Preparation of Ni-Mn-Zn ferrite films on CeO_2/YSZ-buffered Si substrate

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***Abstract*—Ni-Mn-Zn ferrite films were deposited on Si substrate with CeO_2/YSZ(YSZ:yttria-stabilized ZrO2) buffer layer by pulsed laser deposition(PLD). The effect of CeO_2/YSZ buffer layer on the Ni-Mn-Zn ferrite film was studied by XRD, SEM and VSM. The results revealed that the CeO_2/YSZ buffer layer can improve the films crystallinity, smooth the roughness of film, reduce the film crack and lead to a homogeneous microstructure. The saturation magnetization (Ms) higher than 240 emu/cm^3 can be obtained. It also found annealing process can improve the film crystallinity and the magnetic properties, decrease the coercivity (Hc).**

Keywords- ferrite, CeO_2/YSZ buffer, pulsed laser deposition

I. INTRODUCTION

Nickel-zinc(NiZn) ferrites are considered to be low cost optimum magnetic materials which play important roles in technological application[1][2]. It is a kind of mixed spinel ferrites in which tetrahedral(A) sites are occupied by Zn^{2+} and Fe^{3+} ions and the octahedral (B) sites are occupied by Ni^{2+} and Fe^{3+} ions in the formula of AB_2O_4[3]. Substitution of Cu、Mn、Mg in the NiZn ferrites has remarkable influences on the magnetic and electrical properties[4][5]. Nowdays, Ni-Mn-Zn ferrites (NMZF) has been widely used in electronic applications, such as microwave devices [6][7].

With the development of MMIC, microwave devices need to be integrated with other devices. This requires thin ferrites film to be deposited on Si substrates. However, because of the difference of lattice between Si with the NMZF and instability of the Si, it hard to prepare well films directly deposited on Si substrates [8]. Some researchers have already prepared Ni-Zn ferrites films on Si substrates with $ZnFe_2O_4$ and $La_{0.7}Sr_{0.3}MnO_3$ buffer layer [9]. In recent years, YSZ and double CeO_2/YSZ epitaxial growth thin films on Si(001) substrate have attracted much attention due to its applications such as the buffer layers in electronic devices or high-Tc superconductors[10][11]. Usually, the Si substrate is covered by a native amorphous SiO_2 layer. Even after removing it by chemical cleaning, the new SiO_2 layer formed quickly just before film deposition starting at high-temperature and high-vacuum conditions. The use of YSZ as a buffer layer can deoxidize the amorphous SiO_2 thin layer and form a higher quality of epitaxial YSZ films on Si substrates. The CeO_2, which is used as second buffer layer, has a smaller lattice mismatch with YSZ and can prevent the chemical reaction between YSZ and the upper layer NMZF films. However, few studies concerned using CeO_2/YSZ as buffer layer on NMZF films have been reported. In this paper, we reported the preparation of the NMZF films on Si substrates with CeO_2/YSZ as buffer layer by pulsed laser deposition (PLD) method and studied influences of buffer layer and annealing process on the magnetic properties and microstructure of the films .

II. EXPERIMENT

PLD with KrF excimer laser (248nm) was empolyed to prepare all layers for NMZF/CeO_2/YSZ thin films. For the thin film preparation, YSZ, CeO_2 and NMZF ceramic disks were synthesized as targets by solid state reaction method. YSZ, CeO_2 powders were pressed into pellets and sintered at 1450℃ for 3 hours. The NMZF target was prepared by using Fe_2O_3, MnO_4 and ZnO with nominal composition, milling in demineralized water, grinding, pressing at 300Mpa, sintering at 1350℃ for 3 hours.

TABLE I. THE GROWTH CONDITION OF FILMS

Targets	YSZ,CeO_2,NMZF
Substrate	Si(100)
Target-substrate distance	45mm
Deposition time	YSZ : 0.5min,2.5min CeO_2:7.5min NMZF: 300min
Laser energy	300mJ
Substrate temperature	YSZ:650℃ CeO_2:760℃ NMZF:650℃
O_2 gas pressure	YSZ:5x10^{-4},5x10^{-2} CeO_2:3Pa NMZF:4Pa

The films growth condition were summarized in Table 1.The laser beam was focused by a quartz lens up to the rotating targets at angle of 45^o . The distance between targets and substrate was 45mm. The Si (100) substrates were cleaned according to the RCA method. The cleaned substrate was dipped in diluted HF (HF:H_2O=1:5) to remove silicon dioxide just before the deposition. Then the substrate was immediately put into the processing chamber. The substrate was heated up to 650℃ at base pressure of 5X10^{-4} Pa. After the temperature reached 800℃, deposition of YSZ layer was started at base pressure without the introduction of O_2 gas. Thirty seconds after laser pulsing began, O_2 gas was introduced at 5X10^{-2}Pa. After 2.5min deposition time, the YSZ target was changed to a CeO_2 target and deposition of

CeO_2 was carried out at 760℃ under 3Pa for 7.5min. Then substrate temperature was cooled up to 650℃ at 4Pa, the deposition of NMZF films were carried out for 5 hours, lastly, the films were annealing at 800℃for 1hour in air.

The crystallographic structure and microstructure of the films were characterized by X-ray diffraction with Cu $K\alpha$ radiation ($\lambda=1.540\dot{A}$). A vibrating sample magnetometer (VSM) was used to measure the magnetic properties of the films. The morphological characteristics and thickness of the films were measured by scanning electron microscopy (SEM).

III. Results and Discussion

In this part, the effect of CeO_2/YSZ buffer lay is discussed.

Firstly, the NMZF films deposited on Si(100) with buffer and without buffer were tested by XRD respectively, the results were displayed as figure 1. As shown, it could be clearly seen that there is a SiO_2 diffraction peak for the sample without CeO_2/YSZ buffer layer. It is suggested that the surface of Si is easy to be oxidized to SiO_2 in the high substrate temperature before deposition. So is was of no much effect that remove silicon dioxide by chemical method just before the deposition. Naoki has reported that the ZrO_x produced by laser irradiation would react with SiO_2 [10].

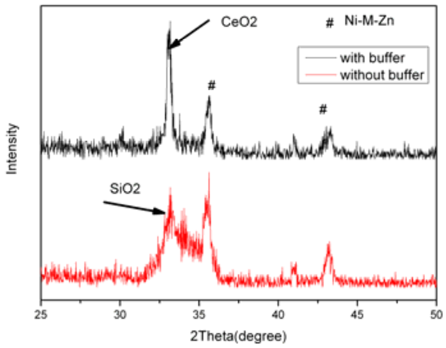
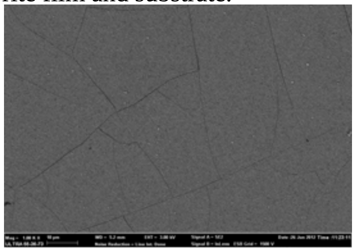


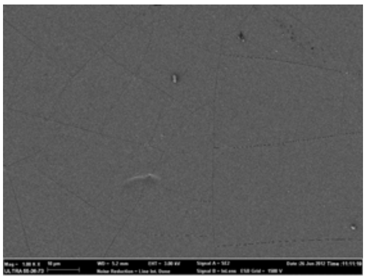
Figure 1. XRD for NMZF film

So the YSZ film was first deposited at base pressure without introduction of O_2 gas. It has been studied that 3Pa of the O_2 gas and 760℃ of the temperature can get high CeO_2(100) orientation film on Si(100) substrate. From figure 1, it can be seen that after deposited with CeO_2/YSZ buffer layer, the SiO_2 peak was disappear and there was a CeO_2(100) peak. The effect of buffer layer on the crystalline of NMZF films can also be seen from figure 1. Both of them represent typical polycrystalline structure. However, from the FWHM of NMZF(311) peaks , one can expect that the buffer lay can improve the films crystallinity.

Figure 2 showed the SEM results for the surface and cross section of NMZF films with or without buffer layer. It is obvious that the CeO_2/YSZ buffer layer can improve the quality of surface of film, smooth the roughness of film, and reduce the film crack. From the cross section of the film, it could be seen that the density of the film was improved and microstructure was more homogeneous. This may be ascribed to that the CeO_2/YSZ buffer layer decreases the strain of the NMZF films by preventing the diffusion of Si into the ferrite films and reduces the crystal lattice difference between the ferrite film and substrate.



(a)



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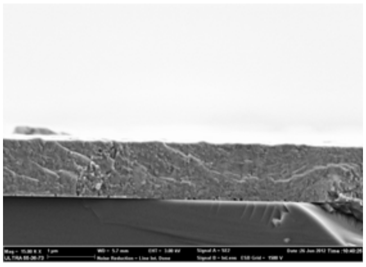
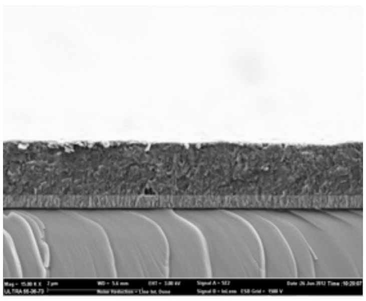


(c)



(d)

Figure 2. SEM for the surface and cross sectional NMZFe films:(a) (c)without buffer ,(b) (d)with CeO2/YSZ buffer

The VSM test results were shown in figure 3. The film got a Ms value higher than 240 emu/cm^3 with CeO_2/YSZ buffer. However, for the one without buffer layer, the Ms can get higher than theoretical value. This phenomenon may be due to the diffusion of Si into NMZF films and the changes of structure or others. Further research need to be done.

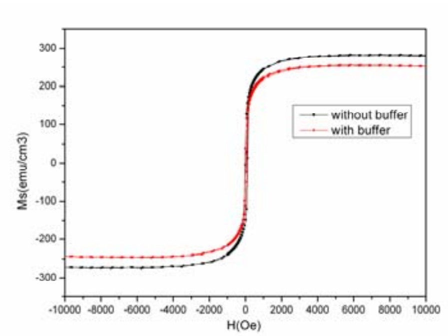


Figure 3. VSM for the NMZF films

Because of hardness of crystallization of NMZF film fabricated by PLD, the annealing process was considered to be one of important conditions to obtain NMZF film with good crystallization. The sample was cut into two parts, one was annealed in the electric furnace at 800℃ for 1 hours. Figure 4 showed the XRD results for the films before-annealing and after-annealing. It could be seen that all the NMZF films represent polycrystalline structure. The FWHM of (311) peak changed from 0.433 to 0.267 after the annealing process, which stands for the crystallinity of film was improved after annealing process. The magnetic properties of the film were tested by VSM, as shown in figure 5. It is clearly that the annealing process can increase the Ms of the film. Furthermore, from the inset in the upper left, it can be found that the Hc of the film decreased after annealing process. This may be due to annealing process promote the grain growth which decrease the amount of boundary.

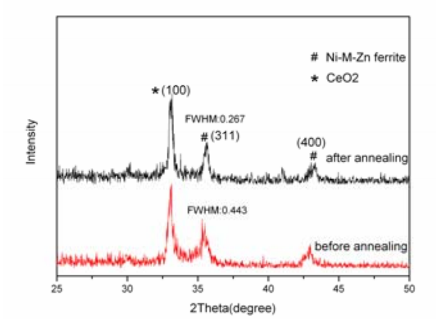


Figure 4 XRD results for the film before-annealing and after-annealing

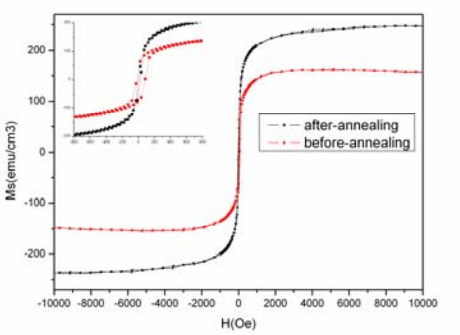


Figure 5. VSM for NMZF film before-annealing and after-annealing

IV. Conclusion

In this study, the NMZF films have been successfully prepared on Si(100) substrates with CeO_2/YSZ as buffer layer. The results showed that the CeO_2/YSZ buffer layer can improve the films crystallinity, smooth the roughness of film, reduce the film crack and lead to a homogeneous microstructure. This phenomenon could be ascribe to that the CeO_2/YSZ buffer lay can decrease the strain of the NMZF films by preventing the diffusion of Si into the ferrite films and have the similar TEC with the ferrite films. The VSM test results exhibited that the film with buffer layer showed a Ms value of 248emu/cm^3, which is much more close to the theoretical value. It is also found that the annealing process can improve the film crystallinity and the magnetic properties and decrease the Hc.

Acknowledgment

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