Superparamagnetic States and Perpendicular Magnetic Anisotropy in Ultrathin MgO/CoFeB/Ta Structures

C.C. Tsai[1], Chih-Wei Cheng[2], Meng-Chiau Tsai[2], and G. Chern[2]

[1]Department of Engineering and Management of Advanced Technology, Chang Jung Christian University, Tainan 71101, Taiwan, ROC

[2]Department of Physics, National Chung Cheng University, Chia Yi 62102, Taiwan, ROC

High perpendicular magnetic anisotropy (PMA) has been observed in MgO/CoFeB/Ta thin films if the thickness of CoFeB is in the range between 1.1 and 1.5 nm. However, both the coercivity and remanence vanish when the thickness of CoFeB is less than 1.1 nm, indicating a characteristic of superparamagnetic state. The magnetization versus external field of these thinner films shows a fit with a Langevin model. In addition, a temperature dependent study identifies a blocking temperature of 160 K by field cool and zero field cool measurements. The particle size of $\sim$ 23 nm in diameter is estimated for a pancake shape cluster and the small particles are probably formed at the CoFeB/MgO interface at the beginning of the growth. Moreover, even the thicker films, which show ferromagnetic response at room temperature, also exhibit the temperature-dependent characteristic of superparamagnetic state due to the pinning at the edge of the small particles.

***Index Terms*—CoFeB, perpendicular magnetic anisotropy, superparamagnetism.**

I. Introduction

SINCE the observation of perpendicular magnetic anisotropy (PMA) reported by Ikeda *et al.* [1] in a stack of MgO-based magnetic tunnel junction with reduced thickness of CoFeB ferromagnetic layers after a post-annealing treatment, much attention have been drawn to the investigation of this system because of its potential applications in realizing the next-generation high density nonvolatile storage media and logic devices. The CoFeB/MgO-based perpendicular magnetic tunnel junctions (p-MTJs), using simply a conventional sputtering deposition technique, are found to exhibit promising traits that are desirable in spin transfer torque (STT-RAM), such as high tunnelling magnetoresistance (TMR) ratios, reduced critical switching currents, as well as a high magnetic stability against thermal agitation. It is further noticed [2], [3] that the magnetic anisotropy in this system can be modified by application of an electric field. This effect of electric fields on the magnetic anisotropy provides a more efficient mechanism of operation power to aid or directly implement voltage-controlled magnetic switching.

Although the origin of the perpendicular magnetic anisotropy in this system is still unclear, it was suggested that interfacial anisotropy from CoFeB/MgO interface plays a major role [1], [4]. Theoretical studies of Fe/MgO and Co/MgO have shown that a large value of PMA can be induced by the hybridization of Fe 3d and O 2p orbitals at the interface [5]. For the study of PMA dependence on ferromagnetic layer thickness, the anisotropy energy density $\mathrm{K_{eff}}$ is commonly expressed as

$$\mathrm{K_{eff}} = \mathrm{K_b} + \frac{\mathrm{K_{interface}}}{\mathrm{t}} - 2\pi \mathrm{M_s^2} \quad (1)$$

where t is thickness of the ferromagnetic layer, $\mathrm{K_b}$ is the bulk magnetocrystalline anisotropy energy density of the ferromagnetic material, $\mathrm{K_{interface}}$ is the interface anisotropy energy density per unit area, and $\mathrm{M_s}$ in the demagnetizing term is the saturation magnetization. According to (1), a linear plot of $\mathrm{K_{eff}} \times \mathrm{t}$ against t is ordinarily obtained and the characteristics of magnetic anisotropy are thus attained from the slope and intercept. Nonetheless, our results show that there is a rollover on the $\mathrm{K_{eff}} \times \mathrm{t}$ versus t plot as the thickness of the CoFeB layer decreases to less than 1.2 nm [6], suggesting that $\mathrm{K_{interface}}$ in (1) cannot be treated as a constant in the system. Similar phenomenon was observed by other groups and the results were consistent with our measurements [7].

The rollover of $\mathrm{K_u}$ at thinner films is generally assumed due to the degrading of the ferromagnetic response but a qualitative understanding is still lacking. Miyakawa *et al.* [8] have investigated the diffusion effects of Ta on the PMA in a stack of Ta/CoFeB/MgO bottom structure of an MTJ at various annealing temperatures. Their results showed that $\mathrm{K_{interface}}$ was significantly reduced as the annealing temperature increased to higher than a certain value (300 °C in their case). It was suggested that the effect of Ta migration to the CoFeB/MgO interface accounts for the reduction of $\mathrm{K_{interface}}$ and thus degradation of PMA at high annealing temperatures. In addition, it has been suggested that superparamagnetic nanoparticles are formed in the thin CoFeB layer adjacent the MTJ interface [9], [10]. In the study of the tunneling resistance as a function of temperature, Feng *et al.* observed an abnormal temperature dependence of the junction resistance [9]. They have suggested that the anomaly may arise either from spin-flip scattering associated with thermal fluctuations of interfacial superparamagnetic nanoparticles [11] or an extra magnetic coupling occurs due to the blocking of the nanoparticles at low temperatures.

In this paper, we present a study of the magnetic response of a series of MgO/CoFeB/Ta films with different ferromagnetic layer thicknesses from 0.9 to 1.9 nm. Our results show that when the thickness of CoFeB increases to 1.6 nm, the magnetic easy axis changes from perpendicular to in-plane. Alterna-

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tively, the hysteresis vanishes when the thickness of CoFeB is reduced to less than 1.1 nm; in addition, the magnetization measurements after the zero-field-cooled and field-cooled processes exhibit superparamagnetic characteristics as the thickness decreases to less than 1.1 nm, indicating presence of nanoparticles, which may form at the interface of the ferromagnetic and nonmagnetic layers. The sizes of the particle will be estimated as well. Moreover, we found that even thicker CoFeB films also showed weak superparamagnetic characteristics indicating that a small amount of nanoparticles may still exist even the ferromagnetic response already dominates. The origin of the formation of the superparamagnetic nanoparticles in these films and the possible diffusion mechanisms will be discussed.

II. Experimental Methods

We have fabricated a series of substrate/Ta(5)/$Co_{40}Fe_{40}B_{20}$(x)/MgO(1)/Ta(1) films with $0.9 < x < 1.9$ (where all the numbers are in the unit of nm and the substrate is oxidized Si) by dc/rf magnetron sputtering. All the samples were vacuum annealed at 300 °C for 1 hour without further application of external magnetic fields. The magnetic properties at room temperatures were measured using a vibrating sample magnetometer (VSM), while the temperature dependence of the magnetization for both zero-field cooled (ZFC) and field-cooled (FC) procedures were measured by using a physical properties measurement system (PPMS).

III. Results and Discussion

Measurement of magnetization at room temperature was implemented under in-plane and out-of-plane magnetic fields for all of the MgO/CoFeB(x)/Ta films after a post-annealing treatment, where the thickness x of the CoFeB layer is between 0.9 and 1.9 nm. Five of the M(H) curves for samples with $x = 1.0$, 1.2, 1.4, 1.5 and 1.6 nm were shown in Fig. 1(a)–(e), respectively, which are in the region where the magnetic easy axis changes between perpendicular and in-plane. Perpendicular magnetic anisotropy is clearly observed in the figures with the M(H) curves under perpendicular magnetic fields showed hysteresis for those samples with the thickness of ferromagnetic layer greater than 1.1 but less than 1.6 nm. The optimal thickness for obtaining perpendicular magnetic anisotropy depends upon the film structure and annealing temperature. The squareness of the loop m_r/m_s (m_r is the remanent magnetization and m_s is the Saturation magnetization) for the 1.4 nm sample, for example, is found to be 0.9. The M-H hysteresis loop of sample with $x = 1.5$ nm still exhibits a reasonable perpendicular magnetic anisotropy with $M_s = 1200$ emu/cm^3, and coercivity $H_c = 25$ Oe, whereas the magnetic anisotropy has changed from perpendicular to in-plane at $x = 1.6$ nm. When the thickness is reduced to less than 1.1 nm, the isothermal M(H) curves show, however, no apparent hysteresis; i.e., both coercivity (H_c) and remanent magnetization (m_r) are close to zero, which implies occurrence of a superparamagnetic state. Plots of $K_{eff} \times t$ against the CoFeB thickness t are shown in the inset of Fig. 1 for both of the bottom Ta/CoFeB/MgO and top MgO/CoFeB/Ta structures for comparison. The effective anisotropy constant K_{eff}, which indicates the difference between the perpendicular and in-plane magnetic configuration,

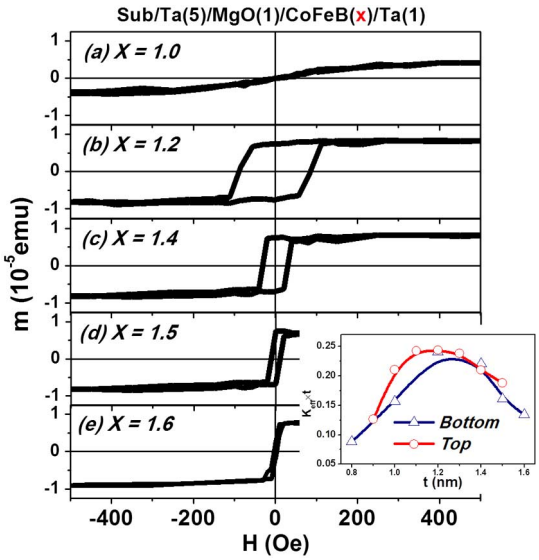

Fig. 1. (a) to (e) M-H curves under out-of-plane magnetic fields for the top stack Ta(5 nm)/ MgO(1 nm)/$Co_{40}Fe_{40}B_{20}$(x nm)/Ta(1 nm) structures with $x = 1.0$, 1.2, 1.4, 1.5 and 1.6 nm, respectively. All the samples were measured after a post-annealing treatment at 300 °C for 1 hour. Inset in the figure shows $K_{eff} \times t$ plotted against t for both bottom Ta/CoFeB/MgO and top MgO/CoFeB/Ta structures, where a rollover occurred at the thickness of $\sim$ 1.2 nm for the top structure.

was estimated from the saturation field along the hard axis of these films. A linear correlation between $K_{eff} \times t$ and t should be expected according to (1). Nevertheless, a rollover of the curve occurs at the thickness of CoFeB layer around the nominal thickness of 1.2 nm, indicating that the contribution of the interface magnetic anisotropy cannot be treated as a constant in our case; i.e., the interface magnetic anisotropy, which plays a major role with the PMA in this system, is dependent on the thickness of the ferromagnetic layer.

The superparamagnetic characteristics observed in the thinner samples are due to the existence of nanoparticles, which may form at the interface of the ferromagnetic and nonmagnetic layers. This usually happens as the ferromagnetic layer thickness is too thin to hold a continuous film. The development of superparamagnetic nanoparticles in our films may also be attributed to the effects of Ta diffusion as mentioned. Here, we focus our investigation on the MgO(1.0 nm)/CoFeB(1.0 nm)/Ta(1.0 nm) sample, which shows apparent superparamagnetic features by various experimental observations. The isothermal M(H) curve of the film at room temperature, Fig. 1(a), already shows nonhysteresis characteristics. The M(H) curves of the MgO(1.0 nm)/CoFeB(1.0 nm)/Ta(1.0 nm) measured at temperatures between 10 K and 300 K are shown in Fig. 2. The isothermal M(H) curves at high temperatures ($T \geq 160$ K) show no obvious hysteresis. However, the isothermal M(H) curves at low temperatures ($T < 160$ K) reveal a noticeable hysteresis with a rather high coercive field of 2000 Oe at $T = 10$ K. It is known that the magnetic anisotropy energy barrier is lowered as the volume of the ferromagnetic particles decreases. When the magnetic anisotropy energy of the particle is reduced to a value smaller than the thermal fluctuation energy at the temperatures above the blocking temperature T_B, the

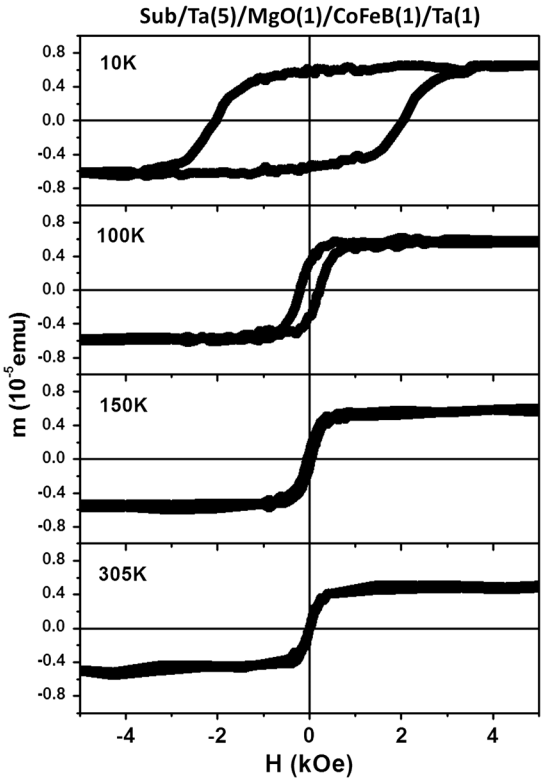

Fig. 2. Isothermal magnetization of MgO(1 nm)/CoFeB(1.0 nm)/Ta(1 nm) structure at various temperatures from room temperature to 10 K. There is no hysteresis loop at room temperature, whereas clear hysteresis loops are observed at low temperatures.

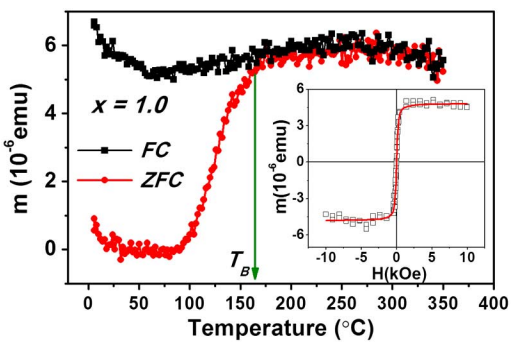

Fig. 3. Temperature dependence of the magnetization (M-T) for the Ta(5 nm)/MgO(1 nm)/CoFeB(1.0 nm)/Ta(1 nm) sample at a field of 50 Oe, measured with ZFC and FC modes. Hump of the ZFC occurs at the divergence of the two curves near the blocking temperature of 160 K. Inset: fitting of the M(H) curve of the MgO(1 nm)/CoFeB(1.0 nm)/Ta(1.0 nm) film at room temperature to (3).

relaxation time of the magnetic spins becomes shorter than the characteristic time of the measurement, which then provokes a paramagnetic-like behavior. On the other hand, when the magnetic anisotropy energy exceeds the thermal fluctuation energy as the temperature is reduced to lower than T_B, the long spin relaxation time compared with the measurement time then results in a development of hysteresis, which reflects the superparamagnetic behavior of M(H) observed in Fig. 2.

To further investigate the superparamagnetic nature of the sample, measurements of magnetization as a function of temperature were carried out after zero-field cooled (ZFC) and field cooled (FC) courses at a small magnetic field of 50 Oe. The results of the $t_{CoFeB} = 1.0$ nm sample are shown in Fig. 3. It can be seen that the M_{FC} and M_{ZFC} curves diverge at temperatures ~ 160 K (indicated by the arrow in the figure), but overlap above this temperature. It is known that the irreversible temperature T_{irr}, where M_{ZFC} curve deviates from M_{FC} curve, can be identified as the blocking temperature T_B for a system with a narrow nanoparticle sizes distribution. It should be noticed that the blocking temperature obtained from the ZFC-FC magnetization measurements depends also on the magnetic field applied during the field cooled process and the blocking temperature identified thereof increases as the external field increases. These behaviors are not expected for ferromagnetism and therefore suggest the presence of superparamagnetism in this film.

The size of superparamagnetic nanoparticles can be estimated from the expression [14], [15]

$$K_{eff}V = 25\,k_B T_B \tag{2}$$

assuming the characteristic measuring time of 100 s ($K_{eff}V$ reduced to $\sim 5\ k_B T$ for those measurements with characteristic measuring time of 10^{-8} s). K_{eff} is the anisotropy energy density, k_B is the Boltzmann constant, V is the volume of particle and T_B is the blocking temperature. Using the value of anisotropy energy $K_{eff} = 1.4 \times 10^6$ erg/cm^3 and $T_B = 160$ K from our measurements, the volume of the superparamagnetic nanoparticles is estimated approximately at 410 nm^3, which corresponds to a diameter of 23 nm for a nanoparticle with the shape of a pancake for the sample with the thickness of the CoFeB layer at 1.0 nm.

For an ideal ensemble of single domain particles, each with a magnetic moment μ, the magnetization under a magnetic field H at temperature T in the superparamagnetic regime can be expressed as [16]

$$M = N\mu\left[\coth\left(\frac{\mu H}{k_B T}\right) - \frac{k_B T}{\mu H}\right] = N\mu L\left(\frac{\mu H}{k_B T}\right) \tag{3}$$

where L is the Langevin function; N is the number of particles. The inset of Fig. 3 illustrates a fitting of the M(H) curve of our MgO(1 nm)/CoFeB(1.0 nm)/Ta(1.0 nm) sample to (3) at $T = 305$ K using M_s value of 1200 emu/cm^3. Magnetization μ of an individual nanoparticle thus obtained is 5×10^{-16} emu, corresponding to 10^5 Bohr magneton. The number of particles in our sample with areal dimensions of 1.0 cm $\times$ 1.0 cm and magnetic layer thickness of 1.0 nm can be estimated from $N\mu \approx M_s V_{sample}$, and the number N of value 2.4×10^{11} is obtained. For nanoparticles with a shape of pancake distributed on the 1.0 cm $\times$ 1.0 cm area of our sample, the particle size is estimated as approximately 430 nm^3, assuming particles are homogeneously distributed. The deduced interparticle distance when compared with the dimensions of the particle acquired previously implies minimal interparticle interactions in the sample. This provides an independent way to compare the particle size and is consistent with the value estimated from (2).

The temperature dependent study of the magnetic response has been extended to the thicker MgO/CoFeB/Ta films. The Hc(T), coercivity as a function of temperature shows a general form as $Hc(T) = H_{c0}[1\text{-}(T/T_B)^{1/2}]$ where the H_{c0} is the intrinsic coercivity at $T = 0$ and T_B is a characteristic temperature similar to the Blocking temperature [17]. The distribution

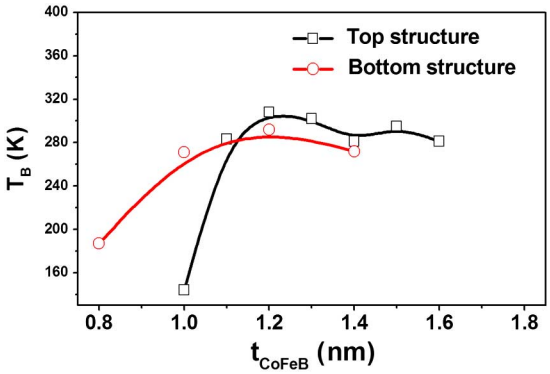

Fig. 4. Magnitude of T_B is plotted against the thickness of the magnetic layer in both of the top (square data points) and bottom structures (circular data points).

of T_B, which is associated with the cluster size as discussed earlier, is given in Fig. 4. The T_B exhibits a constant value $\sim$ 290 K in the ferromagnetic region while the T_B drops substantially to $\sim$ 160 K in the superparamagnetic region. As mentioned earlier, clusters form at the early stage of the growth due to the island growth and amorphous nature of the present films. The films become smoother when the thickness increase or/and the post-deposition annealing starts. However, the Ta diffusion also occurs during the annealing. It is possible that the Ta diffusion follows the route along the edge of the cluster and forms strong pinning site and embeds in the continuous films. This argument proposes a mechanism for the Ta diffusion and cluster formation of the films, which are both crucial for the high quality of the MgO/CoFeB/Ta ultrathin films.

In summary, a series of Ta(5 nm)/CoFeB(x nm)/MgO(1 nm)/Ta(1 nm) films with $0.9 < x < 1.9$ were fabricated. Perpendicular magnetic anisotropy is observed in the range of CoFeB thickness between 1.1 and 1.5 nm but a rollover of the K_{eff} is pointed out. Detailed magnetic characterizations of superparamagnetic state of thinner films are then carried out and pancake shape clusters with diameter of 23 nm are suggested. We further extend the measurements to the thicker films in ferromagnetic region and argue that Ta diffusion may introduce pinning sites along the edge of the clusters which exhibits a characteristic T_B distribution of the MgO/CoFeB/Ta films.

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