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Hydrogen chemisorption on ferromagnetic thin film surfaces

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We report measurements of hydrogen desorption and its effect on the magnetism of pseudomorphic ultrathin films of Fe, Co, and Ni on Cu(001). Hydrogen desorption is measured with thermal desorption spectroscopy (TDS) and changes in the magnetic properties with saturation hydrogen coverage are measured with the surface magneto-optic Kerr effect (SMOKE). TDS of hydrogen shows that Co films less than 2.5 monolayers thick do not completely cover the substrate, and that Co deposited at 300 K does not alloy with the Cu(001) substrate. By carefully controlling the thickness of the Ni films, we can tune the ferromagnetic Curie temperature to below the hydrogen desorption temperature. The thermal desorption of hydrogen from the paramagnetic Ni thin film surface is similar to that from bulk ferromagnetic Ni(001) indicating magnetism has no measurable effect on thermal desorption kinetics. Hydrogen is more weakly chemisorbed on ferromagnetic Co thin film surfaces and more strongly chemisorbed on ferromagnetic Fe thin film surfaces as compared to Ni(001). SMOKE measurements show hydrogen chemisorption produces a magnetically "dead" surface layer on Ni films, a reduction in the surface layer magnetism on Co films, and an enhancement in the surface layer magnetism on Fe films.

I. INTRODUCTION

In a previous publication¹ we showed that reflection high energy electron diffraction (RHEED) and hydrogen thermal desorption spectroscopy (TDS) can be used to determine film morphology for the growth of Co on Cu(001). RHEED is used to determine film thickness and the growth mode. TDS from a freshly deposited film will measure the amount of hydrogen contamination, which is not measurable with Auger electron spectroscopy (AES). TDS of hydrogen probes the chemical composition of the topmost surface layer, since different elements have different chemisorption binding energies confirming the existence of a possible segregated overlayer of substrate material.

Since these films have a Curie temperature that increases monotonically with film thickness, we can compare the desorption kinetics of hydrogen from both ferromagnetic and paramagnetic thin film surfaces by varying the film thickness. Earlier measurements of the desorption parameters from paramagnetic and ferromagnetic Co thin film surfaces suggested there may be a "magnetocatalytic" effect since films less than 2.2 monolayers (ML) thick exhibited anomalously low activation energies.² These anomalously low values are a manifestation of the fact that the Co films do not completely cover the substrate for films less than 2.5 ML thick. For Ni the Curie temperature does not increase as rapidly as for Co, so a comparison of a thicker paramagnetic film to ferromagnetic Ni can be made.

Surface magneto-optic Kerr effect (SMOKE) measurements have shown that the magnetic properties depend on film thickness and layer uniformity.³ SMOKE hysteresis loops obtained from smooth, continuous films have a square shape that is characteristic of a single magnetic domain. Also the approach to criticality of the ferromagnetic/paramagnetic phase transition is sensitive to the uniformity of the film under study because long-range

correlation effects which are sensitive to disorder become more important near T_c . However, little is known about the effects of hydrogen chemisorption on the magnetic properties.

Thin films of Ni, Co, and Fe are all ferromagnetic on Cu(001) with thickness dependent Curie temperatures. These films each have different magnetic anisotropies.³ Ni films have an in-plane magnetization up to a thickness of 5 ML with no evidence of in-plane magnetocrystalline anisotropy. Beyond this thickness, the Ni films develop an out-of-plane magnetization that increases with film thickness. Co films have an in-plane magnetization with no evidence for an out-of-plane magnetization throughout the film thickness range studied. Fe films have an out-of-plane magnetization up to a thickness of 6 ML.⁴

Hydrogen is expected to change the magnetization of the surface layer through the hybridization of the H 1s level with the 3d electrons responsible for the ferromagnetism. This simple picture can be viewed as a "filling" of the unoccupied 3d states above the Fermi energy. The magnetic moment per atom is defined as the difference between the occupation number of majority-spin and minority-spin electrons. The majority-spin 3d subband is completely occupied in Ni and Co, and partially occupied in Fe, so the addition of 3d electrons through hybridization will increase the number of minority-spin states in Ni and Co, and give a net reduction in the magnetic moment of the surface atoms. For Fe, both the majority-spin and minority-spin bands cross the Fermi level, so the addition of 3d electrons at the Fermi level will have a less dramatic effect on the magnetic moment of the surface atoms. In addition, there is a strong dependence of the magnetic moment per atom in fcc Fe on the lattice parameter,^{5,6} so an outward relaxation of the surface atoms upon chemisorption of hydrogen⁷ could produce an increase in the mag-

netic moment of the surface atoms in the absence of any differential band-filling effects.

II. EXPERIMENTAL

The experimental apparatus used for this work has been described elsewhere.¹ The Cu(001) single crystal substrate is commercially available from Monocrystals Inc., Sherwood, OH. The substrate surface is mechanically polished in successive steps down to 1 μm diamond paste and electropolished before insertion into the UHV apparatus. The electropolishing procedure for Cu is found in Tegart.⁸ A solution of 170 ml phosphoric acid, 25 ml sulfuric acid, and 75 ml distilled water is prepared. A Cu plate serves as the cathode and the mechanically polished substrate is the anode. The substrate is placed in the solution for about 1 min, with the potential stabilized at 2.1 V. The electropolishing removes the layers of damage produced by mechanical polishing, and electropolished samples exhibit good low-energy electron diffraction (LEED) patterns and AES spectra after only a few minutes of sputtering followed by annealing to 750 K.

The films were deposited at a substrate temperature of $T_g = 300$ K in a background pressure of 5×10^{-10} mbar. This produces films with typical surface contamination levels of below 5% CO and 10% H₂ as determined by AES and TDS. The deposition rate was held constant in the 1 to 3 ML/min range for each of the experiments using the closed loop feedback system of an Intellemetrics Model IL800 deposition controller. The controller uses the output of a quartz crystal monitor as an input to a proportional integral derivative feedback loop to determine the power output of an electron bombardment evaporator. This keeps the flux of the evaporant constant throughout the duration of the experiment. The tooling factor of the controller is adjusted such that a monolayer is defined as the amount of material deposited between successive maxima in the specular beam intensity of the RHEED experiment.

Film thicknesses were determined with quartz crystal microbalances calibrated with RHEED oscillations as shown in Fig. 1. The RHEED oscillations for Cu and Ni are similar. There is a well-defined maximum corresponding to the completion of the first monolayer, and the oscillations slowly damp out due to increased roughening of the surface. For Co and Fe, the first maximum is not as well defined as the succeeding ones. This indicates a possible bilayer growth mode that has been proposed for these epitaxial systems where the first and second layers grow simultaneously.^{9,10} Recent helium scattering experiments of the Fe/Cu(001) system suggest that bilayer growth is followed by layer-by-layer growth above a critical thickness of 2 ML¹¹ and our measurements show stronger oscillations reappearing after 4 ML of Fe are deposited. This observation is also supported by our LEED measurements.

To determine the amount of surface roughness associated with each of these films, we measured a 3 ML film of each material with LEED. This thickness was chosen to insure that the Cu(001) substrate was completely covered. Henzler¹² showed the diffraction spot width from a rough Si(001) substrate produced by Ar⁺ ion sputtering oscil-

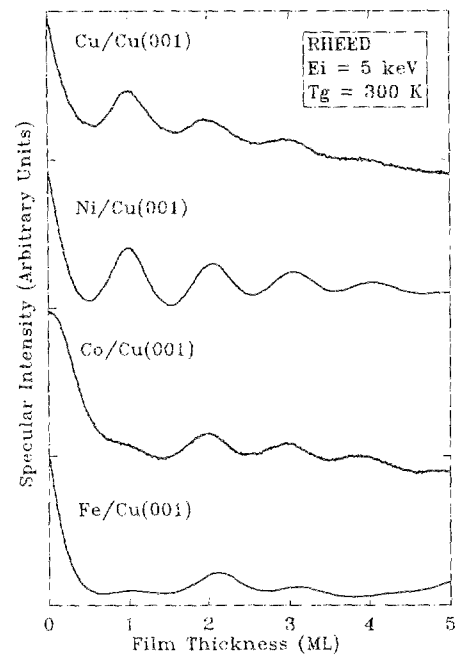


FIG. 1. RHEED oscillations for Cu, Ni, Co, and Fe on Cu(001). The 5 keV electrons were incident at an angle of 82° with respect to the surface normal and the intensity of the specularly reflected beam was measured as a function of deposition time.

lated with incident energy. The maxima occur at energies where electrons diffracted from adjacent layers constructively interfere and the minima occur at energies where they destructively interfere. Figure 2 shows a set of LEED measurements for 3 ML films of Ni, Co, and Fe. The incident electron energy of 140 eV is such that rough films exhibit a maximum in the spot width. Sharp spots are ob-

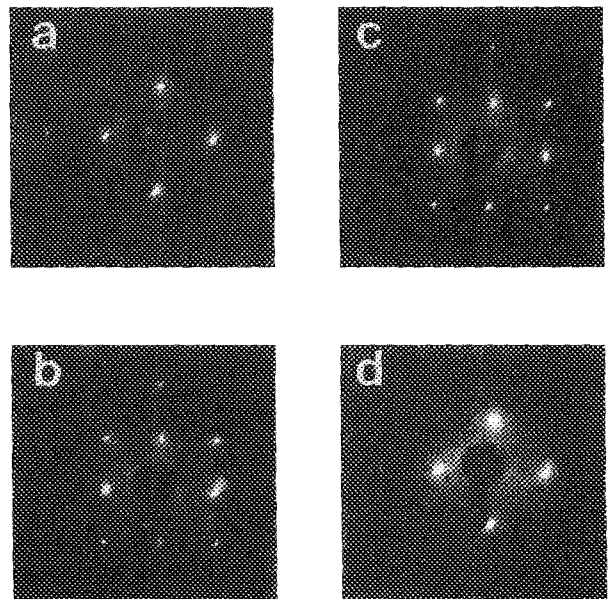


FIG. 2. LEED photos at an incident electron energy of 140 eV (maximum spot width for rough films) for an electropolished Cu(001) substrate (a) and 3 ML pseudomorphic films of Ni (b), Co (c), and Fe (d) grown at a substrate temperature of $T_g = 300$ K.

served for the Ni and Co films, confirming the existence of stable pseudomorphic films. The presence of the $\langle 11 \rangle$ diffraction spots indicates the surface relaxations are different for these films than the relaxation of the substrate, so the films have a tetragonally distorted face centered cubic (fcc) structure as was determined from a complete LEED I - V analysis for the Co/Cu(001) system.¹³ The diffraction spots for the Fe film are broader, which shows the Fe films are rougher due to a number of incomplete layers being present on the surface. If the Fe films grow in a bilayer growth mode for the first four layers on Cu(001),¹⁰ a three-layer film would consist of two complete layers and two-layer thick islands covering half of the surface, producing a LEED pattern with broader spots. These LEED measurements show Ni, Co, and Fe films all grow pseudomorphically on Cu(001), with room temperature growth producing strained layers of fcc Ni(001) and Co(001), and Fe(001).

TDS has been used to probe the chemical composition of the topmost surface layer. TDS measurements are performed by simultaneously heating the sample at a linear rate of $\beta = 1$ K/s, and measuring the desorption rate of gases with an apertured quadrupole mass spectrometer (Leybold-Inficon Model PPC100) which is interfaced to an IBM/PC computer. The surface can be dosed with a precise amount of gas using a homemade flow-controlled gas doser.¹⁴

The Cu(001) substrate surface has an activation energy barrier of about 0.2 eV for dissociative adsorption of molecular hydrogen,¹⁵ so it does not readily adsorb room-temperature H_2 gas since room-temperature gas has an energy of about 1/10 this value. The activation energy barrier is associated with the fully occupied $3d$ band near the Fermi energy.¹⁶ Transition metal surfaces have a partially filled $3d$ band at the Fermi energy, so they have no such barrier and readily adsorb H_2 . Thus, H_2 adsorption can be used as a probe of the composition of the topmost surface layer of a freshly deposited film. The presence of a segregated Cu layer on the surface of a film will prevent it from adsorbing H_2 . Our previous measurements have shown that Co films grown at a higher substrate temperature of 450 K have a segregated layer of Cu on the surface and do not adsorb hydrogen.¹ We have extended these measurements to determine the uniformity of ultrathin epitaxial Co films.

The SMOKE measurements were made with the substrate temperature held at 150 K. Each film was then dosed with 1000 mbar s of hydrogen gas. This amount is sufficient to produce a saturation coverage of hydrogen as was determined from our TDS measurements.

III. RESULTS

The extent to which layers of Co cover the Cu(001) surface was measured with H_2 TDS. Figure 3(A) shows a set of desorption curves for a constant dose obtained from Cu(001) surfaces with varying Co coverage. The initial H_2 coverages, θ_0 , versus Co coverage plotted in Fig. 3(B) increases monotonically as a function of Co thickness up to 2.5 ML. This behavior is similar to TDS measurements of

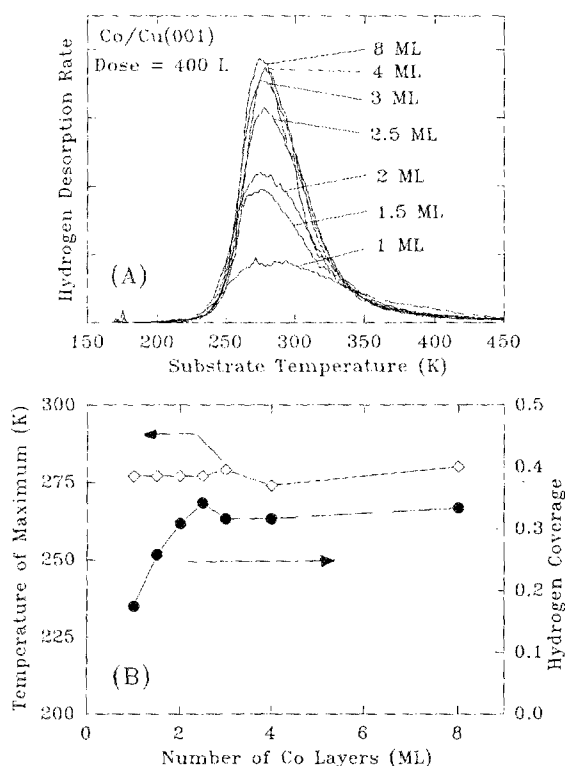


FIG. 3. Hydrogen TDS results for N -layer films of Co/Cu(001) (A) and the data summary (B). The plot of hydrogen coverage versus number of Co layers indicates greater than 2 ML is needed to completely cover the Cu(001) substrate.

hydrogen from Fe films as a function of film thickness.¹⁷ Slight differences may be due to different surface roughness for films above 2.5 ML thickness. There are two possible explanations for these results. Either the deposited Co forms a surface alloy with the Cu substrate for the first few layers or the Co does not completely cover the surface for films less than 2.5 ML thick.

To distinguish between the two possibilities, H_2 TDS measurements were made from 3 ML Co_xCu_{1-x} alloys, with $x = 0.25, 0.5,$ and 0.75 . The alloys were made by codepositing Co and Cu on the Cu(001) substrate with the flux from each of the sources stabilized to give the appropriate stoichiometry. TDS measurements for constant H_2 doses from these alloy films are shown in Fig. 4. Figure 4(B) shows that the temperature of the maximum desorption rate, T_{max} , decreases for increasing Cu concentration. For the $H_2/Cu(001)$ system, T_{max} is 20–60 K higher than for Co(001),^{15,18} so if the H atoms were adsorbed at islands consisting of phase-separated Cu, a high-temperature shoulder would appear in the TDS curve. This "spillover" effect has been observed in Cu coated Ru(0001) catalysts.¹⁹ Since the hydrogen bond is of the order of a single lattice spacing, the alloy surface has some low-energy binding site that is characteristic of chemisorbed hydrogen atoms with a coordination of two different surface chemical species. This low-energy binding site could be produced by an electronic interaction between phase-separated islands of Co and Cu, however our magnetic measurements of codeposited Cu–Co alloy films²⁰ support

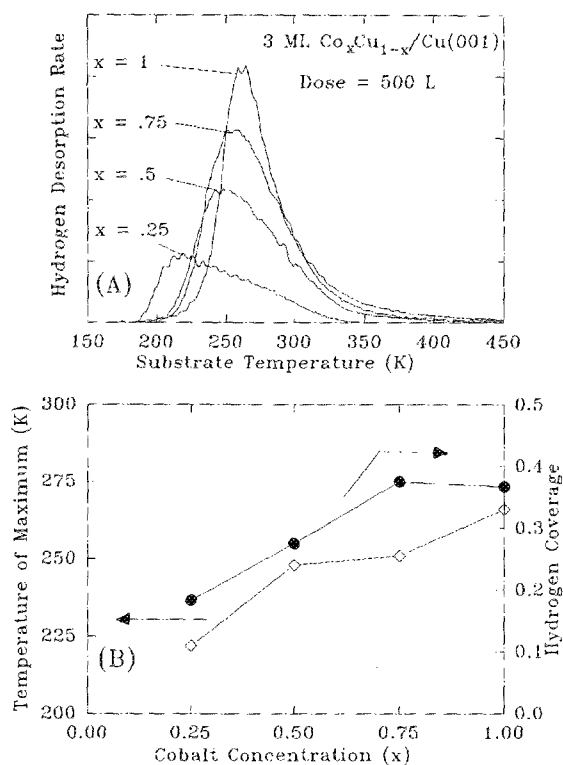


FIG. 4. Hydrogen TDS results for 3 ML $\text{Co}_x\text{Cu}_{1-x}$ alloy films. The monotonic increase with Co concentration of the temperature of the maximum desorption rate indicates the codeposited films are random substitutional alloys.

the hypothesis that the alloy films are metastable random substitutional alloys of Co and Cu. In sharp contrast to these results, the temperature of the desorption maximum is constant for increasing number of Co layers in Fig. 3(B).

$\text{Co}_x\text{Cu}_{1-x}$ alloy films exhibit different TDS curves than the pure Co films, which suggests that Co does not spontaneously form a surface alloy with Cu when it is deposited on the Cu(001) surface. Indeed, the bulk materials are nearly immiscible.²¹ The TDS measurements imply that Co on Cu(001) forms metastable two-layer thick islands in the initial stages of film growth, so film thickness is a rather ill-defined quantity below two atomic layers. This type of film growth is expected from surface energy considerations which predict that Co will not grow in a layer-by-layer growth mode on Cu substrates since Co has a higher surface free energy.²² These measurements support the findings of recent x-ray diffraction measurements of Co/Cu(001) films which showed there is a significant proportion of two-layer thick islands for coverages in the range of 0.5–1 ML.⁹

A comparison of H_2 TDS curves for 3 ML pseudomorphic films of Ni, Co, and Fe on Cu(001) is shown in Fig. 5. The Curie temperature has been determined to be approximately 200 K for a 3 ML Ni film by our SMOKE measurements and it increases by approximately 100 K/ML for thicker films, saturating at the bulk Ni value of 625 K.²³ The curves for the 3 ML Ni film are similar to those observed for bulk ferromagnetic Ni(001)²⁴ with the

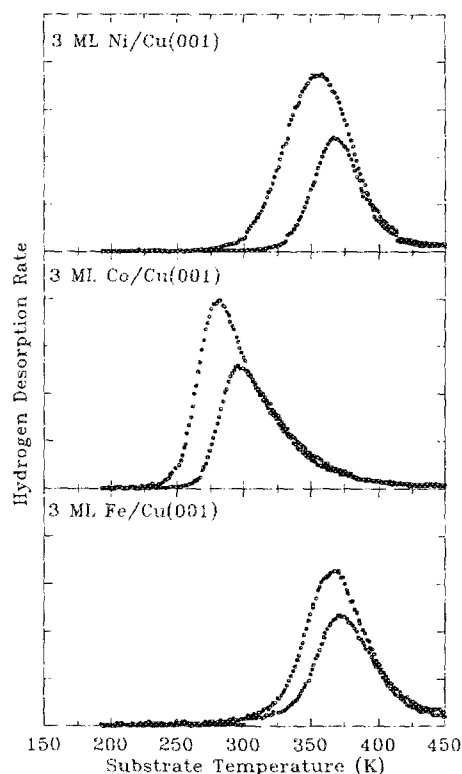


FIG. 5. Hydrogen TDS curves for 3 ML pseudomorphic films of Ni, Co, and Fe on Cu(001). The initial hydrogen coverages in each case are approximately $\theta_0 = 0.5$ for the large-area curves and $\theta_0 = 0.25$ for the small-area curves.

coverage dependent temperatures of the maximum desorption rates for paramagnetic and ferromagnetic Ni equal to within experimental error. Thicker Ni films exhibited similar desorption behavior, in support of the conclusion that the magnetic state of the substrate has no measurable effect on the desorption kinetics. These measurements further confirm the absence of a "magnetocatalytic" effect as was determined from molecular beam studies of the H_2/D_2 exchange reaction on the bulk Ni(001) surface above and below the ferromagnetic Curie temperature.²⁵

The thermal desorption curves from the Co film have an asymmetric line shape, and hydrogen is more weakly bound on Co(001) than on Ni(001) as evidenced by the lower desorption temperatures. The high-temperature "tail" was originally thought to be due to the limited pumping speed of the quadrupole mass spectrometer. This hypothesis has to be rejected since the hydrogen desorption curves from the Ni films are symmetric for similar desorption rates. The curves can be fitted to an Arrhenius expression assuming a coverage dependent activation energy. This behavior is characteristic of a mobile precursor state being involved in the desorption process.²⁶ Detailed fits of the desorption curves for various kinetic models considering these effects will be the subject of a more lengthy publication.²⁷

The desorption of hydrogen from the Fe film is more like the H_2/Ni system, exhibiting second-order desorption, with a slightly higher activation energy. These TDS results show 3 ML films of Ni, Co, and Fe are similar, so differences in their magnetic properties are not due to any gross

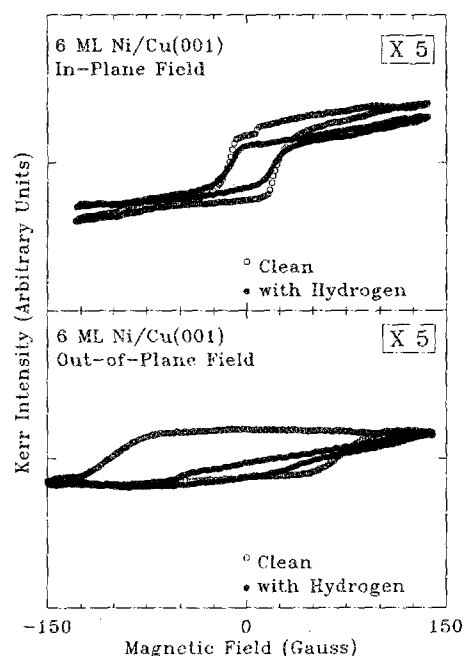


FIG. 6. SMOKE hysteresis loops for a 6 ML Ni/Cu(001) film at 150 K before (open circles) and after (solid circles) a 1000 mbar s dose of hydrogen. The collapse of the out-of-plane hysteresis loop shows that hydrogen demagnetizes the surface layer.

differences in composition and microstructure. This compares well with the LEED measurements of these films presented in Fig. 2.

Ni films 5 and 6 ML thick each have different magnetic anisotropies with a 6 ML Ni film exhibiting an out-of-plane magnetization that is not present for a 5 ML film. This sudden change in the anisotropy offers a means of investigating the magnetic state of the surface layer. If the adsorption of hydrogen demagnetizes the surface layer of a 6 ML film, the out-of-plane magnetization will change drastically. This was indeed observed. Figure 6 shows a net reduction in the in-plane magnetization of a 6 ML Ni/Cu(001) film and a collapse of the observed hysteresis loop in the out-of-plane direction. This indicates hydrogen adsorption is accompanied by the formation of a magnetically dead surface layer on Ni surfaces. These observations are consistent with spin-polarized field-electron emission results that showed the Ni(001) surface is completely demagnetized upon hydrogen adsorption.²⁸

For Co and Fe films we chose a film thickness of 2 ML to study the effect on the magnetism of a saturated layer of hydrogen. For the 2 ML Co film in Fig. 7, there is a 40% reduction in the saturation magnetization of the film. This corresponds to an 80% demagnetization of the top layer which is consistent with the $3d$ band-filling arguments presented above. For the 2 ML Fe film in Fig. 7, the adsorption of hydrogen produces a 15% enhancement in the saturation magnetization. This enhancement is predicted from a bond-order rigid band model of chemisorption²⁹ although the model fails to quantitatively predict the magnitude of the change for Co and Fe.

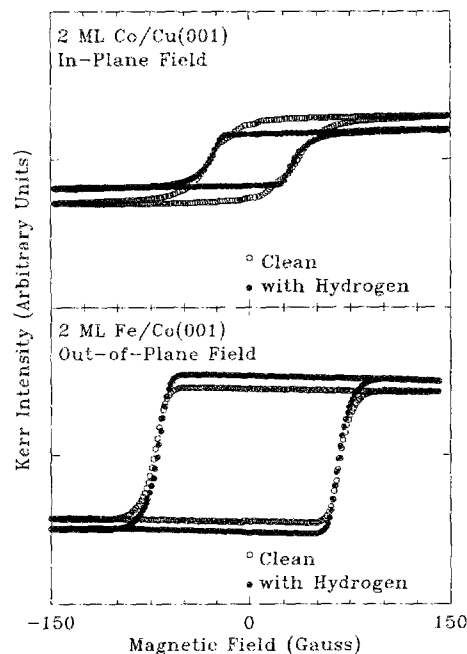


FIG. 7. SMOKE hysteresis loops for a 2 ML Co/Cu(001) and Fe/Cu(001) films at 150 K before (open circles) and after (solid circles) a 1000 mbar s dose of hydrogen. For the Co film, the saturation magnetization is reduced by 40%, and for the Fe film, the saturation magnetization increases by 15%.

IV. CONCLUSIONS

We have shown that pseudomorphic films of Ni, Co, and Fe can be produced by vapor deposition on Cu(001) substrates. However some questions still remain about the initial stages of film growth. By measuring the thermal desorption of hydrogen from the Co films as a function of film thickness we determined that Co films less than 2 ML thick do not completely cover the Cu(001) substrate. The RHEED oscillations from the Co and Fe films show a complicated behavior, where the specular intensity does not show a well-defined maximum with the completion of the first monolayer. Other groups have reported an unusual bilayer growth mode for these systems, where two layers grow simultaneously.^{9,10} This conclusion is supported by our measurements although this interpretation remains controversial.¹¹

Hydrogen desorption from codeposited $\text{Co}_x\text{Cu}_{1-x}$ alloy films suggests that the films form homogeneous alloys that do not undergo phase separation into separate islands of Co and Cu despite the tendency to phase separate in the bulk phase. Phase separation of codeposited $\text{Co}_x\text{Cu}_{1-x}$ alloy films occurs during annealing at 600–700 °C.³⁰ This demonstrates the metastable nature of these ultrathin epitaxial layers.

TDS of hydrogen from 3 ML films that cover the surface was also presented. Desorption from the Ni films, which are paramagnetic at temperatures below the onset of desorption, shows a similar behavior to bulk ferromagnetic Ni(001) indicating the magnetic state of the surface has no measurable effect on the desorption kinetics. Hydrogen is more weakly adsorbed on the Co films, and the thermal

desorption lineshape indicating a possible molecular precursor state is involved in the desorption process. The desorption of hydrogen from the Fe thin film surface is similar to that from Ni(001) with a slightly higher activation energy for desorption.

Our SMOKE measurements show that a saturation coverage of hydrogen on each of these thin film surfaces changes both the saturation magnetization and the magnetic anisotropy. For the Ni films our measurements are consistent with the formation of a magnetically dead surface layer upon hydrogen adsorption. For the Co films, we measure a considerable reduction in the saturation magnetization with hydrogen chemisorption. The saturation magnetization of the Fe films increases slightly with hydrogen chemisorption. However, this may be due to a magnetovolume effect whereby the outward relaxation of the surface following hydrogen adsorption will tend to increase the magnetic moment. The fcc Fe lattice is particularly susceptible to changes in the magnetic moment with changes in the lattice parameter.³¹ This magnetovolume effect may compensate for any changes arising from chemisorption induced density of states effects.

ACKNOWLEDGMENT

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