Flexible Sm–Fe/polyvinylidene fluoride heterostructural film with large magnetoelectric voltage output

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(Received 3 June 2010; accepted 5 November 2010; published online 22 November 2010)

The Sm–Fe/polyvinylidene fluoride (PVDF) heterostructural film was prepared by depositing Sm–Fe nanoclusters onto the flexible PVDF film using cluster beam deposition method. The PVDF film acts as both piezoelectric layer and substrate. The heterostructural film showed the well-defined microstructures in which the Sm–Fe layer was assembled by the nanoparticles, and the interface between Sm–Fe and PVDF layers was clear. The heterostructural film possessed evident magnetic anisotropy with in-plane easy axis and exhibited large voltage output under the magnetic bias. Such flexible heterostructural film with large magnetoelectric output makes it promising to be widely used for the weak magnetic-field detection. © *2010 American Institute of Physics*.
[doi:10.1063/1.3520495]

Recent requirement to develop novel multifunctional integrated devices has drawn intense interest in the multiferroic magnetoelectric films.[1,2] By magnetic-mechanical-electric coupling based on the interfacial stress transferring, the multiferroic composite films combined with piezoelectric and magnetostrictive components could exhibit stronger magnetoelectric coupling than single-phase compound films.[3,4] So in the current stage the multiferroic composite films are ideal candidates in designing integrated magnetic and electronic microdevices, especially in the field of weak magnetic-field detection. Up to now, many efforts have been made to prepare all kinds of multiferroic composite films.[5–8] However, since the multiferroic composite films are generally deposited onto the hard substrates (e.g., $Pt/Ti/SiO_2/Si$ wafer), the coupling interaction between the piezoelectric and magnetostrictive phases is significantly depressed due to the stress clamping effect of the hard substrate, consequently resulting in the weak magnetoelectric coupling. For example, in a typical PZT $[Pb(Zr,Ti)O_3]/CoFe_2O_4/PZT$ heterostructural film deposited on the $Pt/Ti/SiO_2/Si$ wafer, the induced voltage output under external magnetic field is only several microvolts.[8] To measure so small voltage, a complex post-handling circuit with high cost is necessary to enlarge the signal and avoid the noise.

In this letter, we report the large magnetoelectric voltage output in a flexible heterostructural film consisting of nanostructured rare-earth Sm–Fe alloy layer with giant negative magnetostriction and flexible polyvinylidene fluoride (PVDF) polymer film layer. In such heterostructure, the PVDF film acts as both piezoelectric layer and substrate. Since PVDF is so flexible (the Young's modulus is only ~1.5 GPa) (Ref. 9), its stress clamping effect on the Sm–Fe layer could be completely ignorable, consequently leading to more efficient interface stress transfer. Moreover, PVDF has a big piezoelectric voltage constant g_{31} of ~0.22 V m/N, much higher than that of piezoelectric ceramics (e.g., g_{31} ~0.01 V m/N for the typical PZT ceramic),[9] so it is expected that the PVDF layer could generate large induced voltage output even under a small interface stress. In addition, the usage of Sm–Fe alloy with giant negative magnetostriction coefficient ($\sim 1600 \times 10^{-6}$ for the typical bulk[10]) is also crucial for the enhancement of magnetoelectric coupling in the heterostructure. When the Sm–Fe film is under a compressive stress along the film surface, its magnetic easy axis will be parallel to the film surface and consistent with the interfacial stress transferring direction. (This behavior will be further discussed in the result section.) As a result, the magnetic-mechanical-electric coupling based on the interfacial stress transferring will be more efficient.

However, it is difficult to prepare Sm–Fe/PVDF heterostructural film by conventional film preparation means because the phase formation temperature of Sm–Fe alloy film is high, which unavoidably brings about serious structure breakdown of PVDF polymer when the Sm–Fe alloy is deposited onto its surface. In this work, we developed an available method, namely the low energy cluster beam deposition (LECBD) technique, to prepare such heterostructural film. During LECBD, the phase formation of Sm–Fe nanoclusters is formed in the front condensation chamber under high temperature (beyond 500 °C), while the Sm–Fe cluster beam deposition is achieved in the rear vacuum chamber at room temperature. Accordingly, the polymer structure as well as the piezoelectric property of the PVDF film will not be destroyed.

The Sm–Fe clusters were produced by a dc magnetron plasma aggregation cluster source. A $SmFe_2$ alloy plate was used as the sputtering target and the sputtering power was set at 60 W. A self-standing PVDF film (purchased from Mingschin Polymer Co., Ltd., China) with thickness of ~6 μm and piezoelectric strain coefficient d_{33} of 39 pm/V (measured by a piezoelectric d_{33} meter) was used as the substrate. During LECBD, the Sm–Fe cluster was first produced in the former condensation chamber with a pressure of ~100 Pa in the argon ambience. Then the Sm–Fe clusters sprayed out from a skimmer to form a cluster beam and entered into the

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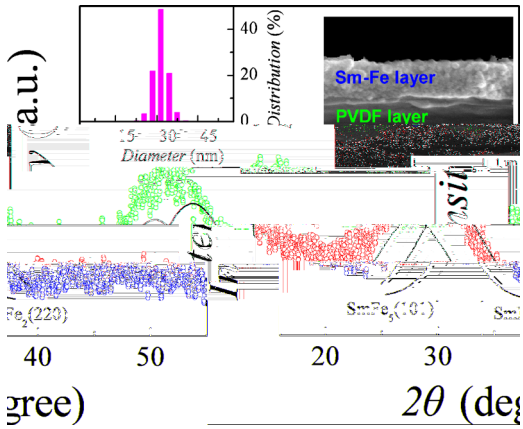

FIG. 1. (Color online) XRD pattern of the Sm–Fe/PVDF film. The broad diffraction peak located at ~31° is fitted into two peaks. The inset is the cross-section SEM image of the Sm–Fe/PVDF film and graph of population vs size distribution of the nanoparticle in Sm–Fe layer.

rear deposition chamber with pressure of 3×10^{-5} Pa. The Sm–Fe cluster was finally deposited onto the PVDF film surface at room temperature to form cluster-assembled Sm–Fe layer with thickness of ~550 nm. For the electric measurement, an Au electrode layer was subsequently deposited onto the Sm–Fe layer surface by ion sputtering method.

Figure 1 presents the x-ray diffraction (XRD) pattern of the Sm–Fe/PVDF film. A broad diffraction peak located at ~31° is observed. Referred to the standard XRD database, we found that this peak is actually a superposition of the $SmFe_5$ (101) diffraction peak at 29.9° and $SmFe_2$ (220) diffraction peak at 34.1°. The inset of Fig. 1 shows the cross-section scanning electron microscope (SEM) image of the Sm–Fe/PVDF film and the graph of population versus the size distribution of the Sm–Fe nanoparticle in Sm–Fe layer. One observes that the Sm–Fe layer is uniformly assembled by the nanoparticles with a narrow lognormal size distribution. The average size of the nanoparticles is ~31.5 nm. In addition, the interface between PVDF and Sm–Fe layers is clear and no transition layer appears. We further measured the piezoelectric property of the PVDF film and found that its d_{33} value still maintained its original value even after it was covered by the Sm–Fe layer. All these indicate that it is successful to prevent the structure breakdown of PVDF during LECBD preparation process.

Figure 2 plots the magnetic field dependence of magnetostriction for the Sm–Fe film. It is seen that the film exhibits a strong negative magnetostrictive effect with a saturation value of $\sim750\times10^{-6}$ at magnetic field of ~7.0 kOe. The inset of Fig. 2 presents both in-plane and out-of-plane magnetic hysteresis loops for the Sm–Fe/PVDF film. One observes that the film is easier to be magnetized along the film plane, indicating that it possesses magnetic anisotropy with an in-plane magnetic easy axis. It is well known that the magnetic anisotropy is related to the magnetostriction and applied stress, which can be described as follows:[11]

$$E_\sigma = -\tfrac{3}{2}\lambda\sigma\cos^2\theta, \tag{1}$$

where E_σ is the magnetic anisotropy energy induced by the stress, λ is the saturation magnetostriction coefficient, σ is the applied stress, and θ is the angle between the magnetization and the plane of the film. According to this equation, under the tensile stress along the film surface, the film with positive magnetostrictive effect would be easily magnetized along the film plane. While for the present cluster-assembled Sm–Fe alloy film, since there exists a small amount of residual argon carrier gas molecules in the film, it is actually subjected to a residual compressive stress.[12–14] Accordingly, under the combining influence of negative magnetostriction and compressive stress, the Sm–Fe film could also generate the magnetic anisotropy with an in-plane magnetic easy axis, which makes the magnetic-mechanical-electric coupling along the interface to be more efficient.

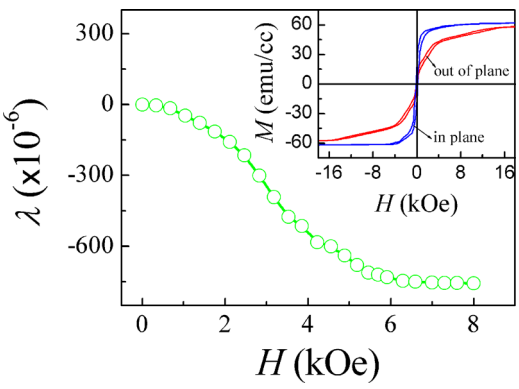

FIG. 2. (Color online) Magnetostriction λ dependence of Sm–Fe film on magnetic field H. The inset is the magnetic hysteresis loops for the Sm–Fe/PVDF film measured at room temperature.

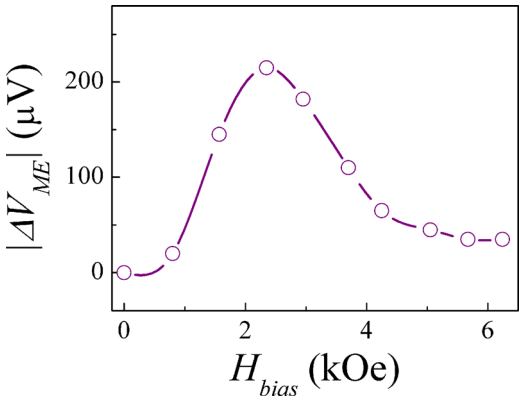

FIG. 3. (Color online) Induced voltage increment $|\Delta V_{ME}|$ as a function of magnetic bias H_{bias}.

For the magnetoelectric coupling measurement, a magnetic bias H_{bias} together with a small alternating magnetic field $H=5$ Oe and frequency $f=1.0$ kHz was applied parallel to the film plane. The induced voltage increment $|\Delta V_{ME}|$ was recorded by a lock-in amplifier. Figure 3 plots the $|\Delta V_{ME}|$ value as a function of H_{bias} for the Sm–Fe/PVDF film. It is seen that the film exhibits a large voltage output under the external magnetic bias. The $|\Delta V_{ME}|$ value increases with increasing H_{bias}, reaching the maximum value of $|\Delta V_{ME}|\sim210$ μV at $H_{bias}=2.3$ kOe, and then drops. Compared with the previous investigations, the magnetoelectric voltage output in the present Sm–Fe/PVDF film is remarkably large, almost being two orders higher than that of typical all-oxide $PZT/CoFe_2O_4/PZT$ film deposited on the $Pt/Ti/SiO_2/Si$ wafer,[8,15] and being about one order of the Tb–Fe/PZT film.[14] The large magnetoelectric output in the Sm–Fe/PVDF film makes it to be significantly sensitive to the magnetic field, thus the posthandling circuit could be greatly simplified. Moreover, since the Sm–Fe/PVDF film is

so flexible, it could be freely tailored to various size or rolled into all kinds of shapes to fit any application requirement, which makes it promising to be widely used for the weak magnetic-field detection in various cases.

To further understand the large magnetoelectric voltage output in the present Sm–Fe/PVDF film, a simple model was introduced to describe it.[16] Assuming that the Sm–Fe/PVDF film is under an in-plane magnetic bias, based on the simple beam theory and plane stress condition, the induced voltage output in the PVDF layer can be derived,[16]

$$V_{\text{out}} = 2 \times g_{31} \times \frac{E_s E_p t_s t_p \Delta\varepsilon_0}{(1-v)(E_s t_s + E_p t_p)}, \quad (2)$$

where E, t, $\Delta\varepsilon_0$, and v are the elastic modulus, thickness, linear strain of PVDF, and passion ratio, respectively. The subscripts s and p denote Sm–Fe and PVDF, respectively. It is seen that the induced V_{out} in piezoelectric layer is directly proportional to g_{31} value. That is to say, the large g_{31} value of PVDF film is important for the large magnetoelectric voltage output. In addition, we notice that the magnetoelectric voltage output is also dependent on the thickness ratio of magnetostrictive and piezoelectric layers. At fixed thickness of the PVDF layer, the V_{out} of heterostructural film increases with increasing the thickness of Sm–Fe layer. Therefore, it may be a suitable strategy to deposit thicker Sm–Fe layer in the practical applications.

The unique cluster-assembled nanostructure in the Sm–Fe layer is also responsible for the large magnetoelectric voltage output in the Sm–Fe/PVDF film. In this work, by adjusting the preparation parameters such as Ar carrier gas flow and condensation chamber length, the average size of nanoparticles in the Sm–Fe layer was well controlled as ~31.5 nm. Miiham *et al.* estimated that the domain wall width of Sm–Fe alloy is ~15 nm.[17] Lewis *et al.* reported that the exchange coupling distance is about twice of the domain wall width for the magnetic nanoparticles.[18] Accordingly, we infer that the nanoparticle size in the Sm–Fe layer is optimal for the efficient magnetic exchange coupling, which could cause the Sm–Fe layer to produce higher magnetoelastic energy. As a result, the magnetoelastic stress transferred from Sm–Fe to PVDF layer increases, consequently enhancing the magnetoelectric coupling of the Sm–Fe/PVDF film.

In summary, the flexible Sm–Fe/PVDF heterostructural film with clear interface has been successfully prepared by the LECBD method. By using the flexible PVDF polymer film as the substrate, the substrate clamping effect on the magnetoelectric coupling of the heterostructural film is completely eliminated. The heterostructural film exhibits large magnetoelectric voltage output, which is mainly attributed to the large piezoelectric voltage constant in the piezoelectric PVDF layer and high magnetic anisotropy with in-plane magnetic easy axis as well as giant negative magnetostriction in the ferromagnetic Sm–Fe layer.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 10904065, 10774070, and 50972055), the Provincial Nature Science Foundation of Jiangsu in China (Grant No. BK2008024), the National Key Projects for Basic Research of China (Grant Nos. 2010CB923401 and 2009CB623303), and the Program for New Century Excellent Talents in University of China (Grant No. NCET-07-0422).

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