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Growth of Co nanoparticles on a nanostructured θ-Al_2O_3 film on CoAl(1 0 0)

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Abstract

We have investigated the growth of Co nanoparticles on θ-Al_2O_3/CoAl(1 0 0) by means of Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (EELS), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Due to Volmer–Weber growth, Co forms particles with a mean diameter of approximately 2.5 nm and height of 0.8 nm. Even on the entirely covered oxide, there is no Ostwald ripening and Co particles stay structurally isolated. The nanoparticles exhibit a small size distribution and tend to form chains, as predetermined by the streak structure of the oxide template. For sufficient high coverages Co-core-CoO-shell nanoparticles may be evidenced, which is explained as a result of surfactant oxygen. The nanostructured particles may open the door to numerous applications, such as in catalysis and magnetoelectronic applications, where large areas of ordered nanodots are desired.

Keywords: Auger electron spectroscopy (AES); Electron energy loss spectroscopy (EELS); Low energy electron diffraction (LEED); Scanning tunneling microscopy (STM); Cobalt; Aluminum oxide; Cobalt oxide; Clusters

1. Introduction

Metallic nanoparticles deposited on oxide films play an important role in nanoscience and nanotechnology. They have applications in, for example, optics, electronics, sensors and heterogeneous catalysis [2]. Moreover, utilization of discrete nanostructures in magnetic materials is a promising concept for future magnetic information storage [3]. Beside elemental magnetic particles, Co-core-CoO-shell particles are also of great interest in the context of exchange biasing [4]. Since CoO is paramagnetic or antiferromagnetic near room temperature ($T_N = 298$ K) [5], the magnetic exchange with the ferromagnetic Co shell opens the path to unique magnetic properties [6]. Generally, electronic, magnetic and catalytic properties of small metal particles differ from those of their corresponding bulk form and depend strongly on their size and shape [7]. However, the investigation or the deployment of the size-dependent properties demands the capability of controlling the nucleation and growth in order to get uniform assemblages of metal particles. Obtaining a homogeneous distribution of nanoparticles, however, is no easy task.

We have chosen a thin crystalline oxide film as substrate to investigate the growth of Co nanoparticles. The process of selective segregation epitaxy, in which one of the components of an ordered intermetallic alloy is oxidized, can achieve such oxide supports [8]. A film of θ-Al_2O_3 (0.9 nm thick) was grown by high-temperature oxidation of a CoAl(1 0 0) crystal [9]. The alumina phase has a monoclinic structure (C_{2h}^3) consisting of oxygen atoms forming face-centered cubic (fcc) cells and Al^{III} ions occupying the octahedral and tetrahedral sites therein. The nanostructured θ-Al_2O_3 surface exhibits a characteristic streak structure. Elongated islands with lengths up to around 100 nm

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are oriented in the two rectangular domain directions of the oxide. These oxide streaks exhibit a height of 0.29 ± 0.08 nm, which is comparable to the lattice constant of the CoAl substrate (0.286 nm) and the O fcc lattice (0.292 nm) in θ-Al_2O_3. The width distribution of the stripes shows pronounced maxima at multiples of the lattice constant $b = 0.564$ nm of θ-Al_2O_3. The appearance of a streak structure was explained by a periodical change of the accumulated energy perpendicular to the oxide film, caused by the lattice mismatch between θ-Al_2O_3 and CoAl(1 0 0) that prevents the lateral oxide growth perpendicular to the streaks. The band gap of the θ-Al_2O_3 film on CoAl(1 0 0) is 4.5 eV.

This paper describes the growth of Co nanoparticles on top of θ-Al_2O_3/CoAl(1 0 0). For that reason the structure, morphology and chemical composition were studied by Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (EELS), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

2. Experimental

The experiments reported here were performed in two separate ultrahigh vacuum (UHV) systems. The first was equipped with a cylindrical mirror analyzer for AES, a three-grid optic for LEED and an EEL spectrometer. The surface sensitivity of AES was improved by decreasing the incidence angle of a second electron gun to 3° (GIAES) in addition to a conventional normal incidence electron gun (NIAES) using the same central mirror analyzer (CMA). Employing the two methods of AES allows us to distinguish between Auger electrons from elements either embedded far or near the sample surface. The EEL spectra were taken in specular geometry at an incidence angle of 57° with respect to the sample surface and at the primary energy of 4 eV. The base pressure of the first UHV chamber was typically 8×10^{-11} mbar. A second UHV chamber was used to record STM images. It was also equipped with facilities for AES and LEED. The STM images were recorded in the constant-current mode utilizing electrochemically etched tungsten tips. The base pressure of the chamber was better than 1×10^{-10} mbar.

A clean CoAl(1 0 0) surface was obtained after treating the sample by repeated cycles of Ar^+ ion sputtering at 1 kV for 20 min (Ar^+ pressure of 5×10^{-6} mbar, sample current of 2 μA), and subsequent annealing under UHV at 1470 K (5 min) by electron bombardment. The 0.9 nm thick θ-Al_2O_3 film was then obtained by exposing the CoAl(1 0 0) surface to 300 L (1 L = 1.3×10^{-6} mbar · s) gaseous oxygen at a sample temperature of 800 K and an oxygen partial pressure of 1.3×10^{-6} mbar. Cobalt was successively deposited in both chambers from a water-cooled evaporator using electron bombardment of a Co rod (99.995% purity, Alfa Aesar). All Co depositions were carried out with the substrate at room temperature and deposition rate of 0.1 nm/min. The amount of evaporated Co was denoted as a nominal film thickness, monitored using a calibrated quartz microbalance thickness monitor.

3. Results and discussion

3.1. STM

Fig. 1 shows STM images with a scanned area of $100 \times 100\ \mathrm{nm}^2$ illustrating the growth of Co on a θ-Al_2O_3/CoAl(1 0 0) substrate at 300 K. In the course of Co evaporation, we had to remove the scanning tunneling microscope from the sample. Thus, every STM image shown in this work represents a different area of the sample surface. However, the orientation of the sample was preserved, and the images demonstrate a surface morphology typical to the particular Co coverage. After the nominal deposition of 0.08 nm Co, the streak structure of the oxide is still clearly observable (Fig. 1a). In addition, Co particles appear as bright contrasts. The mean diameter of the Co particles is $d_m = 1.94 \pm 0.5$ nm, and the mean height amounts to $h_m = 0.67 \pm 0.1$ nm (see histograms in Fig. 1). For this small coverage, nucleation occurs not only at line defects such as steps, where metal atoms presumably bind more strongly [10], but also on streaks (terraces) and in the depressions between the streaks indicating a random nucleation. In the very first stage of Co deposition, surface defects might serve as nucleation centers resulting in the observed random nucleation [11–13]. After the deposition of 0.28 nm Co (Fig. 1b), d_m increases to 2.56 ± 0.7 nm with $h_m = 0.78 \pm 0.1$ nm. Now, the tendency of the particles to order along the oxide streaks becomes apparent. On top of the oxide stripes, the particles start to form chains parallel to the streak direction. After 0.64 nm Co (Fig. 1c), already 90% of the oxide is covered with Co particles. The analysis of the histograms yields $d_m = 2.27 \pm 0.3$ nm and $h_m = 0.86 \pm 0.1$ nm. Most likely, the decrease in d_m is related to convolution effects of the particle shape of adjacent clusters and the tip geometry. Finally, after the deposition of 2.96 nm, particles with mean diameter $d_m = 3.07 \pm 0.4$ nm and height $h_m = 0.91 \pm 0.1$ nm are observed. Even now, when the oxide is entirely covered, most of the Co particles order in elongated chains. The width of parallel Co chains and the orientation of the chains into the direction of the two θ-Al_2O_3 domains indicate that the ordering is predetermined by the stripe structure of the underlying oxide film. The particles stay structurally isolated and show no evidence of Ostwald ripening at the surface. Overall, the Co particles exhibit a strikingly small diameter and height distribution.

The STM images of Co on θ-Al_2O_3/CoAl(1 0 0) reveal the nonwetting behavior of Co on this substrate due to the observed formation of three-dimensional (3D) Co nanoparticles. The Volmer–Weber growth mode can be explained by the large difference of the surface free energy of Co ($\gamma_{Co} = 2709\ \mathrm{mJ/m^2}$) [14] and Al_2O_3 ($\gamma_{Oxide} = 690\ \mathrm{mJ/m^2}$) [15]. Generally, γ_{Co}, γ_{Oxide}, and the surface free energy of the metal/oxide interface $\gamma_{Interface}$ dictate the growth