Canted magnetization in Fe thin films on highly oriented pyrolytic graphite

Wen-Chin Lin,1,a) Fang-Yuh Lo,1 Ya-Yun Huang,1 Chih-Hsiung Wang,1 and Ming-Yau Chern2
1Department of Physics, National Taiwan Normal University, Taipei 116, Taiwan
2Department of Physics, National Taiwan University, Taipei 106, Taiwan

(Received 29 July 2011; accepted 23 September 2011; published online 20 October 2011)

Because of the unique properties of graphene, the combination of perpendicular magnetized materials and a carbon-based template is especially useful. This study examines the effect of highly oriented pyrolytic graphite (HOPG) surface defects on Fe thin films. Numerous Fe thin films were grown on planar HOPG (p-HOPG) and Ar+ sputtered HOPG (s-HOPG), for comparison. X-ray diffraction showed the preferred (110) texture for Fe films on both p-HOPG and s-HOPG. Fe/p-HOPG exhibited only in-plane magnetization. In contrast, Fe/s-HOPG exhibited the coexistence of in-plane and perpendicular magneto-optical Kerr effect hysteresis loops, indicating a stable, canted magnetization. The canted magnetization of Fe/s-HOPG persisted to at least 20 atomic monolayers and might be attributed to a volume-contributed perpendicular anisotropy. These observations are relevant to a combination of ferromagnetic thin films and graphene-related templates. © 2011 American Institute of Physics. [doi:10.1063/1.3654141]

I. INTRODUCTION

Because of their potential applications in high-density data storage and magnetic nanodevices, perpendicular magnetic materials have been studied widely.1,2 The two-dimensional shapes of magnetic thin films and nano-discs always induce a magnetic shape anisotropy, which gives an easy direction on the surface plane. A perpendicular magnetic anisotropy usually originates from crystalline magnetic anisotropy, strain-induced magneto-elastic anisotropy, or surface/interface magnetic anisotropy. Perpendicular magnetization caused by surface/interface anisotropy can only persist for a small number of monolayers (ML) before switching to in-plane direction.3 In other cases, for example, periodic Co/Pd and Co/Pt multilayers and Ni/Cu(100) (Refs. 1, 2, and 4) strain on the crystalline structure leads to a volume-contributed perpendicular anisotropy, which sustains the perpendicular magnetization to a significantly higher thickness. To date, perpendicular magnetization has proved challenging to produce, especially in combination with specific functional substrates, such as carbon-based nanomaterials, which have been shown to possess unique electronic and magnetic properties. For example, graphene exhibits an anomalous quantum Hall effect, high carrier mobility, and micrometer-range spin-relaxation length.5–7 Therefore, the combination of perpendicular magnetic thin films and a carbon-based substrate is important to technical advances in spintronics.

Recently, numerous theoretical reports have been concerned with the magnetism of transition metal adatoms and dimers adsorbed on either graphite or graphene.14,15 However, to the best of our knowledge, only a small number of reports have handled the magnetism of transition metal thin films on either graphite or graphene.9,12,16–18 In 1998, the theoretical calculations of Krüger et al. demonstrated that the Fe, Co, and Ni monolayers on graphite are ferromagnetic.19 In 1999, Edmonds et al. reported a doubling of the orbital magnetic moment in nanoscale Fe clusters on highly oriented pyrolytic graphite (HOPG) by using x-ray magnetic circular dichroism (XMCD).20 In 2004, Fauth et al. studied the magnetic properties of Fe clusters on graphite and concluded that the clusters were forced into a nonmagnetic state by their interaction with graphene.21 In 2009, Kumar et al. performed XMCD studies on Fe-doped HOPG and concluded that Fe atoms are forced into a non-magnetic/paramagnetic state by their interaction with the graphite matrix.22 In 2010, Vo-Van et al. reported on the growth of flat, epitaxial ultrathin Co films on graphene using pulsed laser deposition.12 These Co films displayed perpendicular magnetic anisotropy in a thickness range 0.5–1 nm (approximately 2–5 ML of hcp Co(0001)).

In this study, Fe thin films were deposited on a HOPG substrate. HOPG was chosen because it has the same surface crystalline structure as graphene. The growth of metallic magnetic thin films on HOPG provides valuable information for future applications of graphene. Fe films were grown on a planar HOPG (p-HOPG) and a sputtered HOPG (s-HOPG), and the magnetic properties of each combination were investigated. A previous report identified initial nucleation clusters distributed on s-HOPG with narrower size distribution and significantly higher density than those for p-HOPG. For the Fe thin films investigated here, stable in-plane and canted magnetization were observed in planar and sputtered HOPG, respectively. Canted magnetization was sustained for at least 20 ML Fe. This is different from conventional surface/interface magnetic anisotropy induced perpendicular magnetization, in which the perpendicular moment is usually observed only in the first few monolayers. The sputtered HOPG surface not only changed the Fe/HOPG interface conditions, such as its roughness and defects, but also influenced the total volume of the Fe films, resulting in a volume contributed perpendicular anisotropy.

II. EXPERIMENT

The sample preparation, transferring, and characterization of magnetic properties were performed in an ultrahigh...
vacuum (UHV) with a base pressure of better than $3 \times 10^{-10}$ Torr. The HOPG substrate was cleaved in air, immediately inserted into the vacuum chamber, and then degassed at 400 K for 10h. The HOPG was prepared with either a flat or a sputtered surface. For the sputtered HOPG surface, Ar$^+$ sputtering, with a beam energy of 600 eV, was performed for 180s. The Fe atoms were evaporated by e-beam heating. The Fe deposition rate was calibrated from the epitaxial growth on Cu(100) by using Auger electron spectroscopy. In this experiment, 1 ML is equivalent to the nominal surface atom density of Cu(100), that is, 1 ML = $1.54 \times 10^{15}$ atoms/cm$^2$. This study investigated the magnetic behavior in situ, at room temperature (RT) by using the magneto optical Kerr effect (MOKE) in both longitudinal and polar directions with the lock-in technique. For the characterization of crystalline structure, a x-ray diffraction meter (XRD) with a Cu target was used to obtain the Bragg reflections from the samples. For the purposes of ex situ XRD measurement, the Fe films were covered with a layer of gold to eliminate the possibility of contamination.

III. RESULTS AND DISCUSSION

A. XRD: Crystalline structure

For Fe/HOPG, previous STM investigation had shown that Ar$^+$ sputtering creates a large number of defects on the HOPG surface terraces for the nucleation of deposit, leading to a narrow size distribution for the nucleation clusters. Because of the surface defects, the Fe cluster density is higher and the spatial distribution is more uniform than for growth on p-HOPG. Consequently, the sputtering-induced HOPG surface defects are expected to influence the crystalline structure and magnetic behavior of Fe films.

Fig. 1 shows the XRD patterns for Au-covered Fe films on p-HOPG and s-HOPG, as well as clean HOPG, for comparison. The standard features of HOPG are indicated. Cu-K$\alpha$ x-rays contribute these very large main peaks, (002) and (004), which confirm the highly oriented crystalline structure of the graphite substrate. The other satellite peaks at approximately 12° and roughly 24.5° are Cu-K$\beta$ diffraction peaks of HOPG(002) and HOPG(004), respectively. Because the small peaks at $\theta = 18°$ and $20°$ appear in clean HOPG and all the other two patterns, they may occur because of a number of disordered graphite planes, such as HOPG (110), and are attributed to the background features of the HOPG substrate. As the arrows indicate, a small peak for Fe(110) at $\theta = 22.5°$ is especially pronounced for Au/Fe/p-HOPG. The Fe(110) peak is significantly smaller in Au/Fe/s-HOPG and invisible in clean HOPG.

The crystalline structures of HOPG and body-centered-cubic (bcc) Fe are illustrated in Fig. 2 to explain the Fe(110) peak in XRD. In the ferromagnetic 3d transition metals, Fe, Co, and Ni, the lattice constants of hcp-Co(0001) and fcc-Ni(111) surfaces match the in-plane lattice constants of C(0001) almost perfectly (lattice mismatch <2%), and for bcc-Fe, the lattice mismatch between Fe(111) and C(0001) is significantly larger, at $\approx 5.1\%$ (Figs. 2(a) and 2(b)). The bcc(111) surface is composed of exposed atoms at three different heights and is actually notably rougher than the atomically flat hcp(0001) and fcc(111) surfaces, and therefore, Fe(111) should not be the preferred orientation on HOPG. The lattice constant of Fe(110) matches C(0001) well (lattice mismatch <1%) at one edge of the unit cell, but the lattice mismatch is extremely large at the other edge ($\approx 15\%$). However, for the matching cell shown in Fig. 2(d), seven parts of the HOPG lattice match six parts of the Fe(110) lattice perfectly. Only a slight 5.3° difference is in the angle between the unit vectors. According to this proposed lattice matching, Fe(110) is evidently grown on HOPG. For the sputtered-HOPG, because the surface crystalline structure has been relatively destroyed, the preference for the Fe(110) texture is naturally reduced.

B. MOKE: Magnetism

Fig. 3 shows the normalized MOKE hysteresis loops for n ML Fe/p-HOPG, measured in the perpendicular and in-plane directions. Throughout the examined range for Fe, from 3.6 to 22 ML, only in-plane hysteresis loops were observed. The in-plane hysteresis loop starts to appear at 4.4 ML. Thereafter, the Fe/p-HOPG films exhibit stable, in-plane hysteresis loops with a tilted shape, indicating the in-plane easy direction. In contrast, Fig. 4 shows the normalized MOKE hysteresis loops for n ML Fe on s-HOPG. Within the examined thickness of 2.8–20 ML, Fe/s-HOPG always exhibits square hysteresis loops in both the in-plane and perpendicular directions. The coexistence of in-plane and perpendicular hysteresis loops might originate from either multi-domain structures or canted magnetization. When originating from multi-domain structures, the magnetic structure is a distribution of in-plane and perpendicular domains. When originating from canted magnetization, the magnetic moment is tilted in a direction between the surface normal and surface plane. The MOKE investigation verified that flipping the moment with a perpendicular (in-plane) field fully changes the initial state of the subsequent in-plane (perpendicular) MOKE measurement. This suggests that the in-plane and perpendicular hysteresis loops originate from the
same magnetic moment, resulting in the stable canted magnetization of Fe/s-HOPG films.4

The coercivity field ($H_c$) of the MOKE hysteresis loops, as a function of Fe coverage, is depicted in Fig. 5. For Fe/p-HOPG, the in-plane $H_c$ increases from 5 to approximately 30 Oe and from 3.6 to 6.8 ML. Thereafter, it remains within the range of 30–35 Oe. The point at which $H_c$ becomes almost constant occurs at approximately 7 ML, which implies a possible transition from isolated three-dimensional Fe islands to a two-dimensional Fe network for p-HOPG. For Fe/s-HOPG, the in-plane $H_c$ ranges between 15 and 45 Oe, whereas the perpendicular $H_c$ is one to two times that of the in-plane $H_c$. The coverage-dependent evolution of perpendicular and in-plane $H_c$ is similar. This suggests that both perpendicular and in-plane hysteresis loops originate from the same canted moment. After an initial steep increase until 5 ML, the $H_c$ of Fe/s-HOPG continues to increase gradually. The 7 ML transition point for Fe/p-HOPG is advanced to 5 ML because the sputtering-induced defects on HOPG enable more uniform distribution of Fe nucleation.9 The gradual increase in $H_c$ after 5 ML defines the continuous evolution of

FIG. 2. (Color online) (a)–(c) Crystal-line structures of HOPG, Fe(111), and Fe(110), respectively. The arrows indicate the possible cell for lattice matching. (d) Illustrations of the lattice matching cell for Fe(110) on HOPG, as indicated by the dotted parallelogram.

FIG. 3. Normalized magnetic Kerr hysteresis loops for n ML Fe/planner-HOPG measured at RT.

FIG. 4. Normalized magnetic Kerr hysteresis loops for n ML Fe/sputtered-HOPG measured at RT.
Fe films, regarding their crystalline structure or geometric morphology.

A number of methods, such as ion sputtering and step density control, have been proposed for the modulation of template surface morphology to manipulate the magnetic properties of the subsequently deposited films. However, most of the efforts result in the modification of surface/interfacial anisotropy, which only changes the magnetic behaviors in low coverage regions. For example, the study of the substrate roughness effect on Co/Pd(111) by Kim et al. shows that the sputtered template merely triggers an earlier spin reorientation transition, from the perpendicular to the in-plane easy direction, at lower coverage. Modulation of the substrate surface morphology has two effects. One is the rearrangement of the geometric positions of the substrate and the deposit atoms at the interface, and the other is the strained crystalline structure of the entire film. The first effect is interfacial-contributed and gradually decays with increasing film thickness, whereas the second effect can extend to the volume of thin film and induce magnetoelastic volume anisotropy. The study of Bisio et al. in 2006 successfully isolated the step-induced magnetic (surface) anisotropy from the strain-induced magnetoelastic (volume) anisotropy in Fe/Ag(001) films on which nanoscale surface ripples were produced using the ion sculpting technique. Regarding Fe/s-HOPG in this study, the rough surface created by sputtering may not only change the geometrical arrangement of atom positions at the interface, but may also induce a strain, as well as a volume-contributed magnetoelastic anisotropy in the Fe films, leading to stable canted magnetization.

For discussion, a uniaxial system is considered. The density of magnetic anisotropy can be described as 

\[ E = K_{eff} \sin^2 \theta \]

where \( K_{eff} \) is the effective anisotropy energy and \( \theta \) is the angle between the direction of magnetization and the surface normal. Positive \( K_{eff} \) defines the perpendicular easy direction, whereas negative \( K_{eff} \) defines the in-plane easy direction. \( K_{eff} \) is composed of the surface/interfacial anisotropy and volume contributed shape and crystalline anisotropy. For Fe films, the shape anisotropy of a two-dimensional layer \( K_{shape} = -\mu_B M^2 / 2 = -2.12 \text{ MJ/m}^3 \) prefers in-plane magnetization. \( M_s \) is the magnetic moment density of Fe (2.5 \( \mu_B/\text{atom} \)). The bulk magnetoelastic anisotropy of bcc Fe \( K_{C_{11}} = 0.047 \text{ MJ/m}^3 \), preferring the \( [100] \) directions, is relatively small and unable to overcome the large in-plane shape anisotropy. Therefore, the stable canted magnetization in Fe/s-HOPG films suggests a volume-contributed perpendicular anisotropy that is sufficiently large to compensate for the in-plane shape anisotropy. The sputtering-induced broken carbon bonds on the HOPG surface may bond more strongly to the Fe atoms and lead to strain-induced magnetoelastic anisotropy, which causes canted magnetization.

IV. SUMMARY

In this experiment, a comparative study on the growth and magnetic behavior of Fe films on planar-HOPG and sputtered-HOPG was performed. XRD measurement revealed the (110) texture for Fe/HOPG films. This preference for (110) orientation can be explained by the lattice match between HOPG and Fe. Stable canted magnetization was observed for Fe/s-HOPG within the examined thickness of 3.6–20 ML, which contrasted with the in-plane magnetization of Fe/p-HOPG. The sputtering-induced defects on the HOPG might result in a different crystalline strain, leading to a volume-contributed perpendicular anisotropy. These observations will prove valuable for future studies on the combination of perpendicular magnetism and a graphene template.

ACKNOWLEDGMENTS

This work was supported by the National Science Council of Taiwan under Grant Nos. NSC 99-2738-M-003-001, NSC 99-2112-M-003-009-MY3, NSC 99-2923-M-003-001-MY2, and NSC 98-2112-M-003-007-MY3.