

## Spin-spray deposited multiferroic composite $\text{Ni}_{0.23}\text{Fe}_{2.77}\text{O}_4/\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ with strong interface adhesion

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(Received 15 February 2008; accepted 27 March 2008; published online 15 April 2008)

$\text{Ni}_{0.23}\text{Fe}_{2.77}\text{O}_4$  (NFO)/ $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) multiferroic composites were synthesized by spin-spray deposition of NFO film onto PZT at 90 °C. Strong interface adhesion between NFO and PZT was observed, which was verified by high resolution transmission electron microscopy indicating excellent wetting between the NFO and PZT, and by the strong magnetoelectric coupling in the NFO/PZT multiferroic composite showing an electric field induced remnant magnetization change of 10%. This strong interface adhesion and low-temperature spin-spray synthesis of multiferroic materials provide an alternative route for novel integrated multiferroic materials and devices. © 2008 American Institute of Physics. [DOI: 10.1063/1.2911743]

Multiferroic composite materials with two constituent phases of ferro-ferrimagnetic and ferroelectric phases have drawn an increasing amount of interest due to their potential applications in many multifunctional devices.<sup>1–10</sup> Such materials can display a stress/strain mediated magnetoelectric (ME) effect, i.e., a dielectric polarization variation as a response to an applied magnetic field or an induced magnetization by an external electric field, which enables many device applications. A strong adhesion at the interface between the two constituent phases, ferro-ferrimagnetic and the ferroelectric phases, is crucial in achieving the stress mediated ME coupling.<sup>11–13</sup> Several synthesis methods have been developed for multiferroic composite materials with different levels of strength in interface bonding,<sup>11,14</sup> such as glue bonding with different kinds of glue and glue thickness,<sup>10</sup> solid state sintering<sup>15</sup> for bulk multiferroic composite materials, pulsed laser deposition (PLD),<sup>16–19</sup> physical vapor deposition,<sup>20</sup> and sol-gel process for thin film multiferroic materials.<sup>21–24</sup>

Spin-spray deposition process, which was invented in 1983, is a novel technique to directly plate crystalline spinel ferrite film with different compositions from an aqueous solution at a temperature less than 90 °C.<sup>25</sup> Conventional ferrite film preparation methods such as sputtering, molecular beam epitaxy, PLD, etc., require high temperatures (well above 600 °C), however, spin-spray technique can produce high quality polycrystalline ferrite films at a low temperature in between 25–90 °C. Several chemical reactions are involved in ferrite spin-spray process, which consist of (a) adsorption of  $\text{Fe}^{2+}$  and other ions  $\text{M}^{n+}$  ( $\text{M}=\text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{etc.}$ ) on the substrate surface mediated by OH groups, (b) oxidation process expressed by  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e$ , and (c) ferrite film formation accompanying with hydrolytic dissociation.<sup>26,27</sup> Spin-spray deposited ferrites provide great opportunities for low-temperature synthesized multiferroic composite materials on ferroelectric substrates. Since new chemical bonds are

formed during spin-spray process, strong adhesion between the spin-spray deposited ferrite film and ferroelectric substrate can be expected, which is critical for ME coupling. Typical ferroelectric materials such as  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) can be an excellent supplier of OH groups on its surface, thus facilitating the formation of ferrite film on its surface through spin-spray deposition. In addition, the good lattice match between the perovskite PZT ( $a=4.03 \text{ \AA}$ ) and spinel ferrites ( $a=8.33 \text{ \AA}$ ) may lead to excellent wetting between the ferrite phase and PZT, thus, leading to strong interface bonding that is important for achieving strong ME coupling.

In this work, we report an alternative synthesis method for composite multiferroic materials, in which pure ferrite phase was spin-spray deposited onto PZT. Strong interface adhesion between the ferrite and PZT phase was observed, which was verified by examining the atomic arrangements at the interface by transmission electron microscopy and by the strong ME coupling.

Multiferroic composite material  $\text{Ni}_{0.23}\text{Fe}_{2.77}\text{O}_4$  (NFO)/ $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) was obtained by spin-spray deposition of NFO ferrite on PZT substrates at 90 °C. Commercially available PZT substrate with a thickness of 0.5 mm was used, which was treated in dilute HCl acid solution containing  $\text{Fe}^{2+}$  for 1 min before the spin-spray process to form a seed layer for the ferrite film. An aqueous solution with 1.15 mM  $\text{Ni}^{2+}$  and 13.2 mM  $\text{Fe}^{2+}$ , and a pH value of 4.0 was used as ferrite precursor solution. At the same time, an aqueous oxidation solution with 2 mM  $\text{NaNO}_2$  and 140 mM  $\text{CH}_3\text{COONa}$ , and a pH value of 8.0 was used. Through separate nozzles, these two solutions were simultaneously sprayed at a flow rate of 40 ml/min onto a spinning hot PZT substrate at 90 °C with a rotation speed of 150 rpm.  $\text{N}_2$  gas was blown into the chamber to mitigate the oxidation effects from the oxygen in air. After 30 min of plating, a uniform NFO film on PZT with strong adhesion and the thickness of 1  $\mu\text{m}$  was obtained with a growth rate of ~30 nm/min.

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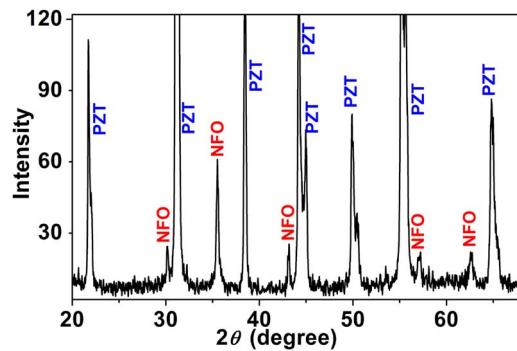


FIG. 1. (Color online) X-ray diffraction pattern of spin-sprayed Ni ferrite film on PZT substrate.

NFO films were deposited using identical spin-spray processing onto three different substrates of glass, alumina, and PZT. Strongest adhesion was observed in the NFO/PZT multiferroic system through simple tape testing. Figure 1 shows the x-ray diffraction pattern of spin-sprayed NFO/PZT. Pure spinel NFO ferrite phase and perovskite PZT phase are clearly identified with no obvious preferential crystallographic orientations. The surface morphology of the NFO was examined by atomic force microscope, which displays the mean grain size of  $\sim 300$  nm and the roughness of 10 nm, or 1% of the ferrite film thickness.

To further understand the origin of the strong adhesion between the NFO/PZT phases, the interface between NFO and PZT was investigated by high angle annular dark field (HAADF) scanning transmission electron microscopy image (Z-contrast), as shown in Fig. 2(a). A uniform ferrite film with a thickness of 1  $\mu\text{m}$  can be identified on the PZT phase, no voids were observed at the NFO/PZT interface. It is interesting to note that the NFO ferrite phase was growing into the small surface crack of the PZT phase with a crack width of  $\sim 100$  nm (area I), as shown in Fig. 2(b), which was proved by the energy dispersive x-ray results. This indicates the excellent wetting between the NFO ferrite phase and the PZT phase during the spin-spray deposition process, which leads to a tight interface and a strong adhesion between the two phases. A high resolution transmission electron microscope (HRTEM) image of the NFO/PZT interface was shown in Fig. 2(c), which shows a clearly tight interface between the ferrite NFO and ferroelectric PZT phases without obvious lattice matching, even though the lattice parameter of the spinel NFO and the perovskite PZT phases are well matched with the NFO lattice parameter being very close to two times of PZT.

Magnetic hysteresis loops of NFO ferrite on PZT are presented in Fig. 3(a). Well-defined magnetic hysteresis

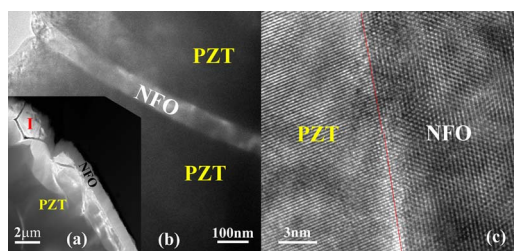


FIG. 2. (Color online) A cross-sectional HAADF image of NFO/PZT (a), HRTEM of Ni ferrite growing in PZT crack (b), and HRTEM ferrite and PZT interface images (c).

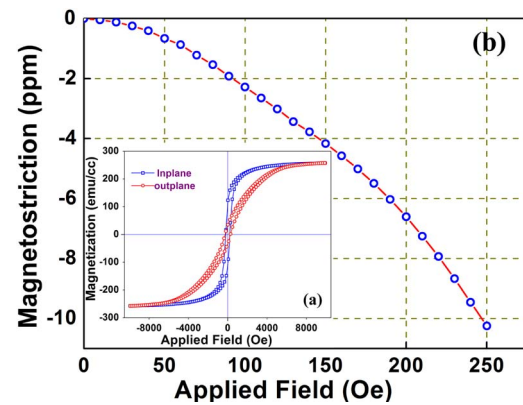


FIG. 3. (Color online) Typical magnetic hysteresis loops (a) and magnetostriction (b) of spin-sprayed Ni ferrite film on PZT.

loops were observed when external magnetic field is applied parallel and perpendicular to the film, showing an in-plane coercivity of 190 Oe and an out-of-plane coercivity of 260 Oe, respectively. The saturation magnetization of the NFO film is determined to be  $245 \text{ emu/cm}^3$ .

The magnetostriction behavior of the NFO ferrite film on PZT substrate was measured by a customer-made magnetostriction tester, as shown in Fig. 3(b). The magnetostriction constant increases with the applied in-plane magnetic field, reaching  $-10$  ppm at 250 Oe, which is smaller than the saturation magnetostriction constant of the pure NFO phase. This may be due to the limited magnetic field strength of our magnetostriction test system, which can supply the highest magnetic field of 250 Oe. The NFO film is clearly not saturated at 250 Oe according to the hysteresis loops in Fig. 3(a).

The ME effect between ferrimagnetic NFO and ferroelectric PZT phases was demonstrated by observing the electric field induced magnetization change. The magnetization curve ( $M$ - $H$  curve) was monitored under different external electric fields across the PZT substrate. Due to the inverse piezoelectric effect, the PZT substrate experiences an in-plane strain when a certain direction electric field is applied through thickness. This in-plane strain is anisotropic in plane due to the beam shape (length  $\gg$  width) of the PZT slab, leading to an anisotropic in-plane net stress in the PZT. This net stress in PZT results in an effective net in-plane magnetic field on the ferrite film through a stress mediated ME coupling between the ferrite film and the PZT substrate, and, therefore, magnetization change of the ferrite films due to the inverse magnetoelastic effect. It is notable that the spin-spray deposited NFO is isotropic in plane, thus, the ME coupling induced magnetization change in the NFO/PZT is different from what we recently observed for the FeGaB/PZT,<sup>28</sup> in which the FeGaB film has well-defined in-plane anisotropy. Much stronger ME coupling is expected for the ME composites with magnetic films with well-defined anisotropy.

The in-plane  $M$ - $H$  curves were measured by applying external electric field of 0 and 1.3 MV/m across the thickness direction of PZT substrate, as shown in Fig. 4. An obvious upward shift of  $M$ - $H$  curve was observed at low external magnetic field and the remnant magnetization was increased by  $\sim 10\%$  when applying electric field of 1.3 MV/m. In addition, we found both  $M$ - $H$  curves reached the same saturation magnetization at high external magnetic field, which indicated ME coupling reduced due to the saturated magnetostriction at high applied magnetic field.

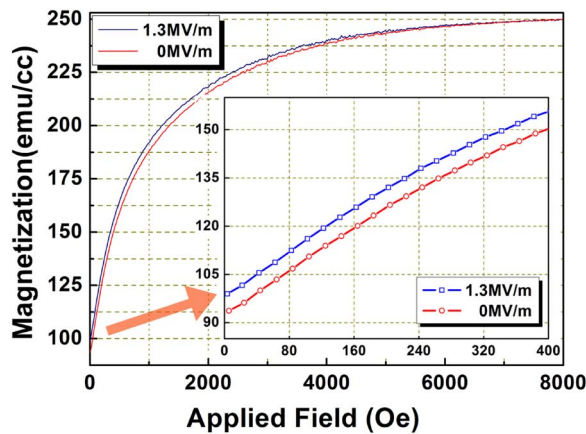


FIG. 4. (Color online) In-plane  $M$ - $H$  curves of spin-sprayed Ni ferrite film on PZT when applying 0 and 1.3 MV/m electric fields through the PZT substrate.

In summary, multiferroic material NFO/PZT was synthesized by spin-spray deposition of NFO on PZT substrate at a low temperature, which displays strong adhesion between the two constituent phases at the NFO/PZT interface. The strong adhesion between the NFO phase and the PZT phase was confirmed by the excellent wetting between the NFO and the PZT phases, as well as a strong strain/stress mediated ME coupling. The strong adhesion observed in the spin-spray deposited NFO/PZT multiferroic composite, as well as the low synthesis temperature, provides a viable route to the synthesis of novel high quality multiferroic materials by spin-spray deposition.

This work is sponsored by the NSF under Award No. DMR-0603115 and ECCS-0746810, the ONR YIP Award No. N00014-07-1-0761, and by the Draper Laboratory through University UR&D program. This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed–Martin Company, for the U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

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