

Change of Magnetic Properties in Ultrathin Fe Films on Pt(111) Induced by Interdiffusion

T.-U. NAHM*

Quantum Photonic Science Research Center and Department of Physics, Hanyang University, Seoul 133-791

Wookje KIM and S.-J. OH

School of Physics and Center for Strongly Correlated Materials Research, Seoul National University, Seoul 151-742

(Received 28 June 2004)

We have studied magnetic properties of ultrathin Fe films grown on Pt(111) substrate by using the *in situ* surface magneto-optic Kerr effect (SMOKE), X-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED). SMOKE measurements show that the Fe layers are not ferromagnetic when the film is thinner than approximately 4.5 ML (monolayers), but the in-plane magnetization is present for a 4.1-ML Fe film on Pt(111) annealed at 550 K. Upon post-annealing at 770 K, a 9.2-ML Fe film does not show any Kerr signal, while a 5.1-ML Fe film has the in-plane Kerr signal with increased coercivity. A diffuse 2×2 LEED pattern was observed for both cases, and the average Fe concentration of the intermixed layers caused by the interdiffusion of Fe atoms into the Pt substrate is estimated to be about 50 and 61 at.% Fe for the 9.2- and 5.1-ML Fe films, respectively. Underlying reasons are discussed on the basis of the XPS results.

PACS numbers: 78.20.Ls, 79.60.Jv, 68.35.Ct

Keywords: Fe films, Pt, Magneto-optic Kerr effect, X-ray photoelectron spectroscopy, Interdiffusion

I. INTRODUCTION

Ultrathin magnetic films have been extensively studied because of their 2-dimensionality and their relation to magnetic multilayers and alloys. The absence of ferromagnetic order in a 2-dimensional spin system at finite temperature proposed by F. Bloch initiated great interest in ultrathin magnetic films on inert surfaces, but nowadays many studies are related to the magnetic properties of artificial structures such as magnetic multilayers. The magnetic properties of (Fe, Co)/(Pd, Pt) multilayer films and alloy films have attracted significant attention both for their potential applications as magnetic recording materials and for their scientific interest as a new artificial structure [1,2]. Extensive studies have been reported for Fe-Pt alloy films as well as for Fe/Pt magnetic multilayers, which have concentrated either on the investigation of the presence of perpendicular magnetic anisotropy (PMA) and its relation to the structure or on the investigation of the local magnetic moments; PMA was observed for FePt(001) films [3], polycrystalline Fe-Pt alloy films [4], Fe/Pt multilayers grown in the [111] direction when the Pt interlayer is thick enough to ensure the low-dimensionality of Fe layers [5], and Fe/Pt multilayers grown in the [100] direction in certain cases

[6,7]. It is also reported that Pt atoms in Fe/Pt multilayers and Fe-Pt alloys have induced magnetic moments [8].

In relation to these novel properties of Fe-Pt alloy films and multilayers, it is necessary to study the role of interface and intermixing between the ad-layer and the substrate. We have previously studied ultrathin Fe films on Pd(111) [9] and found that the morphology of the interface and the degree of intermixing are very crucial to the magnetic properties of ultrathin films.

In this work, we have investigated Fe films grown on Pt(111) by using the surface magneto-optic Kerr effect (SMOKE), X-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED). We found that the Fe layers are not ferromagnetic when the film is thinner than 4.5 ML (monolayers), and that the in-plane magnetization is present for a 4.1-ML Fe film upon post-annealing at 550 K. Thicker films show only an in-plane Kerr signal. Upon post-annealing at 770 K, a 9.2-ML Fe film does not show any Kerr signal, while a 5.1-ML Fe film has an in-plane Kerr signal with increased coercivity. A diffuse (2×2) LEED pattern was observed for both cases, and the average compositions of the intermixed layers caused by the interdiffusion of Fe atoms into the Pt substrate were also estimated.

*Corresponding author; E-mail: tschnahm@hanyang.ac.kr

II. EXPERIMENT

The SMOKE, XPS, and LEED measurements were performed in a home-made ultrahigh vacuum chamber. The base pressure of the chamber was 8×10^{-11} Torr. The Pt(111) substrate was of disk type with diameter 10 mm and thickness 1 mm. The surface was cleaned by several cycles of Ar^+ sputtering at 1 keV and annealing at 870 K in the UHV chamber until a sharp (1×1) LEED pattern was observed. No contamination was detected in the XPS spectrum. The XPS spectra were obtained with unmonochromatized Al K_α radiation with $h\nu = 1486.6$ eV. The overall resolution was 0.9 eV. The light source for SMOKE measurement was a 10-mW He-Ne laser with $\lambda = 623.8$ nm.

The Fe film was deposited on the substrate at room temperature (RT) by an e-beam heating method. An iron wire of 99.99 % purity was heated by electron bombardment from a tungsten filament. The film thickness was first calibrated by using a quartz thickness monitor, and was then cross-checked by XPS by using Fe 2*p* and Pt 4*f* core-level photoelectron (PE) intensities at sub-ML coverage, by assuming no island growth. The values obtained from these two methods agree with each other within an error of 10 %. In this work, the Fe film thickness was represented in units of one monolayer and 1 ML was set as 1.50×10^{15} Fe atoms cm^{-2} , by assuming a pseudomorphic growth of the Fe film on the Pt(111) surface. Most post-annealing was done for 3 min at a given temperature, unless otherwise stated.

III. RESULTS AND DISCUSSION

The results of SMOKE measurement for Fe films grown on Pt(111) surface are shown in Fig. 1. No hysteresis curves were observed for films with Fe thickness less than 4.5 ML. The as-deposited 4.1-ML Fe film does not show Kerr signal for any direction, but upon annealing at 550 K for 15 min, the in-plane Kerr signal is obtained with a coercivity of 2.9 Oe [10]. Similar behavior has been observed in a 2.0-ML Fe film on Pd(111) [9], where both the in-plane and out-of-plane signals are present, but a 2.0-ML Fe film on Pt(111) does not show ferromagnetic behavior upon annealing. In addition to this, the Fe 2*p* and valence band PE lineshapes of a 4.1-ML Fe film on Pt(111) are changed upon annealing, this being different from the 2.0-ML Fe film on Pd(111). This implies that while the post-annealing of the 2.0-ML Fe film on Pd(111) results in better morphology, the post-annealing of the 4.0-ML Fe film on Pt(111) results in intermixing which may make the several layers on the surface ferromagnetic Fe-Pt alloy.

The Kerr intensity of a 5.1-ML Fe film (middle panel of Fig. 1) has a well-defined in-plane hysteresis curve with a low coercivity, and post-annealing at 570 K does not change it much. However, the coercivity increases to

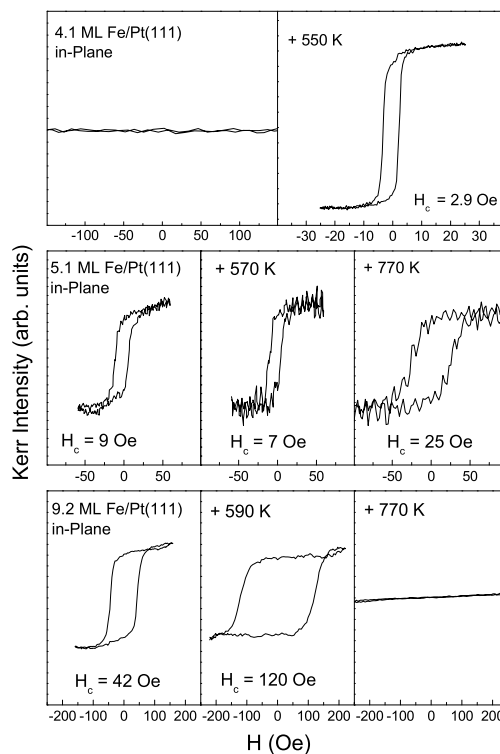


Fig. 1. Kerr signals from 4.1-, 5.1-, and 9.2-ML Fe films on Pt(111) after RT deposition and upon annealing at given temperatures.

25 Oe upon further annealing at 770 K. This increase was also observed for Fe films on Pd(111) at $T = 600 - 660$ K [9], which seemed to result from the formation of compositionally inhomogeneous layers with small domain sizes. Upon post-annealing at 590 K, the coercivity of a 9.2-ML Fe film (bottom panel of Fig. 1) increases, but further annealing at 770 K results in the disappearance of the hysteresis curve. This is not easy to understand when compared with the 5.1-ML case, because it can be expected that thermodynamic equilibrium can be reached easily for thinner Fe films. For the Fe/Pd(111) system, the increase in coercivity was achieved at a lower temperature for a 2.5-ML Fe film than for a 5.5-ML Fe film [9].

In order to figure out the underlying origin of this difference, we first performed LEED experiments. There was a report of observing a (2×2) diffuse LEED pattern in post-annealed Fe/Pt(111) [11], and we also observed such a pattern for both the 5.1- and 9.2-ML Fe films at 570 – 590 K. These spots did not disappear upon annealing at 770 K. This indicates that at least the topmost layers of both films do not differ much. This surface ordering or reconstruction was not observed in Fe/Pd(111) [9]. It is hard to determine the surface structure in real space without I-V characteristic measurement, and we cannot even know the composition of the topmost layer. It was reported that the topmost layer is composed of 45 at.% Fe [11] and, if this was the case, the surface layer

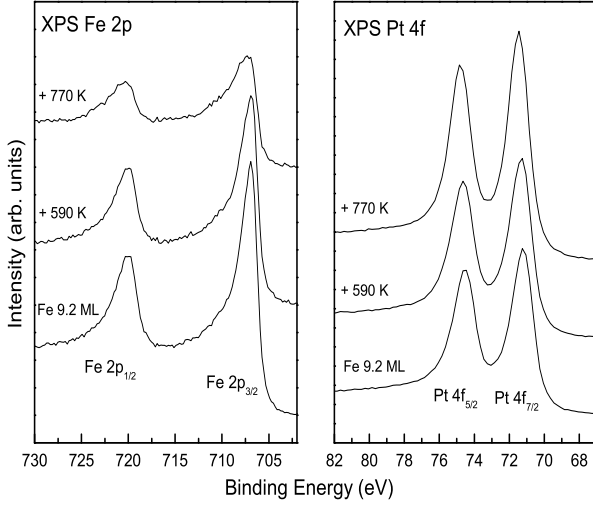


Fig. 2. XPS spectra of a 9.2-ML Fe film on Pt(111) after RT deposition and upon 590 K and 770 K post-annealing.

should be a mixture of $p(1 \times 2)$ and $p(2 \times 1)$, which corresponded to the atomic rows of Fe and Pt on (111) surface. Since it is well known that the topmost layer of $\text{Fe}_{20}\text{Pt}_{80}(111)$ alloy is composed solely of Pt atoms [12], we cannot rule out the possibility of a very complex structure for the topmost layer. The easiest explanation for the $p(2 \times 2)$ LEED pattern is the formation of the surface ordered alloy with composition ratio of 1 : 3, and one may assume the formation of FePt_3 surface ordered alloy upon post-annealing. Since bulk FePt_3 develops antiferromagnetic order below $T_N = 160$ K, it is tempting to conclude that the disappearance of the Kerr signal from the 9.2-ML Fe film upon annealing at 770 K is related to the surface alloy formation of FePt_3 .

Figure 2 represents the core-level spectra of Pt 4f and Fe 2p PE lines. The Fe 2p PE line changes its lineshape greatly upon annealing at 770 K. This implies that there is significant intermixing with Pt atoms due to interdiffusion, but the change is not so severe as in the Fe/Pd(111) case [9]. We can assume that the average composition of intermixed layers is not similar to the post-annealed Fe/Pd(111), where the composition of the thick layer was estimated to be between 9 and 15 at.% Fe.

We first tried to apply Johansson and Mårtensson's method for treating core-level binding-energy shifts in alloys [13] as in Ref. [9] to estimate the Fe concentration of the intermixed layers. This method is based on a Born-Haber cycle involving the heat of formation usually calculated after Miedema [14]. The Pt 4f binding-energy shift calculated in a simplified scheme [13] is $\Delta E = 0.82x$ eV, where x is the average Fe concentration of the intermixed layers. Since the measured value of the maximum shift is + 0.26 eV, the Fe concentration is estimated to be 32 at.%. However, it is apparent that this method does not work in this case; the Fe 2p binding-energy shift calculated in a simplified scheme [13] is $\Delta E = 0.25(1 - x)$ eV, and the measured value of the shift

is + 0.25 eV, implying that the average Fe concentration is almost 0.

On the other hand, if we compare the PE intensity ratio of RT and 770 K annealed films, we can get a rough estimate of the average Fe concentration, since the photoelectrons emitted from the inner layers decay through inelastic scattering [15]. Figure 3 shows the change in the PE intensity upon annealing at given temperatures. By assuming a pseudomorphic behavior for the as-deposited 9.2-ML Fe film, the PE intensity ratio is given by

$$\frac{I_{\text{Fe}2p}}{I_{\text{Pt}4f}} = A \frac{0.8 \sum_{n=0}^8 \exp\left(-\frac{nd}{\lambda_{\text{Fe}}}\right) + 0.2 \sum_{n=0}^9 \exp\left(-\frac{nd}{\lambda_{\text{Fe}}}\right)}{0.8 \sum_{n=9}^{\infty} \exp\left(-\frac{nd}{\lambda_{\text{Pt}}}\right) + 0.2 \sum_{n=10}^{\infty} \exp\left(-\frac{nd}{\lambda_{\text{Pt}}}\right)},$$

where d is the interlayer spacing of $\text{Pt}\{111\}$. The electron inelastic mean free paths have the values $\lambda_{\text{Fe}} = 5.44$ ML and $\lambda_{\text{Pt}} = 7.33$ ML for Fe 2p and Pt 4f photoelectrons excited by Al K_{α} radiation [15]. A constant A represents the ratio of the photoionization cross sections and the effect of analyzer transmission function. If we assume that the surface alloy forms homogeneously with sharp interface upon 770-K annealing, the PE intensity ratio would be

$$\frac{I_{\text{Fe}2p}}{I_{\text{Pt}4f}} = A \frac{x \sum_{n=0}^{l-1} \exp\left(-\frac{nd}{\lambda_{\text{Fe}}}\right)}{(1-x) \sum_{n=0}^{l-1} \exp\left(-\frac{nd}{\lambda_{\text{Pt}}}\right) + \sum_{n=l}^{\infty} \exp\left(-\frac{nd}{\lambda_{\text{Pt}}}\right)},$$

with the constraint

$$x \times l = 9.2,$$

where x is the Fe concentration and l is the thickness of surface alloy in monolayers. This gives $x = 0.49$, much different from the result of Johansson and Mårtensson's method.

The homogeneity of the intermixed layers can be estimated from the change in linewidth of the PE lines. It is well known that the Pt 4f lineshape does not follow the usual Doniach-Šunjić type, but the Mahan type, and it is not easy to determine the real half-width when asymmetry is not treated rigorously [16]. Here we fitted only part of the PE lines where the simple Voigt function worked. Binding energy shifts and the linewidth change of Pt 4f PE lines from the fitting are shown in Fig. 4. The binding energy shift results from the intermixing of Pt substrate with Fe atoms, and its maximum value is 0.26 eV. The values of full width at half maximum (FWHM) of Pt 4f PE lines decrease upon deposition of Fe atoms at RT. This might be related to the change of surface states. The value of FWHM increases upon annealing at 570 and 590 K, indicating that the Pt atoms have many different chemical environments. This can be understood from the

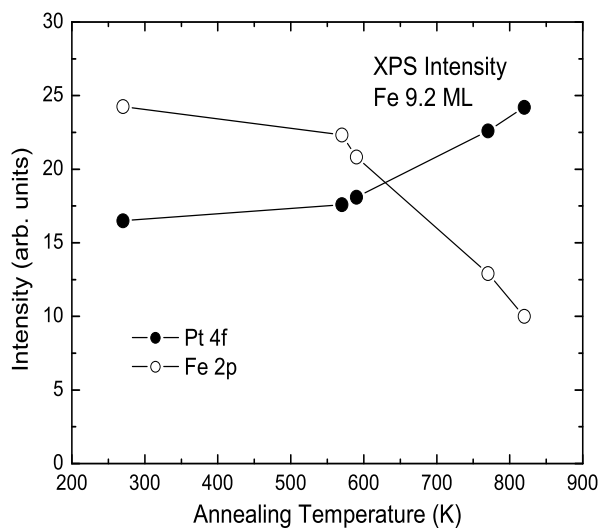


Fig. 3. Photoelectron intensity change from a 9.2-ML Fe film on Pt(111) as a function of post-annealing temperature.

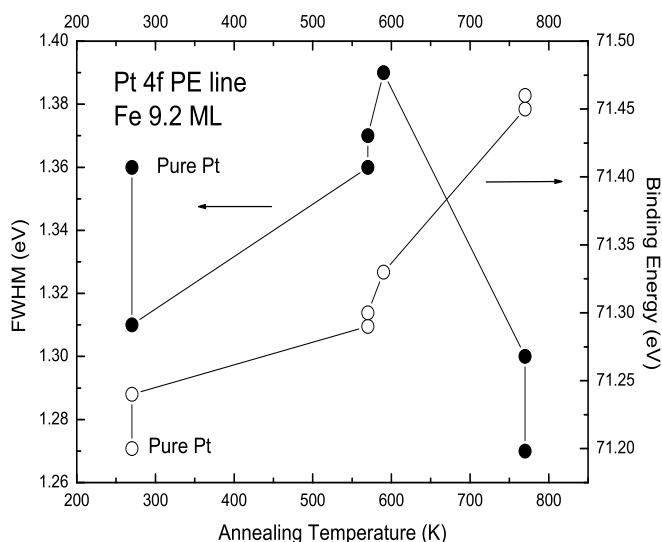


Fig. 4. Binding energy shift (solid circles) and full width at half maximum (open circles) of Pt 4f PE lines as a function of post-annealing temperature. The values for pure Pt(111) are shown for comparison.

normal diffusion phenomena. However, upon annealing at 770 K, the value of FWHM decreases from 1.39 eV to 1.27 eV, and we can conclude that the intermixed layers have more or less homogeneous chemical environments.

From the results, it is clear that the 770-K annealed intermixed layer is composed of nearly equiatomic amounts of Fe and Pt atoms. Since the Fe concentration of the topmost layer was suggested as 45 at.%, it seems that the whole intermixed layer has a homogeneous composition ratio of nearly 1 : 1. Since it is known that there is competition between ferromagnetism and antiferromagnetism in fct FePt [17], the absence of ferromagnetic or-

der in the 770 K annealed 9.2-ML Fe film might be due to the tetragonal distortion and chemical ordering. On the other hand, the 770 K annealed 5.1-ML Fe film has a smaller change in FWHM and photoelectron intensity ratio upon annealing. Similar analysis using Eqs. (1) and (2) gives $x = 0.61$. This probably explains the ferromagnetic order in the latter case. We are currently studying further a 5.1-ML Fe film and the valence band spectra of post-annealed films by comparing them with the XPS and synchrotron radiation PES [18].

IV. SUMMARY

In summary, the magnetic properties of ultrathin Fe films grown on a Pt(111) surface were investigated by using SMOKE, XPS, and LEED. By combining the experimental results, it was found that the Fe layers are not ferromagnetic when the film is thinner than approximately 4.5 ML, but that in-plane magnetization is present for a 4.1-ML Fe film on Pt(111) upon annealing at 550 K. Upon post-annealing at 770 K, a 9.2-ML Fe film does not show any Kerr signal, while a 5.1-ML Fe film has an in-plane Kerr signal with increased coercivity. A diffuse 2×2 LEED pattern was observed for both cases, and the average compositions of the intermixed layers caused by the interdiffusion of Fe atoms into the Pt substrate are estimated to be not less than 49 at.% Fe. The absence of ferromagnetic order observed in a 770 K annealed 9.2-ML Fe film might result from tetragonal distortion and chemical ordering.

ACKNOWLEDGMENTS

This work was supported by KOSEF through q-Psi at Hanyang University, and by the research fund of Hanyang University (HY-2003-NT).

REFERENCES

- [1] S. M. Kim, Y. P. Lee, Y. V. Kudryavtsev, J. Dubowik and J. Y. Rhee, *J. Korean Phys. Soc.* **43**, 1061 (2003).
- [2] J. Y. Rhee, *J. Korean Phys. Soc.* **43**, 792 (2003).
- [3] A. Cebollada, D. Weller, J. Sticht, G. R. Harp, R. F. C. Farrow, R. F. Marks, R. Savoy and J. C. Scott, *Phys. Rev. B* **50**, 3419 (1994) and references therein.
- [4] C.-M. Kuo, P. C. Kuo and H.-C. Wu, *J. Appl. Phys.* **85**, 2264 (1999) and references therein.
- [5] A. Simopoulos, E. Devlin, A. Kostikas, A. Jankowski, M. Croft and T. Tsakalagos, *Phys. Rev. B* **54**, 9931 (1996).
- [6] T. Katayama, Y. Suzuki, Y. Nishihara, T. Sugimoto and M. Hashimoto, *J. Appl. Phys.* **69**, 5858 (1991).
- [7] W. J. Antel, Jr., M. M. Schwickert, T. Lin, W. L. O'Brien and G. R. Harp, *Phys. Rev. B* **60**, 12933 (1999).

- [8] T. Koide, T. Shidara, K. Yamaguchi, A. Fujimori, H. Fukutani, N. Nakajima, T. Sugimoto, T. Katayama and Y. Suzuki, *Phys. Rev. B* **53**, 8219 (1996).
- [9] J.-H. Choi, T.-U. Nahm, W. Kim, W. Kim, J. Chung, J.-Y. Kim, H. Koh and S.-J. Oh, *Surf. Sci.* **495**, 173 (2001).
- [10] In our previous report, W. Kim, J. H. Choi, T.-U. Nahm, S. H. Song and S.-J. Oh, *J. Korean Phys. Soc.* **44**, 722 (2004), we inadvertently made several mistakes in the course of analysis, and hence wrong conclusions. All the previous mistakes have been corrected in this paper.
- [11] D. I. Jerdev and B. E. Koel, *Surf. Sci.* **513**, L391 (2002).
- [12] P. Beccat, J. C. Bertolini, Y. Gauthier, J. Massardier and P. Ruiz, *J. Catal.* **126**, 451 (1990).
- [13] B. Johansson and N. Mårtensson, *Phys. Rev. B* **21**, 4427 (1980).
- [14] A. R. Miedema, P. F. de Châtel and F. R. de Boer, *Physica B* **100**, 1 (1980).
- [15] M. P. Seah and W. A. Dench, *Surf. Interf. Anal.* **1**, 1 (1979).
- [16] L. Ley and M. Cardona (eds.), *Photoemission in Solids II*, (Springer Verlag, Berlin, 1979) p. 351.
- [17] G. Brown, B. Kraczek, A. Janotti, T. C. Schulthess, G. M. Stocks and D. D. Johnson, *Phys. Rev. B* **68**, 052405 (2003).
- [18] S.-H. Song, J.-S. Park, T.-U. Nahm, H.-J. Noh, B.-H. Choi and S.-J. Oh, *J. Korean Phys. Soc.* **45**, 51 (2004).