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# Structures, magnetic properties and thermal stability of CoFeB/MgO films

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## Abstract

The CoFeB/MgO films with various boron (B) contents were prepared by sputtering deposition and post annealed with different temperature. It was found that the films become amorphous and coercivity (HC) decreases with the increase of B content for the as-deposited CoFeB/MgO films. After vacuum annealing, the HC decreases because of the film stress release. The HC decreases more obviously in the CoFeB/MgO films with low B contents than that in the films with high B contents. The reason is that the sample with 12.1% B is amorphous before annealing and it becomes crystalline after annealing at 400 C and the sample with 6.7% B is always amorphous before and after annealing, the competition of the effect of film stress and the crystal anisotropy on the HC makes the slightly variation of HC. Partial crystallization can be achieved in the samples by vacuum annealing. With the increase of the B content, higher annealing temperature is needed to crystallize the sample. The average grain size decreases with the increase of B content in the CoFeB/MgO films. B atoms diffuse to the interface of CoFeB/MgO films and form boron oxide there after annealing, which makes the saturation magnetization (Ms) of the films decrease.

## 1. INTRODUCTION

Magnetic tunneling junctions (MTJs) have recently aroused much interest because of their applications in random access memories and as magnetic sensors in disc drives [1–3]. It has been experimentally confirmed that MgO-based MTJs with CoFeB as the electrode material can exhibit very large TMR values. Djayaprawira et al prepared the CoFeB/MgO/CoFe MTJs by magnetron sputtering and obtained the tunneling magnetoresistance (TMR) ratio up to 230% at room temperature [4]. After that, Lee et al prepared the MTJs by magnetron sputtering and achieved 500% TMR ratio at room temperature [5]. Normally, the MTJs are prepared by sputtering deposition and post treated by annealing. Bea et al found the formation of B oxide and the decrease of Fe oxide in the

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CoFeB/MgO/CoFeB samples after annealing, which lead to the enhancement of the FeCoB electrode polarization and the higher TMR ratio [6]. Schmalhorst et al investigated the variation of TMR with annealing temperature in CoFeB/MgO/CoFeB MTJs, the TMR increases from 20% to a maximum value of 112% with annealing temperature rise. The recrystallization of the Co-Fe-B electrode was observed after annealing. Some of boron diffuses toward or into the MgO barrier and forms a $B_2O_3$ oxide, which lead to the increase of TMR [7]. Burton et al calculated the first-principles total energy of the atomic and electronic structure of crystalline CoFeB/MgO/CoFeB MTJs, the results present that it is energetically favorable for boron to reside at the crystalline CoFeB/MgO interface rather than remain in the bulk of the crystalline CoFeB electrode, the presence of boron at the interfaces is detrimental to TMR [8].

Theoretical and experimental studies have indicated that boron plays an important role in spin-dependent transport in MgO-based MTJs with CoFeB electrode, the device performance is closely relate to the CoFeB electrode and the CoFeB/MgO interface properties after annealing. However, the effect of boron content on structure, magnetic properties, and thermal stability of CoFeB/MgO films has not been addressed in the literature so far. In this work, a series of CoFeB/MgO films with various B contents were prepared. These samples were annealed at 200°C, 300°C, and 400°C. The structures, magnetic properties and thermal stability of CoFeB/MgO films will be discussed in this paper.

## 2. EXPERIMENT

A series of CoFeB/MgO films were prepared by a magnetron sputtering system at 0.34Pa with a base pressure of $6 \times 10^{-5}$Pa at room temperature. The CoFeB layer was deposited by co-sputtering on glass substrate. The power of the $Fe_{65}Co_{35}$ alloy target was kept at 20W and the power of the B target was changed from 20 to 80 W to control the B content in the CoFeB layer. CoFeB layer composition was determined by an IRIS Advantage atomic emission spectrometer. The MgO layer was deposited at 200W RF power at 0.34Pa at room temperature. All the samples were annealed at 200°C, 300°C, and 400°C for 30 minutes in a vacuum of $4 \times 10^{-5}$ Pa. The structures of the CoFeB/MgO bilayers were analyzed by a Rigaku D/Max-2400 X-ray diffractometer (XRD) with Cu $K_\alpha$. A Lake Shore 7304 vibrating sample magnetometer (VSM) was used to measure the magnetic properties of the CoFeB/MgO films at room temperature. To investigate the compositional changes at the interface between CoFeB layer and MgO layer before and after the annealing treatment, the samples were measured by PHI 700 Auger Electronic Spectroscopy (AES).

## 3. RESULTS AND DISCUSSION

The result of atomic emission spectrometer shows that the B concentration in the CoFeB layer was 2.2%, 6.7%, 12.1%, and 16.9% (atomic percent) while the power of the B target was 20W, 40W, 60W, and 80W respectively.

The XRD patterns of the as-deposited CoFeB/MgO films with different B content are shown in Fig. 1. The (110) diffraction peak of $Co_3Fe_7$ is present at $44.75°$ in the CoFeB/MgO films with 2.2% B content. When B content in the CoFeB/MgO films increase to 6.7% and 12.1%, the (110) diffraction peak becomes weaker. The diffraction peak almost disappears when the B content increases to 16.9%. This indicates that the CoFeB/MgO films may become amorphous with high B content. The result is similar to the FeCoB thin films prepared by Kim *et al* [9]. They prepared the FeCoB thin films with different B content and found the film become amorphous when the B content increases to 22.1%. They think boron may segregate on grain boundaries and make it easily to form the amorphous structure.

The variation of coercivity $H_C$ of the as-deposited CoFeB/MgO films with different B content is shown in Fig. 2. The $H_C$ decreases from 215.0Oe to 37.3Oe when B content increases from 2.2% to 6.7%. When B content is 12.1% and 16.7%, the $H_C$ becomes 17.0Oe and 10.1Oe respectively. It can be seen that $H_C$ decreases with the increase of B content in the CoFeB/MgO films. Boron is a well known element to distort α-iron structure and easily segregate on grain boundaries, which facilitates the formation of amorphous or nanocrystalline structure of Fe-based materials [10]. With the increase of B content, the CoFeB/MgO films become more amorphous in nature, accounting for the decrease of $H_C$ by essentially eliminating the crystal anisotropy.
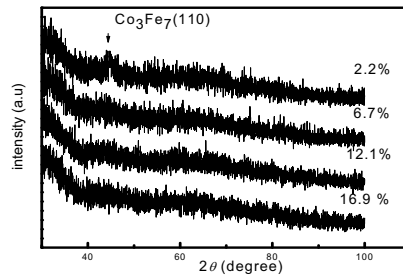
Fig.1. XRD patterns for the as-deposited CoFeB/MgO films with various B content

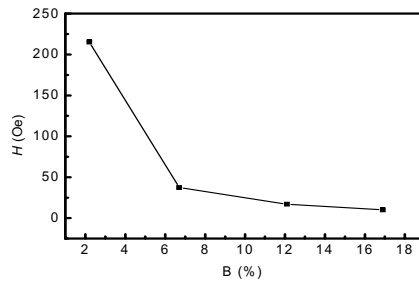

Fig.2. The variation of coercivity HC of the as-deposited CoFeB/MgO films with B content

To investigate the effect of various B content on the structure of the CoFeB/MgO films after annealing, all the samples were vacuum annealed at 200  C, 300  C, and 400  C. Fig. 3 shows the XRD patterns of all the annealed film samples. When the annealing temperature is lower than 400  C, we can identify the minor FeCo (110) crystalline phase in the CoFeB/MgO films with the B contents of 2.2% and 6.7%. No obvious diffraction peak appears for the annealed CoFeB/MgO films with the B contents of 12.1% and 16.9%, indicating that these films are predominantly amorphous. When the annealing temperature is 400  C, the FeCo (110) diffraction peak can be observed in all the CoFeB/MgO film samples, indicating these films crystallize to a certain extent. It can be seen that the higher B content in the CoFeB/MgO film samples, higher annealing temperature is needed to crystallize the film. From Fig. 3 we also can see that when the annealing temperature is 400  C, the diffraction peak becomes broader when B content increases to 12.1% and 16.9%, indicating that the average grain size in the films decrease with the increase of B content in the CoFeB/MgO films. This is because boron can prevent grain growth in the annealing process and facilitate the formation of amorphous or nanocrystalline structure of Fe-based materials [10]. There are no additional diffraction peaks in the XRD pattern of all the annealed film samples, indicating the crystallization of MgO is negligible.
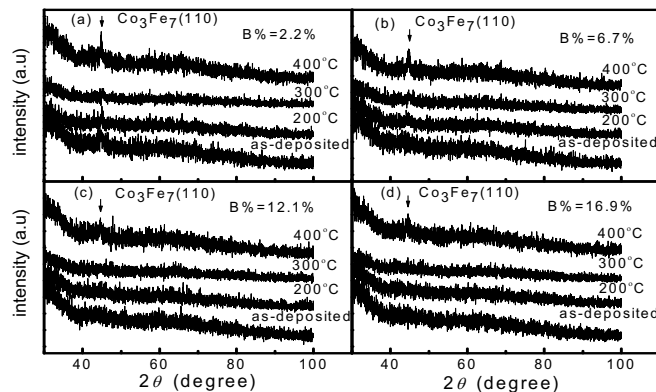


Fig.3. XRD patterns for the as-deposited and annealed CoFeB/MgO films with various B content (a) 2.2%, (b) 6.7%, (c) 12.1%, (d)16.9%.

   The compositional changes of CoFeB/MgO films before and after annealing treatment were measured by AES to investigate the thermal stability of CoFeB/MgO films with various B contents. Fig. 4(a) shows the AES depth profile of the as-deposited CoFeB/MgO films with 12.1% B. B content is about 12.9% in the CoFeB layer, which is in accordance of the result of atomic emission spectrometer. At the interface between CoFeB layer and MgO layer, B content is 3.0% and B is not found in MgO layer. It illuminates no diffusion of boron into the MgO layer for the as-deposited CoFeB/MgO film. Fig. 4 (b) shows the AES depth profile of the CoFeB/MgO films with 12.1% B after annealing at 400$^{o}$C. B content at the interface between CoFeB layer and MgO layer is about 7.0%, which is higher than that of the as-deposited CoFeB/MgO film. At 10.8nm depth in the CoFeB/MgO film, B content is about 3.3% which is much lower than that of the as-deposited film. At 19.2nm depth in the CoFeB layer, the B content is about 5.2% while it increase to 12.9% at 37.6nm depth. It can be seen that the average B content in CoFeB layer decrease after annealing and B content at the CoFeB/MgO interface increase. Some amount of B in the CoFeB layer have diffused to the CoFeB/MgO interface and accumulated there. This is consistent with the theoretical calculation result from Burton *et al* [8]. They present results of first-principles total energy calculations of CoFeB/MgO/CoFeB MTJs and suggest that it is energetically favorable for boron to reside at the CoFeB/MgO interface rather than remain in the bulk of the crystalline CoFeB electrode. Bae *et al* [6] investigated the effect of the heat treatment on the compositional change at the interface between the bottom CoFeB electrode and the MgO barrier before and after annealing. The results indicate that B in the bottom CoFeB layer diffuse into the MgO barrier and boron oxide is formed at the interface of the CoFeB/MgO during the crystallization of the bottom CoFeB layer. The formation of boron oxide in the MgO layer in our film samples can also be observed. Fig. 5 shows the B KLL line shape spectra varying with depth in CoFeB/MgO film with 12.1% B. For the as-deposited CoFeB/MgO film (Fig. 5a), there is no B Auger peak appears in MgO layer, and the B peak appears in the CoFeB layer at 179.2 eV. After annealing at 400$^{o}$C (Fig. 5b), the B peak appears at the interface of CoFeB/MgO film at 169.0 eV which decreases 10.2 eV compared to 179.2 eV. The decrease in the auger kinetic energy may be due to the decrease in electron cloud density around B atoms which indicate the formation of boron oxide [11]. Fig. 4(c) shows the AES depth profile of the CoFeB/MgO film with 6.7% B after annealing at 400$^{o}$C. B content at the CoFeB/MgO interface is 8.2%, which is higher than that of the sample with 12.1% B, and it decrease to 3.1% in the CoFeB layer. It illuminates that large amount of B in the CoFeB layer diffused to the CoFeB/MgO interface and accumulated there after annealing. The B content at the CoFeB/MgO interface is higher in the CoFeB/MgO films with low B contents than that in the films with high B contents after annealing.
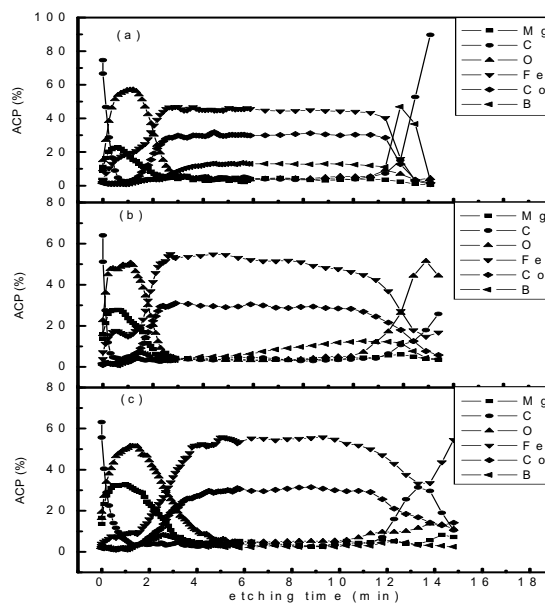


Fig.4. The AES depth profile of CoFeB/MgO films (a) as-deposited CoFeB/MgO films with 12.1% B, (b) 400$^{o}$C annealed CoFeB/MgO films with 12.1% B, (c) 400$^{o}$C annealed CoFeB/MgO films with 6.7% B
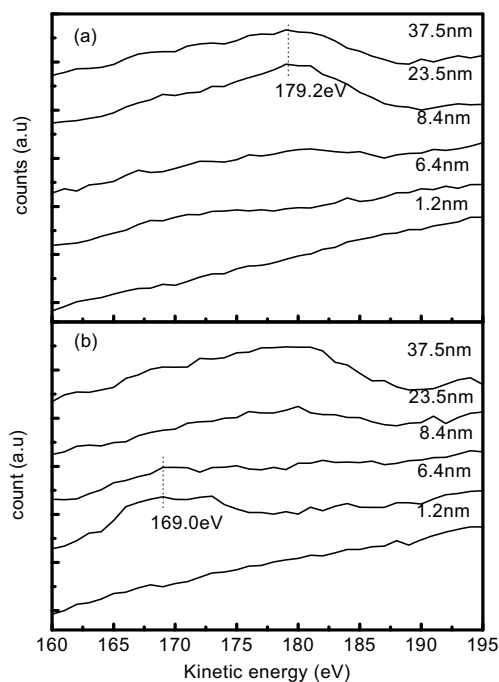
Fig.5. B KLL line shape spectra varied with depth of CoFeB/MgO films with B% of 12.1% (a) as-deposited, and (b) annealed at 400°C

In order to investigate the effect of the B content on magnetic properties of CoFeB/MgO films after annealing, hysteresis loops for the CoFeB/MgO films with various B contents were measured by VSM. Fig. 6 shows the hysteresis loops for the CoFeB/MgO films with various B contents before and after the annealing treatment. For the samples before and after annealed at 200°C, the hysteresis loops show the ferromagnetism characteristic and can be saturated at high field. For the samples annealed at 300°C and 400°C, the hysteresis loops show the ferromagnetism characteristic mainly. But the magnetization curves can not be saturated at high field, the magnetization increases with the magnetic field at high field which shows the paramagnetic phase is formed in the samples. According to the AES result of the CoFeB/MgO films, no diffusion of boron into the MgO layer for the as-deposited samples. After annealing at 400°C, B atoms diffuse from CoFeB layer to the interface of CoFeB/MgO films and form boron oxide, which leads to the films become paramagnetism. Meanwhile, the formation of boron oxide in the CoFeB/MgO films made the variation of the saturation magnetization after annealing, which can be seen from Fig. 6. For the CoFeB/MgO film with the B content of 6.7% (Fig. 6a), the $M_s$ is 14.95KGs before annealing. It decreases to 14.08KGs after annealing at 300°C and to 14.03KGs after annealing at 400°C. For the CoFeB/MgO film with the B content of 12.1% (Fig. 6b), the $M_s$ is 13.64KGs before annealing. It decreases to 12.95KGs after annealing at 300°C and 400°C. The decrease of $M_s$ after annealing can be attributed to the formation of boron oxide in the CoFeB/MgO films. In Fig. 6, the variation of the $H_C$ when the CoFeB/MgO films annealed at different temperature also can be observed. For the CoFeB/MgO film with the B content of 6.7%, the $H_C$ decreases from 37.3 Oe before annealing to 13.3 Oe after annealing at 200°C, and it decreases to 11.0Oe after annealing at 300°C and to 7.4Oe after annealing at 400°C. For the CoFeB/MgO film with the B content of 12.1%, the $H_C$ decreases from 17.8Oe before annealing to 17.1Oe after annealing at 200°C, and it decreases to 15.9Oe after annealing at 300°C and to 12.5Oe after annealing at 400°C. It can be seen that the $H_C$ decreases with the increase of the annealing temperature. The decrease of $H_C$ is more slightly for the sample with the B content of 12.1% than that of the sample with the B content of 6.7%. The effect of film stress should be considered on the variation of the $H_C$ after annealing. There is the film stress in most sputter deposited films [12]. When the films are annealed, the film stress can be released, which results in the decrease of $H_C$ [13]. The slightly variation of $H_C$ after annealing for the CoFeB/MgO film with B content of 12.1% is related with the sample structure. From Fig. 3c we can see that the sample is amorphous before annealing. After

annealing at 400°C, the sample becomes crystalline, the crystal anisotropy will increase the $H_C$. The competition of the effect of film stress and the crystal anisotropy on the $H_C$ makes the slightly variation of $H_C$.
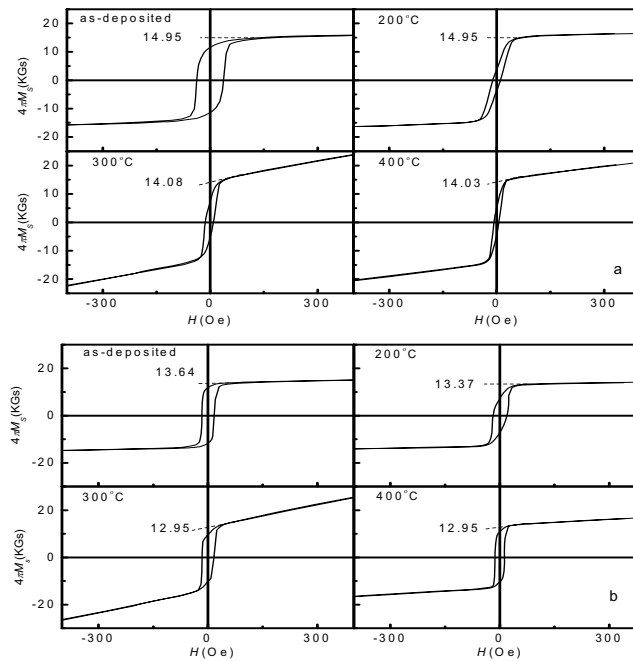


Fig.6. Magnetic loops of CoFeB/MgO films with B content is 6.7%(a) and B content is 12.1%(b) at the as-deposited and annealed state

## 4. CONCLUSION

The B content of CoFeB/MgO films plays an important role in determining their structure, magnetic properties, and thermal stability. For the as-deposited CoFeB/MgO films, the films become amorphous and $H_C$ decreases with the increase of B content. Vacuum annealing make the CoFeB/MgO films crystallize to some extent. With the increase of the B content, higher annealing temperature is needed to crystallize the sample. The average grain size decreases with the increase of B content in the CoFeB/MgO films. AES shows no diffusion of boron into the MgO layer for the as-deposited samples. After annealing, the average B content in CoFeB layer decreases and B content at the CoFeB/MgO interface increases. The B content at the CoFeB/MgO interface is higher in the CoFeB/MgO films with low B contents than that in the films with high B contents after annealing. The formation of boron oxide in the CoFeB/MgO films makes the decrease of $M_s$ after annealing. The $H_C$ decreases with the increase of the annealing temperature for the CoFeB/MgO films. The decrease of $H_C$ is more slightly for the samples with high B content than that of the samples with low B content.

### Acknowledgments

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