Spin-reorientation transition in Ni films on Cu(001): The influence of H_2 adsorption

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The spin-reorientation transition of ultrathin Ni films is investigated by means of *in situ* magneto-optical Kerr imaging as a function of the temperature. A critical thickness d_c of about 11.4 monolayers (ML) at $T=170$ K and 10.3 ML at 370 K has been found. Adsorbates strongly reduce this critical thickness. In particular the adsorption of about 2 langmuir H_2 reduces d_c to 7 ML at 170 K. The magnetocrystalline anisotropy energy of the clean Ni surface $K_{2s}=-153$ μeV/atom is strongly reduced by hydrogen adsorption.
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The anomalous reorientation transition of Ni films on Cu(001) has been investigated quite intensively during the last years.[1–12] The effect of overlayers such as Cu has been studied[10,13–16] but less attention has been paid to the influence of gaseous adsorbates like hydrogen on the magnetic anisotropy of the Ni films. It was found, however, 20 years ago that hydrogen adsorption on Ni surfaces strongly reduces the magnetic moment of the first layer.[17,18] Therefore, a strong effect on the magnetic anisotropy of thin Ni films can be expected as well.

The adsorption and desorption kinetics,[19] the structure,[20–22] as well as possible lattice relaxations induced by H_2 adsorption on nickel,[22] have been investigated quite intensively since the early days of surface science. We briefly summarize the relevant results: H_2 adsorbs dissociatively on Ni(001) in fourfold hollow sites.[20] Adsorption and desorption of hydrogen are completely reversible upon temperature cycling. The isosteric heat of adsorption is 1.0 eV/H_2 molecule. At 300 K and a partial pressure of 3×10^{-11} mbar an equilibrium coverage of about 0.1 is expected[19] [coverage$=1$ corresponds to the Ni(001)-H (1×1) structure]. A decrease in temperature by 20 K or an increase of the hydrogen pressure by a factor of 10 would increase this coverage by more than a factor of 3. In view of the fact that during evaporation of the Ni films typically the pressure rises up to the 10^{-10} mbar range with evaporation rates of the order of monolayer (ML)/min it is not unlikely that films grown at room temperature are precovered with an undetermined but not negligible amount of hydrogen. It is the purpose of this paper to show that hydrogen adsorption strongly affects the surface magnetic anisotropy energy.

Ni grows pseudomorphically on Cu(001). Compared to the Ni bulk the interlayer spacing of the Ni film is reduced by about 3.2% and the in-plane lattice constant is increased by 2.5% to match the Cu substrate lattice.[21] This tetragonal distortion of the lattice induces a second-order magnetocrystalline anisotropy energy K_2. It has been shown that for small film thickness K_2 can be written as $K_2=K_{2v}+(K_{2s}+K_{2i})/d$, with the film thickness d, K_{2v} the thickness-independent ''volume'' magnetization anisotropy energy, and K_{2s} and K_{2i} the ''surface'' and ''interface'' parts.[1,3,15] K_{2v} is found to be positive and therefore favors a perpendicular easy axis of magnetization while $K_{2s}+K_{2i}<0$ favor in-plane magnetization.[1,3] Therefore—opposite to the usual behavior—thin Ni films have the easy axis in plane and at a critical thickness d_c the expression $(K_{2s}+K_{2i})/d_c$ becomes smaller than effective bulk anisotropy energy $K_{2v}-2\pi M_s^2$ and the easy axis switches to the surface normal. d_c values ranging from 7 ML,[4,5,11] 8 ML,[12] and up to 10 ML (Ref. 6) have been reported.

In phenomenological models K_{2v} often is described as a magnetoelastic anisotropy energy $K_{2v}\equiv K_{me}=-3/2\lambda\sigma$, with λ the bulk magnetostriction constant and σ that stress, which in bulk Ni would lead to the 2.5% in-plane lattice expansion observed in the Ni films on Cu(001).[5,14] The surface and interface parts K_{2s} and K_{2i} are either thought to be of entirely ''Néel-type'' origin[5,14] or contain a magnetoelastic component as well.[23] With increasing film thickness the stress in the Ni film induced by the tetragonal distortion increases until dislocation formation sets in, allowing for a (partial) release of the stress by reduction of the tetragonal distortion. Consequently K_{me} becomes now thickness dependent and is reduced in line with the reduced lattice distortion. A second spin reorientation occurs at a thickness d_{2c} where $(K_{2s}+K_{2i})/d_{c2}+K_{me}(d_{c2})$ equals the shape anisotropy $-2\pi M_s^2$. This transition occurs over a much broader thickness range from 37 ML to more than 50 ML.[14,15] Therefore, it is now well accepted that the strain-induced anisotropy component K_{2v} is responsible for the perpendicular magnetization.

In our experiments wedgelike Ni films were grown at $T=298$ K on a Cu(001) single crystal (miscut $<0.2°$) in a molecular beam epitaxy (MBE) apparatus (base pressure $<4\times10^{-11}$ mbar). To avoid morphology changes during the temperature-dependent measurements the film was annealed to 453 K. The flux of the Ni *e*-beam evaporator was calibrated by means of medium energy electron diffraction (MEED) prior to the growth of the wedge. The growth rate was about 0.5 ML/min at a pressure of less than 2×10^{-10}

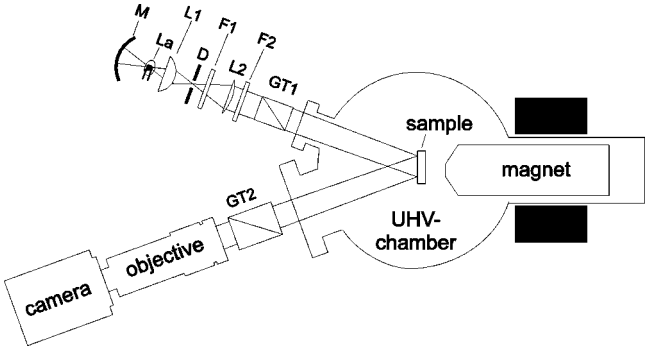

FIG. 1. Schematic view of the experimental Kerr microscopy setup: M, mirror; La, halogen lamp; L1, condensor; D, diaphragm; F1, F2, colored glass filters; L2, lens $f=100$ mm; GT1, Glan-Thompson polarizer; GT2, analyzer (Glan-Thompson).

mbar during evaporation. The thickness of the wedge was cross-checked by Auger analysis after completion of the measurement and by magneto-optical Kerr effect (MOKE) measurements on individual layers. From that we estimate that the error in the thickness calibration is less than 10%.

For the *in situ* Kerr imaging a similar setup as described in Ref. 24 was used (see Fig. 1). The sample was illuminated with the light from a 50 W halogen lamp. A combination of colored glass filters was used to block the blue and infrared light. The light passed a Glan-Thompson polarizer. The incident angle was about 20° with respect to the surface normal. A special ''long-distance'' microscope objective forms an image of the crystal on the chip surface of a ''slow-scan'' charge-coupled device (CCD) camera. For polarization analysis a second Glan-Thompson polarizer is placed in front of the microscope objective. Images for opposite magnetization either in the remanent state or with an external magnetic field of about 300 Oe normal to the surface were taken for the analyzer set close to maximum extinction.

By Kerr imaging a Ni wedge, ranging from 3.9 ML to ≈ 12.5 ML, we observed the spin reorientation during the H_2 exposure. A H_2 partial pressure of 10^{-9} mbar was adjusted and a series of Kerr images of the Ni wedge were taken with the repeated sequence of -300, 0, $+300$, 0 Oe external field. In Fig. 2 the asymmetry image, i.e., the difference of the image for -300 and $+300$ Oe divided by their sum, is displayed for five H_2 exposures of the same selected stripe of 0.6 mm $\times 5$ mm at $T=143$ K. At the low end of the stripe, corresponding to 5.5 ML Ni thickness, the asymmetry is zero, indicating that there is no polar Kerr signal and therefore no perpendicular component of the magnetization. The magnetization component parallel to the film does not significantly contribute to the measured Kerr signal. Using bulk optical constants we estimate the longitudinal Kerr effect to be smaller by a factor of about 12 for the chosen geometry. Experimentally we found an even smaller longitudinal Kerr effect. While for the clean Ni wedge a Kerr asymmetry is observed only for films thicker than about 11 ML the border of the spin reorientation decreases with increasing H_2 exposure down to about 7 ML at 1.4 langmuir (L). The exposure is determined from the pressure as read from the ion gauge without any further corrections. The actual H_2 exposure is considerably larger, approximately by a factor of 3–4. The uptake curve, critical thickness of the spin-reorientation transition versus H_2 exposure, is consistent with a simple first-order adsorption process. At complete hydrogen coverage the critical thickness is reduced by about 4 ML with respect to the clean Ni surface.

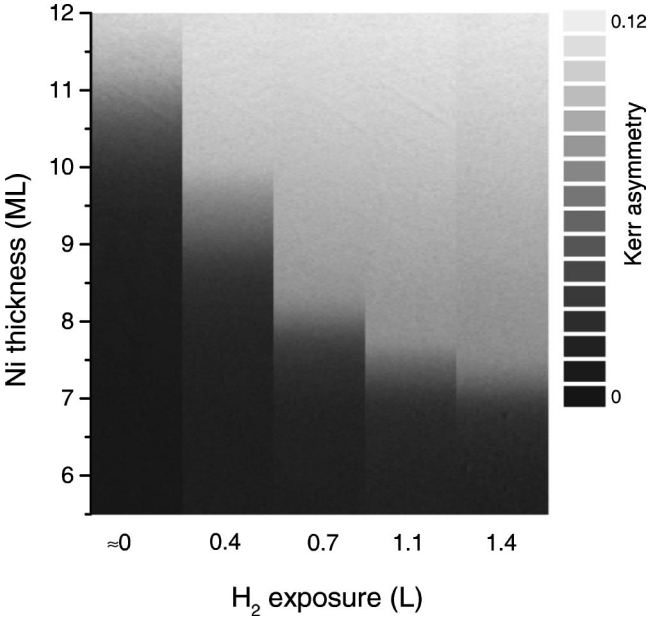

FIG. 2. Polar Kerr asymmetry images of the same section of a Ni wedge on Cu(001) for five H_2 exposures at $T=143$ K. The Ni thickness increases from the bottom to the top of the image as indicated by the scale on the left hand side. The bright area indicates the presence of perpendicular magnetization, the dark area in-plane magnetization.

Figure 3 shows the critical thickness d_c as a function of the sample temperature for the clean (squares) and hydrogen-covered surface (circles). As indicated in the inset, the thickness at which the remanent Kerr signal dropped to 80% (10%) of the extrapolated polar Kerr signal of the same thickness is indicated as solid (open) symbols. The data points for the uncovered Ni wedge were taken for decreasing temperature. Because of unavoidable hydrogen adsorption (of the order of 0.05 L), d_c might be already reduced at low temperatures. From uptake curves, d_c versus hydrogen coverage, we estimate that at the lowest temperature in Fig. 3 this would lead to an increase of d_c (indicated by an arrow) of less than 0.4 ML for the clean film. About 1.7 L of H_2 was adsorbed at 143 K for the hydrogen-covered Ni film. Then Kerr images were taken for increasing sample temperature and d_c was determined in the same way as for the clean film. Because at about 300 K hydrogen desorbs, d_c increases and finally merges into the curves for the clean Ni within the experimental error.

Generally, a very fast increase of the remanent Kerr signal at the reorientation transition was observed that the d_c determined from the drop to 10% or 80% of the full polar Kerr signal at remanence or from the drop to 50% with 300 Oe external field differ only by a fraction of a monolayer. In the following discussion we use always values of d_c determined from the drop to 10%.

Similar experiments were performed for CO adsorption.[25] There d_c (determined from the 10% remanence curve) of about 8 ML was obtained at low temperatures ($T=143$ K). A

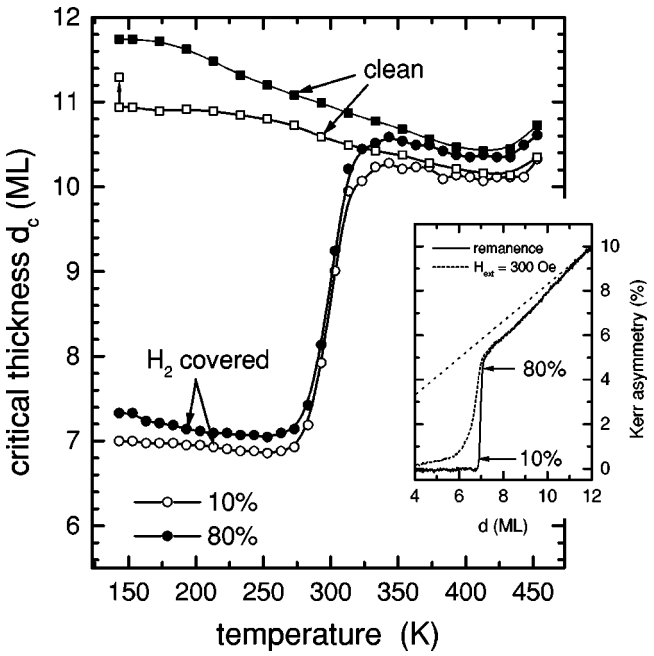

FIG. 3. Critical thickness d_c of the spin-reorientation transition of a Ni film vs sample temperature for the clean surface (squares) and for the surface exposed to 1.5 L H_2 at 143 K (circles). Open (solid) symbols represents the thickness at which the remanent Kerr signal is dropped to 10% (80%) of the (extrapolated) polar Kerr signal of the same thickness. Note that the strong increase of d_c at about 300 K is caused by the desorption of hydrogen at that temperature. The small arrow at the open squares at $T=143$ K indicates an estimate of the reduction of d_c by possibly adsorbed small traces of hydrogen. The inset shows the measured Kerr asymmetry as a function of the Ni thickness d at 233 K for the H-covered film. The dashed line indicates the extrapolated polar Kerr signal used in the determination of d_c.

small fraction of CO remained on the Ni surface even after annealing to 450 K opposite to the case of hydrogen adsorption which is fully reversible. The influence of a Cu cover layer was investigated on a Cu/Ni/Cu(001) double wedge. Largely independent of the Cu cover layer thickness a $d_c=7.4$ ML at $T=300$ K and $d_c=8.1$ ML at $T=143$ K was found for the Cu/Ni/Cu sandwich.

For the above measurement the Ni film was annealed to 450 K for several minutes which results in rather smooth films[26] but does not change the magnetic properties besides a small reduction in the coercive field.[8] It has been shown that surface roughness may affect d_c as well.[27,28] Therefore we compare the d_c obtained from the annealed film with the d_c derived from measurements taken directly after the Ni wedge was grown at 298 K. For the latter we found the critical thickness about 1/3 ML smaller at 300 K. However, repeated temperature cycling after the first annealing did not cause any further change in d_c.

The thickness d_c at which the spin reorientation from in-plane magnetization to perpendicular magnetization occurs is not related to the thickness at which the film starts to develop a dislocation network to reduce the strain.[5,15,21] While earlier work[14,29] reported the onset of misfit dislocations at about 8 ML it was found recently that no significant reduction of the tetragonal distortion occurs for thicknesses up to at least 11 ML.[21] By measuring hysteresis loops with film thickness O'Brien *et al.*[15] found a strong increase of the coercive field at a thickness of 13 ML which is in agreement with our own observation. The above authors interpreted this increase as the onset of misfit dislocation formation. Therefore the spin-reorientation transition of the clean Ni film, which we found to occur at about 10–11 ML, is still below this onset of misfit dislocations.

Magnetization anisotropy energies for Ni/Cu(001) films and Cu/Ni/Cu(001) sandwiches were determined by several groups.[5,9,14,15] The values for d_c, K_{2v}, K_{2s}, and K_{2i} are summarized in Table I. Comparing the values of $K_{2s}+K_{2i}$ of Ref. 5 and K_{2s} of Ref. 14 would imply that the surface/vacuum interface does not contribute significantly. Contrary to this result a recent *ab initio* calculation shows that at $T=0$ K the surface/vacuum anisotropy is much larger than the anisotropy of the Cu/Ni interface.[30] In our experiment we could not determine K_{2v} independently. However, if we take the value of K_{2v} from Ref. 5 and $2\pi M_s^2=7.5$ μeV/atom, we derive with $(2\pi M_s^2-K_{2v})d_c=K_{2s}+K_{2i}$ the values $K_{2i}=-83$ μeV/atom and $K_{2s}=-153$ μeV/atom from our measurements on Ni/Cu(001) and Cu/Ni/Cu(001). We see that the surface magnetocrystalline anisotropy K_{2s} at the Ni/vacuum interface is indeed much larger than that of the Ni/Cu interface in agreement with the ''intuitive'' picture of a stronger disturbance of the electronic structure at the surface. If we extrapolate the measured d_c of the hydrogen covered Ni surface to 300 K we get $d_c=6.8$ ML and $K_{2s}=-70$ μeV/atom. Therefore, the absolute value of the surface anisotropy energy decreases dramatically upon H_2 adsorption. It seems that hydrogen adsorption reestablishes a more bulklike behavior of the surface. Our value of the Cu/Ni interface anisotropy is quite low compared to the values of Ref. 14. However, their value derived from a quite steep

TABLE I. Critical thickness d_c of the reorientation transition and derived surface K_{2s}, interface K_{2i}, and volume K_{2v} anisotropy constants for Ni/Cu(001) (1 mJ/m^2=386 μeV/atom, 1 mJ/m^3=68.3 μeV/atom).

	Our results	From Ref. 5	From Ref. 14	From Refs. 6,15
K_{2v} [μeV/atom]	–	30	37	–
d_c [Ni/Cu(001)] [ML]	10.5	7	–	10/7
d_c [Cu/Ni/Cu(001)] [ML]	7.4	–	–	6
$K_{2s}+K_{2i}$ [μeV/atom]	−236 [a]	−154	–	–
K_{2s} [μeV/atom]	−153 [a]	–	–	−85 [a]
K_{2i} [μeV/atom]	−83 [a]	–	−154	−62 [a]

[a]Derived using $K_{2v}=30$ μeV/atom from Ref. 5.

wedge would imply a critical thickness of about 10 ML, which definitely is not consistent with our data. On the other hand, O'Brien *et al.*[15] found a critical thickness of about 6 ML or $K_{2i}=-62$ μeV/atom for a Cu/Ni/Cu(001) sandwich quite close to our result. Their value for the uncovered Ni wedge, however, $d_c \approx 7$ ML is much too low compared to our result. In view of the difficulties in avoiding hydrogen adsorption even at room temperature, we believe that the reported low values of d_c and therefore of K_{2s} may be caused by such an adsorption. The fact that $|K_{2s}|$ is much larger than $|K_{2i}|$ is also in agreement with the first principles calculation of Uiberacker *et al.* at $T=0$ K.[30]

The temperature dependence of d_c is quite small because of the opposite sign of surface/interface anisotropy energy $K_{2i}+K_{2s}$ and the effective volume anisotropy $K_{2v}-2\pi M_s^2$, largely canceling out temperature dependence. If we take from the temperature-dependent measurements of Ref. 9 the extrapolated value $K_{2v}(0\ \mathrm{K})=72$ μeV/atom and our (extrapolated) $d_c(0\ \mathrm{K})=11.6$ ML for the clean Ni surface, we obtain $K_{2s}+K_{2i}\approx -700$ μeV/atom. This is much larger than the result of the theoretical calculations which are about -100 μeV/atom.[31,30] However, in Ref. 30 the definition of K_{2s} and K_{2i} is different from that used above to analyze the experimental data. In the theoretical work K_{2s} and K_{2i} are essentially the magnetic anisotropy energy of the surface Ni layer and the interface Ni layer, respectively, while in the experimental work K_{2s} and K_{2i} are determined from the *extrapolation* down to zero film thickness. These two definitions lead to the same result only in the case that the magnetic anisotropy energy does not change with thickness in the interior of the film, which is, according to their calculation, not fulfilled.

In conclusion, we have shown that hydrogen adsorption strongly reduced the critical thickness of the spin-reorientation transition d_c in Ni films on Cu(001). For the clean Ni film we observe a d_c of about 10–11 ML. Similarly, CO adsorption or a Cu cover layer reduces d_c. The surface magnetization anisotropy energy for the clean Ni film, $K_{2s}=-153$ μeV/atom, is *larger* than the Ni/Cu(001) interface anisotropy, $K_{2i}=-83$ μeV/atom, at $T=300$ K.

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