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# The effects of annealing temperature and sputtering power on the structure and magnetic properties of the Co-Fe-Zr-B thin films

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ABSTRACT

The microstructure and magnetic properties of the amorphous Co-Fe-Zr-B thin films grown on glass substrates by dc magnetron sputtering are investigated using differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and superconducting quantum interference device (SQUID) techniques. The Co-Fe-Zr-B thin films deposited at room temperature were annealed at temperatures ranged from 683 K to 773 K. Experimental results indicated that the coercivity ($H_c$) of the Co-Fe-Zr-B thin films is significantly influenced by residual stress and crystalline phases within the films. The correlation of the coercivity and the microstructure of Co-Fe-Zr-B thin films are discussed. After annealed at 683 K, the coercivity of the Co-Fe-Zr-B film was as low as 1.2 Oe.



## 1. Introduction

Recently, Co-Fe based metallic glasses and nanocrystalline materials have attracted much interest owing to the excellent soft magnetic properties [1–3]. To extend the application of BMG in the high frequency power converters, the soft magnetic BMG in the films form, i.e., thin film metallic glass (TFMG), can be used in inductors, current transformers and other devices requiring high permeability and low core loss at low frequencies. In order to fit the requirement, soft metallic glass should exhibit a high susceptibility and large saturation [4]. Meanwhile, the magnetic films generally required high electrical resistivity to suppress eddy currents and also increase the skin depth in high frequency applications. Thin film metallic glasses (TFMGs) are thought to be a suitable candidate for MEMS applications because they are isotropic and homogeneous as well as free from defects originating from the crystal structure [5].

In this study, we prepared Co-Fe-Zr-B films by DC sputtering method. It was found that the microstructures of the annealed films as well as the associated magnetic properties are strongly dependent on the sputtering power delivered to the Co-Fe-Zr-B target and the subsequent annealing temperatures.

## 2. Experiment

The Co-Fe-Zr-B films were prepared by DC sputtering method. The $Co_{52}Fe_{20}Zr_8B_{20}$ target was placed on sputtering gun as the source materials. The films were grown on Coring 7059 glass substrates at room temperature for 20 min. The base pressure was $5 \times 10^{-6}$ torr. Ar was used as the working atmosphere and the working pressure fixed at 4 mtorr during growth. The sputtering power delivered to the Co-Fe-Zr-B target ranged from 10 to 50 W. The Co-Fe-Zr-B films were annealed by rapid thermal annealing at a heating rate of 50 K/s, and the annealing temperatures were kept within the range of 683 K–773 K for 3 min. The main reasons of annealing the Co-Fe-Zr-B films in such a short time period were to release the residual stress in the films and to control the grain sizes of the crystalline phase formed in the Co-Fe-Zr-B films in the nanoscale.

The crystal structure and the microstructure of the films were investigated by X-ray diffraction and transmission electron microscopy operated at 200 kV (FEI Tecnai $G^2$). The compositions of the films were examined by electron probe microanalyzer (EPMA). Magnetic properties were studied using a superconducting

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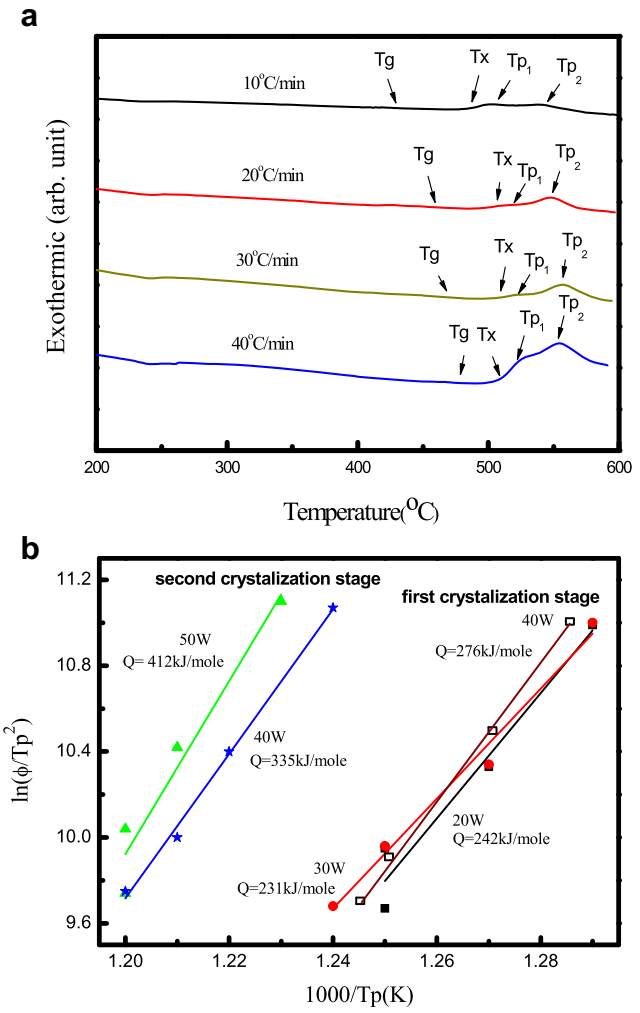


**Fig. 1.** (a) DSC curves with various heating rates of the Co-Fe-Zr-B films grown at 40 W; (b) The Kissinger plots for Co-Fe-Zr-B films grown at various sputtering powers.

quantum interference device (SQUID) at room temperature with a maximum magnetic field of 1.2 kOe.

## 3. Results and discussions

DSC traces of the as-deposited Co-Fe-Zr-B films at different heating rates are used to evaluate the crystallization of the crystalline phase, as shown in Fig. 1. From DSC curves, the glass transition temperature ($T_g$), first crystallization temperatures ($T_x$), and exothermic peak temperature ($T_p$) can be respectively determined. The DSC curves exhibit two exothermic procedures indicating two stages of crystallization. The crystallization temperature of the first crystalline phase, $T_x$, for the Co-Fe-Zr-B films with various sputtering power is in the temperature range of 753–762 K, which does not show apparent dependence with sputtering power. However, the onset glass transition temperature $T_g$ of the Co-Fe-Zr-B films is slightly increased with the sputtering power as listed in Table 1. For bulk metallic glass, the glass transition temperature is related to the content of the free volume in the materials. The relaxation annealing, on the other hand, would lead to the escape of the free volume entrapped during the alloy solidification from the amorphous matrix [6]. During thin films deposition, the sputtering may cause some inhomogeneity and defects in the films, which may

**Table 1**
The $T_g$, $T_x$, $\Delta T_x$ and activation energies of the $Co_{52}Fe_{20}Zr_8B_{20}$ films grown at various sputtering powers.

| Sputtering power (W) | $T_g$ (K) | $T_x$ (K) | $\Delta T_x$ (K) | $Q_{Tp1}$[a] (kJ/mole) | $Q_{Tp2}$ (kJ/mole) |
|---|---|---|---|---|---|
| 20 | 686 | 753 | 67 | 242 | – |
| 30 | 693 | 762 | 69 | 231 | – |
| 40 | 702 | 759 | 57 | 276 | 335 |
| 50 | 698 | 758 | 60 | 253 | 412 |

[a] $Q_{Tp1}$ and $Q_{Tp2}$ are the activation energies of the first and second stages of crystalline phases in the amorphous $Co_{52}Fe_{20}Zr_8B_{20}$ films after annealing.

lead to some empty volume, i.e., some fraction of matter is having a lower atomic coordination than that in a reference region with a denser atomic packing. These sites may be the preferred regions for initiating the glassy structure destabilization caused by glass transition [7]. Therefore, the glass transition temperature of the thin films might be influenced by deposition parameters.

The activation energy for crystallization of the ordering Co-Fe-Zr-B films was determined by means of the Kissinger plot [8],

$$\ln\left(\frac{\varphi}{T^2}\right) = -\frac{E_a}{RT} + const \quad (1)$$

where $\varphi$ is the heating rate, $T$ is the specific temperature, $R$ is the gas constant, and $E_a$ is the activation energy. The plot of the $\ln(b/T^2)$ versus $1/T_p$ ($T_p$ is the peak temperature of crystallization) yielded a straight line and the slope is related to the activation energy of crystallization. The Kissinger plot for Co-Fe-Zr-B films grown at various sputtering power is shown as Fig. 1(b). From the slope, the activation energy of the film was estimated. The activation energy of the first crystallization of the Co-Fe-Zr-B thin films increases from 242 kJ*mole$^{-1}$ to 276 kJ*mole$^{-1}$ with the increasing sputtering power. While the second crystallization was only observed in the Co-Fe-Zr-B films grown at 40 W and 50 W, and the activation energy of the second crystallization of the Co-Fe-Zr-B thin films increases enormously from 335 kJ*mole$^{-1}$ to 412 kJ*mole$^{-1}$ with the increasing sputtering power.

The compositions of the Co-Fe-Zr-B films are identified by EPMA. By varying the sputtering power, there is no obvious difference between the composition of the Co-Fe-Zr-B films and that of the target. Fig. 2 shows the XRD patterns of the as-deposited and annealed Co-Fe-Zr-B thin films. Since the time duration of annealing quite limited, the content of crystalline phase may have

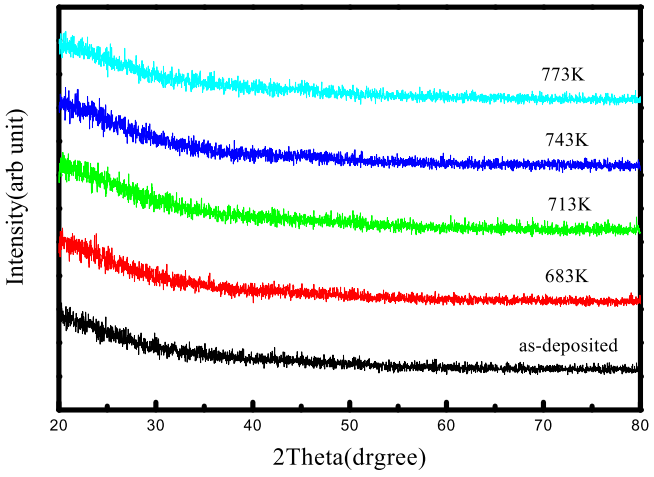


**Fig. 2.** XRD patterns of the Co-Fe-Zr-B films annealed at various temperatures.

been still lower than the detection limits of XRD. As a result, no trace of any crystallized phase can be identified by the result of X-ray diffraction.

For the as-deposited Co-Fe-Zr-B thin films, the TEM observation revealed the morphology of a uniform phase, as shown in Fig. 3(a). The corresponding electron diffraction pattern also confirmed the amorphous feature of the Co-Fe-Zr-B films, which indicates an excellent glass forming ability and homogeneous composition distribution. Fig. 3 (b)~(d) show the conventional transmission electron microscopy photos of the Co-Fe-Zr-B films grown at 40 W and then annealed at 713 K, 743 K and 773 K, respectively. For the Co-Fe-Zr-B films grown at 40 W, the $T_g$ and $T_x$ are 702 K and 759 K, respectively. The Co-Fe-Zr-B films exhibited amorphous feature, while the annealing temperature was below the glass temperature (not shown here). When the annealing temperature was increased to 713 K, which is higher than $T_g$, nanocrystalline phases started to homogeneously precipitate in the amorphous matrix. The grains size of these nanocrystals ranges from 3 nm to 12 nm with an average size of about 6 nm. From the corresponding electron diffraction and composition analysis, the first crystalline phase was identified as the fcc-(Co, Fe) phase. With further increasing the annealing temperature to 773 K, the nanocrystals grew to a larger average grain size of about 9 nm. The corresponding electron diffraction pattern indicated the existences of the second crystalline phases as $CoZr_2$ and $Co_{23}Zr_6$.

According to the TEM results, the evolution of the crystallization of the Co-Fe-Zr-B films is consistent with the DSC results, which showed two exothermic events indicating two crystallization stages. Briefly, the crystallization was triggered when the annealing temperature was raised to higher than glass transition temperature. The fcc-(Co, Fe) nanocrystals with an average size of 6 nm was first to appear at the early stage of crystallization. Afterwards, nanocrystals of fcc-(Co, Fe), $CoZr_2$ and $Co_{23}Zr_6$ were observed to precipitate from the amorphous matrix upon the subsequent stage of crystallization. The crystallization sequence can be briefly summarized below.

$$\alpha \xrightarrow{T>T_g} \alpha' + \mathrm{fcc(Co,Fe)} \rightarrow \alpha'' + \mathrm{fcc(Co,Fe)} + CoZr_2 + Co_{23}Zr_6 \quad (2)$$

where $\alpha$ is the amorphous phase below glass transition temperature, $\alpha$' and $\alpha$" are amorphous phases when the annealing temperature is above glass transition temperature.

Fig. 4 shows the hysteresis loops of the Co-Fe-Zr-B films annealed at (a) 683 K, (b) 713 K, (c) 743 K, and (d) 773 K, respectively. The magnetic measurement was performed along the film direction with a maximum applied field of 1200 Oe. All the as-deposited Co-Fe-Zr-B films are amorphous for various sputtering powers. Owing to the lack of long-range order in atomic arrangement, the crystal anisotropy is absent in the amorphous films. The coercive field ($H_c$) of the as-deposited Co-Fe-Zr-B films grown at 40 W is about 6.8 Oe. With the annealing treatment, the $H_c$ value of the Co-Fe-Zr-B films initially decreased with increasing temperature from 6.8 Oe to 1.2 Oe, presumably due to the relief of residual stresses. However, with the crystallization of fcc-(Co, Fe), $CoZr_2$ and $Co_{23}Zr_6$ phases, the $H_c$ increases with increasing annealing temperature when it is above the glass transition temperature.

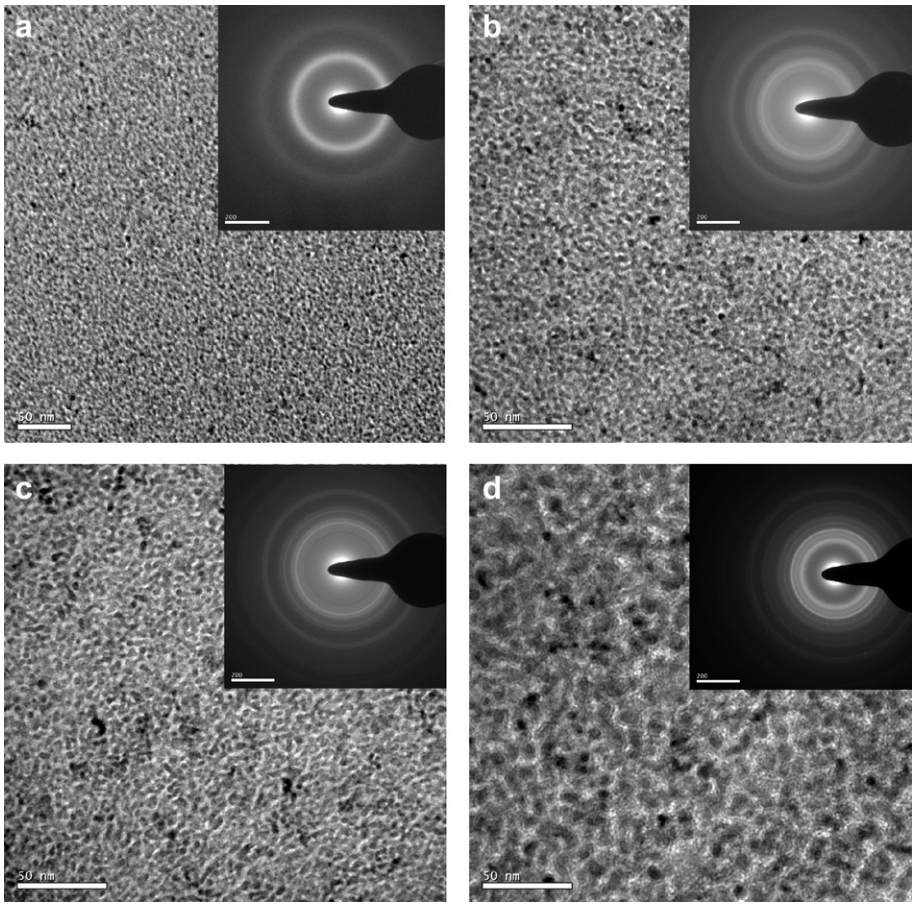


**Fig. 3.** TEM bright field images and the corresponding selected area diffraction patterns of the Co-Fe-Zr-B films, (a) as-deposited, and annealed at (b) 713 K, (c) 743 K, and (d) 773 K.

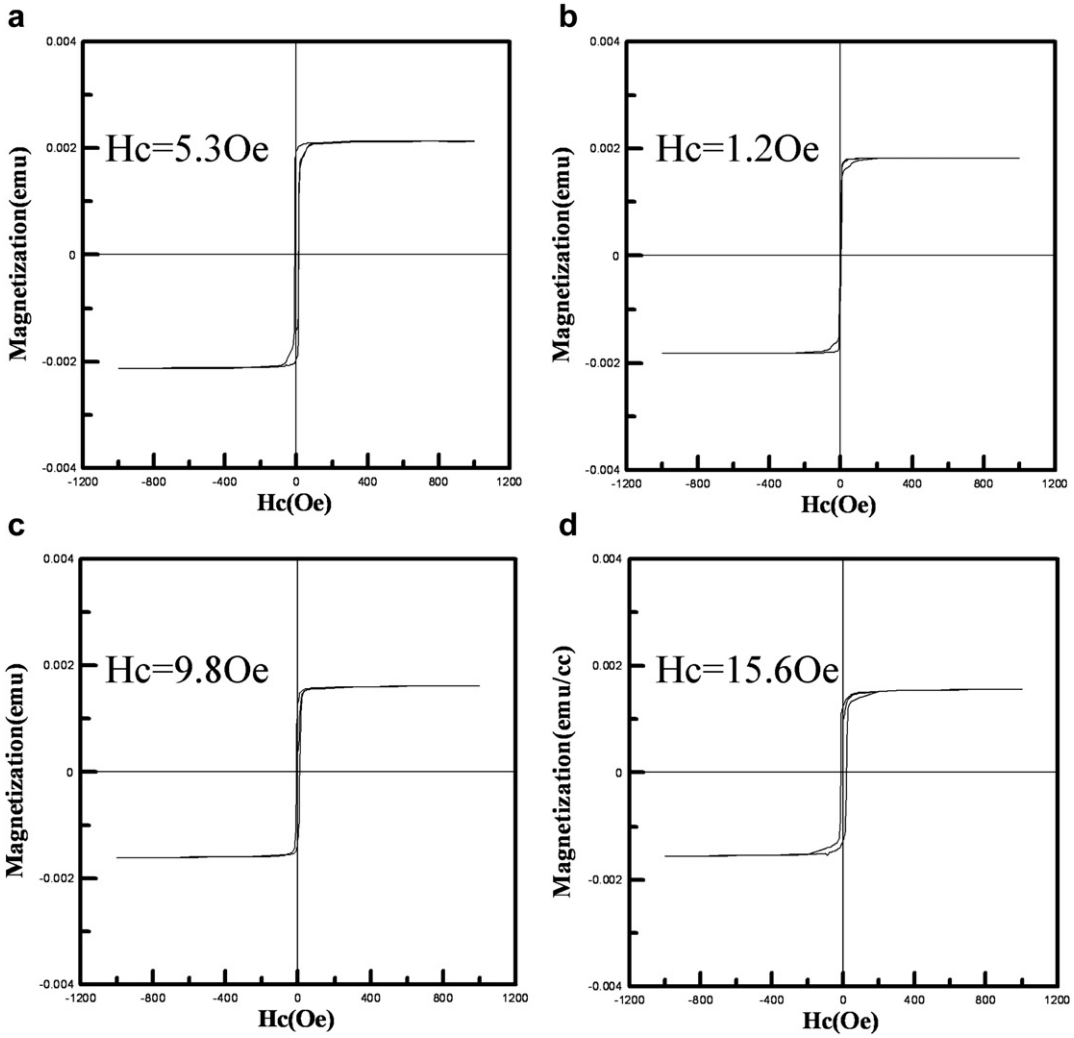


**Fig. 4.** The hysteresis loops of the Co-Fe-Zr-B films (a) as-deposited, and annealed at (b) 683 K, (c) 743 K, and (d) 773 K.

It has been pointed out that the residual stress as well as microstructure irregularities existed in the films might destroy the soft magnetization behavior of films [9]. According to Mayr's model, the intrinsic stress in the amorphous film is closely related to the surface morphology and film thickness [10]. The annealing-induced initial reduction in the coercivity field at low annealing temperatures described above thus might directly correlate to the elimination of the residual stress in the as-deposited films. This could be the primary reason why the film annealed at 683 K exhibited extremely soft magnetizing behavior with $H_c$ as low as 1.2 Oe. When the annealing temperature was elevated to 713 K, the dramatic increase in $H_c$ may, on the other hand, originate from the crystallization of Co-Fe-Zr-B films. As confirmed in the TEM results, the (Co, Fe), $CoZr_2$ and $Co_{23}Zr_6$ phase formed during annealing at high temperatures. Moreover, the average grain size of the ferro-magnetic crystalline (Co, Fe) phase increased with annealing temperature to about 9 nm. Herzer et al. reported on the grain size dependent coercive force $H_c$ of the nanocrystalline soft magnetic materials, which predicted a dependence of $H_c \propto D^6$, where $D$ is the mean diameter of the crystallites in the nanocrystalline material [11]. The present results, thus, consistently confirmed that the magnetic properties of the Co-Fe-Zr-B films are significantly influenced by the detailed nanostructure and the residual stress existing in films.

## 4. Conclusions

In this study, the effects of the sputtering power and annealing temperature on the nanostructure and magnetic properties of the Co-Fe-Zr-B thin films have been investigated. Experimental results showed that the sputtering power has some influences on the glass transition temperatures, which in turn enhances the GFA of the Co-Fe-Zr-B films. In addition, the magnetization behavior of the Co-Fe-Zr-B thin films was found to strongly dependent on the detailed nanostructure of the amorphous film as well as the appearance of the crystalline phases. Below the glass transition temperature, increasing the annealing temperature tends to relieve the intrinsic stress of the amorphous Co-Fe-Zr-B films leading to an extremely low coercive field of 1.2 Oe for films annealed at 683 K. The appearance of nanocrystalline phases, however, would lead to dramatic increase in the coercive field.

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## References

[1] Inoue A, Shen B, Nishiyama N. Development and applications of Late transition metal bulk metallic glasses. USA: Springer; 2007.
[2] Johnson WL. MRS Bull 1999;24:42.
[3] Wang WH. Prog Mater Sci 2007;52:540.
[4] Song JS, Min BK, Jeong DY, Kim HS, Heo JS. J Magn Magn Mater 2001;234:494.
[5] Hata S, Sakurai J, Shimokohbe A. 18Th IEEE Inter Conf Micro Electro Mech Syst; 2005:479.
[6] Jiang WH, Jiang F, Green BA, Liu FX, Liaw PK, Choo H, et al. Appl Phys Lett 2007;91:041904.
[7] Chen M. Ann Rev Mater Res 2008;36:445.
[8] Kissinger HE. Analyst Chem 1957;29:1702.
[9] Chen LH, Chen HK, Hsieh CT, Shih YH, Chen IG, Chen SY, et al. J Appl Phys 2002;91:8450.
[10] Mayr SG, Samwer K. Phys Rev Lett 2001;87:036105.
[11] Herzer G. J Magn Magn Mater 1992;112:258.