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Enhanced magnetoelectric coupling in a composite multiferroic system via interposing a thin film polymer

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Enhancing the magnetoelectric coupling in a strain-mediated multiferroic composite structure plays a vital role in controlling magnetism by electric fields. An enhancement of magnetoelastic coupling between ferroelectric single crystal (011)-cut $[Pb(Mg_{1/3}Nb_{2/3})O_3]_{(1-x)}$-$[PbTiO_3]_x$ (PMN-PT, $x \approx 0.30$) and ferromagnetic polycrystalline Ni thin film through an interposed benzocyclobutene polymer thin film is reported. A nearly twofold increase in sensitivity of remanent magnetization in the Ni thin film to an applied electric field is observed. This observation suggests a viable method of improving the magnetoelectric response in these composite multiferroic systems. © *2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5007655

I. INTRODUCTION

Multiferroics exhibiting both ferromagnetic (FM) and ferroelectric (FE) properties have attracted substantial interest owing to the strong magnetoelectric (ME) coupling behavior between these two ferroic orders. Single-phase multiferroics have relatively low magnetoelectric coupling coefficients due to the reciprocity relations that limit magnetoelectric susceptibilities.[1,2] Compared to single-phase multiferroics, composite multiferroic heterostructures are particularly important for their larger ME coupling effect, where coupling has been demonstrated via several methods, including elastic strain, exchange bias effect, and charge carrier density - all controllable by electric field.[3,4] Among these, the use of electrical field to actuate strain-coupled multiferroic heterostructures has been widely demonstrated in the past few years as an energy-efficient pathway for controlling magnetization in the FM layer.[5–7]

The Villari effect (a.k.a., magnetoelastic effect) describes the behavior where applied mechanical stress σ produces change in the magnetization in a material.[8] Optimizing the transfer of strain and magnetic response in strain-coupled multiferroic heterostructures is key to maximizing the Villari effect, which is at the core of applications such as magnetic random access memory (MRAM), field sensors, and actuators.[9,10] One of the main problems with laminate composites consisting of FM thin

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film and FE single crystal is the large "clamping" effect of the FE onto the FM film which prevents the strain effect of the FE from being exploited fully.[1,11–13]

In this paper, we report that by inserting a thin dielectric polymer layer between the FM Ni thin film and FE $[Pb(Mg_{1/3}Nb_{2/3})O_3]_{(1-x)}$-$[PbTiO_3]_x$ (PMN-PT, $x \approx 0.30$) single crystal, a nearly twofold increase in the electric field-induced FM film's variation in remanent magnetization is observed, when compared with a sample without any polymer layer. The interposed polymer not only serves as a planarization layer that smoothens the surface, but also alters the strain-mediated magnetization response of the magnetic layer in the heterostructure.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

In this study, the two FE specimens used are cut from a polished and unpoled $20 \times 10 \times 0.5$ mm^3 single crystal, (011)-oriented $[Pb(Mg_{1/3}Nb_{2/3})O_3]_{(1-x)}$-$[PbTiO_3]_x$ ($x \approx 0.30$), grown by TRS Ceramics, Inc. (PA, US) following the modified Bridgman method.[14] A 5 nm Ti/50 nm Pt layer, deposited on both sides of the PMN-PT substrate, served as an adhesion layer and surface electrode, respectively.[15] For one of the specimens, adhesion promotor AP3000 and dielectric benzocyclobutene (BCB) monomer of 10 µm thick were spun onto the top electrode, followed by thermal curing in N$_2$ chamber at 250°C. After poling the PMN-PT substrate, 5 nm Ti/15 nm Ni films were deposited by e-beam evaporation. The purpose of poling prior to the deposition of FM layer is to reorient spontaneous polarizations, thereby reducing the ferroelastic energy[16] and prepare the substrate to work in its linear piezoelectric regime. Configurations of the two specimens are illustrated in Fig. 1, where the crystal orientations and piezo-response of the single-crystal PMN-PT substrate, upon application of an electric field, are highlighted. The electric field applied along the [011] direction induces a large uniaxial compressive strain along the [100] direction and a reasonably small tensile strain along the [01-1] direction in the substrate.

B. Characterization

To characterize the FM layers, atomic force microscopy (AFM) images of the surfaces of Ni thin films on both specimens were collected using a Bruker Dimension icon scanning probe microscope. X-ray diffraction (XRD) measurements of FE and FM heterostructures were obtained to confirm the crystal orientation and the structural property of Ni. Synchrotron X-ray diffraction studies were carried out on beamline 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) in grazing Incidence mode (GIWAXS). Data was collected using an X-ray wavelength of 0.9742Å in combination with a Rayonix MX225 CCD 2D detector. In-plane piezoelectric responses were measured by attaching a biaxial strain gauge to the top surface of each of the two samples and applying an out-of-plane electric field. To compare the magnetization response of Ni thin film to the varying electric field, a home-built longitudinal mode magneto-optical Kerr effect (MOKE) magnetometer was used.
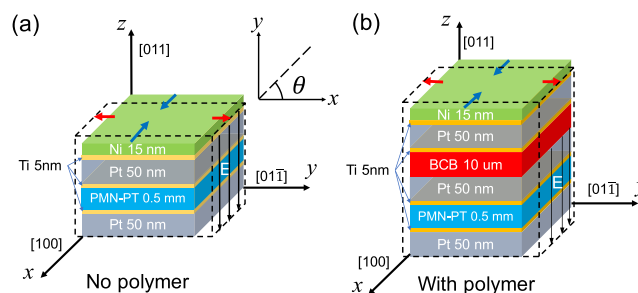

FIG. 1. Schematics of fabricated Ni layer on (011)-oriented PMN-PT heterostructures (a) without polymer and (b) with polymer. Dashed lines outline the piezoresponse of the substrate when an electric-field is applied to the parallel plate elect rode structure.

To ensure the accuracy of measurement, a Kerr hysteresis measurement was performed twice on two sets of such specimens, prepared from two $20 \times 10 \times 0.5$ mm^3 PMN-PT substrates cut from the same crystal.

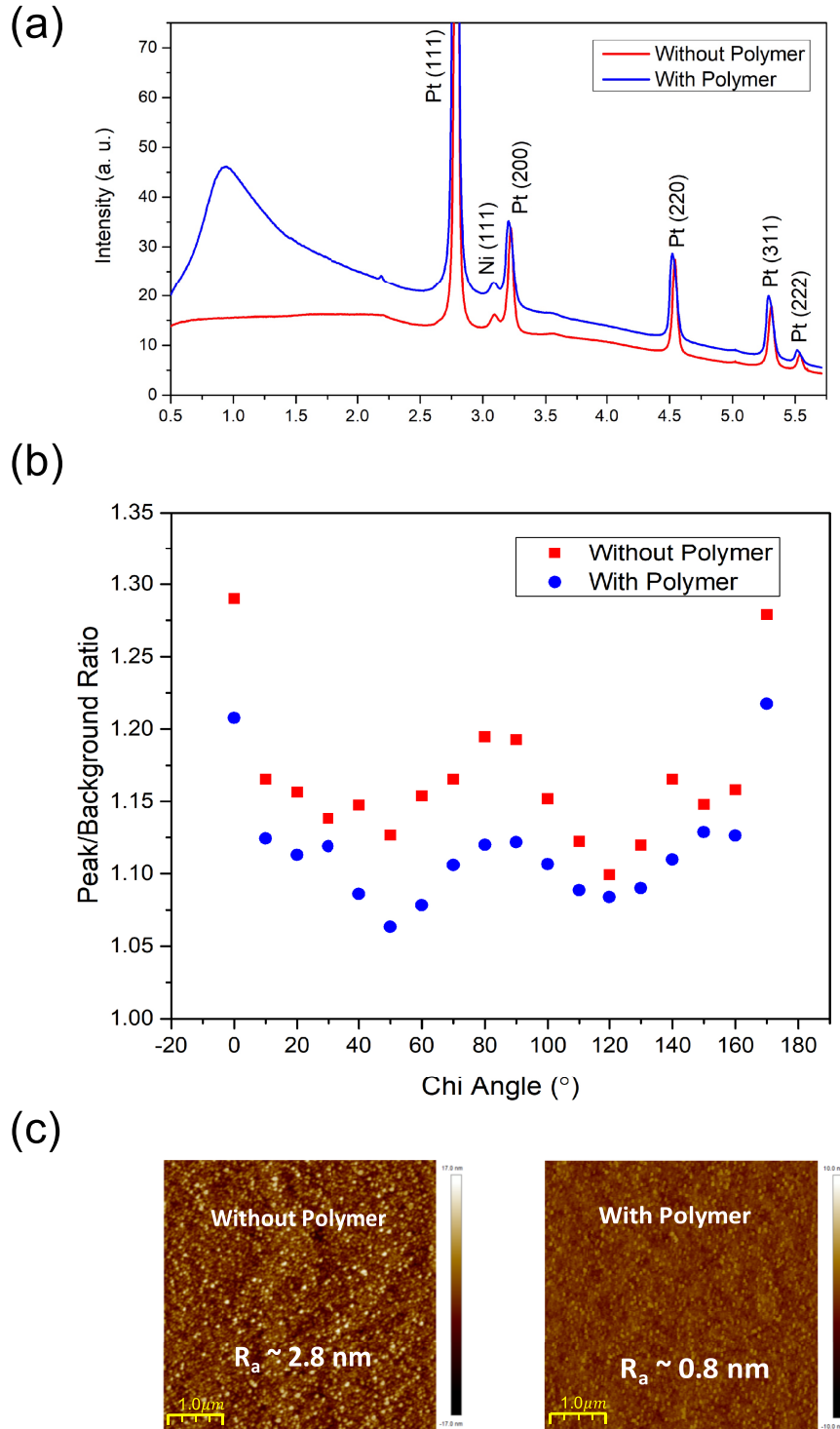FIG. 2. (a) GIWAXS (taken at beamline 11-3 at SSRL) patterns of two heterostructures with and without polymer layer. (b) Ratio of integrated Ni (111) peak height vs. background in 10-degree chi slices, where angle of 0 on the *x*-axis corresponds to integrated 0°-10° slice. Ni (111) peak height value obtained at Q = 3.08, background obtained at Q = 3.00. (c) AFM topography images of Ni thin films on both samples.

III. RESULTS AND DISCUSSION

Synchrotron produced X-rays with a high X-ray flux were used in grazing incidence wide-angle X-ray scattering (GIWAXS) to observe the thin film Ni diffraction (Fig. 2a). The data indicate that the BCB polymer is mostly amorphous, as shown by the broad peak in the blue curve between $Q = 0.5$ and 2.0. The Ni (111) peaks can also be observed in the 1D patterns in Fig. 2a, indicating that the Ni is crystalline. Examination of the raw 2D data indicates that the Ni is polycrystalline, as evidenced by a (111) ring with significant intensity at all angles in both samples. An angular analysis of the Ni (111) peak height compared to the background, however, shows that the Ni is slightly textured in both samples (Fig. 2b), with a small preference for the out-of-plane (90°) and in-plane (0° and 180°) orientations. Regardless, the Ni is surely polycrystalline as evidenced by a (111) peak at all angles in both samples (Fig. 2a). Similar texture is also observed for the more intense Pt peaks. Atomic force microscopy micrographs (see Fig. 2c) of the Ni surface in both samples show that the presence of the polymer decreases the surface roughness of Ni from ~2.8 nm (without polymer) to ~0.8 nm.

Fig. 3 shows the electric-field induced strain from the poled PMN-PT substrates characterized with a biaxial strain gauge. Both unipolar strain curves, measured along [100] and [01-1] directions, are shown for both samples, indicating a linear anisotropic response that can be used to drive anisotropic magnetoelectric response in Ni layer of both samples. According to the strain response measured from both samples, we note that the transition of the strain as a function of electric field on the sample with polymer is, macroscopically speaking, of the same magnitude as that on the one without. Since the strain gauge probes the macroscopic strain response, the anisotropic strain
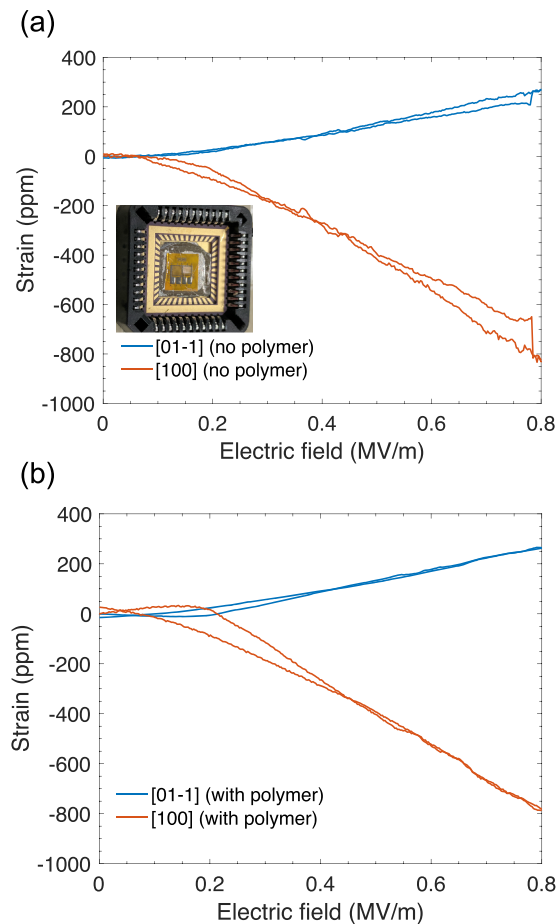

FIG. 3. In-plane piezoelectric strain along [01-1] and [100] directions for sample (a) without polymer and (b) with polymer vs applied electric field. Inset in (a) shows a biaxial strain gauge mounted on the sample without polymer.

generated by both samples are comparable, as shown in Fig. 3 (a) and (b), implying that a complete strain transfer can be achieved even with the addition of the 10 μm thick polymer.

In the specimen with interposed polymer, the electric-field-induced strain in the PMN-PT was first transferred to the polymer and then to the top FM Ni thin film, as opposed to the direct strain transfer usually found in a PMN-PT/Ni composite system.[5,15] To understand the difference in ME response between these two systems, in-plane magneto-optical Kerr (MOKE) magnetometry with in-situ electric fields was employed to study M-H hysteresis loop variation for both samples. The two MOKE specimens were oriented in three directions during the experiment such that the external magnetic field was applied in the direction at an angle θ of 0°, 90° and 45° with respect to the [100] direction of PMN-PT (see Fig. 1(a)).

Fig. 4 shows the normalized Kerr rotation hysteresis curves taken along the three directions mentioned above. Before applying an electric field, negative magnetostrictive Ni on the pre-poled substrate is found to have a magnetic easy direction along [01-1] direction and a hard direction
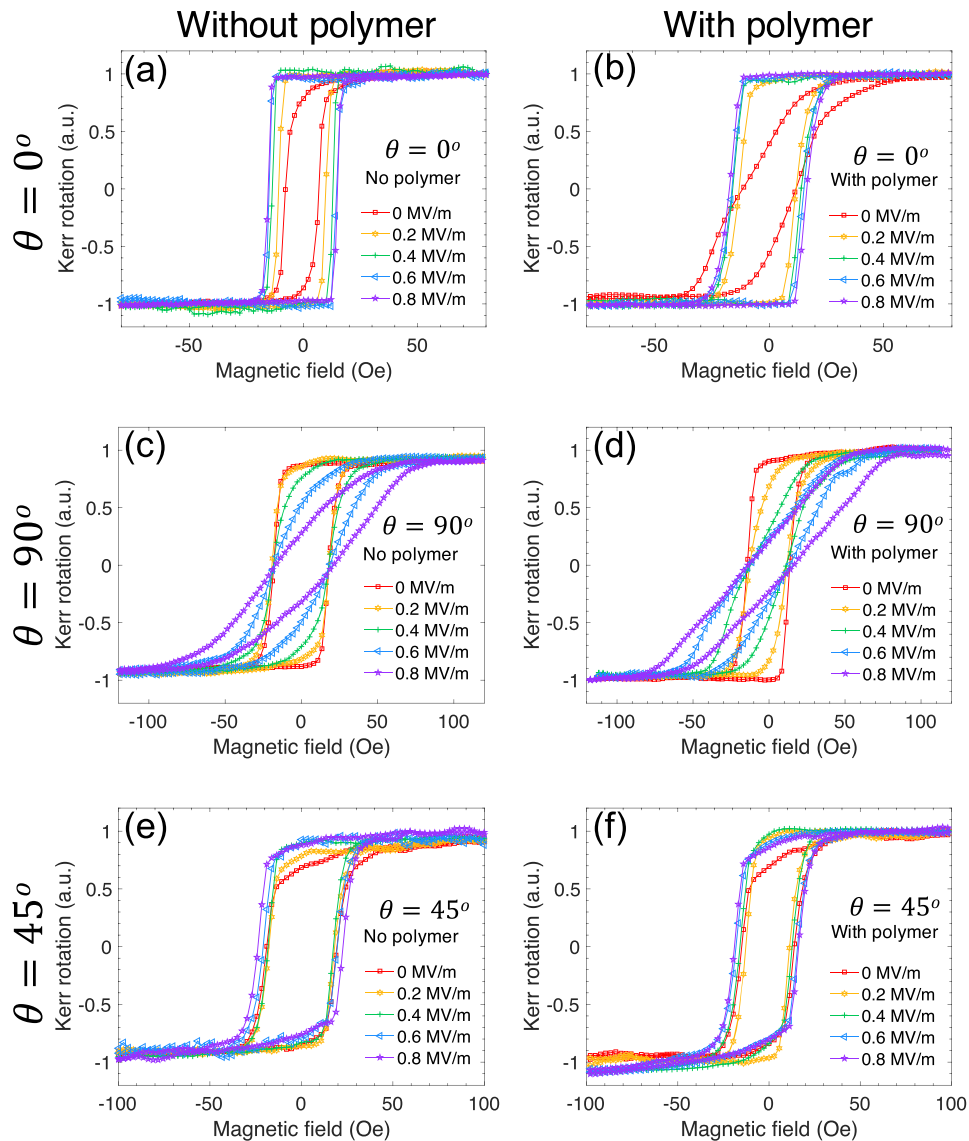

FIG. 4. Normalized magnetic Kerr rotation M-H curves measured at different electric fields with magnetic field parallel to $\theta = 0°$, $\theta = 45°$ and $\theta = 90°$ directions, where θ is the angle between in plane magnetic field H and [100] direction of PMN-PT. (a)(c)(e) Without polymer. (b)(d)(f) With polymer.

along [100] direction, as shown in Fig.4. (a)–(d). Comparing Fig.4(a) and 4(b) showing MOKE M vs H curve for samples without and with polymer, respectively, we note that the presence of the planarization polymer increases the hard-axis anisotropy and thus reduces the remanence-saturation ratio M_r/M_s (normalized remanence). The M_r/M_s measured at an electric field of 0 MV/m in the specimen without polymer is greater than 0.85, while in the specimen with polymer it is below 0.45.

As the electric field increases from 0 MV/m to 0.8 MV/m, the increasingly large anisotropic strain generates a new magneto-elastic uni-axial anisotropy term along the [100] direction. As a result, the magnetic easy-axis rotates from 90° to 0°. i.e., the [100] direction switches from being the hard to the easy axis, and [01-1] from the easy to the hard. M-H curves taken along [100] for both samples show a clear inverse ME effect (Villari effect) with significant strain transfer to the FM. However, in the composite system with a smooth polymer layer, the variation of M_r/M_s as a function of the electric field is more prominent compared to the one without polymer, as shown in Fig. 5, for cases where magnetic field is applied along θ of 0° and 90°. Hence, the ME coupling between magnetic thin film and PMN-PT grows stronger due to the presence of the interposed polymer layer, as shown by the almost two-fold increase in M_r/M_s (θ of 0°) before and after applying the electric field of 0.8 MV/m. The presence of the polymer layer smoothens the strain profile and planarizes the Ni layer, indicating an increased magnetoelastic effect.

Additionally, for magnetic field applied along 45°, bisecting the alternating easy and hard axes, the shape of hysteresis loops remains consistent as the electric field varies. Magnetic moments pointing along this direction are unlikely to change direction as the electric field changes.

When the electric field is ramped down from 0.8 MV/m to 0 MV/m, the magnetization state of Ni film is reversible in both specimens, where the M-H loop overlaps with the one measured at the same electric field while ramping up the voltage. Fig. 6 demonstrates the reversibility of the magnetic behavior in Ni thin film on the polymer layer, with magnetic hysteresis loops measured along [100] direction. Repeatable magnetization states can be switched by electric fields, as shown in Fig. 6 at 0 MV/m, 0.4 MV/m and 0.8 MV/m. For both samples, overlapping of M-H loops, taken when the same electric fields were applied, also verifies the accuracy of the MOKE measurements.

Such enhanced magnetoelectric coupling are believed to originate from several sources. First, the presence of polymer modifies the magnetic property of the Ni thin film deposited on the pre-poled substrates such that along θ of 0° direction, the anisotropy field is larger in the sample compared to the one without polymer. With increased electric field, the thin film in the sample with polymer experiences a stronger change in M_r/M_s, in other words, a larger variation in $\Delta(M_r/M_s)/\Delta E$. Second, the planarization layer smoothes the interface between Ni and substrate. Compared to the sample without polymer where the Ni and Pt interface has grain boundaries, the sample with polymer reduces pinning effect due to lower surface roughness. As a result, the magnetic property of Ni can be largely
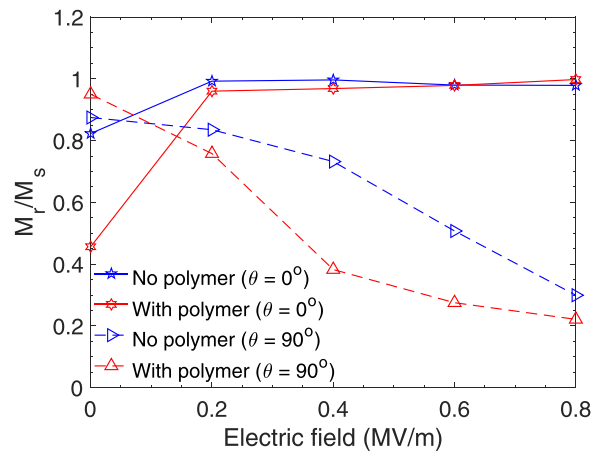

FIG. 5. M_r/M_s, as a function of the applied electric field, for both samples. The magnetic field direction is parallel to $\theta = 0°$ and $\theta = 90°$. A larger change in M_r/M_s vs electric field is observed in both directions for the sample with polymer than the one without.
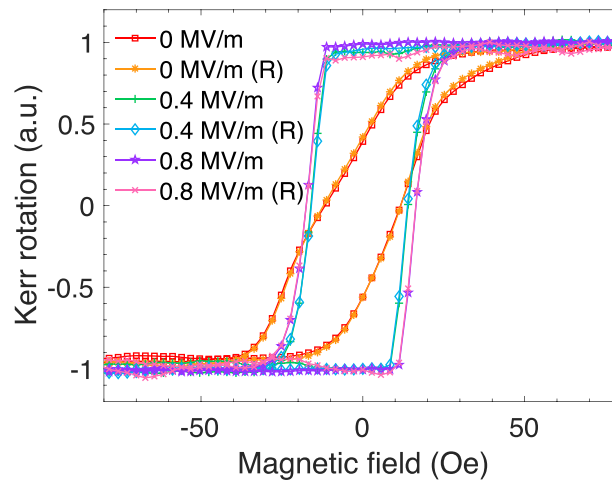
FIG. 6. Reversible magnetic behavior of the Ni thin film in the specimen with interposed polymer layer, measured along [100] direction. Where "R" denotes the M-H loop taken as the electric field was ramped down from 0.8 MV/m to 0 MV/m.

affected, thus contributing to difference in the magnetoelectric properties of the two specimens. The addition of such polymer layer introduces a new degree of freedom of magnetization control in strain-mediated multiferroic systems. Additionally, we used x-ray magnetic circular dichroism photoemission electron microscopy (XMCD-PEEM) to demonstrate the effect of the polymer layer on lowering the electric field which triggers magnetic domain wall motion in lithographically fabricated Ni micro-rings (supplementary material).

IV. CONCLUSION

In summary, we have shown that by interposing a polymer layer in strain-mediated multiferroic structures, enhancement of the magnetoelectric coupling can be achieved. Switching electric-field to operate the (011)-oriented PMN-PT (PT% ≈ 0.30) in the linear regime drives magnetization response in Ni thin films. The Ni thin film above the polymer exhibits an improved sensitivity of remanence to anisotropic strain originating from PMN-PT. Such interposed polymer layer provides an additional pathway to control and enhance the magnetoelectric coupling in composite multiferroic devices.

SUPPLEMENTARY MATERIAL

See supplementary material for the XMCD-PEEM images of Ni micro-rings on devices with and without polymer layer.

ACKNOWLEDGMENTS

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