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Resonant X-ray diffraction revealing chemical disorder in sputtered L1₀ FeNi on Si(001)

Andreas Frisk^{1,‡}, Bengt Lindgren¹, Spiridon D. Pappas¹,
Erik Johansson² and Gabriella Andersson¹

¹ Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden

² ABB AB, Power Devices, Corporate Research, SE-721 78 Västerås, Sweden

Abstract. In the search for new rare earth free permanent magnetic materials, FeNi with the L1₀ structure is a possible candidate. We have synthesized the phase in thin film form by sputtering onto HF-etched Si(001) substrates. Monatomic layers of Fe and Ni were alternately deposited on a Cu buffer layer, all of which grew epitaxially on the Si substrates. A good crystal structure and epitaxial relationship was confirmed by in-house X-ray diffraction (XRD). The chemical order, which to some part is the origin of an uniaxial magnetic anisotropy, was measured by resonant XRD. The 001 superlattice reflection was split in two symmetrically spaced peaks due to a composition modulation of the Fe and Ni layers. Furthermore the influence of roughness induced chemical anti-phase domains on the RXRD pattern is exemplified. A smaller than expected magnetic uniaxial anisotropy energy was obtained, which is partly due to the composition modulations, but the major reason is concluded to be the Cu buffer surface roughness.

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[‡] Corresponding author: andreas.frisk@physics.uu.se

1. Introduction

The need for permanent magnetic materials for energy applications is increasing and will continue to be so when we move towards a more electrified society as a consequence of the ongoing switch to renewable energy [1]. The last years' uncertainty in both availability and prices of rare earth elements (REE), which are utilized in high performance permanent magnets, has motivated a search for possible REE free replacement materials and also for substitution materials with intermediate performance and lower prices [2, 3, 4, 5, 6]. FeNi in the $L1_0$ structure is a possible candidate for such an intermediate material [7, 8].

The intrinsic properties of $L1_0$ FeNi promise a large saturation magnetization, since it only contains ferromagnetic elements. The other relevant intrinsic magnetic property, the uniaxial anisotropy energy, is only intermediate in strength. The magnetic anisotropy is due to the chemical anisotropy created by a structure consisting of monolayers (ML) of alternating Fe and Ni. The FeNi $L1_0$ structure is a stable phase [9, 10] but it is rare in nature, only occurring in meteorites, and it is difficult to synthesize due to the low temperature phase boundary. It has been studied in meteoritic samples [10, 11, 12] and has been synthesized through neutron bombardment (Néel [13] and Pauleve [14]), electron irradiation (Chamberod [15] and Reuter [16]), in thin film form (Kojima and Mizuguchi [8]), through severe plastic deformation (Lee [17]) and recently through a chemical process (Makino [18]). In all of these methods only very small amounts of the phase are produced. For the severe plastic deformation and the chemical process another problem is that the $L1_0$ phase is produced and mixed together with other phases. Determining what part of the sample consists of $L1_0$ is difficult. Mizuguchi and Kojima [8] have created well-ordered samples, although only as thin films. They employed molecular beam epitaxy (MBE), a technique which has thermodynamic restrictions.

Even though the original aim is bulk permanent magnets, studying the intrinsic properties on a model system in thin film form is motivated for increasing our knowledge about the phase. Such thin film fabrication has been shown not to be as straight forward as might first be imagined. But thin film fabrication enables the possibility to grow a structure layer-by-layer which can promote the phase formation.

Magnetron sputtering is more available, scalable and could enable fabrication of larger amounts (in the sense of thin films) to allow more extensive studies of the model system. Synthesis attempts by sputtering on Si substrates have been done previously, but they were not successful in achieving the $L1_0$ phase [19], these attempts did not use layer-by-layer deposition. Also, if silicon substrates could be used, it would open up for applications with the possibility of integration in semiconductor industry.

If equiatomic Fe and Ni are simply mixed the chemically disordered A1 phase will form. This phase has an fcc structure but the distribution of the Fe and Ni atoms are random. A1 thus differs from the $L1_0$ structure in two aspects. Firstly, in the $L1_0$ structure each element is chemically ordered into MLs of Fe or Ni which are stacked along the c axis (stacking of (001) planes), see inset of fig. 1. Secondly, the A1 structure is cubic while the $L1_0$ structure is tetragonal with a c -axis lattice parameter which is larger than the in-plane lattice parameter a , i.e. $c/a > 1$. For $L1_0$ the uniaxial anisotropy is along the c axis and originates in both the tetragonal distortion and in the chemical ordering, where the latter is the main challenge to achieve during synthesis. Therefore it is important to be able to measure and quantify the chemical ordering. Mizuguchi et al. [20] calculated the long range order parameter S , giving a measure of how many atoms are in the correct chemical position, from X-ray diffraction intensities. But there can be "order within the disorder" as will be shown in this article, for this type of disorder S is not a suitable measure.

In this article we show two things. Firstly, it is possible to fabricate FeNi in the $L1_0$ structure through layer-by-layer sputter deposition onto Si substrates. Secondly, we show measurements of different types of disorder in this structure: composition modulations and anti-phase domains. We will qualitatively explain the effects on the X-ray diffraction pattern from these types of chemical disorder.

2. Experimental details

FeNi thin films were deposited using DC magnetron sputtering in an ultra-high vacuum chamber, with a maximum base pressure of 1.6×10^{-9} torr using 99.999% pure Ar as a sputtering gas at a pressure of 2×10^{-3} torr. The sample holder was rotated at 40 rpm to ensure homogeneous films. The films

were deposited on pieces of Si(100) wafers which had been etched in hydrofluoric acid (HF) to remove the natural oxide and to create a hydrogen terminated surface. The wafers were kept in air less than 30 min before loaded into the vacuum chamber. A buffer layer of nominally 1000 Å Cu was deposited at room temperature on the hydrogen terminated Si, which resulted in epitaxial growth of Cu with (001) orientation normal to the surface [21, 22, 23, 24]. On top of the Cu buffer, layers of FeNi were deposited epitaxially on the Cu: nominally 1 monolayer (ML) of Ni followed by 1 ML of Fe, repeated 100 times. A deposition rate of 0.67 Å s^{-1} was used for the Cu and 0.357 Å s^{-1} (or 0.2 ML s^{-1}) was used for the Fe and Ni layers. To protect the films from oxidation a cap layer of nominally 25 Å Ni was deposited. Part of this Ni was expected to transform into a passivating NiO layer of about 15 Å when subjected to air [25].

For each sample, different heat treatment schemes were used. All Cu buffer layers were deposited at room temperature followed by 1 h annealing at different temperatures prior to deposition of the FeNi bilayers, which were also grown at different temperatures. Temperatures between 120 °C and 210 °C were investigated. In addition, samples with 200 and 300 bilayers of FeNi were grown, as well as samples where the deposition time of the individual Fe and Ni layers were shorter than the nominal deposition time for 1 ML. See table 1 for a summary of different samples.

In-house X-ray diffraction (XRD) was measured with Cu $K_{\alpha 1}$ radiation using a Panalytical MRD diffractometer. Normal $\theta/2\theta$ scans, but also rocking scans, reciprocal space maps, texture scans and ϕ -scans were measured to determine the epitaxial structure. Different optics were used depending on the measurement. The $\theta/2\theta$ scans were performed with parallel beam geometry, with a hybrid monochromator mirror and slit defining the incident beam, and a mirror and proportional detector on the diffracted side.

The $L1_0$ ordering can be confirmed if a 001 reflection is present. For a chemically disordered fcc structure (A1 phase) this reflection is forbidden but for the chemical layering of Fe and Ni ($L1_0$ phase) it is allowed due to the different scattering factors of Fe and Ni. Unfortunately the intensity ratio between 001 and 002 reflections I_{001}/I_{002} is only about 1/1000, and in-house XRD is not sufficient. The signal-to-noise-ratio (SNR) is too small, as can be seen in fig. 1. Instead, resonant XRD (RXRD) was measured with synchrotron radiation, which gives a two-fold advantage. Firstly, the much higher intensity of the light gives better SNR. Secondly, by performing XRD at the Fe K absorption edge (7112 eV [26]), the scattering contrast between Fe and Ni is

enhanced and the intensity of the 001 reflection will increase. Scanning the energy around the Fe K-edge gives different intensities of the 001 reflection. These variations are characteristic of the $L1_0$ ordering and can therefore confirm the structure. Resonant X-ray diffraction was measured at MAXLAB beamline I811. $\theta/2\theta$ scans were performed at different energies in the vicinity of the Fe K absorption edge, at 7000–7150 eV. Slits defined the incident beam and virtual slits on a PILATUS area detector defined the diffracted beam.

A Quantum Design MPMS XL Super conducting Quantum Interference Device (SQUID) with a reciprocating sample option head was used to measure magnetic moment as well as the saturation magnetization M_S . In-plane and out-of-plane hysteresis loops were recorded at 35 K. The in-plane magnetization was also investigated by longitudinal magneto-optic Kerr effect (L-MOKE) which was measured at room temperature and at different azimuthal angles ϕ . The applied magnetic field in the range $\pm 700 \text{ mT}$ was measured with a Hall probe. Magnetization loops were taken from the MOKE ellipticity.

A Nanosurf Mobile S atomic force microscope (AFM) was used in contact mode for surface imaging.

For the analysis of the diffraction scans they were compared to diffraction patterns simulated in MATLAB. The simulations employed a simple structure model assuming a one dimensional sample extending only along the film thickness. This thickness profile was represented by a vector where the index of each vector element corresponds to a position and each vector element contains the atomic scattering factors at the corresponding depth. The atomic scattering factors was taken from the calculated values by Sasaki [26]. For mixed FeNi layers the scattering factors were linearly interpolated for the corresponding composition. An X-ray energy of 7120 eV was used. Diffraction patterns were obtained by performing a fast Fourier transform of the thickness profile vectors. For simulations of more than one grain, or with surface steps, the thickness profile vectors for all grains were coherently added and the sum was Fourier transformed.

3. Results and discussion

3.1. Structural Properties

The successful epitaxial growth of both the Cu buffer on the Si(001) surface and the FeNi bilayers on the Cu buffer was confirmed by XRD texture scans and ϕ -scans at the 113 reflection. In fig. 1 a $\theta/2\theta$ -scan shows the (002) plane of both Cu and FeNi being parallel to the Si(004) plane, with no other reflections visible at this sample orientation. The Cu(002/3), FeNi(002/3) and Si(004/3) peaks are assumed to

Table 1. Summary of the different fabricated samples giving their growth conditions and the measured lattice parameters. Fourth column is the FeNi growth temperature, fifth column Cu buffer anneal temperature. c is the out-of-plane and a is the in-plane measured lattice parameter for the Cu buffer layer and FeNi layer. The uncertainty of the lattice parameters are in the third decimal.

Name	Bilayer thickness (Fe ML/Ni ML)	Bilayers (no)	Growth T (°C)	Buffer T (°C)	c_{FeNi} (Å)	a_{FeNi} (Å)	c/a	c_{Cu} (Å)	a_{Cu} (Å)
T120	1/1	100	120	120	3.560	3.604	0.988	3.608	3.617
T150	1/1	100	120	150	3.562	3.605	0.988	3.606	3.624
T180	1/1	100	120	180	3.577	3.592	0.996	3.608	3.633
T150B	1/1	100	150	150	3.570	3.596	0.993	3.603	3.638
T180B	1/1	100	180	180	3.559	3.603	0.988	3.608	3.620
T210	1/1	100	120	210	-	-	-	-	-
T120_x2	1/1	200	120	120	3.580	3.595	0.996	3.615	3.616
T120_x3	1/1	300	120	120	3.578	3.593	0.996	3.606	3.609
T180_0.8Fe0.8Ni	0.8/0.8	100	120	180	3.556	3.615	0.984	3.598	3.633
T180_0.8Fe	0.8/1	100	120	180	3.541	3.628	0.976	3.596	3.647

come from harmonics in the beamline monochromator, since they are at exactly 1/3 of the 002 and 004 reflection positions, respectively. All samples showed a similar behaviour except for samples grown or annealed at temperatures higher than 180 °C. At these temperatures the Si reacted with the Cu and formed copper silicide to varying degrees, and diffraction scans of these samples exhibited both Cu 111 and Ni 111 reflections. The ϕ -scan and pole figure in fig. 2 show that both FeNi and Cu layers are (001) oriented with an in-plane rotation of 45° relative to the Si, i.e. $\text{Cu}[100] \parallel \text{Si}[110]$. In the ϕ -scan of the 113 reflections it is seen that both Si and FeNi have four reflections separated by 90°, consistent with the cubic symmetry. $\phi = 0^\circ$ corresponds to FeNi[100] and Si[110] directions. It is clearly seen that the Si reflections are shifted 45° relative to the FeNi reflections. The 113 reflections are strongest at $\phi = 45^\circ$ and $\chi = 25^\circ$ as expected of a (001) oriented fcc structure. Also visible are peaks at $\phi = \pm 19^\circ$ and $\chi = 72^\circ$, which is also as expected for this orientation. Reflections attributed to 013 and 032 are visible at $\chi = 17^\circ$ and $\chi = 36^\circ$ but no reflections from (111) oriented grains are seen. The crystal alignment in-plane is not perfect since the peaks in the ϕ -scans are quite broad, with a full width at half maximum (FWHM) of 4.8°, meaning there are textured grains. This texturing is also confirmed from reciprocal space maps (RSM) and rocking scans over the (002) and (113) reflections, which give a large mosaicity of about 2° for the Cu and around 1.5° for the FeNi layers, as shown in fig. 3.

From the symmetric (002) and asymmetric (113) reflections, the in-plane and out-of-plane lattice parameters could be calculated [27], and the variations in measured parameters between samples can be seen in table 1.

Figure 1. $\theta/2\theta$ scan for the T150B sample with Cu $K\alpha$ radiation (bottom), 7120 eV synchrotron radiation (middle) and a simulation of the structure (top) to be discussed in section 3.2.1. Arrows identify all reflections. Dashed line is the expected position of the FeNi(001) reflection. The black diamonds are reflections from the sample holder during synchrotron measurements. Inset shows the unit cell of the FeNi $L1_0$ structure where blue (1 and 2) are Fe atoms, orange (3 and 4) are Ni atoms.

3.1.1. Cu buffer layer The purpose of this thick Cu buffer layer was to decrease the strain on the FeNi layer, which would have been large if it was lattice matched directly with Si. Cu was chosen since it has a fcc structure, the same as FeNi, and the lattice parameter is the closest we could find to the one of FeNi, ($a = 3.56$ Å). Epitaxial growth of Cu on Si is strained, therefore by growing a thick layer we let it relax towards the bulk lattice parameter which is closer to the FeNi lattice parameter. This was done while the Cu layer still kept the epitaxial directions of Si enabling further layers to keep the (001) surface orientation, as was shown in previous paragraph. This method was successful and the Cu

Figure 2. (Top) texture measurement with Cu K α X-rays at the FeNi(113) reflection ($2\theta = 91.2839^\circ$) aligned at the substrate Si 004 reflection, which is parallel to the surface normal. (Bottom) ϕ -scan of the FeNi 113 reflection (dashed line) and Si 113 reflection ($2\theta = 56.1702^\circ$).

layer is partially relaxed. In-plane it is stretched slightly with a lattice parameter of 3.61–3.65 Å and the tensile in-plane strain gives a compression out-of-plane with resulting lattice parameter $c = 3.61$ Å which is the same as the bulk lattice parameter. The out-of-plane correlation length (calculated by the Scherrer formula [28]), varies from 180 Å to 210 Å and the mosaicity is around 1.7° to 2.3° . These short coherence lengths are not necessarily bad since the layer is supposed to relax to gain a smaller lattice parameter. From the RSM a similar mosaicity was measured and in-plane coherence lengths were extracted ranging from 400 Å to 1600 Å. These coherence lengths seem to relate to the surface roughness. According to several reports [29, 30, 31], it is found that the surface of epitaxial Cu on Si is mound shaped with island sizes 400–800 Å and an root mean square (RMS) roughness of 5–70 Å, where the better values are for heat treated Cu layers. By AFM we observed similar values in our samples, e.g. 300 Å island size and 4 Å RMS roughness (this value is at the resolution limit). This was measured on a sample composed of only the Cu buffer and Ni cap layers. It was heat treated as the other samples but deposited

at a slower rate, which we hoped would give a better quality, and should hence give best case values. Due to the similar values of island size from AFM and XRD in-plane coherence lengths, we assume the surface islands are connected to the crystal grains.

3.1.2. FeNi layer The FeNi layer has in-plane lattice parameters which are close to but slightly smaller than the Cu, about 3.6 Å. This can be seen in the RSM in fig. 3, where the FeNi(113) reflection has the same $q_{\parallel}$ as Cu(113) while they have different out-of-plane parameters since $q_{\perp}$ differs. The in-plane expansion, compared to bulk FeNi L1₀, gives a compressed out-of-plane lattice parameter of about 3.57 Å. The largest value of c/a is about 0.996 as can be seen in table 1. This is smaller than the expected $c/a > 1$ for ideal L1₀ FeNi. According to calculations by Miura [32] the equilibrium lattice constants are $a = 3.556$ Å and $c = 3.584$ Å giving $c/a = 1.008$. Edström [33] calculated the same values for the lattice parameters, but with less digits, giving $c/a = 1.006$. Kotsugi [12] measured the parameters from meteoritic FeNi L1₀ to be $a = 3.582$ Å, $c = 3.607$ Å, $c/a = 1.007$. This means the tetragonal distortion should be compressive in-plane, which we do not observe in our samples. On the other hand we should be able to compare samples to Kojima [8] who obtained c/a not larger than 0.99. The out-of-plane correlation length in our samples is about 190 Å to 240 Å, so the samples are not fully coherent all the way through the film. As can be seen in the RSM the mosaicity of the FeNi layer varies from 1° to 1.6° i.e. slightly better than in the Cu layer. The lateral coherence lengths, on the other hand, are comparable to the buffer layer and vary from 400 Å to 1500 Å.

Figure 3. RSM measured with Cu K α X-rays at the Cu and FeNi (113) reflections on the T180B sample. $q_{\perp} \parallel [001]$ and $q_{\parallel} \parallel [110]$ is parallel to the sample surface. The upper reflection is FeNi and the lower is Cu. The line goes through the origin and the centre of Cu the peak. $c_{\text{FeNi}} < c_{\text{Cu}}$ since the FeNi peak lies above the line, while $c_{\text{FeNi}} \approx c_{\text{Cu}}$ since both peaks have similar $q_{\parallel}$ positions.

3.2. Chemical ordering

$\theta/2\theta$ scans at energies 7000 eV and 7120 eV of the T120 sample can be seen in the inset of fig. 4. This shows a split peak (001A and 001B) centred at the expected position of the 001 reflection as calculated from the position of the 002 reflection. The intensity variations of these two split peaks versus energy are plotted in the lower panel of the main graph. Here is also plotted the energy variation of one of the sample holder reflections. In the upper panel is shown the intensity variations of the 002 reflections of both the Cu layer and the FeNi layer. The intensities are varying in different ways for different reflections. The sample holder reflection is independent of energy and is more or less constant compared to both the 001 and 002 reflections. The intensities of both 001 peaks have a maximum at the Fe absorption edge (7120 eV) whereas the FeNi(002) reflection has a minimum here. The Cu(002) reflection intensity has a smaller variation, but also decreases at the edge. At the Fe resonance there is an increase in the absorption from the Fe layers, but also a phase shift caused by the real part of the scattering factor. Both these factors decrease the constructive interference between Fe and Ni layers at the 002 reflection, giving a minimum in the scattered intensity. These factors also decrease the destructive interference between Fe and Ni at the otherwise “forbidden” 001 peak. Hence the 001 intensity has a maximum at the absorption edge.

Figure 4. Integrated intensity of different reflections vs energy. Circles are the two 001 reflections (A and B), diamonds is a sample holder reflection. Asterisks are 002 reflections of Cu and FeNi. (Note the different scale of top and bottom panels). Inset is $\theta/2\theta$ -scans on the T120 sample around the 001 reflection measured with synchrotron light of 7120 eV (top) and 7000 eV (bottom). Five peaks are seen: Si(004/3) at $q = 1.54 \text{ \AA}^{-1}$, the split FeNi(001) reflection at (A) $q = 1.68 \text{ \AA}^{-1}$ and (B) $q = 1.84 \text{ \AA}^{-1}$, and two peaks from the sample holder (filled diamonds) at $q = 1.79$ and $2.06 \text{ \AA}^{-1}$.

Figure 5 shows $\theta/2\theta$ scans at the Fe resonance

(7120 eV) over the 001 reflection for several samples. As can be seen, the split 001 peaks looks different from sample to sample. But the intensity variation versus energy of these reflections behaves in the same way as shown in fig. 4, thus confirming these are 001 reflections. All scans were fitted with three Gaussians: one for the sample holder peak (at $q = 1.784 \text{ \AA}^{-1}$) and two separated by a distance $2\Delta q$ centred around the expected 001 position, located at half the value of the 002 reflection position. For the T120 sample a fourth peak was needed at the expected 001 position. In T180_0.8Fe almost no 001 peaks are visible, which is expected since the Fe layers of this sample was deliberately grown thinner than the nominal 1 ML. It can be compared to the sample T180 grown with the same temperatures but with equal layer thickness of Fe and Ni, for which a small and broad reflection centred at the expected 001 position is visible. The T180 sample is suspected to also have a split peak and using two Gaussians gives a better fit compared to only one, although one of the Gaussians is very broad and the separation is almost zero, but with a very large uncertainty. Unfortunately there is also a reflection from the sample holder overlapping with this peak. For the T150B and T120 samples the split 001 reflection can be seen and these samples show a difference in the peak separation Δq . The T120_x2 sample is interesting since Δq is even larger here and there are also two extra reflections which are symmetrically centred around the expected 001 position. For the T120_x3 (not shown) there is an even larger separation and the relative intensities of the four peaks change. Finally, T180B has the highest intensity and the smallest Δq . Here there is a distinct intensity difference between the two peaks. Below we will try to explain the origin of these diffraction patterns, containing a split peak of varying separations.

3.2.1. Models of chemical disorder A perfect epitaxial thin film is very difficult to grow. The lattice mismatch between the Si(001)[110] and the Cu(001)[100] is 6%. This results in a strained epitaxial Cu layer. If the layer is thick enough it will relax to the bulk value of $3.61 \text{ \AA}$ by forming dislocations, which is the case for our films. This can result in a non-flat surface. Additional effects, like miscut of the Si wafer, can also create steps on the surface. Cu is known to not grow flat but instead have a surface composed of mound shaped islands [29, 31, 34] as previously mentioned. All these effects create a surface with atomic steps. Growing the FeNi bilayer on top of this will give Ni and Fe layers which in the lateral direction are out of phase with each other, i.e. in-plane anti-phase domains, fig. 6 c). Depending on the size of these anti-phase domains compared to the coherence width of the X-ray beam,

Figure 5. $\theta/2\theta$ scan around the 001 reflection, measured at resonance (7120 eV), for several different samples, offset for clarity. For each scan the fit used for analysis is also included. The vertical line for each scan shows the expected position of the FeNi 001 reflection calculated from the FeNi 002 position. The arrow defines the 001 peak separation $2\Delta q$. Diamonds indicate sample holder reflections.

there will be an overall decrease in the 001 diffraction intensity compared to an ideal structure (a simulation is shown in fig. 7, curve a). If anti-phase domains of equal size are coherently added there will be no peak at all. This is important to consider when calculating the long range order parameter S . The superlattice peak might appear to have less intensity, which would give a smaller value of S , even though the individual crystal grains might actually be perfectly ordered. A mound shaped Cu island of 300 Å diameter and 4 Å RSM, as is a best case in our samples and within the lateral X-ray coherence length, will have four terraces of 1 ML step height. Each terrace will have a different area fraction of the total island area. An XRD pattern was simulated from such a structure by coherently adding the scattering factor thickness profiles of 100 bilayers Fe/Ni on top of each terrace, scaled with the respective area fraction. In the resulting pattern, the ratio of the intensities I_{001}/I_{002} is decreased by a factor > 10 compared to the ideal case.

If during growth the deposition rate of one element (Fe or Ni) is slightly off, this could result in layers with a larger thickness than 1 ML, e.g. 1.25 ML Ni. If the first element is Ni and the second is Fe the consequences will be the following (see fig. 6 b)): The second layer will contain 0.25 ML of Ni and 0.75 ML of Fe, and the remaining 0.25 ML Fe will end up

in the third layer. The third layer will then have 0.25 ML of Fe and 0.75 ML Ni. This means there will be even more excess Ni, 0.5 ML, which will end up in the fourth layer and so on. This causes a Fe-Ni concentration modulation of the layers which in itself causes a splitting of the “ideal” 001 diffraction peak. A simulation with 0.1 ML excess of Ni is shown in fig. 7 curve b. The size of the splitting depends on the periodicity Δd of the concentration modulation, and the relationship is then $\Delta q = 2\pi/\Delta d$. Any deviation from a single monolayer growth may cause such a modulation. Therefore the deviation of the deposition rates from the nominal will determine the size of the periodicity (and the split). The modulation period will be linked to the deviation from the nominal 50/50 at.% Fe/Ni in the resulting total composition. But a direct connection from the total composition to Δq can not be done, since the case when there is less/more than 1 ML of each element, in both Fe and Ni layers simultaneously, will also result in a modulation period even though the total composition can have the correct nominal value. Nevertheless Δq and composition should be correlated.

A similar splitting of the 001 reflection can also be obtained if extra Ni- or Fe-layers are periodically inserted in the otherwise ideal Fe/Ni stacking (i.e. out-of-plane anti-phase domains [35]), but this situation is less probable regarding our type of growth.

The effects of both composition modulation and anti-phase domains can of course be combined, fig. 6 d). A coherent adding of equally sized lateral domains with 1 ML phase shift results in no intensity, at all, of the 001 reflection. But if the two shifted grains have a composition modulation, the intensity of the split peak is only reduced, not zero as for the ideal ordering. Moreover, the relative intensity of the two peaks can be different as shown in fig. 7 curve c). The coherence width of the beam as compared to the lateral coherence of the sample is thus crucial for the 001 diffraction splitting and intensity. As is the roughness of the Cu surface, since steps on the surface will cause a phase shift in the chemical stacking.

In conclusion the X-ray diffraction seems to indicate that in our samples, although the structural ordering is quite good, the chemical ordering is not. The chemical ordering seems to consist of both shifts in stacking but also a composition modulation. The structural roughness between buffer layer and FeNi film causes steps which gives stacking shifts in the chemical ordering. Deviations from the Fe/Ni monolayer thickness, which are varying from sample to sample, give different composition modulations which are manifested as split diffraction peaks. Taking these effects into account we obtain a fairly good match between simulated diffraction patterns and measured

Figure 6. Schematic of four cases of grains. a) An ideal $L1_0$ grain (corresponding to curve a in fig. 7), b) a composition modulated grain with 25 at.% excess of Ni (curve b in fig. 7), c) anti-phase grains: two ideal grains shifted by 1 ML relative each other, d) composition modulated anti-phase aligned grains (curve c in fig. 7).

Figure 7. Simulations with 100 repetitions of (1 ML) Fe / (1 ML) Ni bilayers on top of 552 Cu layers. a) (black dotted) shows the 001 reflection for ideal Fe/Ni bilayer growth. b) (yellow dashed) shows the splitting of the 001 peak caused by a composition modulation, here 10% excess of Ni compared to an ideal layer growth. Figure 6 d) shows a schematic of a 25% excess structure. c) (red full line) corresponds to both 10% excess of Ni and two domains shifted by one bufferlayer step of one monolayer height, (schematic d) in fig. 6).

scans, as seen in fig. 1.

3.3. Magnetic properties

An example of a SQUID measurement can be seen in fig. 8. The in-plane loop, measured along the easy axis in-plane, is parallel to the vertical axis. By L-MOKE measurements it was seen that the magnetization in-

plane has the easy axis along the $[100]$ direction of the FeNi film. This is in contrast to Ni which normally has its easy axis along the $[110]$ direction. The uniaxial anisotropy energy contribution K_U was calculated from $K_{\text{eff}} = K_U + K_{\text{shape}}$, where K_{eff} was found by integrating the area between the out-of-plane loop and the vertical axis. The sign of the anisotropy was defined such that $K_{\text{eff}} < 0$ for in-plane anisotropy and the shape anisotropy was $K_{\text{shape}} = -\mu_0 M_S^2/2$, where M_S was taken from the in-plane measurement. A positive value of K_U means there is an energy contribution which favours the out-of-plane direction, a negative means in-plane alignment is favoured and zero K_U means that only the shape anisotropy keeps the magnetization direction in-plane. All samples measured except the T180-0.8Fe sample

Figure 8. In-plane and out-of-plane hysteresis loops of sample T180 recorded with SQUID at 35 K. Inset shows an enlargement of the central part of the same hysteresis loops.

have a slight out-of-plane anisotropy as can be seen in fig. 9 where K_{eff} and K_U are plotted vs M_S . K_{eff} is constant at about -1 MA/m which gives an increasing K_U with M_S since K_{shape} is quadratically depending on M_S . These values of K_U are very small compared to previous reports of 0.8 – 0.9 MJ/m³ [11, 8].

Assuming a Slater-Pauling behaviour of M_S the corresponding composition x_{Fe} has been calculated, fig. 10. This assumption has been shown to be valid for an A1 ordered material [36]. Since the expected value of M_S for the $L1_0$ structure [33] is close to that of the A1 structure, these compositions should be a fairly good approximation. All measured values of M_S are less than expected from a 50/50% Fe/Ni alloy. Still most of the values of M_S are in the expected range 1.2 – 1.47 MA/m [11, 8] except for the two samples where less Fe had been deposited deliberately. Also the two samples with 200 and 300 bilayer repetitions have slightly lower M_S , and this we believe is due to drift in the deposition rate over time. When plotting M_S versus total deposited amount of Fe in all samples we see a linear trend. This would also give the deliberately

deviating samples T180_0.8Fe and T180_0.8Fe0.8Ni even less Fe since they were grown last.

It should be noted that an increasing K_U is expected if M_S depends on the Fe composition, since the orbital moment of the Fe atoms is the origin of K_U as shown in previous reports [8, 32]. In this case it will give smaller values of $|K_{\text{eff}}|$ counteracting the increased value of $|K_{\text{shape}}|$ for larger M_S .

Figure 9. K_{eff} (bottom) and K_U (top) calculated from SQUID measurements, plotted versus M_S .

Figure 10. M_S plotted versus the composition modulation period Δd . The right axis shows the corresponding Fe composition x_{Fe} assuming that M_S follows a Slater-Pauling behaviour. Dashed line represents the value of a 50/50 % Fe/Ni composition.

3.3.1. Connecting structural and magnetic properties

In fig. 10 the saturation magnetization M_S is plotted against the composition modulation period Δd (calculated from the 001 peak separations). As has been described, M_S is connected to the composition. Firstly it is seen in fig. 10 that all our samples probably had less Fe than the nominal 50 at.%. Further it can be seen, when the composition comes close to the nominal 50/50 composition, Δd increases in agreement with our model where a small composition deviation will give a long modulation. For 48 at.%Fe the

modulation period becomes very large i.e. there is almost no modulation, and the 001 reflection has a very small split: $\Delta q \approx 0$ for the T180 sample. This would suggest that the T180 sample is the most well ordered sample regarding composition, although the diffraction peak is very broad suggesting disorder and small coherence length, so there is a large uncertainty in determining this peak separation. Such a decrease in intensity can be due to the effect of lateral anti-phase domains as explained in the previous paragraph, and is shown in fig. 7 curve c. A low intensity of the 001 reflection might just mean there is good $L1_0$ ordering within the crystal grains but the grains are laterally anti-phase ordered relative to each other. For the other samples the modulation period is smaller the more the composition differs from the 50/50 composition. It might be that our calculations of M_S are off by 2 at.% since the peak in Δd is at 48 at.%. The reason for this offset from nominal composition is probably the drift of deposition rates of the magnetron targets.

We were interested whether there was a connection between the chemical structure and magnetic properties, therefore we have plotted K_U vs the composition modulation period Δd , but it showed exactly the same shape as when plotting M_S vs Δd , seen in fig. 10. Hence, if there is a connection of K_U to the structure it is through the saturation magnetization. For the samples where there is a large difference of M_S from the nominal value, Δd is small whereas Δd increases for values closer to the nominal magnetization. Since M_S is depending on the Fe composition this is an indication that the peak split Δq is in fact originating in a composition modulation. The more the deposition rate differs from the nominal value the larger will the composition modulation period be, and the more will the overall composition differ from the nominal. This argumentation should hold even if the largest value of Δd is discarded. The uncertainty of this value is large since it was difficult to fit two peaks to this diffraction pattern, even though one very broad peak and one more narrow gave a better fit compared to a single peak.

A plot of K_U versus c/a (not shown) looks exactly the same as the plot versus M_S (fig. 9). This is another indication that it is actually the composition which all parameters depends on, K_U , M_S , and the lattice parameters c and a . The question is still if M_S and K_U depends directly on the composition or indirectly through the lattice parameters.

The small values of K_U and the small increase with M_S (fig. 9) can then be explained to some part by this offset in composition. But the major part of the discrepancy to expected values ($\approx 0.8 \text{ MJ/m}^3$) must be due to a larger chemical disorder caused by the surface roughness, with the mound shaped islands of Cu. Furthermore K_U is predicted to depend on the

tetragonal strain and it should increase with larger c/a [32]. All the samples measure in this report have a c/a slightly smaller than one which would give overall smaller values of K_U .

4. Conclusions

FeNi in the L1₀ structure can be grown epitaxially on a Cu buffer layer on Si substrates by DC-magnetron sputtering. Sputtering has several advantages over MBE which has been used in previous studies, since it is not thermodynamically constrained and there are more parameters to vary during the growth. Having the option of using sputtering for synthesis makes FeNi in L1₀ phase more accessible for study. Even though the quality of the samples presented here is not as good as has previously been shown for MBE grown films [8], there is still room for further improvement of this sputter process. The main point to improve is the surface smoothness of the buffer layer. This might be done by gold and nickel additions as done by Kojima [34].

An important point to consider during characterization of L1₀ materials is if there exists lateral anti-phase domains within the coherence width of the X-ray beam. In such a case the measured intensity of the superlattice reflection will be decreased. If the 001 reflection is used to calculate the long range order parameters S this effect will result in a smaller value, even though individual grains might have a much better ordering than the measured.

We observe a symmetrically split 001 reflection which originates from a composition modulation period in the film. The split is related to the total composition but seemingly not in any direct way.

The measured magnetic uniaxial anisotropy is very small but positive for most samples and it is to a small part connected to the Fe composition with increasing values closer to the nominal 50 at.% Fe. The major part of the discrepancy of K_U is due to that only a small fraction of the film is L1₀ ordered. This disorder is partly explained by the composition modulation but the largest part probably originates in a non-smooth Cu buffer layer surface.

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