Epitaxial growth and magnetic properties of Fe₃O₄ films on TiN buffered Si(001), Si(110), and Si(111) substrates

Hua Xiang,¹,a) Fengyuan Shi,¹ Mark S. Rzchowski,² Paul M. Voyles,¹ and Y. Austin Chang¹,a)
¹Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA
²Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

(Received 25 May 2010; accepted 7 August 2010; published online 2 September 2010)

Epitaxial Fe₃O₄ thin films were grown on TiN buffered Si(001), Si(110), and Si(111) substrates by dc reactive sputtering deposition. Both Fe₃O₄ films and TiN buffer are fully epitaxial when grown at substrate temperatures above 150 °C, with textured single phase Fe₃O₄ resulting from room temperature growth. The initial sputtered Fe₃O₄ formed nuclei islands and then coalesced to epitaxial columnar grains with increasing film thickness. The magnetization decreases and the coercive field increases with decreasing film thickness. There is no in-plane magnetic anisotropy of epitaxial Fe₃O₄(001) on Si(001) but Fe₃O₄ films grown on Si(110) and Si(111) substrates show uniaxial in-plane magnetic anisotropy. © 2010 American Institute of Physics. [doi:10.1063/1.3484278]

Theoretical calculations predict that Fe₃O₄ exhibits not only half metallic properties at room temperature (RT) but also a negative spin polarization at RT and high Curie temperature of ~860 K, Fe₃O₄ is one of the most promising magnetic materials for spintronic devices.¹⁻³ Because of the near-perfect lattice match between Fe₃O₄ and MgO, epitaxial Fe₃O₄ films have been mainly grown on MgO substrates.⁴⁻⁵ However, for the purpose of developing the next generation of spintronic devices, epitaxial growth of high quality Fe₃O₄ films on semiconductors, particularly Si, is of great technological importance.⁶⁻⁷

The crystalline structures of Fe₃O₄ films directly deposited on Si show varying results, from amorphous to polycrystalline, with some reports of oriented growth.⁸⁻¹⁰ Although (111) texture of Fe₃O₄ on Si has been reported,¹¹⁻¹³ the films have undesirable and complex Fe₃O₄/Si interfaces. Examples are magnetic iron silicide, amorphous oxide, and weakly coupled phases of FeO and Fe₂O₃; all of which adversely affect the properties of the resulting Fe₃O₄ films.¹⁴⁻¹¹ Given the relatively large lattice mismatch between Fe₃O₄ and Si, a buffer layer is likely needed to induce the Fe₃O₄ epitaxial growth on Si. Investigations of Fe₃O₄ films deposited on Si with buffer layers of Ti, Ta, SiO₂, and Fe₂O₃ all show results of polycrystalline Fe₃O₄.¹²⁻¹⁵ Hassan et al.⁵ grew epitaxial Fe₃O₄ on Si(001) using an MgO buffer. However, it is reported that the MgO/Fe₃O₄ bilayer suffers interdiffusion at relatively low temperatures, starting from about 250–300 °C and becoming severe above ~430 °C.¹⁴ Reisinger et al.¹⁵ fabricated and characterized epitaxial Fe₃O₄ on Si(001) using TiN/MgO buffer but did not report the magnetic properties. In this paper, we report the preparation of Fe₃O₄(001), Fe₃O₄(110), and Fe₃O₄(111) epitaxial films on TiN buffered Si by reactive sputtering. The effects of the substrate temperature, sputtering power, film thickness, and Si substrate orientations on the crystalline and magnetic properties of Fe₃O₄ films were investigated; and the uniaxial in-plane magnetic anisotropies of epitaxial Fe₃O₄(110) and Fe₃O₄(111) films were reported.

Multilayer stacks with the structure of substrate/TiN(100)/Fe₃O₄(t) (nanometer) were grown by dc magnetron reactive sputtering in a home-built system with base pressure better than 1.0 × 10⁻⁷ Torr. Si wafers with orientations of (001), (110) and (111) were used as the substrates. The TiN buffer was prepared at 550 °C.¹⁶ After the substrate was cooled to RT, the Fe₃O₄ layer with different thickness (t) was deposited on the TiN/Si structure at substrate temperatures (Tₛ) of RT, 150, 250, 300, and 400 °C, by three different dc sputtering powers, 30, 60, and 120 W.

Figures 1(a)–1(c) show the θ–2θ scans of the 270 nm Fe₃O₄ films grown on TiN buffered substrates of Si(001), Si(110), and Si(111) at Tₛ=300 °C respectively. Since our previous studies showed TiN can grow epitaxially on Si, we conclude that the crystallographic relationship of the entire stack is Si(004)[100]/TiN(002)[100]/Fe₃O₄(004)[100]. For Fe₃O₄ deposited on TiN buffered Si(111), the θ–2θ scan shows peaks corresponding to Fe₃O₄(111) family and Si(111), as shown in Fig. 1(b). The inset to Fig. 1(b) shows the epitaxial crystallographic relationship can be determined as Si(111)[100]/TiN(111)[100]/Fe₃O₄(111)[100]. The case of the epitaxial Fe₃O₄ film on Si(110) substrate shows in Fig. 1(c), and the crystallographic relationship of the entire stack is Si(220)[100]/TiN(220)[100]/Fe₃O₄(440)[100].

The substrate temperature plays an important role in determining the epitaxial film quality. For the Fe₃O₄ film grown on TiN buffered Si(001) at RT, x-ray diffraction (XRD) results show that the film is a mixture of (400) pre-

---

⁴Electronic mail: xiang2@wisc.edu and changy@cae.wisc.edu.
ferred texture with some (440) oriented structures (results not shown here). After increasing the $T_s$ to 150 °C, the epitaxial quality of the resulting Fe$_3$O$_4$ film improved drastically with no misoriented structures detected with XRD. Figure 1(d) shows the rocking curve full width at half maximum (FWHM) data of Fe$_3$O$_4$ films at different $T_s$, respectively. The data decrease rapidly with increasing $T_s$, indicating a decreasing mosaic spread. The rocking curve width also decreases with increasing film thickness, i.e., thicker films show better epitaxial quality, and this should be related to the sputtered Fe$_3$O$_4$ film growth mechanism which will be explained in later parts. The inset of Fig. 1(d) shows the FWHM data of 90 nm Fe$_3$O$_4$ films on the three Si substrates prepared using 30, 60, and 120 W dc powers at $T_s$=400 °C, and the Fe$_3$O$_4$ films grown at lower sputtering powers show narrower rocking curves. Typically, the rocking rate decreases with lower powers if the power is the only variable, and slow sweeping rates may be helpful to improve the Fe$_3$O$_4$ film epitaxial quality.

Figure 2 shows the low magnification and high resolution transmission electron microscopy (HR-TEM) images of the epitaxial Fe$_3$O$_4$ film on Si(001) at $T_s$=RT and 250 °C, respectively. From Fig. 2(a), combined with the XRD results, the Fe$_3$O$_4$ film prepared at RT is a mixture of mainly (400) texture and some polycrystalline domains. Figs. 2(b) and 2(c) show the images of Si/TiN/Fe$_3$O$_4$ stack at $T_s$=250 °C along the Si(110) zone axis. With the elevated $T_s$, the Fe$_3$O$_4$ film becomes more condensed and the grain size also increases. The different contrast of these two images is due to the intrinsic antiphase boundaries (APBs). APBs have been well documented in epitaxial Fe$_3$O$_4$/MgO systems, and they are also present in our Fe$_3$O$_4$/TiN structures given the very close lattice parameters between TiN and MgO. Combined Figs. 2(a) and 2(c) we find an initial layer of about 10–20 nm Fe$_3$O$_4$ film grows as island nuclei and then coalesces to epitaxial columnar larger grains with the increasing film thickness.

The 10 nm TiN buffers are very smooth on all three Si substrates, with the atomic force microscopy measured rms=0.21±0.03 nm on Si(001), 0.23±0.03 nm on Si(110) and 0.18±0.03 nm on Si(111). However, the scanning transmission electron microscopy energy dispersive spectroscopy measurements show there is a ∼2 nm intermixing layer at the TiN/Fe$_3$O$_4$ interface, with 8.21±0.56 at. % Ti diffusion into Fe$_3$O$_4$, which may affect the magnetic property. The electron diffraction pattern of the whole stack in Fig. 2(d) confirms the overall epitaxial relationship between Si, TiN, and Fe$_3$O$_4$ is quite good.

Figure 3(a) shows the high resolution x-ray photoemission spectroscopy (XPS) spectra of the Fe 2p region of Fe$_3$O$_4$ films at $T_s$=150 and 400 °C. The broad Fe 2p peaks, attributed to the coexistence of Fe$^{3+}$ and Fe$^{2+}$ states, exclude the possible presence of Fe$_2$O$_3$. Fig. 3(b) shows the RT magnetization hysteresis loops of the 270 nm Fe$_3$O$_4$ films at different $T_s$ on Si(001). The effects of the Si/TiN bilayer have been subtracted in this study. The magnetization (M) of the Fe$_3$O$_4$ film is not completely saturated up to 6000 Oe. This is a well documented behavior of epitaxial Fe$_3$O$_4$ films, attributed to the intrinsic APBs arising from iron sublattice stacking faults. These stacking faults result in strong antiferromagnetic (AF) exchange coupling between adjacent antiphase domains. It is difficult to overcome this coupling and magnetically align adjacent domains even in moderate magnetic field. The $T_s$ has evident effects on

![FIG. 1. (Color online) The θ-2θ scan of 270 nm Fe$_3$O$_4$ films on TiN buffered (a) Si(001), (b) Si(111), and (c) Si(110) substrates; and also (d) the rocking curve FWHM data of the Fe$_3$O$_4$ films prepared at different $T_s$ and by different sputtering powers. (Peak lines indicated by * are from the substrates.]

![FIG. 2. Low magnification and HR-TEM images along the Si(110) zone axis of the 270 nm Fe$_3$O$_4$ films deposited on TiN buffered Si(001) at (a) RT, and (b) and (c) 250 °C; (d) selective area diffraction pattern of the entire Si(001)/TiN/Fe$_3$O$_4$ stack.]

![FIG. 3. (Color online) (a) The high resolution XPS spectra of the Fe 2p region of Fe$_3$O$_4$ films at $T_s$=150 and 400 °C; (b) the RT magnetization hysteresis loops of 270 nm Fe$_3$O$_4$ films prepared at different $T_s$ on TiN buffered Si(001).]
the magnetization improvement of the films, from 290 ± 20 emu/cc at RT to 420 ± 20 emu/cc at \( T_s = 400 \) °C of our 270 nm Fe\(_3\)O\(_4\) films, primarily resulting from a larger domain size and lower APB density with elevated \( T_s \).

The coercive fields (\( H_c \)) are approximately independent of growth temperature, 490 ± 20 Oe for 270 nm films.

We investigated the thickness dependence of the magnetic properties by comparing the 270, 140, and 90 nm Fe\(_3\)O\(_4\) films grown on Si(001) at \( T_s = 400 \) °C. The \( M \) decreases from 420 ± 20, 380 ± 20, to 310 ± 20 emu/cc, and the \( H_c \) increases from 490 ± 20, 530 ± 20, to 570 ± 20 Oe for these thicknesses. The main reason for such a variation in \( M \) and \( H_c \) is likely the shrinking antiphase domain sizes and the increasing effects of APBs with smaller \( t \). Eerenstein et al.\(^{39}\) has reported a \( t^{-1/2} \) power relationship between the Fe\(_3\)O\(_4\) film thickness \( t \) and the APBs density. More APBs mean more AF couplings, intuitively resulting in smaller \( M \).

A second reason is based on the film growth mechanism of initial island nuclei coalescence followed by columnar grain growth. The out-of-plane orientations of the Fe\(_3\)O\(_4\) grains in the initial layer may scatter to a certain extent. However, with increasing thickness, the subsequent epitaxial columnar Fe\(_3\)O\(_4\) grains grow, resulting in relatively lower \( H_c \) due to fewer defects. The third reason could be the relatively larger epitaxial strain in thinner films, which may cause strain-induced magnetic property variations.\(^{1,6,7,10}\)

We also studied the in-plane magnetic anisotropy of the Fe\(_3\)O\(_4\) films on the three Si substrates. There is no magnetic anisotropy between \{100\} and \{110\} directions of the films grown on Si(001) substrates. However, both epitaxial Fe\(_3\)O\(_4\) films on Si(110) and Si(111) substrates show uniaxial in-plane magnetic anisotropy at RT, as shown in Figures 4(a) and 4(b). For the Fe\(_3\)O\(_4\) film on Si(110), the [001] direction is the in-plane easy axis in Fig. 4(a). This is in contradiction to the previously reported results of epitaxial Fe\(_3\)O\(_4\) films on MgO(110) substrate, which have [110] in-plane easy axis.\(^{1,4}\)

By assuming an isotropic 0.3% strain for epitaxial Fe\(_3\)O\(_4\) on MgO(110), Aoshima and Wang\(^{1}\) calculated the magnetoelastic and magnetocrystalline energy of [110] and [001] directions respectively, and found the relatively larger difference of the magnetoelastic energies between these two directions leads to a strain-induced [110] easy axis. However, the lattice mismatch between Fe\(_3\)O\(_4\) and TiN (about 1.1%) is much larger than that between Fe\(_3\)O\(_4\) and MgO, and may cause the difference. Moreover, the \( M \) and \( H_c \) along the [001] direction are 385 ± 20 emu/cc and 1000 ± 20 Oe, respectively.

Fig. 4(b) shows the in-plane magnetic anisotropy of Fe\(_3\)O\(_4\)(111) film on Si(111), with the easy axis determined as [112]. The corresponding \( M \) and \( H_c \) along [112] are 375 ± 20 emu/cc and 730 ± 20 Oe, respectively.

In conclusion, the sputtered epitaxial Fe\(_3\)O\(_4\) films on Si substrates and the corresponding magnetic properties were reported. Both Fe\(_3\)O\(_4\) films grown on Si(110) and (111) substrates show uniaxial in-plane magnetic anisotropy and the easy axes are determined as [001] and [112], respectively. The [001] easy axis of the epitaxial Fe\(_3\)O\(_4\)(110) film on TiN/Si(110) is opposite to the reported results of Fe\(_3\)O\(_4\)/MgO(110), which may relate to the relatively larger lattice mismatch between Fe\(_3\)O\(_4\) and TiN. The magnetization of (110)- and (111)-oriented Fe\(_3\)O\(_4\) films are comparable but the coercive field of Fe\(_3\)O\(_4\)(111) film is much smaller than that of Fe\(_3\)O\(_4\)(110) film. For epitaxial Fe\(_3\)O\(_4\) films on the three Si substrates, both the in-plane and out-of-plane crystallographic directions of Fe\(_3\)O\(_4\), TiN, and the corresponding Si substrates are parallel to one another. The epitaxial growth of Fe\(_3\)O\(_4\) on Si and the reported magnetic properties should be helpful to engineer the magnetic tunnel junctions with Fe\(_3\)O\(_4\) electrodes or other spintronic devices.

This work is supported by the Office of Basic Energy Research of DOE through Grant No. DE-FG02-99-ER45777, the Wisconsin Alumni Research Foundation (WARF), and the Wisconsin Distinguished Professorship.

---