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Magnetoelectric properties of flexible $BiFeO_3$/Ni tapes

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We report ferroelectric (FE), ferromagnetic, and magnetoelectric (ME) properties of $BiFeO_3$ films directly deposited on flexible magnetic Ni tapes. Without use of metal-oxide and/or noble metal buffer layer between the $BiFeO_3$ and the Ni, both ferroelectric and magnetic properties of the film and the substrate are preserved. X-ray diffraction and transmission electron microscopy analyses confirm the formation of preferentially oriented (110) $BiFeO_3$ film on Ni tapes. The $BiFeO_3$ film has a saturation polarization and a piezoelectric d_{33} coefficient of 69 $\mu C/cm^2$ and 52 pm/V, respectively. The $BiFeO_3$/Ni tape shows a magnetoelectric coefficient of 3.5 mV/cm·Oe. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4731780]

Tremendous efforts have been devoted to integrate ferroelectric films with metal substrates since such an integration will lead to devices such as multilayer capacitors, piezoelectric sensors, ultrasonic actuators, energy harvesters, magnetoelectric (ME) sensor, etc.[1–5] Ferroelectric films directly deposited on metal substrate have their great advantages compared with films on ceramics. For example, base metal substrates (nickel, copper, and iron) cost far less than single crystal ceramic substrates. The use of metal as substrates can greatly reduce the cost of the assembly.[2] Metal tapes are flexible compared with commonly used ceramic crystal substrates. Such feature enables the devices (piezoelectric actuator, energy harvester, etc.) to operate under extreme conditions of high strain and vibration environments. Flexible organic ferroelectric films have been demonstrated[6] and may find applications in specific cases. On the other hand, an integration of oxide-based ferroelectric films with flexible metal substrates offers other opportunities for applications since oxide-based ferroelectric materials exhibit much improved ferroelectric and dielectric properties at high temperature. Similar to the superconducting tapes,[7] the growth of ferroelectric films with desired properties on flexible metal tapes makes it possible to produce large area ferroelectric materials. In addition, one would expect to obtain coupled functionality if one can integrate high performance ferroelectric films with flexible magnetic metal tapes. For example, ME film sensors using ferromagnetic metal tapes as substrates are expect to have much better ME performance because ferroelectric films are not constrained by the thin and flexible substrates.[5]

To deposit ferroelectric films on metal substrates with desired physical properties, multilayer metal-oxides or noble metals are usually used as buffer layers. For example, $LaMnO_3$/MgO/IBAD-MgO/Y_2O_3/Al_2O_3 multi-layers have been used as the buffer between the $BaTiO_3$ film and the nickel substrate.[8] Gold has also been used as a buffer between the $BaTiO_3$ and the metglas foil.[5] It has been a technical challenge in the field to directly deposit ferroelectric films on metal substrates with satisfied polarization and piezoelectricity. The main technical difficulty is that metal-oxide thin films are often deposited in an oxygen ambient (~100 mTorr) at a temperature of 700–900 °C. Under such processing conditions, the base metal is quickly oxidized. In previous reports, ferroelectric $BaTiO_3$, (Ba,Sr)TiO_3, Pb(Zr,Ti)O_3 and (Pb,La)(Zr,Ti)O_3 films were directly grown on nickel and copper substrates using pulsed laser deposition (PLD),[9–11] chemical solution deposition (CSD),[2,12–16] and sputtering.[17,18] Most of the reports show the expected structural properties of the films but with limited demonstration of desired dielectric properties.[2,13–18] In fact, only one report illustrated the ability to deposit Pb(Zr,Ti)O_3 film directly on copper foil with satisfied polarization hysteresis loop.[2] There is no report at all on the ME properties even though these ferroelectric films are directly deposited on magnetic substrates such as Ni foils.

In the last several years, $BiFeO_3$ has been extensively investigated as one of the most promising ferroelectric materials due to its large polarization (~60 $\mu C/cm^2$) and piezoelectricity (~75 pm/V) at room temperature.[19] In this letter, we report the demonstration of ferroelectric $BiFeO_3$ films directly deposited on nickel tapes by pulsed laser deposition. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements confirmed the formation of $BiFeO_3$. The $BiFeO_3$ films on Ni showed ferroelectric and piezoelectric properties comparable to the films on crystal ceramic substrates. Importantly, we report the ME effect of flexible $BiFeO_3$/Ni tapes tested by using a traditional AC + DC magnetic field method.

$BiFeO_3$ films were directly deposited on 127 μm thick nickel tapes by pulsed laser deposition. The Ni tapes were polished before the deposition. The thickness of the films was varied between 1 and 1.5 μm, which was confirmed by TEM. The films were deposited using a XeCl excimer laser

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with a wavelength of 308 nm and an energy density of 5 J/cm^2 on the target surface. The substrate temperature and oxygen pressure during deposition were initially optimized for the best structural properties and were then maintained at 540–620 °C and 30 mTorr, respectively. The phases of the films were determined using a Philips X'pert high resolution x-ray diffractometer (XRD) equipped with a two bounce hybrid monochromator and an open three-circle Eulerian cradle. The magnetic properties of the Ni tape were measured at 300 K using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS magnetometer). Polarization and piezoelectricity of the films were measured by home-made Sawyer-Tower measurement system and piezo-response force microscopy, respectively. The top gold electrodes are deposited by sputtering through a shadow mask with a dimension of 37 μm × 37 μm.

XRD, TEM, and energy-dispersive spectroscopy (EDS) were used to identify the phase and structure of the $BiFeO_3$ films on Ni tapes. As shown in Figure 1(a), the $BiFeO_3$ film is preferentially oriented along (110). Except for the diffractions from $BiFeO_3$ and Ni, no other phases are detected, suggesting the formation of pure $BiFeO_3$ films directly on Ni substrate. The cross-sectional TEM image of the film is shown in Figure 1(b). A thin NiO layer between the $BiFeO_3$ and the Ni is observed, which may be formed either before the deposition while the nickel is exposed to the atmosphere or oxygen diffusion through the $BiFeO_3$ at the late stage of the film growth. For instance, an amorphous layer is often observed between the substrate and the film when PLD is used to deposit metal-oxide on Si.[20,21] It should be noted that the chemical information from different regions (see Fig. 1(b)) has also been mapped by EDS, where the sample was prepared by a focused ion beam technique. The EDS results confirm the chemistry from the top to the bottom being $BiFeO_3$, NiO, and Ni even though such a technique does not give an accurate determination of the composition.

The desired structural properties of $BiFeO_3$ lead to high performance $BiFeO_3$ directly on Ni. As shown in Fig. 2(a), polarization-electric field (P-E) loops measured at room temperature are as good as the $BiFeO_3$ films on crystal ceramic substrates.[19] The saturation polarization reaches 69 μC/cm^2 under an electric field of 1300 kV/cm. The remanent polarization of the $BiFeO_3$ film is 53 μC/cm^2. The shift of P-E loop to the right side can be attributed to the internal electric field, which has been also observed in $BiFeO_3$ films by others.[19] Figure 2(b) shows the piezoelectric response of the $BiFeO_3$ film on the Ni tape. The piezoelectric d_{33} coefficient of $BiFeO_3$ film is 52 pm/V at an electric field of 1000 kV/cm. The asymmetric coercive fields observed in the piezoelectric curve further indicate the existence of built-in field in the $BiFeO_3$ layer.

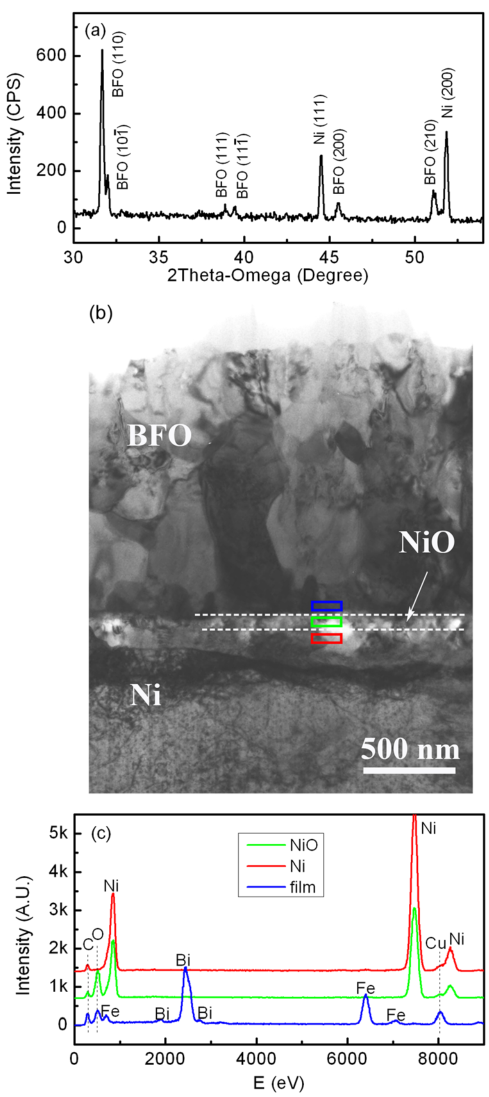

FIG. 1. Structural analysis of the $BiFeO_3$ film directly deposited on the flexible Ni tape (a) XRD pattern; (b) cross-sectional TEM image of the $BiFO_3$/Ni tape; and (c) EDS mapping at different regions of the $BiFO_3$/Ni tape.

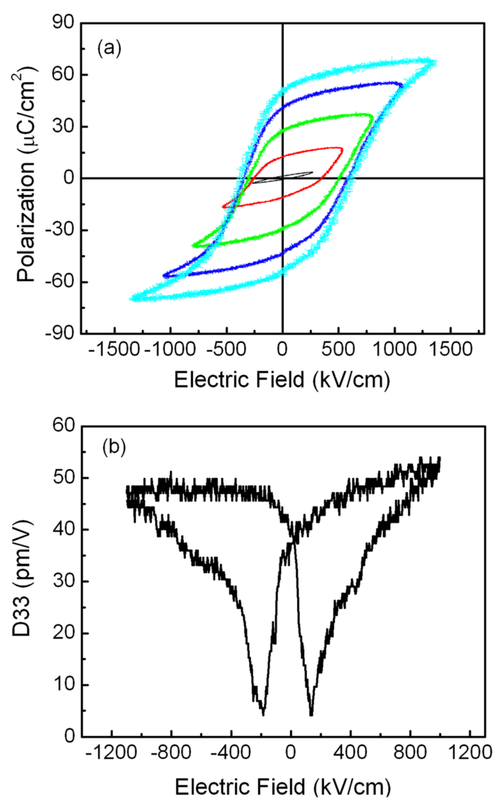

FIG. 2. Polarization and piezoelectricity of $BiFeO_3$/Ni. (a) Polarization as a function of electric field at room temperature and (b) piezo-response hysteresis loops for the $BiFO_3$/Ni tape.

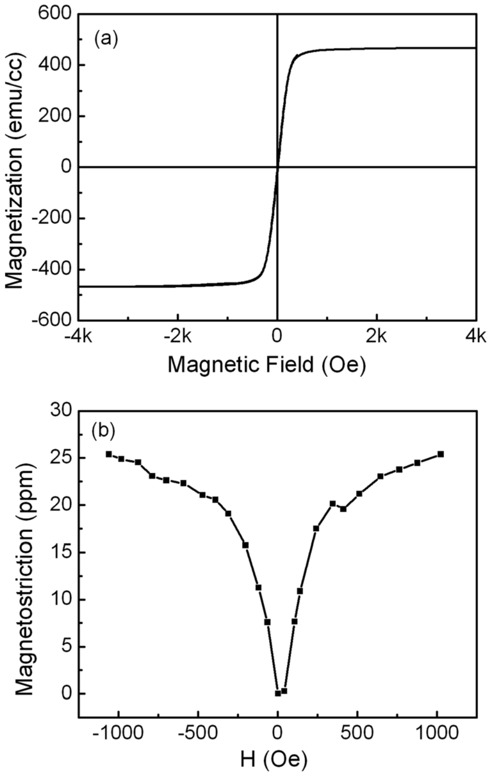

FIG. 3. Magnetization and magnetostriction of Ni substrate. (a) Magnetization as a function of magnetic field at room temperature and (b) magnetostriction as a function of magnetic field of the Ni substrate.

It is noted that the direct deposition of high performance ferroelectric $BiFeO_3$ film on Ni tape does not degrade the magnetic properties of the Ni. This is important for applications if one wants to utilize the combined functionalities of both the film and the substrate. As given in Figures 3(a) and 3(b), the in-plane magnetization hysteresis and magnetostriction curve of nickel tape are measured by SQUID magnetometer and magnetic strain gauge at room temperature. The saturation magnetization is 467 emu/cc. As a comparison, a normal bulk nickel has a magnetization of 490 emu/cc. The maximum magnetostriction of nickel tape used in this experiment is 25 ppm at 1 kOe as shown in Fig. 3(b).

The most significant observation in our experiment is that ME effect is detected when $BiFeO_3$ is directly deposited on Ni tape. In this experiment, we measured the ME response of $BiFeO_3$/Ni by a traditional AC + DC magnetic field method. While AC magnetic field was kept as 1 Oe at 1 kHz, DC magnetic field slowly varied between 1 kOe and −1 kOe. In the measurement, both AC and DC magnetic fields were applied along the in-plane direction, and the electric polarization was measured along the out-of-plane direction. The maximum ME coefficient of $BiFeO_3$/Ni is 3.5 mV/cm·Oe when DC magnetic is around 100–200 Oe, as shown in Fig. 4. The ME output decreases with increasing DC magnetic field. It has been reported that ME output of Ni/PZT/Ni bulk ME sensor with 2-2 structure can have a value as high as 40–400 mV/cm·Oe.[22–24] The ME coefficient of our $BiFeO_3$/Ni is much smaller than this value. It will be important to understand the limiting factors in order to maximize the ME output. It is well know that the ME coefficient of a composite can be expressed as

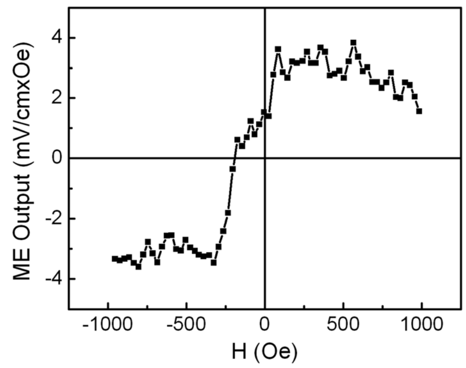

FIG. 4. Magnetoelectric coefficient of a $BiFeO_3$/Ni tape as a function of the external magnetic field.

$$\alpha = \frac{\partial P}{\partial H} = \frac{\partial P}{\partial S} \times \frac{\partial S}{\partial H},$$

where P is the polarization, S is the strain, and H is the magnetic field.[25,26] $\partial P/\partial S$ and $\partial S/\partial H$ represent piezoelectricity and magnetostriction of the ferroelectric and ferromagnetic phases, respectively. Piezoelectric coefficient d_{33} of $BiFeO_3$ film is around 69 pm/V due to the constraint of the substrate, while d_{33} of PZT ceramic could reach 750 pm/V.[27] Ni tape we are using in the experiment is nickel 201 alloy, which is stable at a temperature of 649 °C and has a magnetostriction of 25 ppm. A value as large as 58 ppm has been reported for a regular Ni single crystal by others.[28] Accordingly, a relatively small ME coefficient of $BiFeO_3$/Ni in this report is not unreasonable. One could potentially increase the ME output if the ferroelectric properties of $BiFeO_3$ film are further optimized and Ni tapes with high magnetostriction are chosen.

In summary, we have directly deposited (110) preferred ferroelectric $BiFeO_3$ films on flexible Ni tapes. Our results demonstrated that the $BiFeO_3$ films have desired ferroelectric properties with a saturation polarization of 69 $\mu C/cm^2$ and a piezoelectricity d_{33} of 52 pm/V. The Ni tape, after the growth of $BiFeO_3$, remains ferromagnetic with a saturation magnetization of 467 emu/cc and a maximum magnetostriction of 25 ppm. Additionally, The ME coefficient of the $BiFeO_3$/Ni shows a maximum value of V_{ME} = 3.5 mV/cm·Oe.

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