Transition to the perpendicular easy axis of magnetization in Ni ultrathin films found by x-ray magnetic circular dichroism

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Using soft-x-ray magnetic circular dichroism we have observed a change in the easy axis of magnetization in Ni ultrathin films on Cu(001) from parallel to the surface for 5–9 monolayers (ML) to perpendicular for 10–75 ML. This is an unusual effect which is counter to the predictions of magnetic surface anisotropy arguments. We conclude that the effect is due to a shape anisotropy, introduced either by a change in the Ni lattice structure or by three-dimensional morphological changes in the film.

If an epitaxial film of a magnetic material is made sufficiently thin, the importance of the surface magnetization anisotropy increases to the point where the easy axis of magnetization may become perpendicular to the surface.[1–8] This possibility that the reduced symmetry of surface atoms could affect the magnetic anisotropy was first suggested by Néel.[9] More recently Gay and Richter[1] showed explicitly that a spin-orbit-induced anisotropy at the surface could overcome the magnetic dipole interaction and lead to a perpendicular easy axis for monolayer films. This phenomenon has been observed for a number of ultrathin magnetic films, typically in the 2–5 monolayer (ML) thickness range.[4–8] For thicker films, there is a rotation of the easy axis into the surface plane due to the volume effect of the magnetostatic energy. Perpendicular magnetization arising from interface anisotropy, closely related to the surface anisotropy, is found in multilayer magnetic materials,[10] which are potentially important for high-density magnetic storage media.

In this paper we describe our findings of perpendicular remanent magnetization in ultrathin films of Ni, grown on Cu(001) substrates. For film thicknesses of 5–9 ML we find a parallel magnetic easy axis, with ferromagnetic ordering at room temperature. Surprisingly, for films with thicknesses between 10 and 75 ML, we have found a transition to perpendicular anisotropy, with a Curie temperature above room temperature. This is a very unusual behavior which cannot be explained by standard arguments that attribute perpendicular magnetization to the surface anisotropy.

Our magnetic measurements were made using the technique of x-ray magnetic circular dichroism (XMCD), which has been rapidly established as a powerful method for investigating the element-specific magnetic ordering of ultrathin films.[11] In XMCD of the $3d$ transition elements, the $L_{2,3}$ soft-x-ray absorption spectrum (SXA) is obtained on a magnetized sample using circularly polarized photons. The magnetic dichroism signal, $\sigma_M=\sigma^+-\sigma^-$, is the difference between the SXA spectrum with the photon spin parallel (σ^+) and antiparallel (σ^-) to the sample magnetization. The average of the two spectra, $\sigma_0=\frac{1}{2}(\sigma^++\sigma^-)$, is in most circumstances identical to the linearly polarized SXA spectrum. Recently, Thole *et al.*[12] and Carra *et al.*[13] have derived sum rules which relate the integrated intensity of the dichroism signal σ_M at the L_3 and L_2 edges to the ground-state expectation values $\langle L_z\rangle$ and $\langle S_z\rangle$ for atoms, but the application of these sum rules to band ferromagnetism is still controversial. For this study we need only rely on the direct proportionality between σ_M and the net vector magnetization of the sample; that is, $\sigma_M\sim\boldsymbol{\Sigma}\cdot\mathbf{M}$, where $\boldsymbol{\Sigma}$ is the photon spin and M is the net sample magnetization. As an example, XMCD has been previously used to study the perpendicular magnetization of a 2-ML film of fcc Fe.[7]

Samples were made using ultrahigh-vacuum (UHV) vapor deposition. The Cu(001) substrate was a single crystal which was cleaned by repeated cycles of argon ion sputtering (2 keV) followed by annealing above 1000 K, which results in a sharp (1×1) low-energy electron-diffraction (LEED) pattern. The Ni films were grown *in situ* by evaporation after allowing the Cu substrate to cool to room temperature. Evaporation was done either by passing current through a pure Ni wire or by electron-beam heating the tip of a Ni wire. Film thickness was determined by a combination of techniques. A quartz-crystal microbalance at the sample position was used to measure the evaporation rate. This microbalance has previously been calibrated by monitoring the $c(2\times2)$ electron-diffraction spots by LEED during the evaporation of Mn onto Cu(001).[14] The film thicknesses were further confirmed by monitoring the absorption-edge jump at threshold in the L_3 spectra, and by measuring the Cu and Ni $3p$ photoemission intensities. We estimate our reported film thicknesses to be accurate to within ±20%. Evaporation rates were ~1 ML/min, with a background pressure during deposition in the 10^{-10}-Torr range.

The XMCD experiments were performed on the 10 M toroidal grating monochromator beamline located at the Synchrotron Radiation Center (SRC) of the University of Wisconsin. The beamline is equipped with a water-cooled aperture which allows the selection of either linear, left-handed, or right-handed elliptically polarized photons, with polarization of 85% as determined by calculations and comparison to other MXCD work.[15] Due to the exceptional stability of the photon flux and polar-

ization at the SRC beamline, dichroism measurements with very high reproducibility are obtained by maintaining a constant incident-photon spin direction and measuring σ^+ and σ^- by reversing the sample magnetization. The reliability of this method has been explicitly checked by measuring nonferromagnetic Mn on ferromagnetic Fe, which shows that absolute XMCD intensities as small as 1% can be detected.[15]

After growth, the samples were magnetized under UHV conditions by a 2-kG electromagnet, with the field either perpendicular to the surface or in plane along any chosen axis. All XMCD measurements were made on the remanent sample magnetization at room temperature, in a chamber with a background pressure of 6×10^{-11} Torr. For in-plane magnetization measurements the incident photon beam was directed at 65° from the sample normal. The absorption spectra were measured using total electron yield $Y(\hbar\omega)$, which is related to the absorption cross section according to the relation $Y(\hbar\omega) \propto \hbar\omega\sigma(\hbar\omega)$. The yield spectra were corrected for the incident photon flux on the sample and the linear $\hbar\omega$ dependence using a Au photodiode current, corrected according to the tabulated Au photoyield.[16] This result was confirmed using a Cu diode. An $(\hbar\omega)^{-n}$ background was subtracted from the Ni $L_{2,3}$ spectra to remove the contribution from the substrate.

In Fig. 1 we show the Ni $L_{2,3}\sigma^+$ and σ^- SXA spectra along with the difference (dichroism) spectrum σ_M for a 15-ML-thick sample, which was magnetized perpendicular to the surface. These spectra are shown with minimal manipulation, incorporating only a normalization to the incident photon flux. No corrections or alterations for incomplete photon polarization, smoothing, or energy shifts are needed, and none have been applied. We find good agreement between our results and previously published dichroism spectra for bulk Ni.[17,18] In their

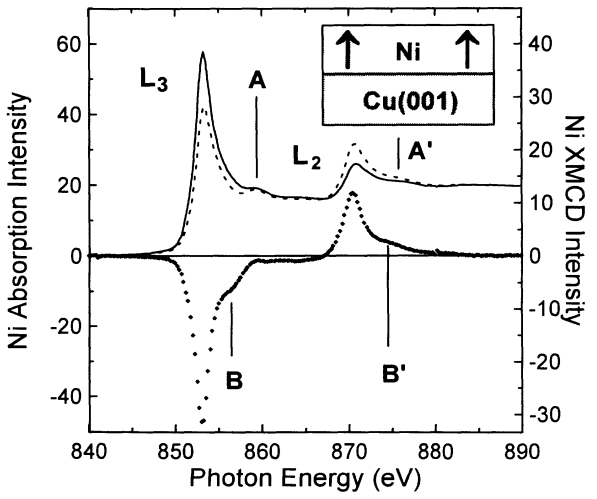

FIG. 1. (Top) Ni $L_{2,3}$ SXA spectra taken with photon spin parallel (dashed line) and antiparallel (solid line) to sample magnetization for a 15-ML Ni film magnetized perpendicular to the surface. (Bottom) Difference spectrum, XMCD, showing ferromagnetic ordering with magnetization perpendicular to surface. Features B and B' appear only in the XMCD spectrum.

analysis of bulk Ni dichroism, Smith *et al.*[18] report values for the intensity ratio $R=I(L_3)/I(L_2)$ of $R_0=2.5\pm0.1$ for the linear (average) absorption σ_0, and $R_M=1.6\pm0.1$ for the absolute value of the dichroism signal $|\sigma_M|$. For the 15-ML Ni/Cu(001) film we obtain values of $R_0=2.8\pm0.2$ and $R_M=2.2\pm0.2$, which is in close agreement with the results of Chen, Smith, and Sette,[17] considering the different approaches taken to calculating the integrated intensities.

To obtain R_0 for the polarization-averaged spectra, we used a step-function background to approximate the contribution to the absorption spectrum from transitions to the continuum. The features B and B', which are present in the dichroism spectrum σ_M but not in the linear SXA spectrum σ_0, were reported by Chen, Smith, and Sette[17] and have been attributed to a multielectron excitation in the final state. The features A and A' are present in the σ^+, σ^-, and σ_0 spectra but not in the σ_M spectrum, and are therefore not intrinsically related to the dichroism. These features are well described by one-electron band-structure calculations.[18] To compare the Ni ultrathin film results with bulk Ni, we have also measured the circularly polarized SXA spectra for a Ni(100) single crystal, magnetized parallel to the surface along the {110} direction. There is no significant difference between the linear absorption spectra of the Ni/Cu(001) films and bulk Ni. However, the normalized dichroism intensity, given by $\sigma_N=\sigma_M/\sigma_0$, is nearly twice as large in the ultrathin films (30%) as it is in bulk Ni(100). This is the largest XMCD signal reported for Ni to date, to our knowledge.

In Fig. 2 we show the normalized dichroism intensity

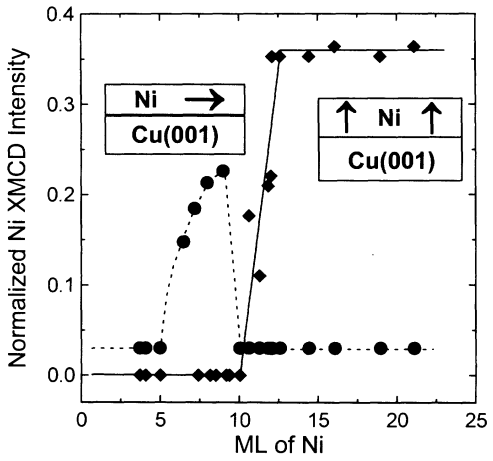

FIG. 2. Normalized Ni XMCD intensity as a function of Ni film thickness. Below 10 ML, the films exhibit remanent magnetization parallel to the surface plane (dots). Above 12 ML, the films show saturated perpendicular magnetization (squares). This behavior persists up to 75 ML. For a small range of coverages near 9–11 ML, there is no evidence of room-temperature ferromagnetic order. The parallel remanence data are offset from zero for clarity. Values for parallel magnetization and perpendicular magnetization have been multiplied by 1.3 and 1.18, respectively, to account for incomplete photon polarization and alignment of sample magnetization to photon spin vector.

σ_N, measured at its maximum absolute value in the L_3 edge, as a function of Ni film thickness. The values for both perpendicular and parallel magnetization reported in Fig. 2 have been corrected for incomplete photon polarization (85%). The values reported for parallel magnetization have been further corrected for the nonparallel alignment of sample magnetization and photon spin vector [(sin 65°)$^{-1}$]. This dichroism signal is a measure of the degree of ferromagnetic ordering, and by separately measuring samples magnetized parallel or perpendicular to the surface we can determine the direction of the net sample magnetization. For films below 5 ML, we find no evidence of remanent magnetization at room temperature, which is in excellent agreement with contemporary determinations of the Curie temperature of the Ni/Cu(100) system, which find that T_C is below room temperature for coverages below 5 ML.[19,20] From this we confirm the 20% accuracy of our film thickness measurements. Between 5 and 9 ML thickness, we find room-temperature parallel remanence according to the XMCD signal, with a magnitude that was somewhat dependent on sample growth history.

The transition from parallel to perpendicular magnetization is very abrupt, occurring over a range of film thicknesses of only about 2 ML. In the region of perpendicular magnetization, we found no evidence of a parallel component of magnetization for 2-kG field strengths along either the {100} or {110} surface directions. In the region of parallel remanence (5–9 ML), we found no evidence of perpendicular moment. One sample, with film thickness near 9–10 ML, displayed no evidence of net magnetization in either the parallel or perpendicular directions. We have also investigated two much thicker Ni films. A 75-ML-thick film has the saturated σ_N value of 35% for perpendicular magnetization and no XMCD for in-plane magnetization. A 150-ML-thick film has σ_N values of 18% and 2%, for in-plane and perpendicular magnetization, respectively. Between 75 and 150 ML, the magnetic properties of the film begin to convert to bulklike.

Conventional arguments based on surface anisotropy cannot explain a transition from parallel to perpendicular magnetization as the film thickness is increased above 10 ML. For films thicker than 10 ML, any surface anisotropy should be overcome by the magnetic dipole interaction, which favors in-plane magnetization. There is evidence from two sets of experiments that *capped* ultrathin films can exhibit such a transition. Egelhoff *et al.*[21] find that a monolayer of Cu on top of 5 ML fcc Fe/Cu(001) causes the magnetization to rotate from in plane to perpendicular. Similarly, Engel *et al.*[8] found that perpendicular magnetization could be induced in 10-Å-thick Co(111) films by a monolayer cap of Cu, Pd, or Ag.

Although we made no deliberate attempt to cap our films with copper, there is some evidence that copper can diffuse through defects in epitaxial films and form a capping layer, particularly if the films are annealed.[22] Given the possible influence on the sample magnetic properties, we executed a careful analysis of the Cu and Ni 3*p* photoemission line shapes and intensities, to determine the limits of possible Cu overlayer contamination. No evidence of surface Cu was found, to a sensitivity limit of 0.1 ML, using highly surface-sensitive soft-x-ray photoemission spectroscopy. Similar negative results were found in a search for potential inadvertent Fe, Co, or Mn contamination. We conclude that the abrupt transition from parallel to perpendicular magnetization is a property of a pure nickel film without a Cu capping layer.

For bulk fcc Ni, the easy axis of magnetization is the [111] direction. This should not favor either in-plane or perpendicular magnetization in the epitaxial films on Cu(100). The reduced value of the normalized dichroism signal, $\sigma_N = 20\%$, for both bulk Ni and (5–9)-ML nickel films, may be in fact due to the formation of multiple domains oriented parallel to the surface in response to having the easy axis ([111]) oriented obliquely to the surface plane. The rapid rise of the perpendicular dichroism to a large, constant value of 35% means that these films are very nearly a single magnetic domain. For comparison, the largest $2p_{3/2}$ MCD signal measured to date is 40%, in Co/Pd superlattices.[10]

We believe the explanation for the parallel-to-perpendicular magnetization transition for (10–20)-ML films must lie in the film morphology. In an earlier study, Zhang *et al.*[23] have determined the structure of 10-ML-thick Ni/Cu(001) films using quantitative x-ray photoelectron diffraction. They found that these films grew with lateral coherence to the substrate (sometimes called pseudomorphic epitaxy), such that the in-plane lattice constant of Ni was identical to the substrate copper. The interlayer Ni spacing subsequently relaxed, resulting in a distorted fcc structure (face-centered tetragonal, fct), with a Ni-Ni nearest-neighbor spacing equal to that of bulk fcc Ni. Above 10 ML, dislocations and other structural defects allow the film to relax back to the equilibrium Ni fcc structure with disorder.

The strained-layer fct structure (0–9 ML) exhibits parallel magnetization, and we conclude that the transition to perpendicular magnetization is due to a relaxation back to a fcc structure accompanied by disorder, as the film exceeds the critical layer thickness for coherent lateral epitaxy. Since the equilibrium Ni lattice constant is smaller than that of the substrate, film relaxation above the critical thickness can result in a lateral contraction of islands in the Ni layer, creating and exposing new surface areas that create, in effect, three-dimensional islands with substantially different magnetic properties from those of the thinner films. Along this line of argument, we note that recent Kerr studies of the temperature dependence of magnetization by Huang *et al.* show a crossover from two- to three-dimensional behavior at Ni film thicknesses above 7 ML.[20] We feel this system deserves further study, using additional structural probes such as scanning tunneling microscopy, to clarify the nature of the structural change that causes the magnetic transformation.

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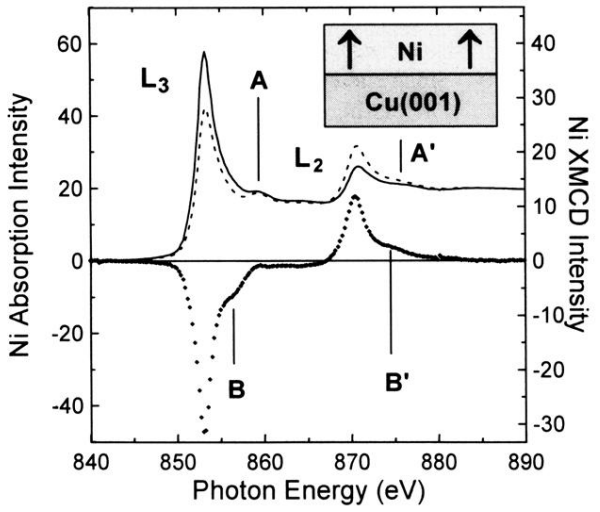

FIG. 1. (Top) Ni $L_{2,3}$ SXA spectra taken with photon spin parallel (dashed line) and antiparallel (solid line) to sample magnetization for a 15-ML Ni film magnetized perpendicular to the surface. (Bottom) Difference spectrum, XMCD, showing ferromagnetic ordering with magnetization perpendicular to surface. Features B and B' appear only in the XMCD spectrum.