1. Introduction

Amorphous TbFeCo films are a high density magneto-optical recording medium due to their large perpendicular magnetic anisotropy. Their magneto-optical property and structure changes induced by oxidation, nitrogenation, thermal treatment, etc. have been studied extensively [1–10]. To protect TbFeCo recording film against corrosion, protection layers, such as Si₃N₄ or SiO₂ layers [4–6], were usually coated on the TbFeCo film. However, side effects occurred as well [6]. It was already reported that the composition diffusion would take place near the interface between TbFeCo and the protection layers so that Tb in TbFeCo film would composition diffusion take place near the interface between TbFeCo film. It was also found that the oxidation would be kept in air at room temperature because previous reports were noticeable changes in torque curve and perpendicular anisotropy. TbFeCo film prepared by magnetron sputtering and did not find noticeable changes in torque curve and perpendicular anisotropy. It seems that bare TbFeCo film can be kept in dry air for over 7 months. However, we still do not know how long the uncoated TbFeCo film can continue to be kept in dry air against corrosion. Meanwhile, it is also unknown how long the uncoated TbFeCo film can be kept in dry air against corrosion. Moreover, it is important because magnetic dynamics is related to recording rate, and hence affects the available recording speed of an aging TbFeCo magneto-optical storage device.

In this article, a bare TbFeCo film exposed to dry air for two years is studied using magneto-optical Kerr spectroscopy and vibrating sample magnetometry (VSM). The out-of-plane hysteresis loop by VSM is found to become slanted and meanwhile, an in-plane loop is also observable. The Kerr loop measured from the exposed surface is also slanted compared to that measured from the substrate-contacted surface, which indicates that the exposed surface is oxidized. So a bilayer structure of the film is proposed. When a pump laser is switched on, the Kerr loops measured from both surfaces at the delay time of ~5 ps become anomalous, showing the occurrence of magnetization reversal across magnetization compensation temperature. Unlike that measured from the substrate-contacted surface, femtosecond laser-induced magnetization dynamics measured from the exposed surface does not show magnetization reversal crossing zero magnetization. This can be explained by the bilayer structure as the compensation effect of demagnetization recovery of the oxidized layer on magnetization reversal of perpendicularly anisotropic TbFeCo layer across magnetization compensation temperature. Above experimental results show that the uncoated TbFeCo film cannot resist oxidation in dry air at room temperature for 2 years while the SiO₂-coated surface can do so for over 2 years.

As a result, it is reasonable to assume that bare TbFeCo film may be oxidized slowly at room temperature. Hong et al. [1] did perform a 7-month oxidation experiment in dry air at room temperature on the bare TbFeCo film prepared by magnetron sputtering and did not find noticeable changes in torque curve and perpendicular anisotropy. It seems that bare TbFeCo film can be kept in dry air for over 7 months. However, we still do not know how long a bare TbFeCo film can continue to be kept in dry air against corrosion. Meanwhile, it is also unknown how long the uncoated TbFeCo film can be kept in dry air against corrosion. Moreover, it is important because magnetic dynamics is related to recording rate, and hence affects the available recording speed of an aging TbFeCo magneto-optical storage device.

In this article, a bare TbFeCo film exposed to dry air for two years is studied using magneto-optical Kerr rotation and VSM. It is found that the hysteresis loops of the exposed surface changed, while those of the protected side on the glass substrate remain unchanged. The femtosecond laser-induced ultrafast dynamics of magnetization is also found to be different on either side of the sample, revealing the effect of oxidation on magnetization speed up with the temperature above 100°C [9].

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structure and property changes and femtosecond laser-induced magnetization dynamics of two-year-old high coercive TbFeCo films

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An uncoated TbFeCo film on glass substrate exposed to dry air for 2 years is studied using magneto-optical Kerr spectroscopy and vibrating sample magnetometry (VSM). The out-of-plane hysteresis loop by VSM is found to become slanted and meanwhile, an in-plane loop is also observable. The Kerr loop measured from the exposed surface is also slanted compared to that measured from the substrate-contacted surface, which indicates that the exposed surface is oxidized. So a bilayer structure of the film is proposed. When a pump laser is switched on, the Kerr loops measured from both surfaces at the delay time of ~5 ps become anomalous, showing the occurrence of magnetization reversal across magnetization compensation temperature. Unlike that measured from the substrate-contacted surface, femtosecond laser-induced magnetization dynamics measured from the exposed surface does not show magnetization reversal crossing zero magnetization. This can be explained by the bilayer structure as the compensation effect of demagnetization recovery of the oxidized layer on magnetization reversal of perpendicularly anisotropic TbFeCo layer across magnetization compensation temperature. Above experimental results show that the uncoated TbFeCo film cannot resist oxidation in dry air at room temperature for 2 years while the SiO₂-coated surface can do so for over 2 years.

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1. Introduction

Amorphous TbFeCo films are a high density magneto-optical recording medium due to their large perpendicular magnetic anisotropy. Their magneto-optical property and structure changes induced by oxidation, nitrogenation, thermal treatment, etc. have been studied extensively [1–10]. To protect TbFeCo recording film against corrosion, protection layers, such as Si₃N₄ or SiO₂ layers [4–6], were usually coated on the TbFeCo film. However, side effects occurred as well [6]. It was already reported that the composition diffusion would take place near the interface between TbFeCo and the protection layers so that Tb in TbFeCo film would react with the oxygen or nitrogen from the protection layers [6,7] or even with the oxygen from glass substrates [8,9]. Consequently, the oxidation of uncoated TbFeCo film in dry air was focused on. A 92 h oxidation experiment of uncoated TbFeCo film at 70°C was reported [10]. It was found that the oxygen would soak into TbFeCo near the surface, leading to the change of magneto-optical properties of TbFeCo film. It was also found that the oxidation would...```
dynamics. All results indicate the change of the structure and magnetic properties of the sample due to the exposure to air as well as the formation of a bilayer-like structure.

2. Experimental

The uncoated high coercive TbFeCo amorphous alloy films were prepared by magnetron sputtering on a glass substrate 2 years ago. The as-deposited film had a magnetization compensation temperature of 380 K, a Curie temperature of 505 K and a thickness of 100 nm. It has been exposed in dry air at room temperature for 2 years so far.

Magnetic measurements are carried out using VSM. Polar magneto-optical Kerr hysteresis loops and the magnetization dynamics are measured by our magneto-optical Kerr experimental setup which has the time-resolution ability and has been described in detail elsewhere [11]. The linearly polarized laser pulses from Ti:sapphire amplifier with a repetition rate of 1 kHz, the duration of 100 fs at the central wavelength of 800 nm and a maximum energy of 0.5 mJ per pulse, are split into pump and probe pulses. The ratio of pump to probe in power is larger than 40. The pump pulses are normally incident and focused to a spot of 150 μm diameter on the sample surface. The probe pulses are incident at a small angle and focused in the central area of the pump spot. The probe spot is nearly half smaller than the pump spot so that the probed area is almost homogeneous in the change of fs-laser induced magnetization. A neutral density attenuator is used to control incident power so that the suitable pump fluence can be set. The polar Kerr rotation of the probe pulses reflected from the sample surface is measured by a balanced optical bridge and read out by a lock-in amplifier referenced at the frequency of an optical chopper that modulates probe beam at the frequency of 324 Hz. External magnetic fields are generated by an electromagnet and have a maximum field of ~9000 Oe [11].

3. Results and discussion

3.1. Magnetic characterization by VSM and discussion

The as-deposited sample was measured by VSM 2 years ago. Its out-of-plane hysteresis loop is plotted in Fig. 1 by the curve with filled squares. It is squared, revealing a strong perpendicularly magneto-crystalline anisotropy. However, it becomes slanted after the sample was exposed to dry air for 2 years (referred to as “aged sample” below), as shown in Fig. 1 by the line with solid triangles. Furthermore, an in-plane hysteresis loop is also observed, as shown by the line with filled circles in Fig. 1, but it is not observable in the as-deposited sample. The emergence of in-plane and slanted out-of-plane loops reveals two possible changes of the as-deposited sample. One is phase segregation, that is, a new in-plane magnetization layer is formed, which is supported by the in-plane loop. The other is the whole change of the sample. Its perpendicular magneto-crystalline anisotropy reduced considerably due to nitrogenation so that the magnetization of the aged sample is extremely slanted toward in-plane magnetization state because nitrogen content in air is the highest, while only ~5% nitrogen content in TbFeCo film can lead to the magneto-crystalline anisotropy changed from out-of-plane to in-plane easy axis [12]. The evidence is from both the in-plane loop and the slanted out-of-plane loop with large coercivity that might be explained by the angular dependence of coercivity [13] because it was well known that the magnetization reversal of rare earth-transition metal (RE-TM) ferrimagnetic films is dominated by the mechanism of domain wall motion [14,15] which results in coercivity increase with the angle between the magnetization and magnetic field applied.

To further identify the two possible changes, a series of minor out-of-plane hysteresis loops are measured by VSM for different reversal fields, as plotted in Fig. 2 by the lines with filled squares. A remanent curve obtained from the minor loops is also plotted in Fig. 2 by the line with open circles. It shows that the magnetization reversal of the aged sample includes reversible and irreversible contributions. In the reverse ranges of A→B and C→D, the flat remanent curve reveals that the magnetization reversal is purely reversible, while the sloped remanent curve in the range of B→C and the fact that the remanent coercivity (HcR) is larger than the coercivity (Hc) of major loop show that the reversal of B→C includes the reversible and irreversible contributions [16]. In other words, reversible magnetization reversal exists in the whole reversal range from A to D. It implies that a soft magnetic layer occurs in the aged sample and it has weak in-plane magnetic anisotropy. The in-plane hysteresis loop in Fig. 1 should just reflect the magnetization behavior of the soft magnetic layer, while the slanted out-of-plane loop should demonstrate the combined magnetic behavior of perpendicular anisotropy layer.
and the in-plane anisotropic soft magnetic layer. The slope of the out-of-plane loop originates just from the reversible magnetization contribution of the soft magnetic layer, as what the remanent curve shows in Fig. 2. Therefore, we conclude that phase segregation or structure change occurred in the TbFeCo film due to the exposure to dry air for two years. The new phase may originate from the oxidation or nitrogenation of TbFeCo film because it was reported previously that the reaction of Tb in TbFeCo film with oxygen or nitrogen could lead to the formation of Fe-rich soft magnetic layer due to the loss of Tb content [25,10]. However, we still cannot locate the soft magnetic layer because both surfaces of the as-deposited sample might react with the oxygen from glass substrate [9] and air.

3.2. Magnetic characterization by magneto-optical Kerr and discussion

To locate the in-plane magnetized soft magnetic layer and even measure its magnetic parameters, polar magneto-optical Kerr hysterisis loops with no pump are first measured, from the air-contacted side (referred to as “the top side” below) and the glass substrate-contacted side (referred to as “the bottom side” below) of the aged sample. They are plotted in Fig. 3(a) and (b) by solid lines, being distinct from each other. The loop measured from the top side in (a) is apparently slanted, revealing the change of the top side. It can be explained well by a bilayer structure film which is a perpendicular magnetization TbFeCo film covered by a thin in-plane magnetization soft magnetic layer. And the magnetic characteristic of the soft magnetic layer can be described by the loop with filled circles in Fig. 1. It well matches the previous report that the soft magnetic layer should be a thin layer of TbOx rather than TbNx, within which Fe and Co were dispersed [10] because oxygen is chemically more active than nitrogen and TbOx is transparent, while the slanted out-of-plane Kerr loop in Fig. 3(a) implies simultaneous measurement of the soft magnetic layer and TbFeCo layer underneath, and thus transparency of the soft magnetic layer is necessary. In contrast, the loop in (b) measured from the bottom side through the glass substrate is squared, being very similar to the loop of the as-deposited sample in Fig. 1. As a result, it can be concluded that the bottom side of the sample has not been changed during the past 2 years, while the top side of the sample has been oxidized. It implies that the SiO2 coating layer (the bottom layer on the glass substrate) can protect the TbFeCo film against oxidation for over 2 years at room temperature. Furthermore, the slope direction of the loop in Fig. 3(a) also provides us with the information on magnetization compensation temperature (Tc) of the bilayer structure film because the Kerr signal at 800 nm wavelength mainly reflects the moments of the transition metal sublattices in RE-TM alloy film [17]. The Kerr signal at saturation field is weaker than that at zero field, revealing that the TM moments in TbFeCo and soft magnetic layers are oriented anti-parallelly at saturation field. Consequently, TbFeCo and soft magnetic layers should have a higher and lower Tc than room temperature, respectively.

To further test the bilayer-structured film and its parameters, such as Tc, polar magneto-optical Kerr hysteresis loops with a pump fluence of 18.0 mJ/cm2 are measured at −5 ps delay time which means the probe pulses are probing the magnetic state long after the pump excitation (~1 ms). The pump-on Kerr loops at −5 ps are measured from both the top and bottom sides, and are also plotted in Fig. 3(a) and (b) by the solid lines with solid circles. The loop looks quite distinct from that without pump. Similar loops were already observed in GdFeCo amorphous film with Tc above room temperature, and were called as the anomalous hysteresis loops [14,15,17]. However, such anomalous loops are reported here for the first time for amorphous TbFeCo films. The physical origin of the anomalous loop was studied in depth in Refs. [14,17]. It was believed to come from multiple-pulse-induced magnetization reversal accumulation and external-field-history-memory effects [14] when the pump-induced transient temperature of the sample is over the Tc as well as the reversed magnetization frozen (irreversibility) on the loop part where applied field is lower than Hk as sample temperature returned to room temperature [14,17]. The anomalous loop in Fig. 3(b) provides direct evidence to the fact that perpendicular magnetization TbFeCo layer of the aged sample has a Tc over room temperature, while the similar slanted anomalous loop in Fig. 3(a) again shows that the soft magnetic layer is in-plane in magnetization and has a Tc below room temperature because the slope of the anomalous loop can still be explained by the reversible magnetization reversal of the soft magnetic layer with a Tc below room temperature under an external field applied perpendicularly, as shown in Fig. 2.

The Kerr hysteresis loop with no pump is once again taken from the top side after the above anomalous hysteresis loop at −5 ps is measured under a pump fluence excitation of 18 mJ/cm2, and it looks nearly identical to the solid line loop in Fig. 3(a), suggesting that the laser pump does not expedite the oxidation of the aged TbFeCo film.

3.3. Magnetization dynamics measurements by time-resolved Kerr spectroscopy and discussion

Magnetization dynamics of oxidized TbFeCo is important because it is related to recording rate of an aging TbFeCo storage device. However, except the study of an ultrafast magnetization dynamics on the as-deposited TbFeCo film [18], nothing more has been reported. Here we study it on the aged sample by means of all-optical time-resolved magneto-optical Kerr spectroscopy.

We first measure the femtosecond laser-induced magnetization dynamics of positive and negative saturation magnetization states from the top side of the aged sample under a pump fluence of 18.0 mJ/cm2. The transient Kerr signals are plotted in Fig. 4(a). It is somewhat surprising that the transient Kerr signal of either positive (+Mk) or negative (−Mk) saturation magnetization states
shown in Fig. 3(a) never crosses over the zero magnetization line \( M = 0 \) in Fig. 3(a)](a) even if the pump fluence increases up to damaging the sample. It is obviously different from the magnetization dynamics reported previously in as-deposited TbFeCo [18] and GdFeCo [15,17] films, where picosecond and subpicosecond ultrafast magnetization reversal dynamics were observed. However, the emergence of anomalous loop in Fig. 3(a) in turn shows that magnetization reversal across \( T_M \) induced by pump heating to the sample indeed occurred. Because it has been reported that there were no exchange coupling effects between the oxidized layer and the TbFeCo film [1], there are two possible causes which can lead to no magnetization reversal observed in Fig. 4(a). One is that the single laser pulse actually is unable to make magnetization reversed even with strong saturation external field applied due to the considerable thickness and limited direct laser-heating depth \( ( < 30 \text{ nm}) \) of the sample, whereas the anomalous loop in Fig. 3(a) was caused by the accumulation and memory effects, respectively, from continuous pump pulse excitation and external field history [14]. The other is that the magnetization reversal of TbFeCo across \( T_M \) took place, but was compensated by the demagnetization recovery of the soft magnetic layer because the total transient Kerr signal is contributed by the summation of Kerr signals from transparent soft magnetic and TbFeCo layers, while both contributions have opposite change trends. The anomalous loop can be observed because it was measured at \( -5 \text{ ps} \). At that time, the demagnetization of the soft magnetic layer has recovered almost to the initial state. Therefore, the compensation effect on the magnetization reversal (irreversible and frozen) of TbFeCo layer across \( T_M \) was not observable.

To confirm two possible causes, we measure the magnetization dynamics of \( -M_s \) state of the bottom side with the same pump fluence as that applied in the measurement of the top side. The transient Kerr signal is plotted in Fig. 4(b) by open circle curve. The magnetization reversal across \( T_M \) is very obvious. The pump fluence leads to \( -80\% \) demagnetization and the temperature of the sample across \( T_M \) during several picoseconds. Then, magnetization reversal takes place and crosses over zero magnetization going towards opposite magnetization state at \( \sim 80\% \), and thereafter maintains the reversal trend in the scanning time scale of 600 ps in spite of some oscillations. Therefore, this result clearly shows that magnetization reversal across \( T_M \) does take place. The phenomenon that magnetization reversal is not observable in the measurement of the top side is believed to arise from the compensation effect of demagnetization recovery of the soft magnetic layer. A quantitative calculation is provided in Fig. 4(b) to further elucidate the compensation effect. The demagnetization recovery dynamics of remanent state is measured and plotted in Fig. 4(b) by the filled circle curve. The average of the transient Kerr signals of magnetization reversal at \( -M_s \) state and demagnetization recovery at remanent state is calculated and also plotted in Fig. 4(b) by the solid line. It is obvious that the average Kerr signal does not show magnetization reversal phenomenon but a slow recovery process. It is well known that the rate of demagnetization recovery is directly proportional to the external field applied for the reversal mechanism of domain wall motion [13]. Therefore, demagnetization recovery dynamics at saturation magnetization state should decay faster than at remanence, so that the compensation effect of demagnetization recovery on magnetization reversal is stronger in saturation state than in remanence. This is why an obvious demagnetization recovery dynamics rather than a magnetization reversal process is observed in Fig. 4(a). However, the magnetization reversal of TbFeCo layer underneath the soft magnetic layer actually takes place. Meanwhile, these dynamic behaviors once again confirm the existence of the soft magnetic layer on the top side of the aged sample. Magneto-optical writing through the soft magnetic layer should be feasible. The formation of the oxidation-induced soft magnetic layer does not affect the magneto-optical recording property of the TbFeCo film underneath. The soft magnetic layer may act as a protection layer against further corrosion of TbFeCo film underneath.

It is noticeable that the rate of magnetization reversal of TbFeCo across \( T_M \) seems much lower than that of GdFeCo though TbFeCo and GdFeCo are very similar in structure and properties. A previous report is in accordance with our result here [18]. Such a phenomenon is to be further studied. Here we speculate that the relatively slow magnetization reversal of TbFeCo film across \( T_M \) may relate to the orientations of local Tb moments randomly canted to some extent from the direction anti-parallel to TM moments [19], while in the GdFeCo film the orientation of Gd moments is strictly anti-parallel to the direction of TM moments.

4. Conclusions

We have studied in depth the structure and magnetic property changes of an uncoated TbFeCo film exposed to dry air for two years by VSM and magneto-optical polar Kerr as well as femtosecond laser-induced magnetization dynamics by all optical time-resolved Kerr spectroscopy. It is found that the out-of-plane hysteresis loop by VSM is slanted, and meanwhile an in-plane hysteresis loop appears. A series of minor loops are measured and the remanent curve is obtained, which reveals that the slope of out-of-plane loop originates from a reversible magnetization reversal. Therefore, it is concluded that the soft magnetic layer occurs in the aged sample which is further characterized from both the top and bottom sides by magneto-optical polar Kerr rotation. Pump-off Kerr hysteresis loops measured from the top side are slanted, but not slanted from the bottom side. When the pump is switched on, the Kerr loops at \( -5 \text{ ps} \) become anomalous on either side. Conclusions can be drawn from those Kerr hysteresis loops that the soft magnetic layer occurs on the top side of the aged sample and has a magnetization compensation temperature below
room temperature. Therefore, a bilayer structure model is proposed. The soft magnetic layer on the top side of TbFeCo is inferred to be TM rich due to the loss of Tb with reaction of the oxygen in air. Femtosecond laser-induced magnetization dynamics is studied from both the top and bottom sides. Unlike that measured from the bottom side, the dynamics measured from the top side does not show magnetization reversal behavior, revealing the compensation effect of the demagnetization recovery of soft magnetic layer on magnetization reversal dynamics of TbFeCo across TM. This compensation effect also confirms the bilayer structure of the aged sample. It is found that the rate of magnetization reversal of TbFeCo film is much lower than that of GdFeCo film. Our experiment results show that the SiO₂ coating layer on TbFeCo film may protect it from oxidation over 2 years at room temperature, but it is shorter than 2 years for TbFeCo exposed to dry air. However, oxidation-induced soft magnetic layer does not affect magneto-optical recording of TbFeCo film underneath, and hence it may act as a natural protection layer against further corrosion of the TbFeCo film underneath it.

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