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The magnetoelectric effect in Ni–Fe alloy/ZnO nanorod array composites

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Abstract

Ni–Fe alloy/ZnO nanorod composites were fabricated and the magnetoelectric effect was demonstrated. The ZnO and Ni–Fe alloy serve as the piezoelectric phase and the magnetostrictive phase in the nanocomposite, respectively. Since the nanorod structure possesses the inherent nature of a large surface-to-volume ratio, it greatly enhances the interplay between the piezoelectric and magnetostrictive coupling. Besides, the substrate clamping effect can be avoided. Our newly devised composite therefore provides a different species for magnetoelectric applications. It is interesting that the magnetoelectric voltage coefficient determined by the direct measurement method can reach a value as high as $0.48 \text{ mV cm}^{-1} \text{ Oe}^{-1}$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The magnetoelectric (ME) effect in composites has been extensively investigated in the last few decades [1–3]. The effect is defined as the induction of electric polarization by a magnetic field, or inversely the induction of magnetization by an electric field. An ME composite generally consists of a piezoelectric phase and a magnetostrictive phase, and it is the strain coupling between the two phases that makes this composite show magnetoelectricity. Recently, several research groups have successfully fabricated magnetoelectric nanocomposites by pulsed laser deposition, in which perovskite ceramics and magnetic oxides were used as epitaxial compositions [4–6]. In general, perovskite ceramics, such as BaTiO_3 and lead zirconate titanate (PZT), are the most widely used piezoelectric material in ME composites. To the best of our knowledge, there has been no report on the introduction of semiconductors into the piezoelectric phase of ME composites.

Zinc oxide is a semiconductor that has drawn extensive attention in research because of its potential application in light-emitting devices, gas sensors, and power generators. Recently, ZnO nanorods have been successfully demonstrated as a good nanogenerator based on their excellent piezoelectric properties [7]. This study is aimed at creating a nanocomposite consisting of nickel–iron magnetic alloy and ZnO nanorods

composite with a large magnetoelectric effect, with Ni–Fe and ZnO serving as the magnetostrictive phase and the piezoelectric phase, respectively [7, 8]. There are two main reasons to extract a magnetoelectric effect in our newly designed nanocomposite. First, we are able to take advantage of the unique property of ZnO, which simultaneously has good piezoelectric as well as semiconducting behavior. Second, with the inherent nature of the large surface-to-volume ratio of nanorods, the interaction between piezoelectric and magnetostrictive phases can be greatly enhanced. Besides, compared with 2–2 type (laminar–laminar) ME nanocomposites, the nanorod arrays can avoid the clamping effect of the substrates [9], so a stronger ME coupling is expected. We consider our alloy/nanorod array composites as a mixture of 2–2 type and 1–3 type phase connectivity, which contains the stronger ME coupling in 1–3 type and easier direct ME measurement in 2–2 type samples [6, 9].

2. Experimental details

The ZnO nanorod arrays were synthesized by an electrochemical deposition method, which was performed in a conventional electrochemical reaction cell with a standard three-electrode configuration. A Zn foil and a standard saturated calomel electrode (SCE) in saturated KCl solution were used as the counter electrode and the reference electrode, respectively.

The ITO substrate was used as the working electrode. Right before the electrochemical deposition, the ITO substrates were ultrasonically rinsed in acetone, alcohol, and distilled water successively. The electrolyte was an 300 ml aqueous solution containing 1 mM $\text{Zn}(\text{NO}_3)_2$, 0.1 M KCl, and 10% formamide. The reaction temperature was kept at 65 °C and the initial pH value of the electrolyte was 6. A stationary potential of -1.1 V versus SCE was applied on the working electrode. After two hours of electrochemical deposition, ZnO nanorod arrays were obtained on the ITO substrate.

To prevent direct contact of the ITO and Ni-Fe alloy (described later), a thin layer of ZnO was spin-coated on an as-synthesized ZnO sample by the sol-gel method described in [10]. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was first dissolved in methanol and a 0.20 M solution was prepared. The solution was spin-coated on an as-synthesized ZnO nanorod sample at 3000 rev min^{-1} , and then dried in air at 80 °C. The sample was subsequently annealed in air at 530 °C. Three cycles of the procedure were applied, and a thin layer of ZnO was obtained on the surface of the whole sample.

A thin layer of Ni-Fe (wt 75%–25%, thickness 100 nm) alloy was prepared by a high vacuum magnetron system with a base pressure lower than 1.0×10^{-8} Torr. It was deposited on the ZnO nanorods by dc power with deposition voltage of 320 V in a 5×10^{-3} Torr Ar ambient. The morphology of the ZnO nanocomposites was observed by a field emission scanning electron microscopy (FE-SEM, JSM-6500F) equipped with energy-dispersive spectrometry (EDS) equipment. The microstructural characterization of the nanocomposites was performed using field-emission-gun transmission electron microscopy (TEM, FEI Tecnai F20), operated at 200 keV. X-ray diffraction (XRD) was carried out with a PANalytical X'Pert Pro diffractometer with Cu $K\alpha$ radiation at 45 kV and 40 mA.

The ME voltage coefficients were measured by the direct ME measurement method [11]. A thin layer of Au sputtered on the Ni-Fe alloy and the ITO substrates served as electrodes and was connected to a lock-in amplifier (Stanford SR830). The ME composites were operated in both TM (transverse magnetization) mode and LM (longitudinal magnetization) mode, with the directions defined with respect to the axes of the ZnO nanorods. The sample was placed into a set up which contained the combination of a dc bias magnetic field and an ac magnetic field. The sample was shielded from stray electric fields. An electromagnet and a Helmholtz coil were used to apply a bias magnetic field H and an ac field δH in parallel, respectively. To enhance the accuracy of our measurement, lock-in detection was implemented. The lock-in amplifier measured the induced ME voltage δV_H , and the ME voltage coefficient α_H was then given by

$$\alpha_H = \delta V_H / \delta H t, \quad (1)$$

where t is the thickness of the sample.

3. Results and discussion

Figure 1(a) shows an SEM image of as-synthesized hexagonal ZnO nanorods. The nanorods have an average diameter of

Figure 1. As-grown ZnO nanorods on ITO glass substrate: (a) bird's eye view SEM image of the nanorod array; (b) 2θ scan x-ray diffraction pattern.

about 100 nm. A typical XRD pattern is shown in figure 1(b). The strong (002) peak in the XRD pattern clearly indicates the nanorods prefer [002] growth. Comparing figure 1(a) with figure 1(b), we can conclude that the ZnO nanorods have the wurtzite structure and are aligned along the direction perpendicular to the ITO substrate.

To confirm the magnetron sputtered layer of Ni-Fe on ZnO, we also conducted an EDS spectrum measurement, and the result is shown in figure 2(a). The zinc and oxygen atoms both come from the ZnO nanorods, while the nickel and iron atoms come from the coating alloy. Analyzing from the EDS spectrum we find that the weight ratio of Ni to Fe is approximately 3:1, which is the same as the magnetron sputtered target. This result provides good evidence to confirm that the Ni-Fe alloy has been successfully sputtered on the ZnO nanorods, as expected. Figure 2(b) is a magnified SEM image after Ni-Fe alloy was coated on ZnO nanorods. The surfaces of the nanorods are covered by a granular layer, and the roughness is comparatively larger than that of as-synthesized nanorods. Figure 2(c) shows a cross-sectional SEM image of the sample. A ZnO buffer layer, fabricated by the sol-gel method, can be clearly seen on the substrate. The average length of the ZnO nanorods is about 1 μm , and therefore we use the sample thickness $t = 1 \mu\text{m}$ for the calculation of ME coefficients, as indicated in equation (1).

Figure 2. (a) EDS spectrum, (b) magnified SEM image, and (c) cross-sectional view of the Ni-Fe coated ZnO nanorods.

In order to examine the microstructure quality of the nanocomposite consisting of a Ni-Fe coating layer and ZnO nanorods, we obtained transmission electron microscopy (TEM) images as shown in figure 3. Figure 3(a) shows a representative TEM bright-field (BF) image of the ZnO nanorods with coated Ni-Fe alloy, and the inset is the enlarged image of figure 3(a). It reveals a core-shell structure: the core is the ZnO nanorod, ~500 nm in diameter, and the shell is the Ni-Fe coating layer, ~60 nm in thickness. A further inspection of the selected area diffraction pattern (SADP) of the ZnO@Ni-Fe core-shell structure, shown in figure 3(b), revealed the mixture of regular spots with a dashed hexagonal and ring pattern, indicating the single-crystal nature of the ZnO nanorod and polycrystalline nature of the Ni-Fe coating

Figure 3. (a) TEM BF image of a ZnO nanorod with a coated thin layer of Ni-Fe alloy. The inset is the enlarged image of (a). (b) The corresponding SADP of the core-shell structure. (c) A representative HRTEM image of the Ni-Fe alloy from the square region in (a).

layer, respectively. Furthermore, the representative high-resolution TEM (HRTEM) image, enlarging the square region in figure 3(a), also indicates the polycrystalline nature of the Ni-Fe coating layer with particle size of ~5 nm, as shown in figure 3(c), and consistent with the SADP in figure 3(b). As mentioned above, we can clearly observe that both the Ni-Fe coating layer and the ZnO nanorods have excellent crystalline structures, and the interface is rather sharp. This result is beneficial for our measurement of the ME effect.

Figure 4. Transversal (TM mode) and longitudinal (LM mode) magnetolectric voltage coefficients α_H (the lines are to guide the eye).

Direct measurements of the ME voltage coefficient were obtained under an ac magnetic field $\delta H = 1.40$ Oe at a frequency of 1.0 kHz and in a bias field H range 0–6.0 kOe. Figure 4 shows the ME voltage coefficients in the TM and LM modes. Both the transversal (TM mode) and the longitudinal (LM mode) ME coefficients increase monotonically as the bias H increases. However, the longitudinal ME coefficients increase more quickly than the transverse ones. The maximum observed longitudinal and transversal ME coefficients in our measurements, corresponding to bias field 6.0 kOe, are $0.48 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ and $0.34 \text{ mV cm}^{-1} \text{ Oe}^{-1}$, respectively.

As we can clearly see from figure 4, the longitudinal ME coefficients are relatively larger than the transversal ME coefficients. The difference of ME coupling may originate from the shape anisotropy of ZnO nanorods. In general, the ME voltage coefficients are directly proportional to the magnetostrictivity $q = \delta\lambda/\delta H$, where λ is the magnetostriction and H is the magnetic field. However, considering the demagnetization effect, the effective magnetostrictivity of a sample can be expressed as [12]

$$q' = q / \left(1 + \frac{D}{4\pi} \chi^\sigma \right), \quad (2)$$

where q is the theoretical magnetostrictivity, D is the demagnetization factor, and χ^σ is the susceptibility under constant stress condition. For a nanorod, the demagnetization factor for fields perpendicular to its axis is larger than that for fields along the axis, i.e. $D_\perp > D_\parallel$ [13]. Thereby we obtain

$$q'_\perp < q'_\parallel, \quad (3)$$

where $q'_\perp$ and $q'_\parallel$ correspond to the transverse fields (TM mode) and the longitudinal magnetic fields (LM mode), respectively. Hence the stronger ME coupling in transversal magnetic fields may be attributed to the discrepancy between the demagnetization factors resulting from the shape anisotropy of the nanorods. In order to demonstrate the enhanced ME effect in nanocomposites, we have performed a similar experiment

with a sample with Ni–Fe alloy thin film deposited on ZnO thin film. It is found that the detected ME signal is in the noise level, which can be neglected.

The observed ME coefficient in our experiment, $0.48 \text{ mV cm}^{-1} \text{ Oe}^{-1}$, is not high compared with concurrent values observed in perovskite composites [5, 6]. The leakage current may account for this result. Since ZnO is an n-type semiconductor with relatively lower resistivity than perovskite materials, such as BaTiO_3 , leakage current may occur during the direct measurement, resulting in significant loss of ME signals. We suggest that, on reducing the leakage current by adopting a different piezoelectric semiconductor with higher resistivity than ZnO, a higher ME coefficient can be obtained

4. Summary

In summary, we have successfully fabricated an ME composite consisting of magnetostrictive Ni–Fe alloy and piezoelectric ZnO nanorods. XRD and SEM confirmed the good alignment of the nanorods, and TEM images and EDS spectrum confirmed that the Ni–Fe alloy had been successfully coated on the nanorods. The magnetolectric voltage coefficients in LM and TM modes exhibit different coupling strength, which may be explained by the difference between the demagnetization factors in these two operation modes. Compared with reported ME composites, the large ME coefficient shown here demonstrates that a nanocomposite consisting of a semiconductor and a magnetic alloy may open up an alternative pathway for the study of the magnetolectric effect.

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References

- [1] Ramesh R and Spaldin N A 2007 *Nat. Mater.* **6** 21
- [2] Fiebig M 2005 *J. Phys. D: Appl. Phys.* **38** R123–52
- [3] Nan C W, Bichurin M I, Dong S X, Viehland D and Srinivasan G 2008 *J. Appl. Phys.* **103** 031101
- [4] Zheng H *et al* 2004 *Science* **303** 661
- [5] Zavaliche F *et al* 2005 *Nano Lett.* **5** 1793
- [6] Zhang Y, Deng C Y, Ma J, Lin Y H and Nan C W 2008 *Appl. Phys. Lett.* **92** 062911
- [7] Wang Z L and Song J 2006 *Science* **312** 242
- [8] Boroth R M 1993 *Ferromagnetism* (Piscataway, NJ: IEEE Press)
- [9] Nan C W, Lin G, Lin Y H and Chen H 2005 *Phys. Rev. Lett.* **94** 197203
- [10] Natsume Y and Sakata H 2000 *Thin Solid Films* **372** 36
- [11] Srinivasan G, Rasmussen E T, Gallegos J, Srinivasan R, Bokhan Yu I and Laletin V M 2001 *Phys. Rev. B* **64** 214408
- [12] Clark A E and Wun-Fogle M 1989 *IEEE Trans. Magn.* **25** 3611
- [13] Whitney T M, Jiang J S, Searson P C and Chien C L 1993 *Science* **261** 1316