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Citation: *Appl. Phys. Lett.* **109**, 252902 (2016); doi: 10.1063/1.4972304

View online: <http://dx.doi.org/10.1063/1.4972304>

View Table of Contents: <http://aip.scitation.org/toc/apl/109/25>

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# Nonvolatile transtance change random access memory based on magnetoelectric P(VDF-TrFE)/Metglas heterostructures

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(Received 17 October 2016; accepted 28 November 2016; published online 19 December 2016)

Transtance change random access memory (TCRAM) is a type of nonvolatile memory based on the nonlinear magnetoelectric coupling effects of multiferroics. In this work, ferroelectric P(VDF-TrFE) thin films were prepared on Metglas foil substrates by the sol-gel technique to form multiferroic heterostructures. The magnetoelectric voltage coefficient of the heterostructure can be switched reproducibly to different levels between positive and negative values by applying selective electric-field pulses. Compared with bulk multiferroic heterostructures, the polarization switching voltage was reduced to 7 V. Our facile technological approach enables this organic magnetoelectric heterostructure as a promising candidate for the applications in multilevel TCRAM devices. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4972304>]

With rapidly advancing information technologies, a universal memory device with non-volatility, high read/write speed, high density, huge endurance, low power consumption, and inexpensiveness is highly demanded.<sup>1</sup> Currently, charge-based flash memory has been the most popular type of memory due to its large-scale application in portable and mobile electronic devices. However, due to the fundamentally limited cycling index and scaling ability, people are pursuing other memory technologies with different physical storage mechanisms as alternatives to flash memory. In this context, some non-volatile memory technologies, such as magnetic random access memory (MRAM),<sup>2</sup> ferroelectric random access memory (FeRAM),<sup>3</sup> phase change memory (PCM),<sup>4</sup> resistance random access memory (ReRAM),<sup>5,6</sup> and magnetoelectric random access memory (MeRAM),<sup>7</sup> have emerged.

Multiferroics, which combine ferroelectricity and magnetism to allow strong magnetoelectric (ME) coupling effects, have attracted much attention due to their potential application in MeRAM.<sup>8,9</sup> The strength of the ME coupling can be described by the ME coefficient,<sup>10</sup> which is defined as  $\alpha_d = dP/dH$  for the direct ME coupling, i.e., the change of polarization  $P$  by applying magnetic field  $H$ , and  $\alpha_c = \mu_0 dM/dE$  for the converse ME coupling, i.e., the change of magnetization  $M$  by applying electric field  $E$ , where  $\mu_0$  is the vacuum permeability. As we have discussed in detail,<sup>11,12</sup> an ME device with the two-terminal electrode/ME medium (multiferroics)/electrode has a direct linear (nonlinear) relationship between two basic circuit variables, magnetic flux ( $\varphi$ ) and charge ( $q$ ), and thus is regarded as the fourth fundamental circuit element (memelement), which is termed as transtor (memtranstor) corresponding to resistor (memristor), capacitor (memcapacitor), and inductor (meminductor).<sup>11–14</sup> In the

transtor and memtranstor, the  $q$ - $\varphi$  relationship of the ME device actually defines a physical quantity—transtance<sup>11</sup>

$$dq = g \frac{\alpha_d}{\mu_0 \mu_r} d\varphi, \quad (1)$$

$$d\varphi = \frac{1}{g} \frac{\alpha_c}{\epsilon_0 \epsilon_r} dq, \quad (2)$$

where  $g$  is a geometric factor,  $\epsilon_0$  ( $\mu_0$ ) is the permittivity (permeability) of vacuum, and  $\epsilon_r$  ( $\mu_r$ ) is the relative permittivity (permeability) of the ME medium, respectively. The transtance,  $T = g \frac{\alpha_d}{\mu_0 \mu_r}$  or  $\frac{1}{g} \frac{\alpha_c}{\epsilon_0 \epsilon_r}$ , is parallel to the resistance defined by current ( $i$ )-voltage ( $v$ ) relationship, capacitance defined by the  $q$ - $v$  relationship, and inductance defined by the  $i$ - $\varphi$  relationship. Meanwhile, the ME coefficient reflects the strength and sign of transtance via the direct and converse ME coupling effects, respectively.

Based on the established circuit elements, we proposed recently a storage mode, called transtance change random access memory (TCRAM),<sup>15,16</sup> in which the transtance, or the ME voltage coefficient ( $\alpha_E = dE/dH \propto \alpha_d$ ), was directly used as the physical quantity for information storage. In order to positively match the technological requirements of the TCRAM application, a strong ME effect at room temperature and a thin ME device with lower polarization switching voltage are necessary. So far, ME composite multiferroics consisting of interface-coupled magnetostrictive and piezoelectric components produce the largest ME values at room temperature, much larger than those of single phase multiferroics or linear ME media.<sup>17</sup> Many piezoelectric materials, e.g., PMN-PT,  $\text{Pb}_{1-x}\text{Zr}_{1-x}\text{Ti}_x\text{O}_3$ , and  $\text{BaTiO}_3$ , can be composited with magnetic materials to form ME heterostructures.<sup>17</sup> In comparison with the inorganic piezoelectric materials, polymer-based piezoelectric materials, such as polyvinylidene fluoride (PVDF), can be easily fabricated by conventional low temperature processing into a variety of forms, such as thin films, and exhibit improved mechanical properties.<sup>18</sup> It is low-cost, lightweight, flexible, environment-friendly, and easily

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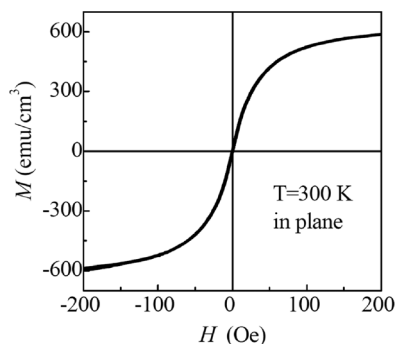


FIG. 1. Magnetization curves of the Metglas foil at 300 K. The sample size is  $4 \times 4 \times 0.025 \text{ mm}^3$  and the in-plane shape anisotropy is almost negligible.

processable.<sup>19,20</sup> A major advantage of PVDF is the ability to be deposited as a thin film at room temperature on many materials. Poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) is one of the most promising PVDF ferroelectric copolymers.<sup>21–24</sup> In this work, we prepared P(VDF-TrFE) thin films with a thickness of  $1 \mu\text{m}$  on Metglas foil substrates with a thickness of  $25 \mu\text{m}$  to form ME heterostructures and investigated their ME coupling and transitive properties. The potential application of the P(VDF-TrFE)/Metglas heterostructures as a nonvolatile TCRAM device has been demonstrated. Compared to the bulk ME devices that we used previously,<sup>15,16</sup> the thinner ME devices are more practical, because the polarization switching voltage, that is, the writing voltage of the TCRAM, was decreased largely.

The random copolymer P(VDF-TrFE) powders with 70:30 molar ratio were purchased from Solvay. Metglas foils with a thickness of  $25 \mu\text{m}$  were used as substrates. Thin P(VDF-TrFE) films were spin-coated directly onto the Metglas foil surface at 3000 rpm from a 5 wt. % solution in methylethylketone. The average thickness of the films, as measured with a DEKTAK surface profilometer, is about  $1 \mu\text{m}$ . Then, the film was annealed at  $140^\circ\text{C}$  in air for 2 h to improve the crystallinity of the ferroelectric  $\beta$  phase of the film. The crystal structure was characterized by X-ray

diffraction (XRD) (Bruker D8 Discover X-ray diffractometer with an X-ray radiation of  $\lambda = 1.5406 \text{ \AA}$ ).

For electrical measurements, Cu top electrodes with a thickness of 150 nm and a size of  $1 \times 1 \text{ mm}^2$  were first deposited onto the polymer film surface through a shadow mask using the thermal evaporation technique. The current density–electric field ( $J$ - $E$ ) measurements were performed with a Keithley 2611 Source Meter in a home-made probe station at room temperature. During the measurements, a voltage was applied to the top electrode with the bottom electrode being grounded. The ME voltage coefficient  $\alpha_E$  was measured using a dynamic method. A small  $ac$  magnetic field  $H_{ac}$  at a frequency of 100 kHz, generated by an  $ac$  current source (Keithley 6221) to a solenoid, in the presence of a simultaneous  $dc$  bias magnetic field, was applied to the composite sample. In response, the change in the electric signal ( $V_{ac} = V_x + iV_y$ ) across the sample resulting from the applied  $H_{ac}$  was recorded using a lock-in amplifier (Stanford Research SR830) synchronized with the  $ac$  current source. The  $\alpha_E$  is calculated by  $\alpha_E = V_x/(H_{ac}t)$ , where  $t$  is the thickness of the P(VDF-TrFE) film. The sample was plugged into an Oxford TeslatronPT superconducting magnet system, which supplies the  $dc$  magnetic field. All the electrical measurements were performed at 300 K.

Figure 1 shows the in-plane  $M$ - $H$  hysteresis loop of the Metglas foil measured by a vibrating sample magnetometer (VSM) at 300 K. Due to the thin and square shape of the Metglas we used, the in-plane shape anisotropy is almost negligible. It can be seen that the Metglas is a typical soft ferromagnet with the coercive field of only several Oe and the saturation field about 200 Oe.

Figure 2(a) shows the 300 K XRD spectra of the prepared P(VDF-TrFE) film annealed at  $140^\circ\text{C}$ . The diffraction peak at  $2\theta = 19.9^\circ$  was assigned to the reflections of the (110) and (200) planes related to the  $\beta$  phase of P(VDF-TrFE)—the polar phase with a large spontaneous polarization along the  $b$  axis which is parallel to the C-F dipole moments, and perpendicular to the polymer chain direction ( $c$  axis) (see inset in Figure 2(a)).

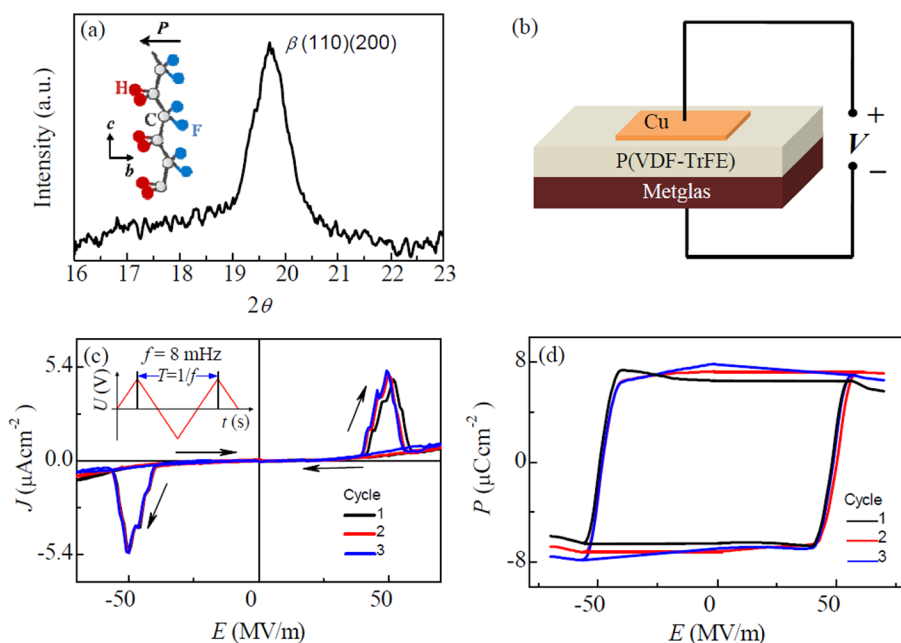


FIG. 2. (a) XRD pattern of the P(VDF-TrFE) films prepared by the sol-gel technique. Inset in (a) shows the schematic molecular structure and ferroelectric polarization direction. (b) Schematic illustration of the device structure and the measurement setup. (c)  $J$ - $E$  curves of the P(VDF-TrFE)/Metglas heterostructures measured between  $-70 \text{ MV m}^{-1}$  and  $+70 \text{ MV m}^{-1}$  with a field-frequency of 8 mHz. (d)  $P$ - $E$  loops calculated from  $J$ - $E$  curves in (c) by Eq. (3).

To characterize the spontaneous polarization of the P(VDF-TrFE) films,  $J$ - $E$  loop measurements were performed on the P(VDF-TrFE)/Metglas heterostructures by sweeping the electric-field in the range of  $\pm 70 \text{ MV m}^{-1}$  (i.e., 7 V) with a ramping rate of  $3.33 \text{ MV m}^{-1} \text{ s}^{-1}$ , corresponding to a field frequency of 8 mHz, as shown in Figure 2(c). After several cycles, the  $J$ - $E$  behavior became reproducible. Two current peaks were observed and they correspond to the polarization switching of the P(VDF-TrFE) film. For an ideal ferroelectric material, that is, a perfect insulator, the leakage is negligible. The current-density during the field ascending ( $J_a(t)$ ) is totally induced by dipole reversal. Since the leakage exists in our samples, the current density value of the second-half sweep curves ( $J_s(t)$ ) that show no current peaks can be taken as the leakage for correction. Therefore, the quasi-static  $P$ - $E$  loops can be calculated by the integration of current density with time using the data of the  $J$ - $E$  loops according to

$$P(t) = \int_0^{t_{end}} [J_a(t) - J_s(t)] dt. \quad (3)$$

Figure 2(d) shows the calculated  $P$ - $E$  loops with a field frequency of 8 mHz. It is clear that the  $P$ - $E$  loops are typical saturated, square hysteresis loops of ferroelectric materials. The spontaneous polarization  $P_s$  is  $\sim 8 \mu\text{C cm}^{-2}$  and the coercive field  $E_c$  is  $\sim 50 \text{ MV m}^{-1}$ . These values are similar to those reported previously.<sup>25</sup>

Figure 3(b) shows  $\alpha_E$  of the heterostructure as a function of  $H_{dc}$  at an off-resonance frequency of 1 kHz. The  $H_{dc} + H_{ac}$  was applied in-plane to control the magnetization of the Metglas layer, while the electric-field was applied out-of-plane to tune the sign and magnitude of the polarization of P(VDF-TrFE), as schematically shown in Figure 3(a). Before the  $\alpha_E$  measurements, an electric-field sweeping from zero to either  $+70 \text{ MV m}^{-1}$  or  $-70 \text{ MV m}^{-1}$  was exerted to the P(VDF-TrFE) films to set the direction of  $P$  to either fully upward or fully downward, respectively. Then, the  $\alpha_E$

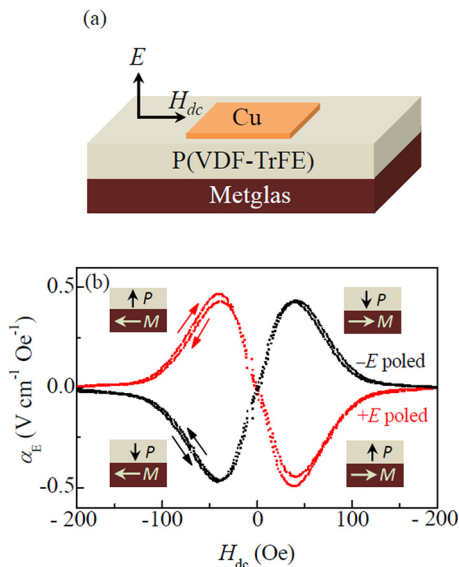


FIG. 3. (a) The configuration of the  $\alpha_E$  measurement. (b) The ME voltage coefficient  $\alpha_E$  of the P(VDF-TrFE)/Metglas heterostructure as a function of  $H_{dc}$  bias. Insets illustrate schematically the change of relative orientation between  $M$  and  $P$  during the measurement.

was measured with an in-plane  $H_{ac}$  of 12.07 Oe as a function of the bias in-plane  $H_{dc}$ . When  $P$  is set to upward (the red curve), with increasing  $H_{dc}$ ,  $\alpha_E$  increased quickly from almost zero at  $H_{dc} = -200 \text{ Oe}$  to a maximum value ( $\sim 0.5 \text{ V cm}^{-1} \text{ Oe}^{-1}$ ) at a particular  $H_{dc}$  ( $\sim -38 \text{ Oe}$ ) and then declined to zero for  $H_{dc} \sim 0 \text{ Oe}$ . In contrast, when  $P$  is set to downward (the black curve), the  $H_{dc}$  dependence of  $\alpha_E$  is totally the opposite, being negative for positive  $H_{dc}$ , and positive for negative  $H_{dc}$ . The  $H_{dc}$  dependence of  $\alpha_d$  can be phenomenologically written as<sup>26</sup>

$$\alpha_d = \frac{dP}{dH} = kqe, \quad (4)$$

where

$$q = \frac{dS}{dH} \quad \text{and} \quad e = \frac{dP}{dS}, \quad (5)$$

where  $k$  is the coupling factor ( $0 \leq k \leq 1$ ) between the consecutive phases,  $S$  is the strain, and  $q$  and  $e$  are the piezomagnetic coefficients of the Metglas and piezoelectric coefficients of the P(VDF-TrFE) films, respectively. Under zero magnetic field,  $q$  is almost zero because negligible magnetostriction takes place in the Metglas, leading to an almost zero  $\alpha_d$  (or  $\alpha_E$ ). With increasing the  $dc$  magnetic field, the magnetostriction reaches the maximum value at  $\sim 38 \text{ Oe}$ , resulting in the peak values of  $\alpha_E$  in Figure 3(b). As the  $dc$  magnetic field continued to increase to 200 Oe, the magnetization of the Metglas fully saturated (see Figure 1) and the magnetostriction gradually disappeared ( $q \sim 0$ ). Therefore,  $\alpha_E$  gradually approached to zero. Besides the  $\alpha_E$  values, it should be noted that the sign of  $\alpha_E$  can also be variable. The sign of  $\alpha_E$  depends on the relative orientation between  $M$  and  $P$  (see inset in Figure 3(b)). Once the direction of  $H_{dc}$  is fixed, i.e., the sign of  $M$ , and consequently that of  $q$ , is fixed, the sign of  $\alpha_E$  is only determined by the direction of  $P$ . Thus, the sign of  $\alpha_E$  can be switched by reversing  $P$  with  $E$  under the condition that the reversal of  $P$  has no influence on the direction of  $M$ . This opens a promising way to realize the nonvolatile memory operation by employing the ME voltage coefficient  $\alpha_E$ .

We first demonstrate the nonvolatile two-level memory by using this multiferroic heterostructure. Figure 4(a) shows the repeatable switch of  $\alpha_E$  of the P(VDF-TrFE)/Metglas heterostructures. The electric-field pulses with the magnitudes of  $+70 \text{ MV m}^{-1}$  and  $-70 \text{ MV m}^{-1}$  and a width of 10 ms were applied alternatively to the P(VDF-TrFE) films to change the polarization direction. After each electric-field application,  $\alpha_E$  was measured for 100 s continuously. During the measurements, a small  $H_{dc}$  bias of 10 Oe was applied to make each state distinguishable. As we expected, a clear switching of  $\alpha_E$  between two levels of  $\pm 0.115 \text{ V cm}^{-1} \text{ Oe}^{-1}$  was obtained, and each state shows good stability after removing the external electric-field. Therefore, the two levels of  $\alpha_E$  can be encoded with binary information of “0” and “1” to realize the nonvolatile memory application. It should be pointed out that, because the thickness of P(VDF-TrFE) is only  $1 \mu\text{m}$ , the corresponding operation voltage is only 7 V, which is much lower than that in the bulk ME devices and more practical for the device application.<sup>15,16</sup> Moreover, the reading of  $\alpha_E$  is non-destructive but an independent coil is

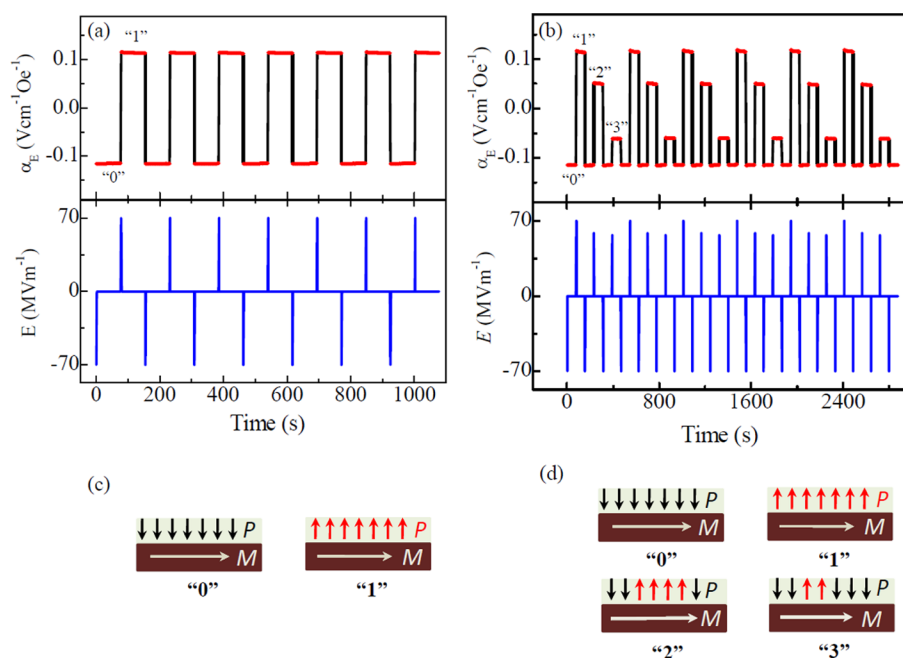


FIG. 4. (a) Two-level switching of  $\alpha_E$  (up panel) and the applied electric-field pulses with the magnitudes of  $+70 \text{ MV m}^{-1}$  and  $-70 \text{ MV m}^{-1}$  and a width of 10ms as a function of time (bottom panel). (b) Four-level switch of  $\alpha_E$  (up panel) and the applied electric-field pulses with varied magnitudes and fixed width of 10ms as a function of time. The "0," "1," "2," and "3" states were obtained by applying  $E$  of  $-70$ ,  $+70$ ,  $+58$ , and  $+56 \text{ MV m}^{-1}$ , respectively (bottom panel). (c) and (d) show the schematic illustration of the change of ferroelectric domains in the P(VDF-TrFE) films during  $\alpha_E$  switching, while the magnetization direction in the Metglas remains unchanged.

required to generate a small reading magnetic field. Because all the memory cells can share a single coil, the reading operation as well as device fabrication can be greatly simplified.

According to Eqs. (4) and (5), the  $\alpha_d$  (or  $\alpha_E$ ) value is also related to  $e$ , which can be changed by tuning the polarization value of the P(VDF-TrFE) films. That means, if we modulate the strength of  $E$  applied to the P(VDF-TrFE) films, different  $e$  as well as  $\alpha_d$  (or  $\alpha_E$ ) values can be obtained, which allows the nonvolatile multilevel memory. Figure 4(b) shows the multilevel switching of  $\alpha_E$  of the P(VDF-TrFE)/Metglas heterostructures. Four  $\alpha_E$  levels encoded as "0," "1," "2," and "3" were obtained by applying  $E$  of  $-70$ ,  $+70$ ,  $+58$ , and  $+56 \text{ MV m}^{-1}$ , respectively. The change of  $\alpha_E$  can be understood in terms of the partial switching of polarization in the P(VDF-TrFE) films under non-saturated  $E$ , as schematically illustrated in Figure 4(d). By means of the different  $\alpha_E$  levels, a multilevel memory mode can be conceived. For example, applying  $+E$  with different strengths, in which several  $\alpha_E$  levels will be induced due to partial reversal of the ferroelectric domains in the P(VDF-TrFE) film, can act as the SET operation. Each state can be used to store different information. And applying a fixed  $-E$ , which is large enough to fully reverse all the ferroelectric domains to the opposite direction, can be used as the RESET operation to erase the saved information. It means that such a multilevel mode device will have a memory ability equivalent to several devices with binary mode without changing the device size. Thus, a multiplied memory density could be expected.

Note that fatigue of the polarization switching is the main disadvantage of the ferroelectric memories. One of the main reasons for that is due to the destructive readout process, in which a polarization switching is required for each readout and then a rewriting process is also needed to switch back the polarization. In the memtransistor-based memory, although the electric-writing process is the same as that of the ferroelectric memories, the destructive readout is avoided. The polarization direction does not need to be changed during the readout of

ME coefficients. Since the majority of operations in real memory devices is readout, our device with nondestructive readout would be helpful to save the problem of fatigue of polarization switch. Moreover, the device is made of insulating materials so that no considerable currents pass through the device to cause Joule heating, and a low power consumption is expected. Last but not least, due to the flexible and easy processable properties of the P(VDF-TrFE) thin film, it is promising to be used as flexible nonvolatile memory devices. To realize these kinds of nonvolatile memory applications, the ME coupling performance is still required to be improved.

In summary, we have prepared ferroelectric P(VDF-TrFE) thin films with a thickness of  $1 \mu\text{m}$  by the sol-gel method on Metglas foil substrates with a thickness of  $25 \mu\text{m}$  and studied the electric-field-induced reversible switching of the ME voltage coefficient  $\alpha_E$  in the P(VDF-TrFE)/Metglas multiferroic heterostructures at room temperature. Several  $\alpha_E$  levels can be obtained by modulating the strength of the applied electric-field. This multilevel switching of  $\alpha_E$  can be attributed to the partial polarization switching of the ferroelectric P(VDF-TrFE) films. Compared with the previous results,<sup>15,16</sup> the operation voltage, that is, the polarization switching voltage, was reduced to 7 V, which is more advantageous to the memory device application. The present results demonstrate the feasibility of the P(VDF-TrFE)/Metglas multiferroic heterostructures in multilevel TCRAM devices.

This work was supported by the National Key Research Program of China (Grant No. 2016YFA0300700) and the National Natural Science Foundation of China (Grant Nos. 11534015, 51371192, 11227405, 11274363, and 51671213).

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