Interdiffusion in Fe–Pt multilayers

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Fe/Pt multilayers with modulation periods \( \Lambda = 24.1 \pm 0.2 \) and \( 37.2 \pm 0.1 \) Å and [110][111] bcc-fcc texture were fabricated by magnetron sputtering on thermally oxidized Si wafers. The structural evolution of the multilayers with annealing temperature in the range of 300–600 K was studied by \textit{in situ} x-ray diffraction (XRD) and x-ray reflectivity. Two temperature regimes were found from the XRD data. Below 534±4 K slow, short-range diffusion is observed without significant broadening of the satellite peaks or changes in the texture. Above 534 K fast, long-range diffusion is observed accompanied by significant broadening of the satellites and rapid increase of the misorientations of the grains. The multilayers crystallize at about 583 K into the tetragonal FePt phase with a small degree of ordering and strong [111] texture. The transition resembles a first-order phase transition with a critical exponent \( \beta = 0.48 \pm 0.01 \) which practically does not depend on \( \Lambda \). The bulk interdiffusion coefficient, determined from the decay of the -1 satellite of the (001) Bragg peak of the multilayers, can be expressed in Arrhenius form as \( D(T) = (1.37 \pm 0.26) \times 10^{-6} \exp(-1.7 \pm 0.6/k_BT) \) m²/s. The gradient-energy coefficient \( k \), entering the Cahn-Hilliard diffusion equation [Acta Metallurg. \textbf{9}, 795 (1961), \textbf{10}, 179 (1962); J. Chem. Phys. \textbf{28}, 258 (1959)], was estimated from the \( \Lambda \) dependence of the diffusion coefficient to be \((-6.8 \pm 0.2) \times 10^7 \) eV/cm.

\( c \) is the concentration of the grains. The multilayers crystallize at about 583 K into the tetragonal FePt phase with a small degree of ordering and strong [111] texture. The transition resembles a first-order phase transition with a critical exponent \( \beta = 0.48 \pm 0.01 \) which practically does not depend on \( \Lambda \). The bulk interdiffusion coefficient, determined from the decay of the -1 satellite of the (001) Bragg peak of the multilayers, can be expressed in Arrhenius form as \( D(T) = (1.37 \pm 0.26) \times 10^{-6} \exp(-1.7 \pm 0.6/k_BT) \) m²/s. The gradient-energy coefficient \( k \), entering the Cahn-Hilliard diffusion equation [Acta Metallurg. \textbf{9}, 795 (1961), \textbf{10}, 179 (1962); J. Chem. Phys. \textbf{28}, 258 (1959)], was estimated from the \( \Lambda \) dependence of the diffusion coefficient to be \((-6.8 \pm 0.2) \times 10^7 \) eV/cm.

I. INTRODUCTION

Heat treatment of Fe/Pt multilayers (MLs) has recently attracted attention as a possible reaction pathway for the synthesis of FePt hard magnetic thin films. Such thin films are attractive for high-density magnetic recording devices as a possible reaction pathway for the synthesis of FePt hard magnetic thin films. Such thin films are attractive for high-density magnetic recording devices due to the very large magnetocrystalline anisotropy of the L1\(_0\) FePt phase.\(^6\) However, the mechanisms and kinetics of the transformation of Fe/Pt MLs are still poorly understood, and data for the interdiffusion coefficients, required for proper selection of annealing temperatures (\( T \)) and times (\( t \)), are very scarce. Most previous Fe–Pt interdiffusion experiments were carried out at temperatures \( T > 1173 \) K,\(^{11-13}\) while for practical applications lower temperatures are desirable. Recently, Endo et al.\(^7\) have reported data for Fe–Pt interdiffusion coefficients of Fe\(_{1-x}\)Pt\(_x\) alloys with \( c = 0.15-0.50 \) obtained in the temperature range of 523–673 K using an (Fe 1000 Å/Pt 1000 Å) diffusion couple. At such temperatures, the interdiffusion coefficient (\( D \)) is expected to be relatively low and the corresponding diffusion path \( L = (Dt)^{1/2} \) to be very short. That is why direct measurements of \( D \) at low temperatures using standard techniques such as radioactive tracer diffusion or bilayer diffusion couples cannot be easily applied due to the relatively small depth and spatial resolution of Rutherford backscattering (RBS), Auger electron spectroscopy (AES), or energy dispersive x-ray (EDX) techniques used for determination of the concentration profiles after annealing. On the other hand, studies of the decay of the intensity of ML satellites with annealing time using x-ray reflectivity (XRR), neutron reflectivity, or x-ray diffraction (XRD) permit interdiffusion coefficients as low as \( 10^{-27} \) m²/s to be measured for reasonable annealing times.\(^{14}\)

The thermal annealing (TA) of metallic MLs at a given temperature usually leads to a continuous decrease of the initial compositional modulation and the formation of a homogeneous alloy. In this respect, it is the inverse of spinodal decomposition (SD) in which a homogeneous alloy develops a compositional modulation with time. The early stages of SD correspond to the later stages of TA of MLs and vice versa. A general equation describing the later stages of SD with composition-dependent bulk diffusion coefficient \( D(c) \) has been proposed by Cahn,\(^{15}\)

\[
\frac{dc}{dt} = D_1(c)\nabla^2 c - D_2(c)\nabla^4 c + D_1'[0] \nabla [(c - c_0) \nabla c] + \frac{1}{2} D_1''[0] \nabla [(c - c_0) \nabla^3 c] + \cdots ,
\]

(1)

where

\[
D_1(c) = D(c)(1 + 2\eta^2 Y/f''),
\]

(2)

\[
D_2(c) = 2(k/f'')D(c).
\]

(3)

\( D_1'[0] \) and \( D_1''[0] \) are the first and the second derivatives of \( D_1 \), evaluated at the average composition \( c_0 \); \( c(z,t) \) is the occupancy (fraction) of one of the components at a time \( t \) on a position \( z \) along the growth direction; \( \eta = d \ln(a)/dc \) is the logarithmic derivative of the lattice parameter of the homogeneous phase; \( Y \) is the biaxial modulus of the material along the growth direction, which for elastically isotropic materials is equal to \( E/(1-\nu) \), where \( E \) is Young’s modulus and \( \nu \) is Poisson’s ratio; \( f'' \) is the second derivative of the Helmholtz free energy \( f \) with respect to \( c \); and \( k \) is the coefficient of the
first term, $k\nabla^2 c$, in the expansion of $f(c)$ due to the presence of steep compositional gradients.\textsuperscript{15,16}

Equation (1) contains, in addition to Fick’s term $\nabla^2 c$, four additional terms which are necessary for the proper description of TA of MLs. The term $2\eta Yf''/f'\nabla c$ takes into account the presence of coherent strains between the atomic layers. The term $2(k/f'')D(c)\nabla^2 c$ makes allowance for the effects of steep compositional gradients at the interfaces. The last two terms in Eq. (1) describe the nonlinear compositional dependence of the interdiffusion coefficient $D(c)$ and the other parameters in Eq. (2).

The solution of Eq. (1) can be treated only approximately using a complicated iterative procedure\textsuperscript{15} and could not be applied for the study of the Fe/Pt system because the compositional dependence of $D(c)$ is not known. However, if the derivatives $D_t(0)$ and $D_t''(0)$ can be considered equal to zero, Eq. (1) is reduced to the Cahn-Hilliard\textsuperscript{16-18} equation,

$$\partial c/\partial t = D\nabla^2 c + 2\eta Yf''D\nabla^2 c - 2(k/f'')D\nabla^4 c,$$

(4)

which can be treated rigorously. Equation (4) is usually applied to the early stages of SD or vice versa to the later stages of TA of MLs, where the compositional modulations are expected to be small.

Under the assumption that the parameters in Eq. (4) are independent of $c$, Eq. (4) has the discrete solution\textsuperscript{19}

$$c(p,t) = \sum_m A_m(t)e^{iQm_n(p)},$$

(5)

where $c(p,t)$ is the concentration at the $p$th atomic plane ($p=1, 2, \ldots, N$, where $N$ is the total number of atomic planes in the superlattice period), $Q_m = (2\pi\Lambda m$ $(m=0, 1, 2, \ldots)$, and $A_m(t)$ is the amplitude of the $m$th Fourier component at a time $t$. The latter is related to the amplitude $A_m(0)$ at $t=0$ by

$$A_m(t) = A_m(0)[e^{-md\Lambda B^2(\Lambda)t}],$$

(6)

where $D\Lambda$ is a $\Lambda$-dependent interdiffusion coefficient

$$D\Lambda = D(1 + 2\eta Yf''/f'') + 2(k/f'')DB^2(\Lambda)$$

(7)

and $B^2(\Lambda)$ is an orientation-dependent lattice function. $B^2(\Lambda)$ is equal to

$$B^2(\Lambda) = (2/d_0^2)[1 - \cos(2\pi d_\Lambda/\Lambda)]$$

(8)

for wave vectors along [110] or [100] directions in bcc or along [111] as well as [100] directions in fcc structures,\textsuperscript{20} $d_0$ being the average lattice spacing. Equation (7) shows that the interdiffusion coefficient $D\Lambda$ can be smaller than the true interdiffusion coefficient $D$ if $k/f''>0$.

In the kinematic approximation the integrated intensity $I(t)$ of the $+1$ satellite around the (000) Bragg peak (denoted (000)$^+$ hereafter) is proportional to the square of the amplitude of the first Fourier component of the compositional profile,\textsuperscript{19,21}

$$I(t) \sim |A_1(t)|^2.$$  

(9)

Combining Eqs. (6) and (9) one obtains

$$I(t) = I(0)e^{-2D\Lambda B^2(\Lambda)t},$$

(10)

where $I(0)$ is the scattered intensity at $t=0$.

Because the compositional dependence of the parameters in Eq. (2) is usually not known, a linearity of $\ln[I(t)/I(0)]/B^2(\Lambda)$ vs $t$ is the main criterion to determine whether the parameters in Eq. (2) are independent of composition and Eq. (4) is applicable for the description of the TA of MLs or not.

In most previous studies on interdiffusion in metallic MLs, the decay of the (000)$^+$ satellite was measured by XRR and Eq. (10) used for determination of the interdiffusion constants. Philofsky and Hilliard\textsuperscript{22} as well as Cook and Hilliard\textsuperscript{24} have compared the decay of (000)$^+$ with the decay of the $+1$ satellites around higher-order Bragg peaks, measured by XRD, and concluded that the interdiffusion coefficients derived are similar. More recently, Prokes et al.\textsuperscript{24} as well as Aubertine et al.\textsuperscript{25} have compared the decay of the satellites around the (000) and the (004) Bragg peaks of Si/SiGe epitaxial MLs and concluded that accurate interdiffusivity data can be extracted from the decay of the high-angle satellite peaks. A detailed study was also made of the interdiffusion in (GaAs)$_m$(AlAs)$_n$ MLs (Ref. 26) by measuring only the intensities of the high-angle satellites, and a good agreement with previous optical absorption and electron microscopy results was found. In situ XRD is experimentally less demanding than XRR with regard to sample alignment and stability and allows the simultaneous study of coherence and texture of the MLs with temperature as well as follows in situ the growth kinetics of the high-temperature phase.

Based on these considerations we decided to study the interdiffusion in Fe–Pt MLs using mainly in situ high-angle XRD. In situ high-temperature XRR measurements of the second Fe/Pt ML (see below) show a linearity of $\ln[I(t)/I(0)]/B^2(\Lambda)$ as a function of time $t$, justifying the use of Eq. (4). The interdiffusion coefficients, derived from the in situ XRD measurements, are in reasonable agreement with the in situ XRR measurements.

The main goals of the present study are (i) better understanding of the processes occurring during thermal annealing of Fe/Pt MLs with different interface roughnesses, (ii) testing of the application of Eq. (4) to the Fe–Pt system and determination of the Fe–Pt interdiffusion coefficient in the temperature range of 523–603 K using the ML technique, and (iii) experimental estimation of the gradient-energy coefficient $k$.

II. EXPERIMENTAL PROCEDURES

A. Sample preparation

Homogeneous Fe/Pt MLs were prepared by magnetron sputtering using two different deposition systems. (Fe 7 Å/Pt 18 Å)$_{40}$ multilayers (denoted hereafter as ML1) were deposited in a von Ardenne CS 730S system, and (Pt 17 Å/Fe 20 Å)$_{50}$ multilayers (denoted hereafter as ML2) were deposited in a custom-built UHV deposition system from DCA Oy. The main deposition parameters are given in Table I. The MLs were deposited on thermally oxidized (100) Si wafers without additional heating of the substrates. ML1 was deposited by repeatedly moving the substrate past two separate, stationary Fe and Pt elemental targets. ML2...
was deposited by repeatedly moving a linear shaft, on which the magnetrons with the elemental targets were mounted, above the stationary substrate. The MLs were deposited on the wafers as $3 \times 3$ mm$^2$ defined by photoresist masks. The wafers were then diced into $4.3 \times 4.3$ mm$^2$ samples for subsequent measurements. The composition of the samples in both cases is close to Fe$_{0.50}$Pt$_{0.50}$ (Table I) as determined by EDX using Leo Supra55 field emission gun scanning electron microscope (FEG-SEM), Si:Li detector, INCA software, and 15 kV and 1000 s/measuring point.

The two sputter systems have different target-substrate distances ($L_{TS}$). It is known$^{27,28}$ that the kinetic energies of the particles arriving at the substrate (and thus the surface roughness as well as morphology) depend strongly on the product $L_{TS}P$, where $P$ is the sputtering gas pressure, in this case pure Ar. Thus, using MLs with similar compositions but deposited at different $L_{TS}P$ values allows study of the effects of interface roughness on the kinetics of the phase transition.

B. Room temperature x-ray reflectivity measurements

Specular and diffuse XRR measurements were done at room temperature (RT) on a Bruker D8 Discovery powder diffractometer equipped with a double Göbel mirror, cylindrical primary beam collimator ($\phi=1$ mm), $\frac{1}{3}$ Eulerian cradle using Cu Kα radiation (40 kV, 40 mA, $\lambda=1.5417$ Å), and a scintillation detector. The sample-detector distance was about 340 mm and the rectangular detector slit was 0.2 mm, giving an in-plane resolution of about 0.034°. A cutting edge in front of the sample stage was used to decrease the instrumental background. Diffuse scattering curves were measured five times using offset $\theta/2\theta$ scans and offset angles from 0.3° to 0.5°.

C. In situ measurements

The high-temperature experiments were done on the same diffractometer in Bragg-Brentano geometry using a $T_C$ Eulerian cradle heating stage from materials research instruments (MRI) GmbH. A flat two-dimensional (2D) Histar detector was used for the XRD measurements and a scintillation detector for the XRR measurements. In situ XRD using a 2D detector allows simultaneous measurement of diffraction patterns in a large $2\theta$ range under identical conditions. The $2\theta$ range depends on the sample-detector distance and was about $\sim 30^\circ$ $2\theta$ in this case.

For the XRD measurements the samples were mounted on a boron nitride-coated graphite (Borolec®) heater and pressed against the surface with a thin (thickness of 0.12 mm) stainless-steel foil using special metal frames in order to achieve better mechanical stability of the samples and better thermal contact to the heater. The stainless-steel foil has a hole ($\phi=3.6$ mm) which allowed entrance and exit of the x rays to the samples. The diameter of the hole was selected in such a way that it touches the MLs only slightly at the corners. For the XRR measurements, the ML2 samples were also mounted directly on the heater and pressed against it with two opposing brass foils (thickness of 0.29 mm), which did not touch the ML surface, because the size of the ML is smaller than the size of the samples. Nevertheless, several samples were measured after XRD and XRR experiments with EDX to check for possible contamination. No differences in the composition (within the EDX precision of $\pm 0.5$ at. %) were found.

The water-cooled heating stage was covered with a Be hemispherical dome (100 mm diameter, 0.5 mm thickness) and evacuated. The averaged pressure in the chamber during the high-temperature experiments was 1.6±0.5 Pa. The temperature was measured using a type-K thermocouple inserted in a hole in the heater near the hot zone and controlled with an accuracy of $\pm 3$ K. Four ML1 and five ML2 samples were heated for XRD measurements with initial heating rates of 11.3±5.0 K/min (for ML1) and 20.2±3.5 K/min (for ML2) up to 373–423 K and then stepwise with a slower rate (to prevent overshooting) to various higher temperatures where isothermal experiments were performed. Several ML2 samples were heated with similar temperature profiles for XRR measurements (average initial heating rate of 25±3°/min).

The XRD intensities at RT of the $-1$ satellite of the first ML Bragg peak [denoted (001) hereafter] show that the different samples from each wafer were not completely identical—the intensity variations were 10% for the ML1 and 4.5% for the ML2 samples. The integral XRR intensities at RT of the (000)$^*$ satellite show 30% variations from sample to sample. Several samples were measured in the heating stage repeatedly at RT over periods of up to 24 h, and an excellent reproducibility of the intensity measurements was established.

III. RESULTS AND DISCUSSION

A. X-ray reflectivity

The specular XRR curves at RT were corrected for diffuse scattering by subtracting the offset scans (offset angle 0.3°) and are shown in Fig. 1 together with the corresponding simulations. For an ideal step profile with equal layer thicknesses, the even Fourier components in Eq. (5) should be zero. The presence of weak second-order peaks for both MLs indicates nonequal layer thicknesses. The subsidiary
maxima (Kiessig fringes) between the main peaks are strongly damped. The simulated reflectance was written in the form

$$R(Q) = R_0(Q) \exp(-\alpha^2 Q^2) + b,$$

where $R_0(Q)$ is the reflectivity of the ideal multilayer, calculated using Parratt’s recursion method.\(^8\) The Fe/Pt and the Pt/Fe interface roughnesses are taken to be equal to an average $\sigma_f$, and $b$ is an adjustable instrumental background. Allowance was made during the calculations for small random variations in the thickness ($\Delta t \sim 0.1$ Å), the electron density $\rho$ ($\Delta \rho \sim 0.1 e/Å^3$) and the absorption coefficient $\mu$ ($\Delta \mu \sim 2 \times 10^{-2}$ cm$^{-1}$) of each atomic layer. The simulations were done with a self-written program, DIFF-ML. The basic ML parameters derived from these simulations are given in Table II. The modulation period of ML2 ($\Lambda = 37.2 \pm 0.1$ Å) is larger than that of ML1 ($\Lambda = 24.1 \pm 0.2$ Å), which allows determination of the bulk interdiffusion coefficient using Eqs. (7) and (8). The electron densities of the Fe and Pt layers in both MLs show, in comparison with the bulk values $\rho_{Fe}^{bulk} = 2.21 e/Å^3$ and $\rho_{Pt}^{bulk} = 5.15 e/Å^3$, that some interdiffusion takes place during the deposition. The average interface roughness of ML2 is larger than that of ML1, which explains the faster decay of the ML2 reflectivity. The discrepancies between the shape of the calculated and experimental reflectivity maxima suggest that there are some nonrandom local deviations from the ideal layer thicknesses and electron densities in the investigated MLs.

### B. Multilayer-FePt phase transition

Typical high-angle XRD patterns of ML1 and ML2 samples at different temperatures are shown in Fig. 2. The measurement time at each temperature was 600 s. The strong peak at about $41^\circ 2\Theta$ is the (001) Bragg peak of the MLs (denoted as 0 satellite in Fig. 2), which corresponds to the average $d$ spacing of the MLs. In the ML1 samples only the ±1 satellites are observed at about $36.8^\circ$ and $44.25^\circ 2\Theta$, respectively. In the ML2 samples the (001)$^{-2}$ satellite at about $36.4^\circ 2\Theta$ is observed in addition to the (001)$^{-1}$ satellite at about $38.8^\circ 2\Theta$ and the (001)$^+$ satellite at about $43.7^\circ 2\Theta$. As expected, the satellites move closer to the Bragg reflection and grow in intensity with increasing $\Lambda$. In both MLs the (001)$^+$ satellite overlaps with two weak peaks from the stainless-steel holder (denoted with $H$ in Fig. 2). That is why only the (001)$^{-2}$ and (001)$^+$ satellites were further analyzed quantitatively. The weak peak at about $48.7^\circ 2\Theta$ arises from the Be hemisphere.

For both MLs, the intensities of the satellites decrease continuously with temperature but the modulation periods remain practically unchanged. No indication for an amorphization solid-state reaction, as in Ni/Ta MLs (Ref. 30) or Fe/Nb MLs,\(^31\) is observed. At the same time a new peak starts to develop at about $47.1^\circ 2\Theta$ above 533 K due to the formation of a FePt phase. Two Bragg peaks of the fcc (disordered) FePt phase could appear\(^32\) in the measured angular range: the (111) peak at about $40.95^\circ 2\Theta$, and the (200) peak at about $47.62^\circ 2\Theta$. Four Bragg peaks of the $L1_0$ FePt

![Graph](image-url)

**FIG. 1.** Comparison of the corrected specular XRR curves: measurements (+) and simulations (thick lines).

### Table II. Structural parameters of the investigated multilayers at room temperature, obtained from simulations of specular XRR curves and XRD patterns. Estimated standard deviations are given in parentheses.

<table>
<thead>
<tr>
<th>Multilayer</th>
<th>No. of bilayers</th>
<th>$t_{Fe}$ (Å)</th>
<th>$t_{Pt}$ (Å)</th>
<th>$\Lambda$ (Å)</th>
<th>$\sigma_f$ (Å)</th>
<th>$\rho_{Fe}$ (e/Å$^3$)</th>
<th>$\rho_{Pt}$ (e/Å$^3$)</th>
<th>$\mu_{Fe}10^2$ (cm$^{-1}$)</th>
<th>$\mu_{Pt}10^2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML1</td>
<td>40</td>
<td>6.7(2)</td>
<td>17.4(2)</td>
<td>24.1(2)</td>
<td>4.7</td>
<td>2.6</td>
<td>4.7</td>
<td>27.0</td>
<td>41.0</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>6.68(3)b</td>
<td>17.6(1)b</td>
<td>24.3(1)b</td>
<td>0.36(1)b</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ML2</td>
<td>50</td>
<td>17.1</td>
<td>20.1</td>
<td>37.2(1)</td>
<td>5.8</td>
<td>2.5</td>
<td>4.5</td>
<td>28.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Bulk</td>
<td></td>
<td>2.2</td>
<td>5.2</td>
<td></td>
<td>24.0</td>
<td></td>
<td></td>
<td></td>
<td>43.0</td>
</tr>
</tbody>
</table>

*From XRD simulations.

*XRD results averaged over the four ML1 samples.*
phase exist in this range: the (110) peak at about 32.98° 2Θ, the (111) peak at about 41.1° 2Θ, the (200) peak at about 47.36° 2Θ, and the (002) peak at about 49.0° 2Θ. The position of the (001) satellite is very close to the (111) peak of both the fcc and the fct FePt phases. The theoretical position of the (002) superstructure peak of the L1₀ FePt phase overlaps with the Be peak, the intensity of which practically remains constant at all temperatures. No diffraction peak is observed at about 33° 2Θ in the XRD patterns measured in situ. Initially, these results suggested that the MLs transform into the disordered fcc FePt phase. However, it could not be ruled out that the L₁₀ FePt phase with a strong (111) texture was actually formed. That is why diffraction patterns were measured on samples cooled down from 593 K using long accumulation times (≈1800 s) and inclination angle χ =57.4°, where χ is the angle between the normal to the film surface and the diffraction plane. These XRD patterns clearly showed the presence of weak (110) and (201) superstructure peaks as well as partial splitting of the (200) and (002) reflections. The low intensity of the superstructure peaks and the small (002)- (200) splitting indicate that the MLs transform into the fct FePt phase with a strong (111) texture and a small degree of ordering.

In order to determine consistently the integral intensities and the full widths at half maximum (FWHMs) of the (001), (001), and (001) peaks, all XRD patterns were fitted by least squares in the range of 33°-47° 2Θ using pseudo-Voigt functions pV(2Θ)=γL(2Θ)+(1−γ)G(2Θ) for the Kα₁ and Kα₂ components of each diffraction peak plus an overall linear background, where L(2Θ) is the Lorentzian part, G(2Θ) is the Gaussian part, and γ is the mixing parameter. Although the shape of the satellites is not necessarily pseudo-Voigt, this gave in all cases goodness-of-fit factors (GOF) between 2% and 5%. Plots of the ratio of the integral intensities I₁(T)/I₁(RT) of the (001) satellite for ML1 and ML2 are shown in Fig. 3. A remarkable similarity between the two MLs is observed despite the differences in Λ and the interface roughnesses. Two different regimes can be distinguished. In the temperature range from RT to approximately 530 K for ML1 and 538 K for ML2 the relative intensity decreases linearly with temperature T: I₁/T₀=1.165 (1−0.000475T) for ML1 and I₁/T₀=1.12 (1−0.000347T) for ML2. The XRD patterns show that there is no phase formation as the MLs are annealed in this temperature range. Evidently, this is a regime of slow short-range interdiffusion. The rate of degradation of the ML1 samples is slightly faster, which might be expected since the individual layers in ML1 are thinner.

Above the average cross-over temperature T_i=534±4 K the relative intensities decrease as a power law...
The critical temperature $T_c$ of the phase transition ML $\rightarrow$ FePt is practically independent of $\Lambda$ and equal to $583 \pm 1$ K. The critical growth exponents $\beta$ are also similar: $\beta = 0.50 \pm 0.01$ for ML1 and $\beta = 0.48 \pm 0.01$ for ML2.

The similar critical temperatures for the two MLs having different total thicknesses $L_T$ ($L_T \sim 964$ Å for ML1 and $L_T \sim 1815$ Å for ML2) are quite interesting. According to the finite-size scaling theory, $T_c$ is a function of $L_T$ and should decrease monotonically with decreasing $L_T$.

Figure 4 shows the averaged (over all measured samples from a given ML) FWHM of the (001)$^-$ satellite as a function of temperature. The vertical lines mark the positions of the cross-over temperatures, determined from Fig. 3. For both MLs, the FWHM remains constant below $T_{co}$ and increases rapidly above $T_{co}$. Since the FWHM of the satellites is proportional to the variations in $\Lambda$, these results indicate that in the first regime the interdiffusion is similar at the different interfaces of the MLs.

On the contrary, above $T_{co}$ the thickness of the bilayers decreases faster in some places and slower in other places, leading to a broadening of the satellites. This aspect of the structural behavior of MLs upon annealing has received little attention, but similar dependence of the FWHM on temperature was reported for CoMoN/CN amorphous MLs. The (001)$^-$ satellite of ML2 has a similar temperature dependence to the (001)$^-$ satellite. However, the average FWHM of the (001)$^2$ satellite is larger than the average FWHM of the (001)$^-$ satellite [FWHM($-2$) = $0.72 \pm 0.06^\circ$ 2$\Theta$ while FWHM($-1$) = $0.55 \pm 0.06^\circ$ 2$\Theta$ at RT]. An increase of the linewidths of the satellites with the distance from the Bragg peak has also been reported for epitaxial Fe/Pt MLs and is an indication of the presence of cumulative roughness disorder.

The change of the texture of the MLs with temperature was analyzed by comparing the distribution of the intensity along the Debye-Scherrer rings. The intensities of (001)$^0$ from $\chi = -28^\circ$ to $\chi = +27^\circ$ (accessible in the present in situ experiments) were fitted with pseudo-Voigt functions. The FWHM of the $\chi$ distributions as a function of temperature are shown in Fig. 5 for samples from both MLs. The FWHM of ML2 is practically independent of temperature below $T_{co}$ and smaller than the FWHM of ML1. It can be seen again that there is a kink at $T_{co}$—above $T_{co}$ the misorientations of the grains along the growth direction increase rapidly.

C. Compositional profiles

The XRD patterns of selected ML1 and ML2 samples were modeled in the kinematic approximation. It was as-
The average $d_s$ spacings of the Fe atomic layers are 2.08 Å for ML1 and 2.04 Å for ML2, both of which are only slightly larger than the bulk $d^{\text{Fe}}$ value ($\sim 2.03$ Å). The employed Laue function included a random $\Lambda$ disorder. The atomic scattering factors were calculated from the nine-parameter equation of Crommer and Mann, including anomalous dispersion corrections. The Debye-Waller factors were set to 0.28 and 0.49 Å$^2$ for Pt and Fe, respectively. In order to account for the presence of interdiffusion at the interfaces (see Sec. III A), the scattering amplitude $f_i(Q)$, where $Q = 4\pi \sin(\theta)/\lambda$, and the $d_i$ spacing of the $l$th atomic layer ($l=1,2,\ldots,N_{\text{Pt}}+N_{\text{Fe}}$) were written as $f_i(Q) = f_{\text{Pt}}(Q)c(l) + [1-c(l)]f_{\text{Fe}}(Q)$ and $d_i = d_{\text{Pt}}c(l) + [1-c(l)]d_{\text{Fe}}$. They depend on one and the same compositional profile $c(l)$, which was selected in the form

$$c(l) = 2e^{-lt\tau} \sinh(N/\tau)/(1 + 2e^{-lt\tau} \cosh(N/\tau) + e^{lt\tau}),$$

(12)

where $\tau$ is a dimensionless diffusion parameter. Several other analytical profiles have been proposed in the literature, but they have not been tested yet. A typical XRD simulation at 563 K is shown in Fig. 6 for a ML1 sample. The experimental XRD patterns were corrected for polarization and Lorentz factors, while the calculated profiles were convoluted with a Gaussian instrumental resolution function. Despite the simplicity of the model, the quantitative agreement with the experimental data is good—the GOF factors for all studied ML1 samples are between 0.5% and 0.9%. The structural parameters for ML1 at RT, derived from these simulations, are in very good agreement with the XRR results (Table II). The variation of the $d$ spacing modulation with temperature for one of the investigated ML1 samples is shown in Fig. 7. The $d$ modulation deviates already at RT from the rectangular shape for an ideal multilayer (average $\tau_{\text{ML1}} = 0.71 \pm 0.19$), showing that some interdiffusion took place during the deposition, as was inferred from the values of the electron density as well (Table II). With increasing temperature, the diffusion parameter $\tau$ increases for this particular sample from 0.57 to 1.73, the amplitude of the $d$ modulation (as well as of the scattering form factors not shown in Fig. 7) decreases, which leads to the observed decrease of the intensities of the (001)$^-$ satellites (Fig. 2). Similar results were obtained for other ML1 samples.

The above model, with only random $\Lambda$ disorder and interdiffusion at the interfaces, indicates that the initial intermixing of the Fe and Pt layers in the ML2 samples, as inferred from the $\tau$ parameters (average $\tau_{ML2} = 1.3 \pm 0.3$), is larger than the intermixing in the ML1 samples (average $\tau_{ML1} = 0.71 \pm 0.19$). But it does not reproduce well the positions of the (001)$^-$ and (001)$^+$ satellites, suggesting the presence of cumulative $d$ spacing disorder. More elaborate analysis of the ML2 compositional profiles will be presented elsewhere.

D. Determination of the $\Lambda$-dependent interdiffusion coefficients

Isothermal annealing XRD experiments were performed at three different temperatures (538, 548, and 558 K) in the second temperature range, where the interdiffusion is faster. The samples were measured for 60 s after different delay times. The XRD decay curves for the two MLs are given in Fig. 8. The corresponding XRD patterns do not show (within ±6% statistical counting errors of the background) the presence of the characteristic FePt peak at about 47.3° 2θ. This guarantees that only interdiffusion processes are studied. The interdiffusion constants $D_\Lambda$ were obtained by fitting Eq. (10) to the linear part of the plots at longer annealing times. The values are given in Table III. The annealing of one ML2 sample was repeated at 558 K. The two $D_\Lambda$ values deviate by 4%, which gives an estimate of the variations of the interdiffusion coefficients from sample to sample. The intensity of the (001)$^-$ satellite of ML2 is very low (see Fig. 2) even at RT and precluded systematic analysis as a function of annealing time.
The XRR decay curves are shown in Fig. 9. The corresponding $D_A$ values are given in Table III. The estimated standard deviations of $D_A$, determined from XRR, are larger than for the XRD data because of the larger noise/signal ratios of the XRR data.

The XRR decay curves show a linear behavior with time, which indicates that the first Fourier component of the compositional profile $A_1(t)$ in Eq. (5) decreases linearly with time and justifies the use of Eq. (4). Small deviations from linearity are only observed at the beginning of the annealing experiments. Similar initial nonexponential decay of the (000)$^+$ satellite is observed for many MLs.\textsuperscript{21,23,25,42} Such effects do not necessarily indicate composition-dependent parameters in Eq. (2) because structural relaxation of non-equilibrium defects, diffusion-induced stresses, or recrystallization could also affect the initial diffusivities.

The interdiffusion coefficients for ML2, determined from the (000)$^-$ and (000)$^+$ satellites, are in reasonable agreement, taking into account the larger XRR standard deviations and the possible variations from sample to sample. This justifies the use of the XRD data for determination of the bulk interdiffusion coefficient and the gradient-energy coefficient $k$ (Sec. III F).

### E. Crystallization kinetics of the FePt phase

A peak of the new FePt phase starts to develop in the ML2 samples after relatively long annealing times (after 2500 s at 538 K, after 1250 s at 548 K, and after 600 s at 558 K). Using the corresponding XRD patterns (which are not included in the determination of $D_A$), the kinetics of the FePt crystal growth in ML2 was studied at 548 and 558 K. The FePt and the Be peaks were fitted with pseudo-Voigt functions. The GOF factors are relatively high (4.5%–6.7%) because the intensity of the FePt peak is rather weak and the signal-to-noise ratio relatively large for accumulation times of only 60 s used in these \textit{in situ} experiments. The integral intensity of the FePt peak at $T=548$ K is shown in Fig. 10 as a function of annealing time. The results for $T=558$ K are similar. Despite the relatively large estimated errors, the data are better described by a linear growth model ($I = I_0 - t$), typical

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Lambda$ (Å)</th>
<th>$D_A \times 10^{24}$ (m$^2$ s$^{-1}$)</th>
<th>Satellite</th>
</tr>
</thead>
<tbody>
<tr>
<td>538</td>
<td>24.1</td>
<td>16±2</td>
<td>(001)$^+$</td>
</tr>
<tr>
<td></td>
<td>37.5</td>
<td>103±1</td>
<td>(001)$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>75±10</td>
<td>(000)$^+$</td>
</tr>
<tr>
<td>548</td>
<td>24.1</td>
<td>48±1</td>
<td>(001)$^+$</td>
</tr>
<tr>
<td></td>
<td>37.5</td>
<td>307±6</td>
<td>(001)$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>270±8</td>
<td>(000)$^+$</td>
</tr>
<tr>
<td>558</td>
<td>24.1</td>
<td>90±10</td>
<td>(001)$^+$</td>
</tr>
<tr>
<td></td>
<td>37.5</td>
<td>400±14</td>
<td>(001)$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>385±15$^a$</td>
<td>(001)$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>401±27</td>
<td>(000)$^+$</td>
</tr>
</tbody>
</table>

$^a$Second independent measurement at 558 K.
for reaction-controlled growth, rather than by a diffusion-controlled growth ($I \sim t^{1/2}$).^{43}

### F. Determination of the bulk interdiffusion coefficient and the gradient-energy term

The $D_L$ values for ML1 and ML2, determined from the XRD data, are plotted in Fig. 11 as a function of $B^2(\Lambda)$. The intercepts and slopes are given in Table IV. Using data for FePt (Ref. 44) and disordered fcc Fe$_{1-x}$Pt$_x$ alloys,^{32,45} a regression equation for the lattice parameter $a$ as a function of $c$ at RT was constructed: $a(c) = 3.692 \pm 0.011 + (0.23 \pm 0.01)c$. Extrapolating this equation to $c=0.5$ gives $\eta=0.06$. This $\eta$ value was used in the analysis of the interdiffusion coefficients since there are no high-temperature data for the lattice parameters of Fe$_{50}$Pt$_{50}$ alloys.

In the case of [111] textured layers, $Y_{111}$ is equal to $6c_{44}(c_{11} + 2c_{12})/(c_{11} + 2c_{12} + 4c_{44})$ (Ref. 17) and represents the true (isotropic) [111] biaxial elastic modulus, where $c_{ij}$ ($i,j=1,2,\ldots,6$ in the Voigt notation) are the zero-pressure elastic constants. Using $c_{ij}$ for fcc Pt at RT (Ref. 46) this equation yields $Y_{111} = 1.7 \times 10^{24}$ eV/cm$^3$. In the case of [110] textured layers, $Y_{110}$ is anisotropic and is taken to be equal to $\frac{1}{2}(c_{11} + 2c_{12})/(c_{11} + c_{12} + 6c_{44})/(c_{11} + c_{12} + 2c_{44})$,^{17} which represents the Voigt average of $Y$ for the [110] texture.^{47} Using the zero-pressure elastic constants of bcc Fe at RT,^{48} this equation yields $Y_{110} = 1.69 \times 10^{24}$ eV/cm$^3$, which is increased by 30% to $Y_{110} = 2.08 \times 10^{24}$ eV/cm$^3$ in order to take into account uncertainties in the elastic constants of the MLs and the averaging procedure. Since the elastic constants of L1$_0$ FePt are not known, we have interpolated the Pt and Fe $Y$ values, obtaining $Y = 1.9 \times 10^{24}$ eV/cm$^3$ at $c=0.5$. Using the above estimates, the $2\eta^2Y$ term in Eq. (7) is equal to $1.368 \times 10^{22}$ eV/cm$^3$, which was used for all three temperatures studied (Table IV). It is interesting to note that the $2\eta^2Y$ values for Cu/Pd MLs, determined experimentally by Philofski and Hilliard,^{22} are practically constant in the range of 628–713 K.

The second derivative of the free energy $f''$ can be written in the form

$$f'' = N_V k_B T \left[ c(1-c) \right]/(1/c) \frac{\partial f}{\partial \bar{c}},$$  

(13)

where $N_V$ is the number of atoms per unit volume, $k_B$ is the Boltzmann’s constant, and $f''$ is the excess free energy of mixing per unit volume. The lowest temperature data for $f''$ are published by Heald.^{49} There $f''$ is expressed using a Redlich-Kister power series as $f''/k_B N_V T = 2.3c(1-c)[B + C(2c-1) + D(2c-1)^2 + \cdots]$, where $f''$ is the excess free energy of mixing per mole and $N_V$ is Avogadro’s number. The coefficients $B$, $C$, and $D$ were determined^{49} from a fit to the Fe activity coefficient measured in the temperature range of 923–1123 K. That is why in the present work $\delta f'/'\partial \bar{c}$ was calculated at 923 K using the published Redlich-Kister coefficients^{49} and introduced in Eq. (13) without extrapolation to lower temperatures. The values given in Table IV represent upper bounds for $f''$. The weak temperature dependence of $f''$ comes mainly from the first term in Eq. (13).

Using the estimated $\eta$, $Y$, and $f''$ values, $D$ and $k$ were calculated from Eq. (7) using the intercepts and slopes, obtained from Fig. 11. As can be seen from Table IV, $k < 0$ in the investigated temperature range. Such a behavior is expected for binary solutions with a tendency for ordering. The negative sign of $k$ means that $D_A$ increases with increasing $\Lambda$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$D_{11} (1 + 2\eta^2 Y/f'') \times 10^{20}$ (cm$^2$/s)</th>
<th>$2k/f'' \times 10^{19}$ (cm$^3$/s)</th>
<th>$2\eta^2 Y \times 10^{-22}$ (eV/cm$^3$)</th>
<th>$f'' \times 10^{-22}$ (eV/cm$^3$)</th>
<th>$D \times 10^{20}$ (cm$^2$/s)</th>
<th>$k \times 10^{-7}$ (eV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>538</td>
<td>154</td>
<td>2211</td>
<td>1.368</td>
<td>8.08</td>
<td>132</td>
<td>−6.79</td>
</tr>
<tr>
<td>548</td>
<td>460</td>
<td>−6644</td>
<td>1.368</td>
<td>8.23</td>
<td>394</td>
<td>−6.94</td>
</tr>
<tr>
<td>558</td>
<td>570</td>
<td>−7744</td>
<td>1.368</td>
<td>8.38</td>
<td>489</td>
<td>−6.62</td>
</tr>
</tbody>
</table>

Table IV. Measured values of $D_{11} (1 + 2\eta^2 Y/f'')$, $2k/f''$, $D$, and the gradient-energy coefficient $k$.
The predicted average value of \( f^* \) \((8.2 \pm 0.1) \times 10^{22} \text{ eV/cm}^3\) is very close to the estimated values for Co/Pt MLs \((9.5 \times 10^{22} \text{ eV/cm}^3)\) (Ref. 42) and Fe/Ti MLs \((5.7 \times 10^{22} \text{ eV/cm}^3)\).\(^{50}\) The predicted values of \( k \) are practically constant \(\{6.8 \pm 0.2\} \times 10^7 \text{ eV/cm}\) in the temperature range studied. This average value is comparable with the estimated \( k \) values for Cu/Pd MLs at 627 K \((k=-6.4 \times 10^6 \text{ eV/cm})\);\(^{22}\) \(\text{Ag}_{0.727}\text{Au}_{0.273}\) MLs at 516 K \((k=-1.6 \times 10^6 \text{ eV/cm})\);\(^{23}\) Co/Pt MLs at 623 K \((k=-4.4 \times 10^6 \text{ eV/cm})\);\(^{24}\) Fe/Ti MLs at 458 K \((k=-2.6 \times 10^7 \text{ eV/cm})\);\(^{50}\) and Cu/Au MLs at 533 K \((k=-3.4 \times 10^6 \text{ eV/cm})\).\(^{51}\)

**G. Temperature dependence of the bulk interdiffusion coefficient**

By plotting \(\ln(D)\) vs 1000/\(T\) (Fig. 12) the effective activation energy of interdiffusion \(H_a\) and the pre-exponential factor \(D_0\) in the Arrhenius equation \(D(T) = D_0 \exp(-H_a/k_BT)\) were determined. The diffusion data for the investigated Fe–Pt MLs can be expressed as

\[
D(T) = (1.37 \pm 0.26) \times 10^{-6} \exp(-1.7 \pm 0.6/k_BT). \tag{14}
\]

The interdiffusivity of the investigated Fe/Pt MLs, extrapolated to 458 K \((D=2.9 \times 10^{-25} \text{ m}^2/\text{s})\), is slightly smaller than the interdiffusivities for Co/Pt \((D=3.4 \times 10^{-25} \text{ m}^2/\text{s})\);\(^{42}\) Fe/Mo \((D=4.1 \times 10^{-25} \text{ m}^2/\text{s})\);\(^{50}\) and Fe/Ti MLs \((D=1.8 \times 10^{-24} \text{ m}^2/\text{s})\).\(^{50}\) The interdiffusivity, extrapolated to \(T=1733\) K \((D=1.5 \times 10^{11} \text{ m}^2/\text{s})\), is similar (within error limits) to the interdiffusion coefficient of the disordered (fcc) FePt phase \((D=3.4 \times 10^{-13} \text{ m}^2/\text{s})\), determined by Kushida et al.\(^{12}\)

The activation energy obtained \((H_a=1.7 \pm 0.6 \text{ eV})\) is higher than the activation energy of 0.3 eV, determined by Endo et al.\(^{7}\) in the temperature range of 523–673 K using a diffusion couple (Fe 1000 Å/Pt 1000 Å) and AES. At the same time it is approximately one-half of the activation energies for fcc FePt \((3.1 \text{ eV})\) and for \(L_1\) FePt along the [100] direction \((3.17 \text{ eV})\), determined in the range of 1333–1493 K by Kushida et al.\(^{12}\) using radioactive tracer diffusion. The differences in these \(H_a\) values suggest either different concentration of vacancies and in-plane grain boundaries or different interdiffusion mechanisms.

**IV. CONCLUSIONS**

Fe–Pt interdiffusion was studied by high-temperature XRD and XRR from RT to 603 K, using Fe/Pt MLs deposited by magnetron sputtering on thermally oxidized Si wafers. Two interdiffusion regimes can be distinguished from the XRD data. In the first regime, up to a cross-over temperature \(T_{cr}=534 \pm 4\) K, only slow, short-range diffusion takes place. The initial texture of the MLs remains practically constant. In the second regime above \(T_{cr}\), the interdiffusion is much faster and leads to a rapid increase with temperature of the broadening of the satellites as well as the misorientations of the grains, perpendicular to the film plane.

The integral intensity of the XRD satellites decreases with temperature above \(T_{cr}\) according to a power law \((1-T/T_{cr})^{2\beta}\). The critical exponent \(\beta=0.48 \pm 0.01\) as well as the critical temperature \(T_c=583 \pm 1\) K are independent of the modulation lengths studied and are practically not affected by the differences in the interface roughness and the degree of layer intermixing of the as-deposited MLs. This interesting effect will be studied further on MLs with different \(\Lambda\).

The MLs transform into \(L_1\) FePt alloy with strong [111] texture and a small degree of ordering. In a narrow temperature range around \(T_c\), peaks of both the FePt phase and satellites of the MLs are observed, indicating that the transformation resembles a first-order phase transition, although the critical exponent \(\beta\) is, within error limits, equal to the Landau (mean-field)\(^{32}\) value for a second-order phase transition. The XRD data suggest that the growth of the FePt phase is reaction controlled.

Isothermal annealing experiments were done at three different temperatures (538, 548, and 558 K) above \(T_{cr}\). The linear decay with annealing time of the intensities of the (000)* XRR satellite for ML2 justifies the use of the Cahn-Hilliard equation. The interdiffusion coefficients for ML2 derived from XRR and XRD experiments are in reasonable agreement. Analysis of the XRD data using both MLs show that the gradient-energy coefficient \(k\) is negative and equal to \((-6.8 \pm 0.2) \times 10^7 \text{ eV/cm}\). The bulk interdiffusion coefficient \(D\) obeys an Arrhenius equation, \(D(T) = (1.37 \pm 0.26) \times 10^{-6} \exp(-1.7 \pm 0.6/k_BT)\).


FIG. 12. Arrhenius plot of \(\ln(D)\) vs 1000/\(T\).