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Magnetoelectric composite thick films of PZT–PMnN + $NiZnFe_2O_4$ by aerosol-deposition

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Abstract

Highly dense magnetoelectric composite films with 10 μm-thick of high piezoelectric voltage coefficient material, $0.9Pb(Zr_{57}Ti_{43})O_3$–$0.1Pb(Mn_{1/3}Nb_{2/3})O_3$ (PZT–PMnN) and magnetostrictive material, $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF), were fabricated on a platinized Si substrate using aerosol deposition (AD). With increasing magnetic NZF content, dielectric and ferroelectric properties were gradually decreased while magnetizations were improved. The 20% NZF added composite thick film were found to exhibit the maximum ME coefficient. This optimal NZF content is the same as that of bulk ME composite materials. It is noticeable that AD can control the content ratio of ME composite films by controlling the powder composition. The fabricated ME composite films have high ME voltage coefficient coupling because of high density without severe inter-reactions of two phases.

Keywords: Piezoelectric; Magnetostrictive; Thick film; Aerosol deposition

1. Introduction

Magnetoelectric (ME) effect typically refers to the coupling between the piezoelectric and magnetostrictive effect [1,2]. Through the ME effect, magnetization could be induced by an electric field or polarization by a magnetic field. This coupling phenomenon between magnetic and electronic and the potential applications to sensors, transducers, and energy harvester, etc. have attracted the great interest from many researchers worldwide [1–9].

ME effect could be observed in the single phase materials including $BiFeO_3$ and $YMnO_3$ or composites of piezoelectric and magnestostrictive materials [2,3]. However, as the ME effect in the single phase materials is usually very small and comparatively few single phase materials are stable at atmospheric pressure [2], great effort has been devoted to develop the composites that possess large ME coupling coefficients. Since the composite of the piezoelectric $BaTiO_3$ and a ferromagnetic $CoFe_2O_4$ in 1970s, many ME composites with the different compositions have been fabricated [4].

In ME composites, the magnitude of coupling is determined by the extent of the mutual elastic strain coupling occurring at the interface of piezoelectric and magnetostrictive phases. For the effective coupling, the ME composite films with different geometry were synthesized by several different methods such as pulsed laser deposition, chemical solution deposition and aerosol deposition (AD) method [5–9]. While most of the reported ME nanocomposite films were limited in overall thickness which might be related to difference in thermal mismatch between individual phases and substrate, it was reported that AD method was adequate in fabricating thick films (>10 μm) with highly dense microstructure [8,9]. In addition, AD has an advantage on controlling the microstructures and complex connectivity [10], which are related with ME coupling. Thus, we pursued the synthesis of ME 3-0 nanocomposite thick films comprising of ferroelectric and magnetostrictive phases using AD.

For 3-0 composite films, we selected $0.9Pb(Zr_{57}Ti_{43})O_3$–$0.1Pb(Mn_{1/3}Nb_{2/3})O_3$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ for piezoelectric matrix material and magnetostrictive particles, respectively.

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Among various piezoelectric compositions, $0.9Pb(Zr_{57}Ti_{43})O_3$–$0.1Pb(Mn_{1/3}Nb_{2/3})O_3$ can be good candidate for ME composite because of its high piezoelectric voltage coefficient [11] which is most important figure of merit for ME composite. We previously reported that the ceramics with this composition had over voltage coefficient of 23 mVm/N [12].

2. Experimental

$0.9Pb(Zr_{57}Ti_{43})O_3$–$0.1Pb(Mn_{1/3}Nb_{2/3})O_3$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ powders were separately synthesized by conventional solid state oxide method by using reagent grade raw materials of PbO, ZrO_2, TiO_2, $MnCO_3$, and Nb_2O_5 and of NiO (99.9%, Kojundo Chem.), ZnO, and Fe_2O_3 (99.9%, all from Sigma–Aldrich Co. except NiO). For AD, PZT–PMnN and NZF powders was mixed with various weight ratio from 15 to 30% NZF. For homogenous mixing of two particles, shear mixer was employed. The mixed powders were combined with carrier gas to form an aerosol flow in chamber and ejected onto the Pt-coated silicon wafer. The film thickness was controlled in the range of 10–13 μm. The as-deposited film was annealed at 700 °C for 1 h in air atmosphere. A Pt-top electrode with diameter of 1.0 mm was deposited on the film by DC sputtering method.

XRD (D-MAX 2200, Rigaku Co., Tokyo, Japan) was used to identify the phases of the annealed films. The microstructures of the films were monitored by SEM (JSM-5800, JEOL Co., Tokyo, Japan). Dielectric properties were measured by Agilent 4294A impedance analyzer, and ferroelectric properties were characterized by P-LC100-K ferroelectric test system (Radiant Technologies, Albuquerque, NM). The magnetization of the composite films was measured vibrating sample magnetometer (7300 Series, LakeShore Cryotronics, Inc., Westerville, OH). The ME composite films were poled in silicone oil at 150 °C for 30 min before ME measurement. For the ME voltage coefficient measurement, an electromagnet was used to apply DC magnetic field, and the samples were placed in the center of the Helmholtz coil under an AC magnetic field (H_{ac} = 1 Oe). The charge induced from the ME composite films were measured and ME voltage coefficient was calculated with measured charge and capacitance of the film.

3. Results and discussion

Fig. 1 shows XRD patterns of 700 °C annealed films with NZF content variation. The composite films showed co-existence of perovskite (PZT–PMnN) and spinel (NZF) phases. Polycrystalline PZT–PMnN phase showed sharp peaks while NZF phase exhibited broad peaks might be due to its nanocrystalline structure [8,10]. Typically nanocrystalline with small amount of amorphous ceramic films are formed by AD and crystallization and/or grain growth occur during annealing process [11]. Based on above, the nano grains of PZT–PMnN phase was grown during annealing, but NZF phase was not markedly done. With increasing NZF content, peak intensities from NZF phase were slightly increased. Although the data was not shown in this article, energy dispersive spectroscopy also

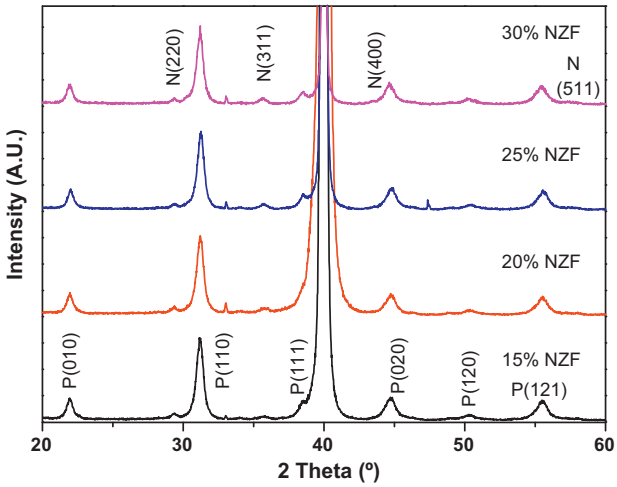

Fig. 1. XRD patterns of 700 °C annealed PZT–PMnN + NZF composite films (N: NZF phase).

showed the Pb/Fe ratio changes with NZF content variation. Thus, we can notice that AD can control the composition ratio of composite films by controlling raw power mixture.

The microstructures of the films were investigated by SEM and 20% NZF added composite film's cross-sectional micrographs are depicted in Fig. 2. All of other compositions also showed very similar microstructures with Fig. 2. It is illustrating highly dense microstructure and good adhesion with the substrate even after thermal annealing. The thickness of films was estimated to be in the vicinity of 10 μm.

Fig. 3(a) and (b) shows the variation of dielectric constant and loss factor before and after thermal annealing at 700 °C for 1 h. The dielectric constants and loss factors of as-deposited films at 1 kHz was measured to be around 80 and 0.05, respectively, regardless of composition. This low dielectric constant is due to low crystallinity of nano size grain [13]. To obtain enough dielectric and ferroelectric properties from the AD films, gains growth and crystallization are required via post annealing process [11]. As can be seen in Fig. 3, after annealing the films, dielectric constants were drastically improved and measured as 700–400. With increasing the NZF content, the dielectric constant of PZT–PMnN was linearly decreased because of rule of mixture [11,14]. Compared with general ME composite bulk materials [15], these values are almost in the

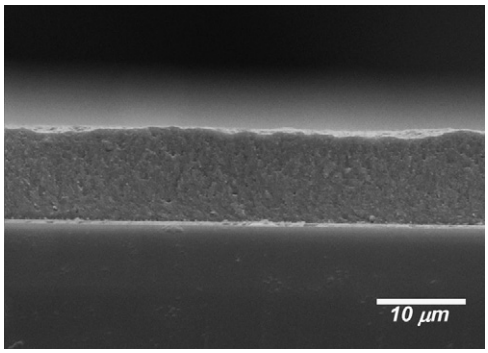

Fig. 2. SEM cross-sectional micrographs of PZT–PMnN + 20% NZF composite film.

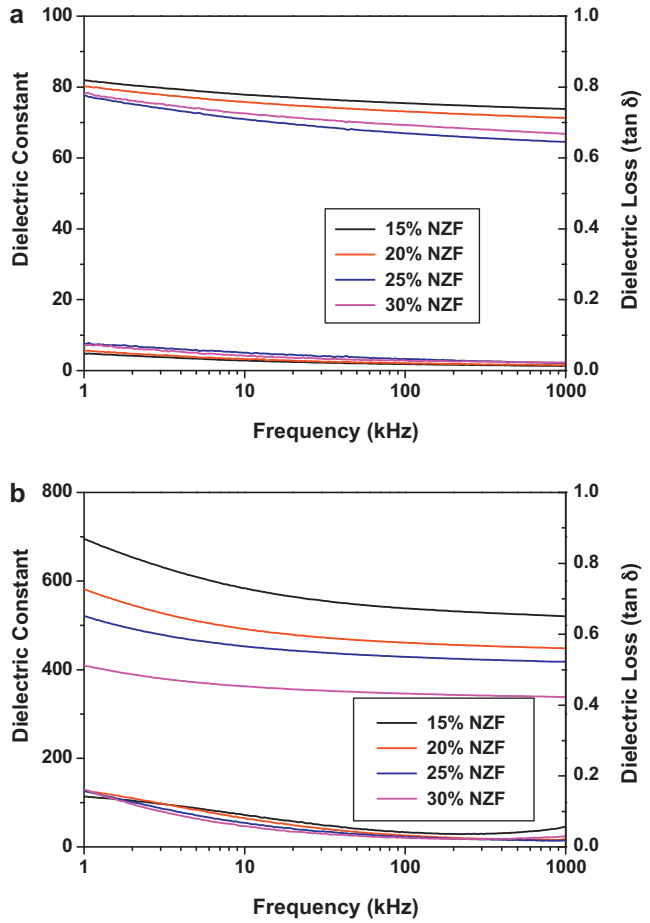

Fig. 3. Dielectric constants and losses according to the frequency of PZT–PMnN + NZF films with various NZF content. (a) As deposited and (b) annealed films.

similar range, which means the excellent quality of films. With increasing frequency, dielectric constant and loss factor decreased.

Fig. 4 shows the polarization–electric field curves for composite films at frequency of 100 Hz. Remnant polarization

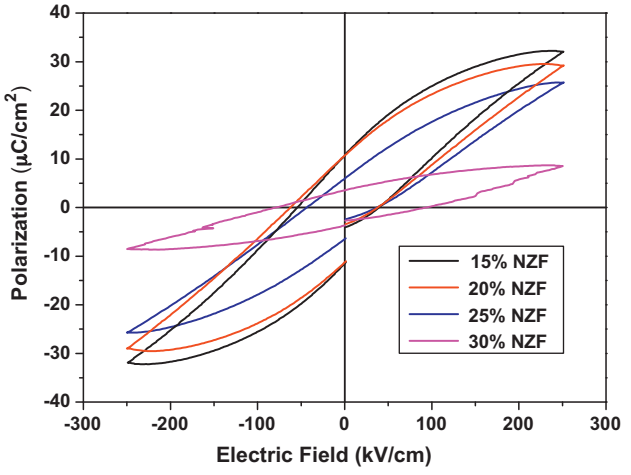

Fig. 4. *P–E* hysteresis loops PZT–PMnN + NZF films with different NZF content.

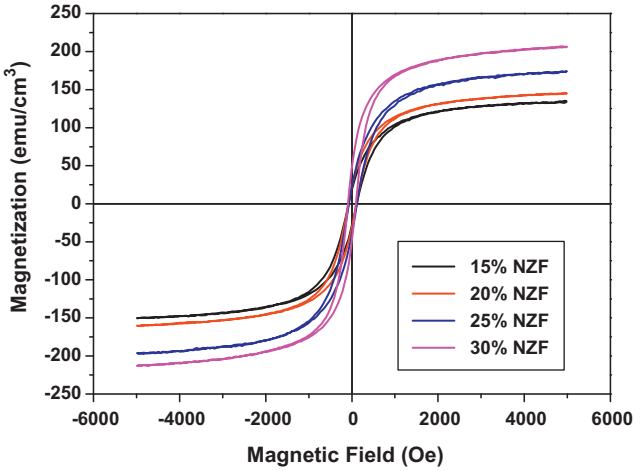

Fig. 5. *M–H* hysteresis loops PZT–PMnN + NZF films with different NZF content.

(P_r) decreased with increasing NZF content gradually. 30% NZF added films showed very low P_r and higher E_c compared to those of other lower content composite films. 30% NZF addition might cause inter-reaction of two phases, especially Fe diffusion into PZT–PMnN matrix making the piezoelectric materials harder. At an applied electric field of ~250 kV/cm, the magnitude of P_r and E_c of 20% NZF added film were measured to 10.5 μC/cm^2 and 40 kV/cm respectively.

The magnetization of films was measured using vibrating sample magnetometer as shown in Fig. 5 reflecting the ferromagnetic characteristics. With increasing NZF content, the remnant and saturated magnetizations were gradually increased and coercive magnetic fields were keeping the almost same value. This indicates that NZF content variation did not severely affect its own magnetic characteristics. The maximum ME voltage coefficient was measured by using an electromagnet to apply DC bias with films placed in the center of Helmholtz coil and driven with an AC magnetic field, H_{ac} = 1 Oe. The maximum ME voltage were monitored using a charge amplifier and oscilloscope, and Fig. 6 shows the result.

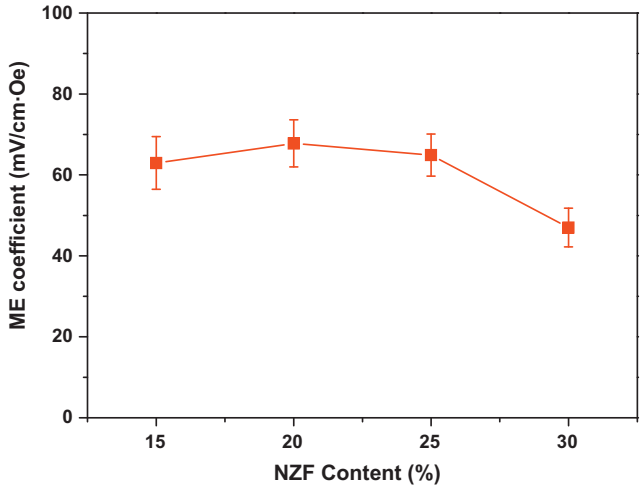

Fig. 6. Maximum ME coefficient of PZT–PMnN + NZF composite films as a function of NZF content.

The ME coefficients were not changed severely in that NZF content range of 15–25%, but there was drop when 30% NZF was added. The maximum ME output voltage was obtained to be 68 mV/cm Oe from 20% NZF added composite film. This magnitude is higher than that of the nanocomposite films made by other thin film process which had maximum ME output voltages under 40 mV/cm Oe [5–7].

4. Conclusions

ME composite thick films of PZT–PMnN and NZF were deposited on a Pt-coated Si substrate using AD with different NZF content. With increasing NZF content, dielectric and ferroelectric properties were gradually decreased while magnetizations were improved. The 20% NZF added film were found to exhibit the maximum ME coefficient of the order of 68 mV/cm Oe which is higher than that of ME composite films by other thin film processes. It is noticeable that AD can control the composite content ratio rather easily.

Acknowledgements

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