Oscillatory Spin Polarization and Magneto-Optical Kerr Effect in Fe_3O_4 Thin Films on GaAs(001)

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The spin dependent properties of epitaxial Fe_3O_4 thin films on GaAs(001) are studied by the ferromagnetic proximity polarization (FPP) effect and magneto-optical Kerr effect (MOKE). Both FPP and MOKE show oscillations with respect to Fe_3O_4 film thickness, and the oscillations are large enough to induce repeated sign reversals. We attribute the oscillatory behavior to spin-polarized quantum well states forming in the Fe_3O_4 film. Quantum confinement of the t_{2g} states near the Fermi level provides an explanation for the similar thickness dependences of the FPP and MOKE oscillations.

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Spintronics strives to revolutionize semiconductor electronics by utilizing the electron's spin in addition to charge for integrated memory and logic functions [1]. For spin injection and detection, magnetite (Fe_3O_4) is an attractive material because theory predicts a complete density of states (DOS) spin polarization at the Fermi level (i.e., half-metal) [2,3], experiments measure a large spin polarization (55%–80%) [4,5], and the Curie temperature of 858 K is much higher than room temperature. Following the successful growth of Fe_3O_4 thin films on GaAs [6], the recent demonstration of spin injection establishes Fe_3O_4 as an important material for semiconductor spintronics [7].

One interesting aspect of magnetic thin films and multilayers is the confinement of electron waves to form quantum well (QW) states. Because the QW states are spin polarized, this produces oscillatory interlayer magnetic coupling [8,9] and modulates magnetic properties such as the magnetic anisotropy [10] and magneto-optical Kerr effect (MOKE) [11,12]. Fe_3O_4 is particularly appealing in this regard because its relatively low carrier density ($\sim 10^{21}$ cm^{-3}) compared to metals and large spin polarization should lead to strong modulation of spin dependent properties that could be tuned by electrostatic gates. While evidence for quantum confinement in Fe_3O_4 has been reported for thin films and nanoparticles [13,14], their effect on spin dependent properties has not been established.

In this Letter, we report strong oscillations and sign reversals in the spin polarization and MOKE of Fe_3O_4 films as a function of thickness, which we attribute to the formation of spin-polarized QW states. High quality Fe_3O_4 films on GaAs(001) are fabricated by molecular beam epitaxy (MBE), and the Fermi level spin polarization of Fe_3O_4 is probed using the ultrafast optical measurement of ferromagnetic proximity polarization (FPP) [15,16]. The systematic thickness dependence of FPP and MOKE are measured on wedged Fe_3O_4 films on GaAs(001), and similar oscillatory behaviors are observed even though the two measurements rely on different mechanisms (spin dependent electron reflection for FPP, optical transitions for MOKE). Quantum confinement of the t_{2g} states near the Fermi level provides an explanation for the similar thickness dependences of the FPP and MOKE oscillations. Our results demonstrate the tuning of spin dependent properties of Fe_3O_4/GaAs hybrid structures by quantum confinement, suggesting potential applications in semiconductor spintronic devices.

Samples are grown by MBE with the following structure: Al cap(2 nm)/Fe_3O_4/GaAs(123 nm)/$Al_{0.7}Ga_{0.3}As$(400 nm)/GaAs(001), with n-type doping of the GaAs epilayer (Si: 7×10^{16} cm^{-3}). The GaAs template is grown in a separate III-V chamber and capped with As, transferred in air to a second chamber for Fe_3O_4 growth, and the As is desorbed to produce a (2×4) surface reconstruction. A single crystalline Fe (5 nm) film is deposited at RT, with thickness determined by a quartz deposition monitor. Next, molecular oxygen is leaked into the vacuum chamber ($P_{O2} = 5 \times 10^{-7}$ torr [6,17]) and the sample is heated to 175 °C for the formation of Fe_3O_4. The reflection high-energy electron diffraction (RHEED) pattern evolves from Fe streaks into a typical Fe_3O_4 RHEED pattern [6,7] within three minutes after reaching 175 °C. Figures 1(a) and 1(b) show the corresponding RHEED patterns along the [110] and [010] in-plane directions of GaAs after 30 min of oxidation, indicating epitaxial growth of Fe_3O_4 (10 nm) on GaAs. We assume the Fe is completely oxidized and 1 nm of Fe corresponds to 2.086 nm of Fe_3O_4.

The magnetic properties of the Fe_3O_4 films are characterized by MOKE and vibrating sample magnetometry (VSM). Figure 1(c) shows the hysteresis loop of Fe_3O_4 (10 nm) measured at 80 K along the [110] in-plane direction of GaAs, and other directions show almost identical magnetic behavior. The magnetization measured by VSM at RT is 4.1 ± 0.1 Bohr magnetons (μ_B) per Fe_3O_4 formula unit [Fig. 1(c), inset]. The square hysteresis loop with magnetization value close to the ideal value of $4\mu_B/Fe_3O_4$ [2,3] indicates the high quality of the film, large magnetic domains, and the absence of antiphase boundaries [18].

Figure 1(d) shows the temperature dependence of the remanent magnetization as determined by the MOKE measurement. Upon cooling from RT to 4 K, the magnetization increases slightly as typical of ferrimagnetic behavior, and the coercivity also increases as the temperature is lowered. There is a small decrease in magnetization as the sample is cooled below 120 K, which is a suppressed Verwey transition, consistent with previous studies of ultrathin Fe_3O_4 films [19,20].

We investigate the spin polarization of the Fe_3O_4 film through time-resolved Faraday rotation (TRFR) measurements of the FPP effect. This is described in detail in the supplementary online materials [21] and in Ref. [22]. Briefly, unpolarized conduction electrons are optically excited in the GaAs by a linearly polarized pump pulse tuned near the band gap. Immediately following the excitation (within 50 ps [16]), the electrons gain in-plane spin polarization, S_{FPP}, by reflecting off the FM/GaAs interface (i.e., FPP effect). We are most interested in the value of S_{FPP} because it provides a measure of the spin polarization of the FM's density of states at the Fermi level [23,24]. Because the Faraday rotation of a linearly polarized, normally incident probe beam is proportional to the out-of-plane component of spin while the S_{FPP} is oriented in-plane, S_{FPP} is determined by measuring electron spin dynamics in a tilted magnetic field (B_{app}, oriented 30° out of plane) which generates the measurable out-of-plane component, as illustrated in the Fig. 2 insets. The out-of-plane component of the Larmor spin precession about a cone is given by

$$S_z = (\sqrt{3}/4)S_{FPP}(\hat{m}\cdot\hat{e}_y)(\exp(-\Delta t/T_1) - \cos(2\pi\nu_L\Delta t)\exp(-\Delta t/T_2^*)), \quad (1)$$

where $\nu_L = g\mu_B B_{app}/h$ is the Larmor frequency, g is the g factor of GaAs (-0.44), μ_B is the Bohr magneton, Δt is the pump-probe time delay, $\hat{m}$ is the unit vector along the magnetization, and the T_1 and T_2^* are longitudinal and transverse spin lifetimes, respectively. For convenience, we express S_z and S_{FPP} in units of the Faraday rotation angle. The value of S_{FPP} is extracted by fitting the TRFR data with this equation.

Figures 2(a) and 2(b) show TRFR curves on Fe(4 nm)/GaAs and Fe_3O_4(8 nm)/GaAs prepared by oxidation at 175 °C for 60 min. The delay scan for the Fe(4 nm)/GaAs hybrid structures show positive S_{FPP}, consistent with previous studies [16,22]. On the other hand, the S_{FPP} for Fe_3O_4/GaAs is negative ($S_{FPP} = -73$ μrad) and has a larger magnitude than for the Fe/GaAs sample

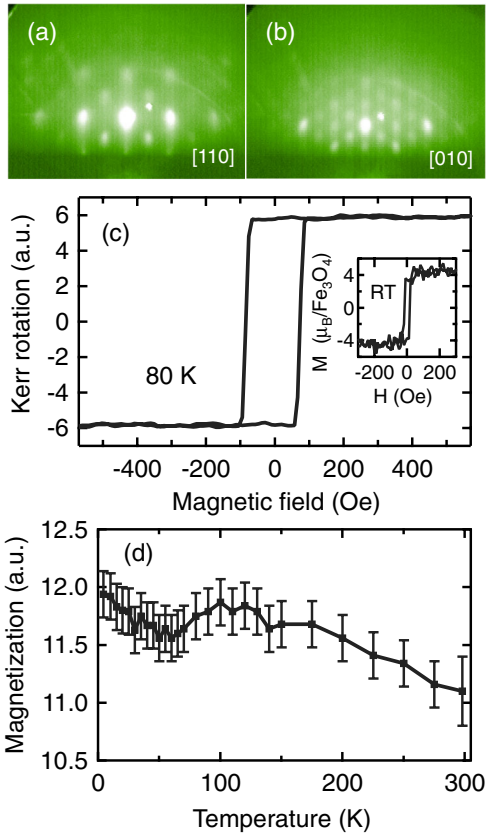

FIG. 1 (color online). (a),(b) RHEED patterns of Fe_3O_4(10 nm)/GaAs(001) along [110] and [010] directions of GaAs. The beam energy is 15.0 keV. (c) Hysteresis loop measured by longitudinal MOKE at 80 K. Inset: hysteresis loop measured by VSM at RT. (d) Remanent magnetization vs temperature measured by MOKE.

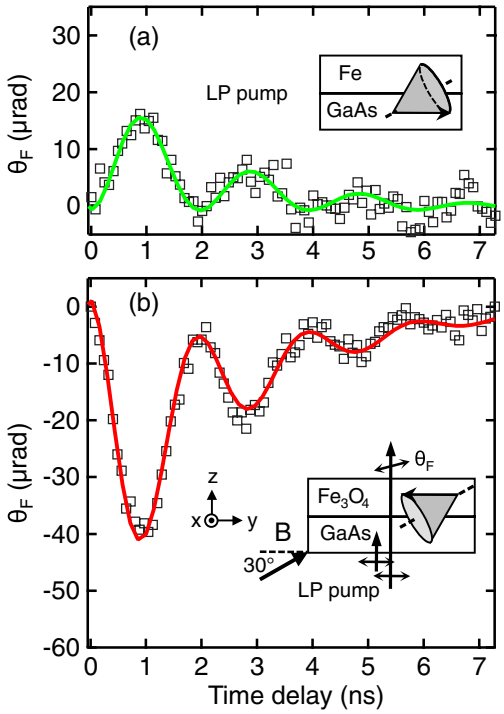

FIG. 2 (color online). (a),(b) Representative TRFR curves on Fe(4 nm)/GaAs and Fe_3O_4(8 nm)/GaAs, respectively. The measurements are performed at 80 K and with a linearly polarized pump pulse to directly measure the FPP. The open squares are data points and the solid lines are fits by Eq. (1). Insets: FPP measurement geometry.

($S_{FPP} = 28$ μrad). The opposite S_{FPP} in Fe_3O_4/GaAs compared to Fe/GaAs is expected because the DOS at the Fermi level in bcc Fe has a positive spin polarization (majority spin) while the Fermi level DOS of Fe_3O_4 is theoretically predicted to have 100% negative spin polarization [2,3]. This result demonstrates the spin dependent reflection in Fe_3O_4/GaAs and the sign and magnitude of S_{FPP} are consistent with theoretical expectations.

We utilize wedged Fe_3O_4 films to investigate the thickness dependence of the FPP. Figure 3 shows S_{FPP} vs film thickness for four different oxidation temperatures (150 °C, 175 °C, 225 °C, and 275 °C). For all samples, the RHEED patterns are characteristic of Fe_3O_4 (see supplementary material, Fig. S3) [21]. Interestingly, the curves for 150 °C and 175 °C exhibit oscillations in S_{FPP} as a function of film thickness. For the 150 °C sample, S_{FPP} oscillates between negative and positive values through nearly two oscillations with a period of ~4.2 nm. For the 175 °C sample, S_{FPP} oscillates mainly between a negative value and zero with a period of ~5.0 nm. The oscillatory behaviors have been observed on two samples prepared at 150 °C and two samples prepared at 175 °C, with consistent results for sign reversal and period (within 20%). For oxidation at 225 °C, S_{FPP} is negative and the oscillations are no longer present. At the higher oxidation temperature of 275 °C, no FPP signal is observed.

The oscillations in S_{FPP} as a function of thickness could be explained by the formation of spin-polarized QW states in the Fe_3O_4 film, which causes the Fermi level spin polarization of the Fe_3O_4 to oscillate between positive and negative values. In principle, there are two distinct wavelengths for spin up and spin down electrons in magnetic

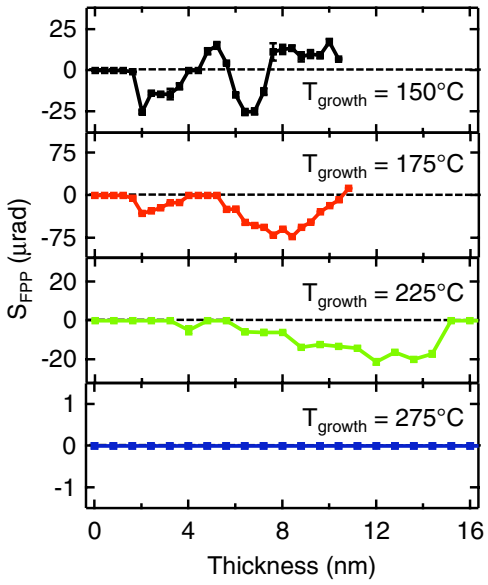

FIG. 3 (color online). S_{FPP} as a function of thickness for wedge samples oxidized at 150 °C, 175 °C, 225 °C, and 275 °C, respectively. Error bars for all the data points are displayed, or smaller than the size of the data points.

films and QW states form according to the quantization condition

$$2k_{\uparrow,\downarrow}d + \phi_{\uparrow,\downarrow} = 2\pi n, \quad (2)$$

where n is an integer, d is the film thickness, and $k_\uparrow(k_\downarrow)$ and $\phi_\uparrow(\phi_\downarrow)$ are the wave vector and the phase accumulated for spin up (down) electrons upon reflection at the boundaries, respectively. This produces oscillations in the Fermi level (ε_F) DOS as a function of thickness with periods of $\pi/k_\uparrow(\varepsilon_F)$ and $\pi/k_\downarrow(\varepsilon_F)$. Theoretically, Fe_3O_4 is predicted to be a half-metal with only spin down electrons, but spin-polarized photoemission experiments find DOS spin polarization below 80% [4,5]. Therefore, we consider both spin polarizations at the Fermi level. For the 150 °C sample, the sign of S_{FPP} oscillates between positive and negative values, indicating that both spin states are present at the Fermi level. The oscillation could be due to quantum confinement of one spin species or both spin species. For the 175 °C sample, S_{FPP} oscillates between zero and negative values, so it is possible that there are only spin down states confined at ε_F. The oscillation period of 4–5 nm is longer than typical periods observed in metallic QWs (less than 1 nm), which could result from smaller Fermi wave vectors associated with the lower electron density of Fe_3O_4 ($\sim 10^{21}$ cm^{-3} [25,26]) compared to metals ($\sim 10^{23}$ cm^{-3}). Furthermore, earlier work on QW states in Fe_3O_4 [13,14], suggests a de Broglie wavelength ($2\pi/k_F$) of ~10 nm (i.e., QW oscillation period of ~5 nm), which is consistent with our data. A quantitative investigation of the oscillatory period would require a direct comparison of the Fermi surface and QW states via angle-resolved photoemission spectroscopy (ARPES) [27]. At higher temperatures, the interface is expected to degrade through interdiffusion or overoxidation and therefore the QW states would be destroyed. Apart from the spin polarization of the Fermi level DOS of the Fe_3O_4 film, there are other factors that could affect the sign of the FPP signal such as the Schottky barrier height and carrier concentration of the GaAs [23,24]. However, these effects are ruled out as the origin of the FPP oscillations as discussed below.

To further explore the origin of the oscillations, we measure the magnetic properties of the Fe_3O_4/GaAs hybrid structure along the wedge by longitudinal MOKE (835 nm at RT and 80 K), which depends only on the properties of Fe_3O_4 layer. Figures 4(a)–4(c) show the MOKE hysteresis loops taken on the 150 °C sample at different film thicknesses at 80 K. Interestingly, the sign of the MOKE also depends on the film thickness. A more detailed scan of the remanent MOKE signal as a function of thickness [Fig. 4(d)] displays oscillations at 80 and 300 K with similar shape as the FPP thickness dependence. This implies that the oscillations in both FPP and MOKE are related to the properties of Fe_3O_4 layer, as opposed to Schottky barrier or parameters of GaAs. While the quantitative calculation of the MOKE coefficient in magnetic

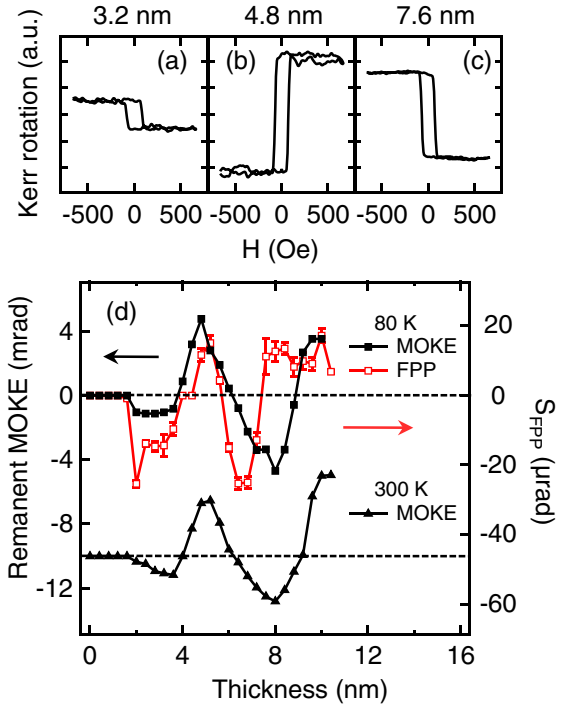

FIG. 4 (color online). (a)–(c) MOKE hysteresis loops on Fe_3O_4 thicknesses at 3.2 nm, 4.8 nm, and 7.6 nm, respectively. (d) Remanent MOKE (Kerr rotation) along the wedge sample oxidized at 150 °C, measured at 80 K (black squares) and 300 K (black triangles, offset by −10 mrad), and S_{FPP} (red or gray square) is plotted for comparison. The errors of the data points are within the size of the data points.

metals is rather complicated [28–30], it is known that the photoexcitation process is determined by Fermi's golden rule, with $h\nu = \varepsilon_f(k) - \varepsilon_i(k)$, where $\varepsilon_i(k)$ and $\varepsilon_f(k)$ are initial and final states of photoexcitation, respectively. Modulating the density of the initial or final states by quantum confinement should induce oscillations in the MOKE. Theoretically, the Kerr rotation in Fe_3O_4 for 1.49 eV photon energy (835 nm) involves the minority t_{2g} states [29,30]. Because the t_{2g} states are also responsible for the spin polarization at the Fermi level [2,3], quantum confinement of the t_{2g} bands can account for the oscillations in both the MOKE and FPP signals. Moreover, this explains why two experiments that rely on different physical processes (optical transitions for MOKE, electron reflection for FPP) exhibit similar oscillatory behavior. The differences in the oscillation periods of MOKE and FPP are likely due to the fact that the MOKE not only depends on the states at the Fermi level but also states away from the Fermi level, which can produce different periods because of the energy dispersion of the wave vector [27].

In conclusion, we have successfully fabricated epitaxial Fe_3O_4 films on GaAs(001) by post oxidation of single crystalline Fe and observe oscillations in both the FPP and MOKE signals as a function of film thickness. The oscillations are strong enough to induce sign reversals of both the spin polarization via FPP and the Kerr rotation. We attribute the oscillatory behavior to the formation of spin-polarized QW states in the Fe_3O_4 film. Future studies utilizing direct probes of the electronic structure (e.g., ARPES [27]) should be performed to further investigate the oscillatory behavior.

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