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Nonvolatile programmable two-terminal diodes using a ferroelectric semiconductor

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The conductance of diodes formed by epitaxial $(Pb, La)(Zr, Ti)O_3$ on $SrTiO_3$ doped with Nb is programed using the relaxation semiconductor characteristics of a ferroelectric. Namely, a three-terminal device function is given to a two-terminal device by time-domain control. The conductance modulation programed by a short-voltage pulse is perfectly retained for ten days at room temperature and is nondestructively read. The relaxation current at very low bias is also programmable. When the current is regulated by a metal/ferroelectric contact, the pulse modulation is obscure and is not retained. This implies that the surface layer at the metal/ferroelectric contact is negligibly thin or thinner than the tunneling distance. © *2000 American Institute of Physics.* [S0003-6951(00)02002-7]

The functionality of perovskite oxides is rapidly expanding since the discovery of the high-T_c superconductor by Bedenorz and Müller. Diodes possess one of the simplest device structures and operate in a two-terminal configuration,[1–4] which is advantageous in high-density-integrated circuits (IC). However, an external control of the rectifying characteristics as in three-terminal devices is desired, especially for memory application.

Ferroelectric perovskites possessing a high resistance and a large permittivity change the spontaneous polarization (P_s) by application of a short-voltage pulse while they conduct the carrier when a dc voltage is applied.[5–7] Namely, the ferroelectric behaves as an insulator in a short time scale and as a semiconductor in a long time scale and is regarded as a relaxation semiconductor.[8] These properties allow a time-domain control of a three-terminal device-like-operation of diodes. The present letter reports programing of the diode conductance, i.e., a memory write by a short-voltage pulse, ten day perfect retention, and a nondestructive memory read by a dc voltage. Relaxation current is found also to exhibit similar behavior. These operations were possible in *pn* junctions-like ferroelectric heterostructures formed by $Pb(Zr, Ti)O_3$ and $SrTiO_3$. The current–voltage ($I-V$) characteristics of ferroelectric films are usually unstable due to degradation. However, the $I-V$ characteristics reported below are extremely stable and unchanged over hundreds of measurements. The results are interpreted as a P_s control of the diode current. On the other hand, in ferroelectric Schottky contacts, P_s control of the current was not identified. This fact limits experimentally the thickness of an intrinsic surface layer with $\nabla P \neq 0$ restricting the ferroelectric size limit.[9,10] An advantage of this approach over ferroelectric field-effect devices[11,12] is the reduction of the wiring for high-density integration. Furthermore, using the present diodes, synapse elements in a neural circuit and ferroelectric diode disk memories can be developed.[13]

A few works reported dc voltage modulation of the current through epitaxial ferroelectric heterostructures. After a high V_{dc} was applied to a low-resistance film, the resistance modulation was retained over a day, although the repeatability is not reported.[14] After a low-dc voltage (V_{dc}) was applied, the current increased and decreased repeatedly, reproducibly by a factor of 10–100, but the modulation was retained only for an hour.[15] These observations have been explained by the change of bandbending due to (i) charge injection at the ferroelectric surface or (ii) spontaneous polarization (P_s). Furthermore, analysis of the carrier-transport process suggested a kind of *pn* junction formation in some ferroelectric heterojunctions, e.g., $Pb(Zr, Ti)O_3/SrTiO_3$, where the *p* type is the hole carrier type and the *n* type is the electron carrier type.[16]

c-axis-oriented $Pb_{0.95}La_{0.05}Zr_{0.2}Ti_{0.8}O_3$ (PLZT), $Pb_{0.95}La_{0.05}TiO_3$ (PLT), and $PbZr_{0.2}Ti_{0.8}O_3$ (PZT) films without secondary phases were epitaxially grown by pulsed-laser deposition on (100) $SrTiO_3$ doped with 0.5 wt % Nb (STON), as well as on 100-nm-thick $La_{1.99}Sr_{0.01}CuO_4$ (LCO). The Zr concentration is chosen to achieve a good lattice matching and acceptable switching properties. The ferroelectric layer is approximately 200 nm thick. Au and Pt films with surface areas of 0.2 and 1 mm^2 were deposited as the top electrodes, and the bottom conductive layer or the substrate was grounded. P_r measured by the Sawyer–Tower method is 2–5 $\mu C/cm^2$ at maximum applied voltage of 8 V at 10–100 kHz. The current was measured by applying V_{dc} across a ferroelectric film at room temperature (RT), where V_{dc} was first increased from zero to the maximum ($+V_{max}$), then decreased to the minimum ($-V_{max}$), passing through zero, and finally returned to zero. One $I-V$ curve consists of 200 points of 1 s intervals.

First, the results of a PLZT/STON diode are discussed. Similar results were found in PZT/STON and PLT/STON diodes, while the PLZT/STON diodes showed the best reproducibility among the three. PLZT/STON showed $I-V$ characteristics of a *pn* diode, and the forward bias polarity was positive (Fig. 1). The +6 V 25 μs pulse increased the forward bias current, and the −6 V 25 μs pulse decreased it. Four pairs of $I-V$ curves after ±6 V 25 μs pulses are shown

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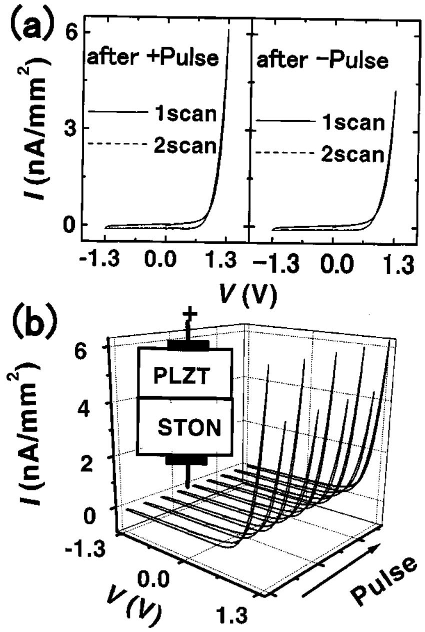

FIG. 1. $I-V$ characteristics of PLZT/STON (*pn* junction-like) after ±6 V 25 μs pulses (b). The +6 V 25 μs pulse increased the forward bias current, and the −6 V 25 μs pulse decreased it. For each pulse, two $I-V$ curves taken consecutively are displayed. Two $I-V$ curves measured after +6 V (left) and −6 V pulse (right) are shown but are completely overlapped (a), indicating that the reading process is nondestructive.

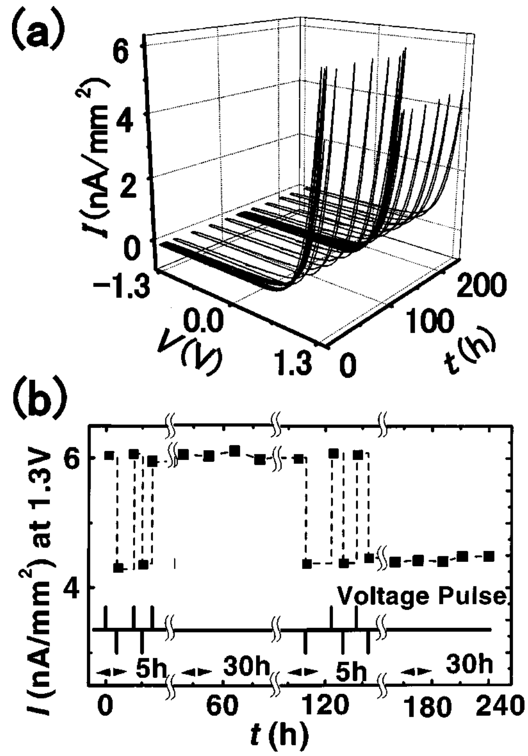

FIG. 2. Long time retention of $I-V$ characteristic modulation in PLZT/STON (*pn* junction-like) by ±6 V 25 μs pulses (a). For each measurement, two $I-V$ curves taken consecutively are displayed. As a summary of the retention, the current density I at $V_{dc}=+1.3$ V from (a) is replotted in (b). (I is taken from the third $I-V$ on each day to eliminate the effect of trap emissions.) Abscissa have a dual scale: The arrows of the length of one division show the scales.

in Fig. 1(b). All the $I-V$ curves after the +6 V 25 μs pulses were identical, and those after the −6 V 25 μs pulses were also identical. After each pulse, the $I-V$ curves were measured twice and were indistinguishable, as demonstrated in Fig. 1(a). This shows that the ''read'' process by the $I-V$ measurements is nondestructive.

The $I-V$ modulations were retained for at least five days (Fig. 2). On the first day of the retention test, the $I-V$ characteristics were measured by applying ±6 V 25 μs pulses. The last pulse was positive, and no pulse voltage was applied afterwards for 120 h. The $I-V$ measurements after the last positive pulse confirmed that the $I-V$ characteristics were completely reserved [Fig. 2(a)]. After these measurements, the $I-V$ characteristics were measured again by applying ±6 V 25 μs pulses. The last pulse was negative, and no pulse voltage was applied afterwards. The $I-V$ measurements after the last negative pulse confirmed that the $I-V$ characteristics were completely reserved. The retention characteristics are summarized in a plot of the current density at 1.3 V after the last pulse [Fig. 2(b)]. The retention at another electrode was found to be over ten days in a 21 day test, although its current density was slightly scattered from day to day by poor room-temperature control.

The results suggest that P_s controlled the current through the *pn* junction-like ferroelectric diodes. The forward bias $I-V$ relation is expressed by $\exp[e(\langle\Phi\rangle - V_{dc})/vkT]$, where e is the elementary charge, Φ is the barrier height, $\langle\rangle$ means an average over the leakage paths, k is the Boltzmann factor, T is the absolute temperature, and v is the ideality factor. A typical $I-V$ curve is replotted in Fig. 3 from Fig. 1(a), and the curve at increasing V_{dc} is fitted with $v=1.56$. The change of the $I-V$ characteristics is explained by $\delta\langle\Phi\rangle$, the change of $\langle\Phi\rangle$ due to the polarization reversal near the leakage paths. The $\delta\langle\Phi\rangle$ estimated from the fitting to Fig. 3 is 11.9 mV. In comparison with theory,[16] this small value indicates that P_s near the leakage path is pinned tightly. The value of 11.9 mV suggests that less than 3% of the domain switched near the leakage path.

Similar experiments on nm-scale contacts were performed using an atomic force microscope with a conducting tip. No reproducible $I-V$ modulation was observed for pulse voltages smaller than 13 V, which may be related to the aforementioned small fraction of domain switching near the leakage path.

In contrast with the diode-like $I-V$ characteristics, the low-voltage $I-V$ characteristics were dominated by a relaxation current that likely originates from the emission and the absorption of carriers by traps. Nevertheless, pulse modulation was also observed (Fig. 4). The +6 V 25 μs pulse decreased the width of the hysteresis and the slope of the $I-V$ curve ($\Delta I/\Delta V$) and the −6 V 25 μs pulse increased them.

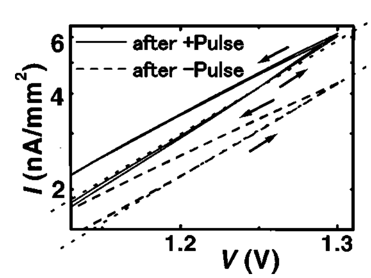

FIG. 3. Log I vs V_{dc} plot of typical $I-V$ curves of PLZT/STON in Fig. 1 after ±6 V 25 μs pulses. For each pulse, two $I-V$ curves taken consecutively are displayed.

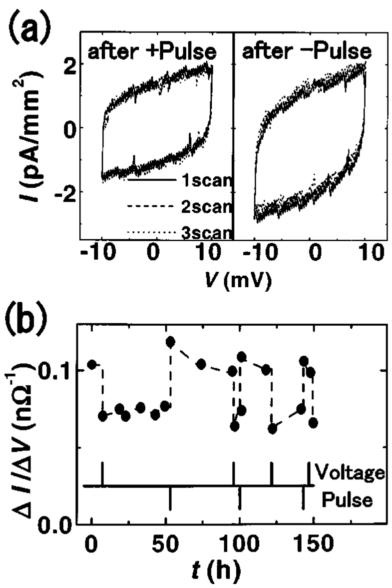

FIG. 4. Low-voltage $I-V$ characteristics of PLZT/STON (*pn* junction-like) after ± 6 V 25 μs pulses (a). The hysteresis is due to relaxation. For each pulse, three $I-V$ curves taken consecutively are displayed and are almost identical, indicating that the reading process is nondestructive. Retention of the slope of the $I-V$ curves (b).

Consistently with the diode current modulation, the modulations are explained by the decrease of the resistance by the $+6$ V pulse and the increase by the -6 V pulse, because the current is mainly due to the capacitive response and increases with the *RC* time constant. The modulation was retained at least for two days.

Contrary to the PLZT (PLT, PZT)/STON diodes, most of the metal/PLZT (PLT, PZT)/LCO diodes did not exhibit reproducible $I-V$ modulation, which agrees with a recent report.[17] An exception was found in Au/PLT/LCO (Fig. 5). The PLT/LCO exhibits $I-V$ characteristics of a metal/*p*-type semiconductor diode, and the forward bias polarity is negative. The -8 V 100 μs pulse increased the forward-bias current, and the $+8$ V 100 μs pulse decreased it. However, the $I-V$ characteristics were noisy, and unlike PLZT/STO, the $I-V$ curves of the first and second measurements do not completely overlap. The modulation was not retained even for 9 h [Fig. 5(b)]. These results would suggest that P_s switching did not affect the current through the ferroelectric Schottky diodes.

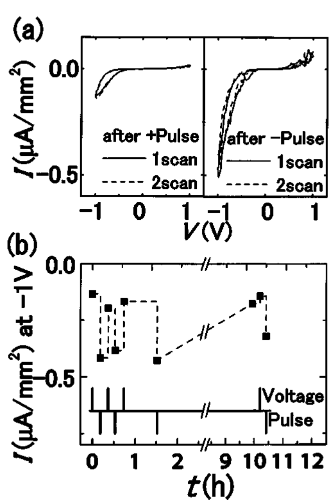

FIG. 5. $I-V$ characteristics of a Au/PLT/LCO (Schottky diode-like) after ± 8 V 100 μs pulses (a) and retention (b). For each pulse, two $I-V$ curves taken consecutively are displayed in the main figure, showing worse reproducibility than that in Fig. 1.

Theoretically, modulation of the $I-V$ characteristics by domain switching is also expected at the ferroelectric/metal contact, if a nonconducting dead layer formed by chemical reaction or a layer with $\nabla P \neq 0$ exists on the ferroelectric surface.[16] The above result suggests that the thickness of such a layer at a clean metal/ferroelectric interface is less than the tunneling distance, if it exists. This is consistent with the recent report of two-dimensional ferroelectric films demonstrating that an intrinsic thickness limit is negligibly small.[18] However, the present conclusion does not exclude the possibility that such an ultrathin layer may reduce the net dielectric constant of the film.

In conclusion, nondestructive reading and nonvolatile writing of a two-terminal device, i.e., a diode, were repeatedly performed, exploiting the difference of the time-domain response of a semiconducting ferroelectric. Namely, the conductance of a *pn* junction-like diode was changed by the voltage pulse, was undisturbed by read processes, and was perfectly retained for 5–10 days. The whole operation can be regarded as a quasi-three-terminal device operation in the time domain. Such modulation was not retained when the current was regulated at the metal/ferroelectric interface.

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