

Reorganization of small Co particles on Al₂O₃ surfaces monitored by ferromagnetic resonance

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Changes of the magnetic properties of ferromagnetic Co particles deposited on the $\sqrt{31} \times \sqrt{31} R \pm 9^\circ$ reconstructed α -Al₂O₃(0001) as well as on a thin alumina film grown on a NiAl(110) substrate were investigated as a function of thermal annealing. On the thin film changes of the magnetic response were found above 500 K which correlates with changes in the particle size distribution. Annealing to 870 K leads to a permeation of the metal through the oxide film which causes significant changes in the ferromagnetic resonance response. On the α -Al₂O₃ single crystal sintering of particles requires temperatures above 600 K being about 100 K higher as compared to the thin alumina film. For large clusters intraparticle redistribution takes place already below 600 K a phenomenon not observed for the small clusters. In addition, a significant dependence of the measured g values from the substrate as well as the thermal treatment is found which can be understood in terms of the structural properties of the systems. © 2005 American Institute of Physics. [DOI: 10.1063/1.1884598]

I. INTRODUCTION

Small metal particles deposited on oxide surfaces play an important role in various fields. The catalytic activity of such systems, in particular, has triggered considerable interest in properties of these systems such as geometric and electronic structure, adsorption, and reactivity. To elucidate these properties and correlate them at a molecular level, model systems where particles are deposited either on bulk oxide single crystals or ordered thin oxide films have been investigated in detail over the last years.¹⁻⁵ Magnetic properties of small metal particles can serve as a valuable probe to detect structural changes in nanoparticle systems because of the tight correlation between magnetic and structural properties of the system (e.g., Refs. 6 and 7). This turns out to be useful if bulk insulating materials are investigated where electron based techniques cannot be used due to charging. In this contribution we use the magnetic properties as measured by an *in situ* ferromagnetic resonance experiment to investigate the thermal stability of metal particles on an oxide support. It should be noted in passing that the use of magnetic properties is not limited to this particular question. We have shown that adsorption of molecules, oxidation, as well as interactions at the particle substrate interface can be probed via magnetic properties.⁸⁻¹⁰ In this paper Co particles deposited on a thin alumina film were compared to particles grown on a bulk α -Al₂O₃ single crystal. The study focuses on the effect of interparticle rearrangements such as sintering or internal rearrangements such as crystallization of noncrystalline particles on the magnetic properties of the particles such as magnetic anisotropy or g value.

II. EXPERIMENT

The ferromagnetic resonance (FMR) experiments were carried out in a specially designed UHV apparatus which has been described previously.¹¹ The spectra on the sapphire single crystal were recorded with a commercial X-band (9.4 GHz) electron spin resonance spectrometer (Bruker, B-ER 420) which has been equipped with a new microwave bridge (Bruker, ECS 041 XK) and a new lock-in amplifier (Bruker, ER 023M) to improve the noise level of the machine. The spectra on the thin film were taken with a Bruker EMX spectrometer in a chamber of similar design.¹² A clean $\sqrt{31} \times \sqrt{31} R \pm 9^\circ$ reconstructed sapphire (0001) surface was prepared by annealing the sample several times for 20 min to $\approx 1000^\circ\text{C}$. Epipolished sapphire single crystal substrates with exceptional low paramagnetic impurities were purchased from Crystec GmbH (Berlin). The spectrum of the prepared sapphire surface showed no electron paramagnetic resonance or FMR signal on the scale of the noise of the presented spectra. The temperature was calibrated by a thermocouple (NiCr-CuNi) mounted in a small hole near the upper edge of the crystal. The clean surface shows neither carbon nor other impurities within the sensitivity of Auger spectroscopy. The reconstruction of the surface after this treatment was verified by low-energy electron diffraction (LEED). The thin aluminum oxide film was grown on a NiAl(110) single crystal as described in detail elsewhere.^{13,14} The structure of the film was monitored by means of its characteristic LEED pattern. Metal was deposited by an electron beam evaporator (Focus/Omicron EFM3). The particles were grown at 300 K with a deposition rate of 1 Å/min as calibrated by a quartz microbalance. Note that the sample was biased to the voltage of the evaporation material to avoid an acceleration of metal ions onto the surface. The pressure during metal evaporation never rose above 6×10^{-10} mbar and the base pressure in the apparatus was bet-

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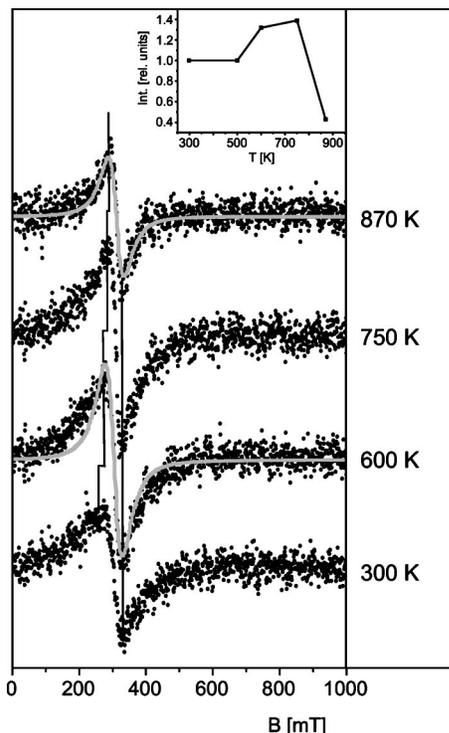


FIG. 1. FMR spectra of 2 Å Co deposited at room temperature on $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ after annealing to the temperatures given. Inset shows the intensity of the spectra with respect to the annealing temperature. Gray traces are fits using a single Lorentzian line.

ter than 3×10^{-10} mbar. The coverage given throughout this paper is meant as the height of a hypothetical, homogenous film of cobalt on the surface.

All FMR spectra shown throughout this paper are taken at room temperature with the static magnetic field being oriented in the surface plane unless stated otherwise.

III. RESULTS

A. Cobalt on a thin alumina film

The nucleation of Co particles on a thin Al_2O_3 film grown on $\text{NiAl}(110)$ has already been discussed in the literature.^{9,15} Deposition at room temperature leads to an almost random distribution of particles on the surface. Co particles nucleate not only at domain boundaries known as relatively strong nucleation sites, but also at point defects on the regular terraces of the thin film known to be weaker adsorption sites. This behavior renders Co to be a metal with a relatively strong metal/oxide interaction. The ferromagnetic resonance spectrum of 2 Å Co deposited on the thin alumina film at 300 K is shown in Fig. 1. The spectrum shows a resonance at 303 mT and a peak to peak linewidth of 72 mT. The line shape of the FMR spectrum is asymmetric with a broader maximum at the low field side and a sharper high field minimum. Furthermore, it exhibits a uniaxial out of plane anisotropy with an easy axis of magnetization in the surface plane which holds true for all systems investigated here. The anisotropy of the resonance field (H_a) determined by the difference of the resonance field measured with the

static magnetic field perpendicular minus the resonance field parallel to the surface of the crystal ($H_a = H_{r,\text{perp}} - H_{r,\text{par}}$) is 21 mT.

The influence of annealing on the morphology of the particles has recently been studied by scanning tunnel microscope (STM).^{16,17} Annealing to 570 K was shown to reduce the particle density slightly by about 15%. Annealing to 770 K and 870 K shows a further decrease of the particle density to 60% and 40% of the initial value, respectively. Concomitantly, the size of the particles increases. This behavior is readily explained by a sintering of the particles at elevated temperatures. However, it is important to note that the total amount of metal on the surface decreases upon heating above 570 K. From an analysis of the STM pictures it was concluded that metal diffuses into the support at the line defects of the oxide film.¹⁶ In the case of Co deposits additional features on the terraces of the film suggest that Co particles may also “dissolve” into the support at their adsorption site.¹⁶ The STM images taken after annealing at 870 K show a bimodal size distribution where the apparently smaller particles look as if they were partially incorporated into the alumina film. The FMR spectra taken for 2 Å Co deposited on the $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ surface after annealing to 600 K, 750 K, and 870 K are also shown in Fig. 1. Annealing to 500 K does not alter the spectrum of the pristine deposit which is in line with temperature programmed desorption results showing a thermal stability of the Co deposits up to 530 K.^{18,19} Annealing to higher temperatures shifts the resonance field monotonously towards higher fields from 303 mT for the pristine particles to 312 mT for the deposits annealed to 870 K. Furthermore, the spectra show a shift of the low field maximum towards higher fields whereas the high field minimum is virtually unaffected as indicated by the lines in Fig. 1. Therefore, the apparent linewidth of the spectrum as well as the asymmetry of the resonance line decreases with increasing annealing temperature. The line shape of the spectrum taken at 870 K can be described by a single Lorentzian line with a peak to peak width of 28 mT as shown by the solid line in Fig. 1. All other spectra show deviations from a symmetric line shape (a Lorentzian line is added to the spectrum taken after annealing to 600 K for comparison). Concomitantly, the difference of the resonance positions between parallel and perpendicular orientation drops from 21 mT for the pristine deposits to 5.7 mT after annealing to 870 K.

The intensity of the spectra as obtained by a double integration of the derivative spectra is presented in the inset of Fig. 1. Upon annealing the intensity remains constant up to 500 K. At 600 K the reduction in particle density as seen by STM is accompanied by an increase of the FMR intensity by about 30%. Further annealing to 750 K increases the intensity slightly. After annealing to 870 K, however, the intensity drops by a factor of 3.5 to about 40% of the initial value. Annealing to 900 K reduces the intensity further; however, a quantitative evaluation is hampered by the very poor signal to noise ratio of the spectrum. A further increase of the annealing temperature leads to a complete loss of the FMR signal.

The change of the FMR spectra caused by an increase of

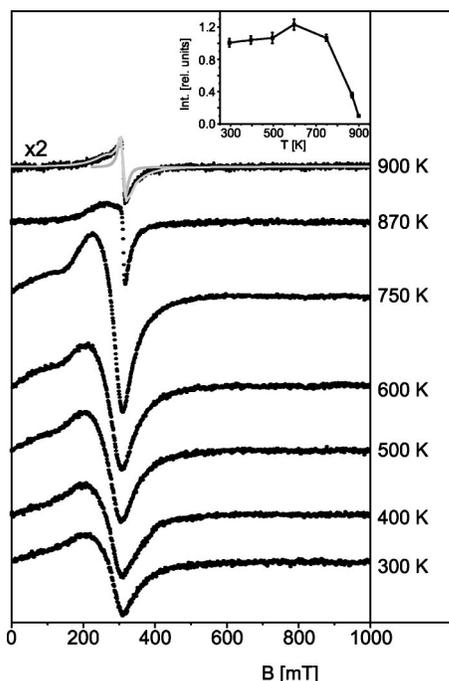


FIG. 2. FMR spectra of 6.5 Å Co deposited at room temperature on Al₂O₃/NiAl(110) after annealing to the temperatures given. Fit to the top-most spectrum using one and two Lorentzian lines. For details of parameters see text. Inset shows the intensity of the spectra with respect to the annealing temperature.

particle size as prepared by a deposition of 6.5 Å Co on the thin alumina film is shown in Fig. 2. For the pristine deposit an anisotropic line shape with an apparent resonance position of 276.6 mT is observed. The corresponding peak to peak linewidth is 98 mT. Similar to the situation of the smaller particles described above the spectrum exhibits a sharp minimum at the high field side and a broad maximum at low field values. However, the spectra extend almost to zero field in contrast to the smaller deposits. Upon annealing to 600 K the apparent resonance field changes only slightly. Further heating results in an increase of the resonance field being 309.3 mT after annealing to 900 K. The line shape changes moderately up to 750 K. The broad low field tail of the spectrum separates into a broad feature at lower fields and a relatively sharp peak close to the resonance field which becomes sharper in the course of the treatment. However, annealing to higher temperatures alter the line shape strongly. After annealing to 870 K the spectrum sharpens considerably and the resonance position shifts to 308.9 mT but in contrast to the 2 Å deposit the line shape of the spectrum remains asymmetric with a broad low field maximum and a sharp high field minimum. The asymmetry of the line shape is markedly reduced after annealing to 900 K resulting in a spectrum with a peak to peak linewidth of just 14 mT. However, the wings of the line are considerably broader than expected for a simple Lorentzian line. A reasonable fit shown in Fig. 2 can be achieved by assuming two symmetric Lorentzian lines with a linewidth of 14 and 62 mT and resonance positions of 309.3 and 300.5 mT, respectively.

The drastic change in the line shape is also reflected in the intensity of the spectra shown in the inset of Fig. 2. Whereas annealing to 750 K changes the intensity of the

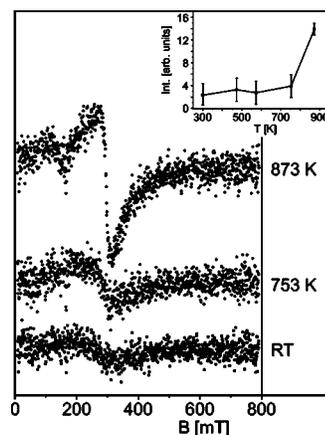


FIG. 3. FMR spectra of 2.4 Å Co deposited at room temperature on the $\sqrt{31} \times \sqrt{31} R \pm 9^\circ$ reconstructed α -Al₂O₃(0001) surface after annealing to the temperatures given. Inset shows the intensity of the spectra with respect to the annealing temperature.

spectra only slightly it drops to 35% and 8% of the initial value upon heating to 870 K and 900 K, respectively. It is noteworthy that the increase in peak to peak amplitude in the derivative spectra clearly seen upon annealing to 750 K is compensated by the reduction of linewidth. In fact, the intensity remains almost constant upon annealing to 500 K. It increases by about 20% at 600 K and comes back to the value at 500 K after heating to 750 K.

B. Cobalt on an α -Al₂O₃ single crystal

Figure 3 shows the FMR spectra as well as their intensity of 2.4 Å Co deposited on the $\sqrt{31} \times \sqrt{31} R \pm 9^\circ$ reconstructed α -Al₂O₃ (0001) single crystal surface with respect to annealing temperature. For the pristine deposit a very weak absorption centered at 272 ± 5 mT is detected for parallel orientation of surface and static magnetic field. The corresponding anisotropy of the resonance field H_a between perpendicular and parallel orientations is small (7 ± 5 mT). This spectrum is unchanged upon heating up to 573 K. Further annealing to 753 K increases the intensity of the spectrum by $\approx 60\%$. The linewidth of the spectrum is changed very little while the resonance position is shifted slightly towards higher fields (282 ± 5 mT). After treatment at 873 K the situation changes drastically. First, the spectrum gains intensity roughly by a factor of 7 with respect to the pristine deposit. Concomitantly, the resonance field shifts further towards higher fields, namely, from 272 mT to 294 mT. The angular dependent measurements reveal an increase of the anisotropy of the resonance fields to 23 ± 2 mT. The line shape of the spectrum shows a small broadening at the low field side and a peak to peak linewidth of 52 mT.

The corresponding change in the metal distribution was monitored by Auger spectroscopy. Due to the small mean free path of electrons the intensity ratio between Co and substrate (here oxygen) transitions is very sensitive to the arrangement of the Co atoms on the surface. The squares in Fig. 4 show the behavior of the relative intensity ratio between the Co transition at 785 eV and the oxygen transition at 502 eV of the 2.4 Å deposit with respect to the annealing temperature. Up to 573 K no change in the intensity ratio is

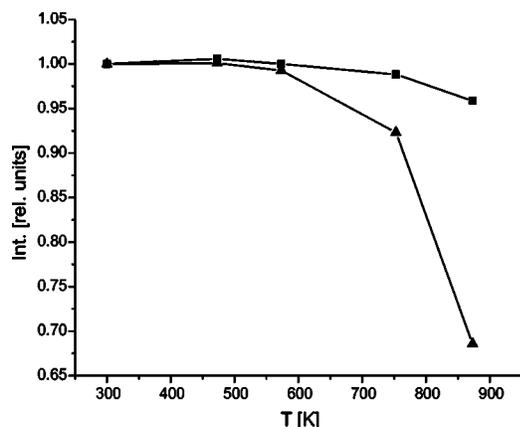


FIG. 4. Normalized ratio of the Auger intensities measured for Co and O. Squares correspond to measurements of the 2.4 Å Co deposit on the reconstructed sapphire surface. Triangles belong to a 6.5 Å Co deposit on the same surface.

observed. However, annealing to 753 K decrease the Co/O intensity ratio slightly being more pronounced after heating to 873 K. The decrease of the intensity ratio is expected for a sintering of particles. During this process the large particles grow in size whereas the density of particles decreases, in turn the amount of uncovered oxide area increases. The resulting gain of the substrate signal from the bare surface overcompensate the increased attenuation due to the higher particles. On the contrary, the Co signal decreases because of an enhanced attenuation of the Auger electrons for thicker particles.

The behavior is very similar for 6.5 Å Co deposits on this surface as indicated by the triangles in Fig. 4. The intensity ratio remains again constant up to 573 K, while a progressive reduction of the intensity ratio is observed after heating to 753 K and 873 K. Figure 5 shows the corresponding FMR spectra. The pristine deposit shows a Lorentzian line centered at 243 mT and a linewidth of 107 mT. Upon annealing the line shape becomes asymmetric and the center of gravity shifts towards lower fields. However, the apparent resonance positions of the signals remain almost constant during this treatment. The difference of the resonance fields between perpendicular and parallel orientation increases from 110 ± 5 mT for the pristine case to 158 ± 5 mT for the annealed deposit. The thermal treatment leads to a strong increase of the integral intensity as shown in the inset of Fig. 5. In contrast, to the proceeding cases annealing to 450 K already increases the intensity significantly by about 50%. In the course of the annealing the intensity increases monotonously. Overall it gains a factor of 4 after heating to 873 K as compared to the pristine deposit. It should be noted that the FMR intensity of the pristine 6.5 Å deposit is more than an order of magnitude larger than the one observed for the 2.4 Å case.

IV. DISCUSSION

As revealed from STM images the particle density for 2 Å Co deposited on the thin aluminum oxide film is $9.6 \times 10^{12} \text{ cm}^{-2}$.¹⁸ This leads to an average particle size of 190 atoms and a corresponding diameter of ≈ 16 Å assuming

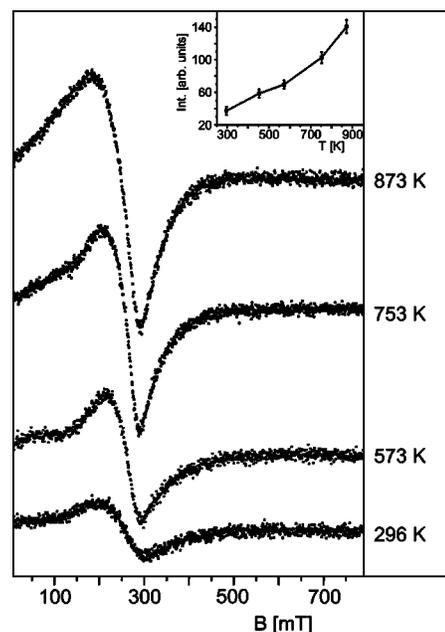


FIG. 5. FMR spectra of 6.5 Å Co deposited at room temperature on the $\sqrt{31} \times \sqrt{31} R \pm 9^\circ$ reconstructed $\alpha\text{-Al}_2\text{O}_3(0001)$ surface after annealing to the temperatures given. Inset shows the intensity of the spectra with respect to the annealing temperature.

spherical particles which is consistent with the height of a large fraction of particles of $\approx 15\text{--}20$ Å measured by STM. For particles of this size superparamagnetic behavior is expected which means a thermal activated fluctuation of the magnetization in space. This fluctuation has two important consequences for FMR experiments. First, the intensity of the FMR spectrum decreases considerably as compared to the situation without fluctuations. With increasing temperature a Langevin-like behavior of the intensity is expected for systems showing superparamagnetic behavior. Second, the resonance position determined by the anisotropy energy in the ferromagnetic limit collapses to an isotropic line centered at the g value for fast fluctuations on the time scale of the FMR experiment. The latter situation is usually called isotropic superparamagnetism.²⁰ This description already indicates that the term superparamagnetic is not rigorously defined. In fact, it depends on the time scale of the experiment as compared to the time scale of the fluctuation whether a certain sample behaves as a superparamagnet at a given set of experimental conditions.

In a FMR experiment the resonance position of a system with certain anisotropy energy will shift from the low temperature limit towards the isotropic g value with increasing rate of fluctuation. Therefore a shift towards the g value is expected with increasing temperature. Depending on anisotropy energy and temperature, any intermediate situation between the two limits can be observed.

For the pristine particles prepared by evaporation of 2 Å Co at room temperature a small uniaxial anisotropy of 21 mT was observed with the easy axis of magnetization being oriented in the surface plane. This small anisotropy is consistent with the expected superparamagnetic behavior of the particles. For systems with sufficiently high fluctuations of the magnetization the effect of the thermal fluctuations

can be taken into account by modulating the anisotropy constants which enter the ferromagnetic resonance equation.^{21,22} This approach has been successfully used in the past to simulate FMR spectra of small particles and the same approach was adapted here.²³ Analyzing the angular dependent FMR spectra taken at room temperature within this framework and using the particle sizes determined by STM gives a uniaxial anisotropy constant of $(2.4 \pm 0.5) \times 10^5 \text{ Jm}^{-3}$ assuming a bulk magnetic moment of $\mu_{\text{Co}} = 1.72 \mu_{\text{B}}/\text{at}$. The corresponding g value was found to be 2.22 ± 0.015 . This set of values allows a consistent description of angular dependent measurements for temperatures down to 70 K, which corroborates the extracted parameter further. The g value is in good agreement with measurements by Respaud *et al.* on colloidal Co particles. They found values of 2.20 and 2.22 for Co particles with 150 and 310 atoms, respectively.²⁴ A similar g value of 2.20 was also found by Wiedwald *et al.* for Co particles with a diameter of 9 nm.²⁵

The easy axis of magnetization is observed in the surface plane. One important contribution to account for this observation is the shape anisotropy of the particles. Only a small deviation from an ideal sphere has to be assumed to account for the observed anisotropy. For pure shape anisotropy an aspect ratio $c/a = 0.90$ would explain the observed anisotropy assuming a symmetric ellipsoid with bulk magnetization. However, it is not expected that the observed effect is purely due to shape effects. In particular, surface contributions may also play an important role for such small particles. This was shown to be the case by Respaud *et al.* They found values of the effective anisotropy constant of 9×10^5 and $7.5 \times 10^5 \text{ Jm}^{-3}$ for particle sizes of 150 and 310 atoms, respectively, which are considerably larger than the ones observed here.²⁴ Assuming spherical particles they extracted the surface contribution to be $K_{\text{S}} = 2 \times 10^{-4} \text{ Jm}^{-2}$ and the corresponding volume contribution $K_{\text{V}} = 1.5 \times 10^5 \text{ Jm}^{-3}$ using the phenomenological equation $K_{\text{eff}} = K_{\text{V}} + 6K_{\text{S}}/D$. An estimation of the surface contribution can be made for the present case using the larger particles as prepared by deposition of 6.5 Å. These particles consist of 2400 atoms on average according to STM results.¹⁷ From the angular dependent FMR measurements a uniaxial anisotropy of $(1.5 \pm 0.2) \times 10^5 \text{ Jm}^{-3}$ and a g value of 2.22 ± 0.015 were determined. Temperature dependent measurements down to 120 K could be consistently described using these values. Assuming independent spherical particles one can use the same phenomenological approach described above. For the present case a surface contribution $K_{\text{S}} = 4.2 \times 10^{-5} \text{ Jm}^{-2}$ and a corresponding volume part $K_{\text{V}} = 8.2 \times 10^4 \text{ Jm}^{-3}$ can be extracted. This indicates that surface contributions play indeed an important role for the behavior of the particles. It should be emphasized that although the g value of the two situations is identical which indicates a similar environment of the Co atoms in the clusters this analysis neglects all changes of the particle shape or changes of the bulk magnetic anisotropy constants, thus it should be taken as an estimate only.

Annealing of the 2 Å deposits to 870 K changes the situation considerably. STM investigations show a bimodal size distribution of the particles. The size of the larger ones corresponds to particles with approximately twice the number of

atoms as compared to the pristine deposit while the smaller ones show a reduced size as compared to the initial situation.¹⁷ However, a determination of the size of the smaller ones is hampered by the fact that these particles seem to be incorporated into the oxide film.¹⁷ Using the size of the larger particles an anisotropy constant of $(5 \pm 0.5) \times 10^4 \text{ Jm}^{-3}$ was extracted from the FMR results which is a factor of 5 lower than the one observed for pristine deposits. For the “smaller” particles this analysis was not possible because of the uncertainty of their size. In addition, to the decrease of the anisotropy constant the g value of the particles is reduced to 2.18 ± 0.015 after annealing to 870 K as compared to 2.22 observed for the pristine deposit. This is identical to the value for hcp Co (2.18) described in literature. Similar to the pristine case these constants allow a description of temperature dependent measurements between 70 K and 600 K.

The reduction of the g value upon annealing is not restricted to the 2 Å deposit. The same decrease of the g value to 2.18 was found for the 6.5 Å deposits shown in Fig. 2, as well. What is the reason for this decrease of the observed g value?

Respaud *et al.* have found that the structure of the particles showing a g value of 2.22 is rather complex, being a mixture of bcc and hcp components, indicating that structural changes towards less densely packed structures might be responsible for the increased g value.²⁶ A similar deviation of the g value was observed for thin Co films grown on Cr(001).²⁷ For thin films a strong distortion of the hcp lattice towards a bcc structure was observed.²⁸ The distortion relaxes with increasing thickness of the film and concomitantly a reduction of the g value is observed.²⁷ A distorted structure of the pristine particles is expected due to the lattice mismatch between the alumina film and the Co particles and the low deposition temperature which prevents the formation of thermodynamic equilibrium structures.¹ This is corroborated by STM results which show no sign of faceted crystallites expected in thermodynamic equilibrium which have been observed, e.g., for Pd grown under these conditions.^{18,29} Upon annealing the kinetically trapped structure of the particles will relax towards thermodynamic equilibrium.¹ Thermodynamically fcc or hcp structures are expected, which give rise to lower g values of 2.14–2.16 and 2.18, respectively (see Ref. 30 and references therein).

From an electronic point of view the reduction of the g value can be interpreted as a reduction of the ratio between the orbital (μ_{L}) and spin (μ_{S}) magnetic moment, which is given by

$$\frac{\mu_{\text{L}}}{\mu_{\text{S}}} = \frac{g - 2}{2}$$

for small orbital contributions.^{31,32} Thus, the orbital contribution to the g value decreases from 11% in the case of the pristine deposits to 9% for the annealed system. An increase of the orbital contribution can be interpreted as a narrowing of the 3d band due to a reduced atomic coordination. The same increase of the orbital contribution with decreasing atomic coordination was observed for Co atoms at the perimeter of monolayer islands on Au using x-ray magnetic

dicroism.³³ Obviously, the surface atoms have a reduced atom coordination and should possess a larger orbital contribution. In fact, the existence of low coordinated Co atoms on the surface of the pristine deposits was shown by chemical means.³⁴ However, the same g values were observed for fairly different cluster sizes. Therefore, it can be concluded that the increase of the g value is not governed by the surface rather than by structural rearrangements in the bulk of the particles.

It is interesting to note that the line shape of the 2 Å deposit after annealing to 870 K is a symmetric Lorentzian line, despite the fact that the particle size distribution is bimodal according to STM. This does no longer hold true for the 6.5 Å deposit after annealing. Here, the line shape of the FMR spectrum resembles the bimodality of the particle size distribution as indicated by the fit to the spectrum after annealing to 900 K using two Lorentzian lines. Almost 90% of the intensity is located in the broad resonance. This resonance is also characterized by a larger anisotropy as compared to the sharp component. From these observations the broad resonance is tentatively assigned to the apparently small particles which were incorporated in the alumina support. The shift of the resonance position and the observed linewidth is explained by the increased interaction of these particles with the support. In addition, these particles are the majority species (70%) on the surface as seen by STM.¹⁷ The lack of a measurable anisotropy in the line shape of the 2 Å deposit might be due to an overlap of both components. In fact it is possible to fit the topmost spectrum in Fig. 1 assuming two components with slightly different resonance fields (3 mT) and different linewidth (28 mT vs 18 mT). However, due to the poor signal to noise ratio of the spectrum the assumption of two components cannot be justified based on the fits.

This interpretation can be corroborated by measuring an intermediate thickness. After annealing of 4.5 Å Co to 870 K the line shape of the spectrum can be described by two components. Besides, a broad component with a linewidth of 50 mT and an integral intensity corresponding to 70% of the total intensity, a sharp one with a linewidth of 18 mT is observed.

In comparison to the thin film a similar amount of Co deposited on a reconstructed sapphire surface show some similarities but also considerable differences. The most intriguing difference occurs at high annealing temperatures. Whereas the thin film becomes permeable for the Co deposit leading to a strong decrease of the FMR intensity the opposite takes place on the sapphire surface. This excludes any significant desorption from the surface or diffusion into the bulk, also reaction with the surface resulting in an oxidation of the particles can be excluded. The lateral mobility of the Co atoms on the surface starts above 600 K in the case of the reconstructed sapphire surface. It is ≈ 100 K higher than in the case of the oxide film which points towards a stronger interaction of the Co with the reconstructed single crystal as compared to the thin film. This behavior is not unexpected since this surface is characterized by an oxygen deficiency in the top layers.³⁵

Does the increased interaction between the sapphire sur-

face and the Co particles influence the structure of the particles? To answer this question it is helpful to resort again to angular dependent measurements. An analysis of the spectra for the pristine 2.4 Å deposit results in a g value of 2.28 ± 0.02 corresponding to a fraction of the orbital contribution to the magnetic moment of 14%. A similar analysis of the 6.5 Å deposit is hampered by the fact that this system shows already a fairly large anisotropy of 165 mT in the pristine case. In addition, a considerable fraction of the linewidth is due to the particle size distribution, namely, changes of the resonance field with the particle size. For this situation the determination of the g value from measurements at a single frequency is fairly inaccurate. Under these conditions one should resort to measurements at different frequencies as it has been done, e.g., by Wiedwald *et al.* for monodispersed Co particles prepared by colloidal chemistry.³⁶ As an estimate we have analyzed the data assuming spherical particles and a uniaxial anisotropy. This gives a g value of 2.26 ± 0.02 , where the error given is just the uncertainty within the model and does not take systematic errors into account. The latter will increase the uncertainty to at least 0.05.

The observed g value for the smaller particles on sapphire is considerably increased as compared to the pristine particles on the thin alumina film indicating that the structure is characterized by a reduced average coordination of the Co atoms as compared to the film. Qualitatively the same behavior is observed for the larger particles although the effect is less pronounced. This behavior can be understood by the large lattice mismatch of Co on the reconstructed sapphire surface and the increased metal support interaction that was already suggested by the thermal stability of the particles. The analysis of the FMR spectra of the 2.4 Å deposits after annealing to 870 K reveals a decreased g value of 2.18 ± 0.015 which is identical to the situation on the thin film after annealing. This indicates that the structure of the particles changes towards a higher coordination of the Co atoms upon annealing. For the thicker deposit the analysis gives a g value of 2.20 ± 0.06 using the same assumptions mentioned above. Although the g value is larger than the one observed for the smaller particles and the situation on the film after annealing, the difference is well within the systematic error of the simplified analysis.

The behavior of the FMR intensity for the two cases deserves special attention. For the 6.5 Å deposit a monotonous increase of the intensity is found for temperatures above room temperature (see inset Fig. 5) whereas the Auger analysis reveals that the particle size distribution is unchanged below 600 K. If the number of atoms in each particle remains constant, the increase in FMR intensity can only be explained by internal structural rearrangements in the particles.

Temperature dependent measurements show that the increase in intensity is not due to a change of the Curie temperature, which might cause large changes of the FMR intensity if the system is close to the Curie point. Therefore, the observed increase of the FMR intensity is due to an increase of the average magnetic moment per Co atom in the particles. On the contrary, no change of the FMR intensity is observed up to 600 K for the smaller particles produced by

deposition of 2.4 Å Co. However, after annealing to 870 K an increase of the FMR intensity by a factor of 7 is observed. At this temperature sintering of the particles, i.e., a growth of the large particles at the expense of the small ones, occurs as monitored by Auger spectroscopy. However, the increase of the particle size and concomitant decrease of thermal fluctuations cannot account for the increase in intensity since the overall number of atoms on the surface remains constant. Thus it has to be concluded that sintering of the Co particles also increases the average magnetic moment per Co atom. It is likely that at the higher temperatures both effects, namely, internal rearrangements as well as growth in size will occur simultaneously.

For a kinetically controlled growth of atoms the structure of the resulting aggregates is imposed by the energetics of the different processes involved, namely, the interaction energies (metal/surface; metal/metal), diffusion properties as well as activation barriers for different processes.² In particular, the lattice mismatch between surface and metal will cause substantial structural changes as long as metal support interaction is substantial. However, this stress will be released with increasing height of the particles.

To explain the observations presented here it is assumed that the Co atoms located close the sapphire interface contribute less to the magnetic moment of the particle as compared to those at larger distance to the surface due to the change of the environment close to the support. Therefore, metal atoms close to the interface can serve as a “reservoir” for magnetic moment as soon as their structural environment is changed towards a regular closed packed Co structure.

What is the reason that internal restructuring of the particles does only occur for the larger particles? In order to predict this behavior one would need to know the activation energy for internal rearrangements as compared that of atom detachment as a function of particle size and structure. Unfortunately, this information is not available. However, it is obvious that if the activation energy of detachment is lower than the one for internal rearrangements, sintering of the particles will occur prior to a rearrangement, while an internal rearrangement will be observed for the reverse situation. For strong metal support interaction it is expected that the activation for internal rearrangements will be high for atoms close to the interface while it decreases with increasing height of the particle. Therefore, it is possible that the higher particles can rearrange parts being further away from the surface, while small particles cannot undergo internal rearrangements due to their strong metal support interaction. The corresponding process is schematically summarized in Fig. 6 were the contribution of the atoms to the total magnetic moment of the particle is indicated by their gray scale. It should be noted in passing that the presence of Co atoms with smaller effective magnetic moment at the interface does also explain the observed discrepancy between the intensity enhancement (factor 10) and the change of the metal amount (factor 2.5) for the two different deposited amounts discussed here. For the annealed situation the discrepancy is markedly reduced to 2:1.

It is worthwhile to have a closer look at the line shape of the pristine deposits on the sapphire surface in comparison to

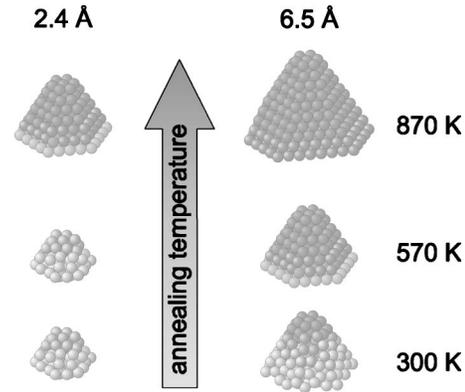


FIG. 6. Schematic representation of the rearrangements occurring upon heating on the $\alpha\text{-Al}_2\text{O}_3$ single crystal surface. Darker gray tones belong to stronger ferromagnetic coupling.

the situation on the thin film. On the one hand, an almost symmetric line shape is observed for the pristine deposits on the sapphire, whereas the spectra on the thin film exhibit an asymmetric one. On the other hand, the line shape observed for the annealed systems on sapphire corresponds very closely to the ones observed for the pristine deposits on the thin film. It is important to understand if the asymmetric line shape is an intrinsic property of the particles or if it is an ensemble effect. Berger *et al.* have discussed the importance of intrinsic effects, namely, different relaxation processes, on the line shape of small particle systems.³⁷ They have shown that other relaxation processes than a simple exponential decay of the magnetization can explain strongly asymmetric line shape observed for samples of small ferromagnetic particles in matrices. However, for the present system this does not hold true. This can be seen by looking at the line shape of angular dependent spectra. Figure 7(a) shows the FMR spectra of 6.5 Å Co deposited on the reconstructed sapphire surface after annealing to 900 K for three different

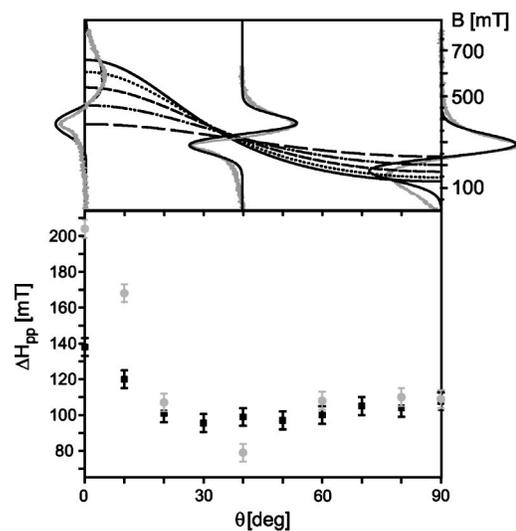


FIG. 7. (top) FMR spectra of 6.5 Å Co deposited on the reconstructed sapphire surface after annealing to 900 K for different polar angles. Gray lines are simulated line shapes for the model used see text. (bottom) Peak to peak linewidth measured for different polar angles. Filled squares pristine 6.5 Å Co deposit on the reconstructed sapphire surface. Filled gray circles: after annealing to 900 K.

polar angles. It can be seen that the asymmetry of the line shape observed for the in-plane orientation ($\theta=90^\circ$), namely, a broad low field side and a sharp high field minimum, is reversed for the perpendicular orientation. For the latter geometry the linewidth is substantially increased as compared to the parallel configuration. However, at intermediate polar angles the linewidth is reduced and the line shape is much more symmetric. The apparent peak to peak linewidth measured at different polar angles is plotted in Fig. 7(b) (filled gray circles).

The present line shape can be understood by a simple model, where a log-normal distribution of spherical particles (average diameter 3.1 nm; normalized width 0.25) with uniaxial anisotropy of $2.5 \times 10^5 \text{ J/m}^{-3}$ and a surface anisotropy of $1 \times 10^{-4} \text{ J/m}^{-2}$ was assumed. The resonance position was calculated in the same way as described above and a constant Lorentzian line of 70 mT was assumed for all particle sizes. The line shapes calculated by this model are shown in comparison to the observed spectra in Fig. 7(a). The calculated line shapes are in good agreement with the observed ones. The only larger deviation occurs at low magnetic field for the parallel configuration. The deviation at the low field end is most likely due to the fact that the magnetization of the sample changes significantly with the field in this range which is not taken into account in the analysis and is known to give intensity at low magnetic fields.³⁶ The reason for the reduction of the linewidth and the more symmetric line shape at intermediate polar angles is indicated by the lines in Fig. 7(a) which sketch the angular dependence of the resonance position for a given effective magnetic anisotropy. Particles with large effective anisotropy have the lowest resonance field for the parallel configuration and the highest for the perpendicular one. The situation is reversed for the particles with small magnetic anisotropy. Due to the functional form of the resonance equation the spread of resonance positions is larger for the perpendicular orientation than for the parallel one, resulting in a larger apparent linewidth for perpendicular geometry in accordance with the observed spectra. The crossover takes place at polar angles of $\approx 40^\circ$ which depends on the magnitude of the magnetic anisotropy. For these angles all particles have similar resonance position resulting in a reduced overall linewidth. Since the reduction in linewidth is connected with a more symmetric line shape it can be concluded that the intrinsic line shape for these clusters at 300 K is fairly symmetric.

For the pristine deposits on the reconstructed sapphire the line shape remains symmetric over the whole range of polar angles although the line shape deviates from a simple Lorentzian line for small polar angles. The linewidth for the different polar angles is plotted in Fig. 7(b) (filled squares). In comparison to the annealed system the behavior is qualitatively similar. However, quantitative differences are found. The linewidth for the parallel orientation is fairly similar in both cases, while the reduction of the linewidth at intermediate polar angles as well as the increase for parallel orientation is markedly reduced. The behavior of the linewidth can be understood in the same way as it was discussed above, however, the spread of magnetic anisotropy within the particle ensemble is smaller for the pristine case. This is

partly due to the smaller size of the particles and the increasing importance of thermal fluctuations. The reduced spread of the magnetic anisotropy in combination with comparable linewidth for the parallel orientation and a larger linewidth at intermediate polar angles is interpreted as increased linewidth of the individual resonance of each cluster. It has been shown for thin magnetic films that the linewidth of the FMR spectra is correlated with the structural homogeneity of the system (e.g., Refs. 38 and 39). Therefore, it is expected that the linewidth of the strongly distorted particles on the reconstructed sapphire surface show a larger linewidth than the less distorted ones prepared by annealing which is in line with the analysis of the g values discussed above.

V. CONCLUSION

In conclusion, we have shown that ferromagnetic resonance is capable to monitor intraparticle as well as interparticle redistribution of atoms and thus provide important insight into the thermal stability of supported particles. It was shown that the g value of the FMR spectra is a valuable probe to detect structural properties as well as changes thereof, e.g., induced by thermal annealing. A stronger interaction of the Co deposits with the reconstructed sapphire surface as compared to the thin aluminum oxide film was found, which is reflected in the 100 K temperature difference between the onset temperatures for sintering, as well as significant shift of the g value for both systems. In addition, pristine Co-particles grown on the reconstructed sapphire surface show a strongly reduced magnetic moment of the atoms close to the sapphire interface due to the strong metal support interaction.

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