposited at a constant rate (ca. 0.02 ML/s) onto the bare and oxide film/NiAl(100) surfaces by using an Oxford Scientific e-beam evaporator. The Co coverage on oxide film was calibrated by STM [15], showing the formation of Co clusters aligned mainly along the protruded stripes on the ordered alumina oxide surface [15,16]. The RHEED results show diffuse ring patterns for both bare and oxide/NiAl(100) surfaces after Co deposition at room temperature.

3. Results

We are interested in the crystalline structure and the diffusion behavior of Co clusters deposited on naked NiAl(100) and oxidized NiAl(100) surfaces. The reciprocal lattice (rel) of Co clusters is deduced from RHEED, where the rel-distances $\mathbf{b_i}$ of a $(hkl)^*$-plane in RHEED are calculated by the relation $\mathbf{r_i} = \mathbf{L}\cdot\boldsymbol{\lambda}\cdot\mathbf{b_i}$, where $\mathbf{L}$ is the camera length (the distance between the specimen and the RHEED screen), and $\boldsymbol{\lambda}$, $\mathbf{r_i}$ are the wavelength of the electron beam and the distance between the zero- and the reflection-spot, respectively. It is convenient to index the extra reflection spots on the basis of the unit mesh ($\mathbf{a}^*, \mathbf{b}^*$) of the NiAl(100) substrate. The 2D-unit vectors $\mathbf{a}^*$ and $\mathbf{b}^*$ of the NiAl(100) substrate are parallel to the [100] and [010] directions of (001)oxide (Θ-Al_2O_3) [16] and their magnitudes (0.346 $Å^{-1}$) are equal to the rod spacing between the (00) and (10), (01) substrate reflections, respectively. The detailed analysis of RHEED patterns has been described elsewhere [16]. Ring patterns in RHEED can be useful for qualitative identification of the materials deposited on oxide surface.

3.1. Cobalt deposition onto the bare NiAl(100) surface

Prior to Co deposition the ordering and the cleanliness of the bare NiAl(100) surface were monitored by RHEED (Fig. 1a) and AES (Fig. 2a). The clean NiAl(100) surface shows weak Auger O- and C-signals in Fig. 2a, which probably arise from the CO adsorbate of the rest gas in UHV, however, they would be removed via $CO + O_2 \rightarrow CO_2$ during the growth of oxide film on NiAl(100) [15,16]. LEED pattern (not shown) for NiAl(100) covered by the Co deposit shows only strong background, and the spots of the substrate and the $c(\sqrt{2}\times3\sqrt{2})R45°$ phase seen in the clean NiAl(100) surface are no longer visible. However, the diffuse rings are observed in RHEED, characteristic of the presence of randomly orientated Co particles on bare NiAl(100) surface (Fig. 3a). The presence of Co deposit on NiAl(100) is also confirmed by the pronounced Auger Co-signals at 656 and 716 eV (not shown, but similar to Fig. 2b). Moreover, the additional transmission spots denoted by arrow developed at the (10) and (−10) substrate reflections. The reciprocal distance of the extra spot, 0.491 $Å^{-1}$ is equal to that of the 110-substrate reflection (0.49 $Å^{-1}$). While this reciprocal distance is ca. 9.8% larger than that of the 202-oxide reflections (0.443 $Å^{-1}$) [16], and the formation temperature of the oxide, 800 K is

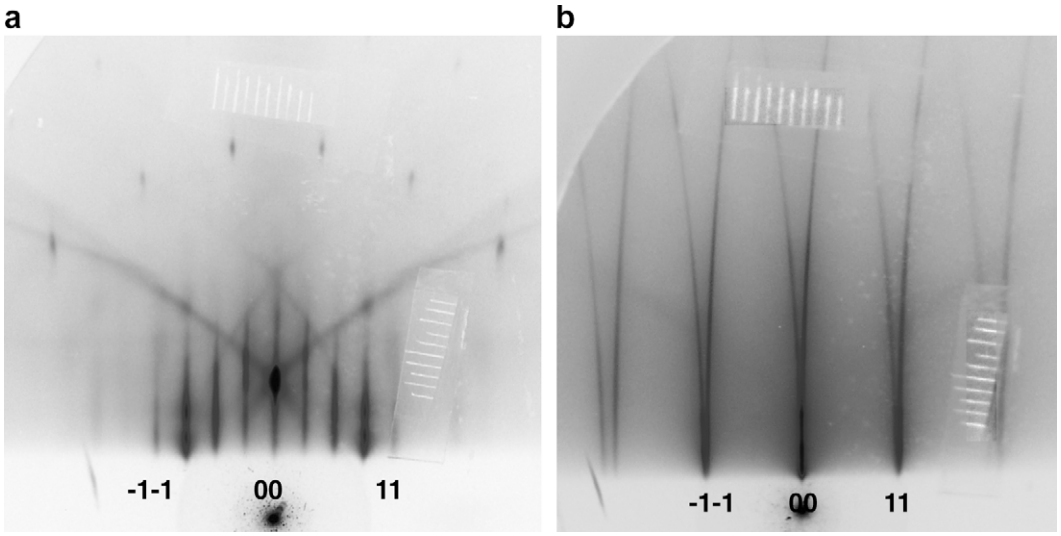

Fig. 1. (a) RHEED patterns ([0 −1 1] azimuth) for (a) a clean NiAl(100) surface, showing the reflections of the $c(\sqrt{2}\times3\sqrt{2})R45°$ phase, (b) for an oxidized NiAl(100) surface, showing the curved streaky reflections due to the oxide film.