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Resistance switching in $BaTiO_{3-\delta}/Si$ *p-n* heterostructure

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The resistance switching characteristic and electric displacement-voltage hysteresis loop have been observed in $BaTiO_{3-\delta}/Si$ *p-n* heterostructures fabricated by laser molecular beam epitaxy. The ferroelectric response of $BaTiO_{3-\delta}$ can be enhanced by the interface polarization of the junction. The resistance switching property observed in the $BaTiO_{3-\delta}/Si$ *p-n* junction can be attributed to the irreversibility of polarization in the polarization and depolarization processes. The present results indicate a potential application of resistance switching in the heterostructures consisting of oxides and Si. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2821369]

Recently, a great deal of effort has been devoted to exploring materials with multifunctional properties in perovskite-type oxides for their potential applications. Especially, resistive hysteresis effect, which reflects resistance switching under external stimuli, has attracted wide attention due to their potential application in nonvolatile resistance memory.[1] Some research groups have observed resistive hysteresis effect on ferroelectric thin films[2–4] and artificial heterostructures.[5–9] Compared with thin films, the heterostructures have great potential in designing and tailoring devices to specific applications.[10–14] So far, most of the heterostructures with resistive hysteresis effect are found in all-oxide materials or metal/oxide semiconductor.[5–9] From the view of application, however, it would be important if we can realize resistance switching in the heterostructures made of oxides and Si, which means we could have the possibility of realizing this functional property in the semiconductor integration.

In previous work, we have observed the ferroelectric hysteresis loop in $BaNb_{0.3}Ti_{0.7}O_3/Si$ *p-n* junction.[10] In this work, not only the electric displacement-voltage (*D-V*) hysteresis loop but also more interesting hysteresis current-voltage (*I-V*) characteristic are found in the $BaTiO_{3-\delta}/Si$ *p-n* junction. The results present the possibility of realizing resistance switching in oxide-silicon *p-n* junctions.

In order to form *p-n* junctions with high-quality interfaces, a computer-controlled laser molecular beam epitaxy (laser MBE) was used to fabricate the $BaTiO_{3-\delta}/Si$ *p-n* junctions. We chose 2 in. *p*-type Si (001) wafers with resistivity of 4 Ω cm as the substrates, and epitaxially grew $BaTiO_3$ thin films on Si substrates under a low oxygen pressure to obtain *n*-type $BaTiO_{3-\delta}$. As mentioned in our previous report,[10] at first, about two-unit cell thick $BaTiO_{3-\delta}$ were deposited on the Si substrates at room temperature to prevent the formation of amorphous SiO_2 layer, and then the Si substrates were heated to 620 °C under the oxygen pressure of 2×10^{-4} Pa. The growth process of the $BaTiO_{3-\delta}$ was monitored by *in situ* reflection high-energy electron diffraction (RHEED). When the RHEED streak pattern of the $BaTiO_{3-\delta}$ layer appeared, the $BaTiO_{3-\delta}$ with a thickness of 300 nm were continuously deposited at an oxygen pressure of 2×10^{-4} Pa. Hall measurement confirmed that the $BaTiO_{3-\delta}$ thin film was electron conductive and the resistivity was 1.7×10^{-2} Ω cm at room temperature.[15] For electrical measurement, indium (In) electrodes of 0.5 mm^2 were used on $BaTiO_{3-\delta}$ and Si, respectively.

The current-voltage (*I-V*) characteristic of the $BaTiO_{3-\delta}/Si$ *p-n* junction was measured by a pulse-modulated voltage source at room temperature. Figure 1 shows a *I-V* curve of the $BaTiO_{3-\delta}/Si$ *p-n* junction. The schematic of the measurement circuit is shown in the left inset of Fig. 1. The sweeping direction of the applied bias voltage was from −6 to +6 V. The junction exhibited a good rectifying characteristic. In addition, the in-plane resistance-temperature curve of the $BaTiO_{3-\delta}$ thin film is also shown in the right inset of Fig. 1 measured by the four-probe method. It is seen that the $BaTiO_{3-\delta}$ thin film exhibited semiconductor behavior in the temperature range of 150−300 K.

The resistance switching characteristic was observed in $BaTiO_{3-\delta}/Si$ *p-n* junctions. Figure 2 shows the typical hysteresis *I-V* curve. As shown in Fig. 2, the voltage was swept as $-6\rightarrow0\rightarrow+6\rightarrow0\rightarrow-6$ V and the numbers from 1 to 4 indicate the direction of the voltage sweep. It is clearly seen that the junction exhibited a low resistance state when sweeping voltage from 0 to +6 V, and exhibited a high resistance state when sweeping voltage from +6 to 0 V. We also measured hysteresis *I-V* characteristic for different V_{max}.

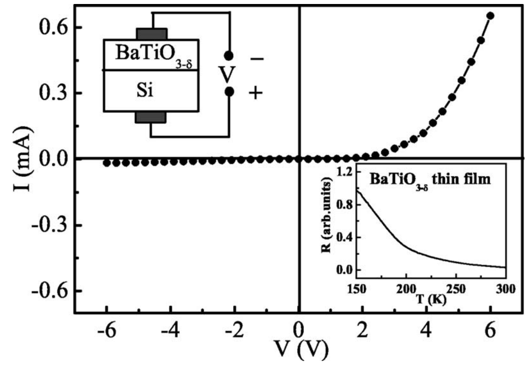

FIG. 1. Current-voltage curve of $BaTiO_{3-\delta}/Si$ *p-n* junction at room temperature. The left inset shows the schematic circuit of the sample measurement and the right inset shows the resistance vs temperature curve of $BaTiO_{3-\delta}$ thin film.

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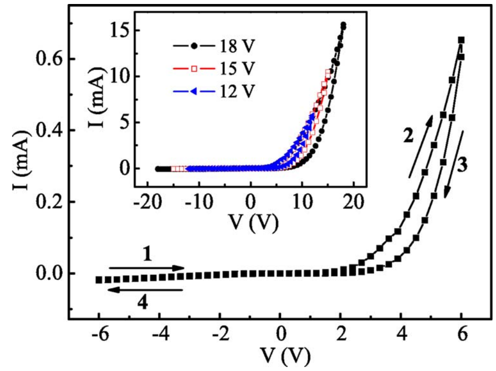

FIG. 2. (Color online) Hystersis *I-V* characteristic of $BaTiO_{3-\delta}$/Si *p-n* junction. The bias voltage was swept as $-6 \rightarrow 0 \rightarrow +6 \rightarrow 0 \rightarrow -6$ V and the numbers from 1 to 4 indicate the direction of the sweep. The inset shows the hystersis *I-V* curves of the junction under various V_{max}.

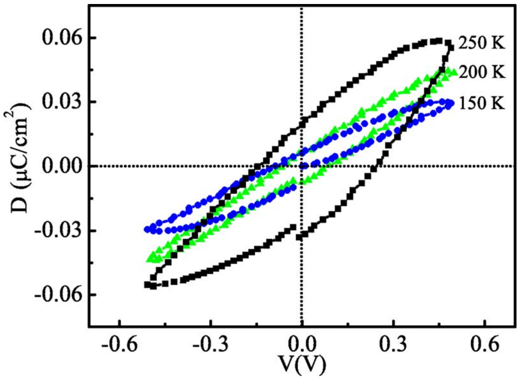

FIG. 4. (Color online) The *D-V* loops of $BaTiO_{3-\delta}$/Si *p-n* junction at different temperatures.

The voltages were swept as $-V_{max} \rightarrow 0 \rightarrow +V_{max} \rightarrow 0 \rightarrow -V_{max}$. As shown in the inset of Fig. 2, all of the *I-V* curves exhibited similar hysteresis property. To avoid the electrical damage to sample, the maximum bias voltage applied to the $BaTiO_{3-\delta}$/Si *p-n* junction was limited to 18 V. It is interesting to note that the junction showed larger *I-V* loop with larger V_{max}, which indicates that the saturated hysteresis loop should be obtained at a maximum voltage larger than 18 V.

The polarization related resistance modulation is usually observed in some ferroelectric films and heterostructures.[9,16] To verify whether the resistance switching is related to ferroelectric response, we measured the electric displacement versus voltage (*D-V*) loops of the $BaTiO_{3-\delta}$/Si *p-n* junction with different applied voltages, the results are shown in Fig. 3. The *D-V* hysteresis loop is an appropriate way to describe the ferroelectric response in ferroelectric systems with a finite conductivity.[17] From Fig. 3, it can be seen that the area of the hysteresis loops became greater under larger applied voltage. To prove whether the *D-V* hysteresis loops resulted from $BaTiO_{3-\delta}$ thin film, we also grew $BaTiO_{3-\delta}$ thin film on $SrRuO_3$/$SrTiO_3$ (SRO/STO) substrate under the same deposition conditions as those for the $BaTiO_{3-\delta}$/Si *p-n* junction. We did not observe the hysteresis loop in the $BaTiO_{3-\delta}$ thin film on SRO/STO substrate due to the large leakage current, in which the SRO is metallic.[18] To check the origin of the hysteresis loops (shown in Fig. 3), we also measured the temperature-dependent hysteresis loops of the $BaTiO_{3-\delta}$/Si heterostructure and the result is shown in Fig. 4. It is seen that the $BaTiO_{3-\delta}$/Si junction exhibited weaker ferroelectric response in lower temperature. This observation cannot be understood merely by the ferroelectric property of $BaTiO_{3-\delta}$. Since the resistivity of $BaTiO_{3-\delta}$ is increased with decreasing temperature, the $BaTiO_{3-\delta}$ thin film was supposed to exhibit stronger ferroelectric response in lower temperature due to the decrease of leakage current. On the other hand, our recent theoretical study[19] has revealed that the carrier densities are increased with the increase in temperature at the interface region, as well as the space charges and the polarization at the interface of heterostructures. Therefore, we suspect that the hysteresis loops in $BaTiO_{3-\delta}$/Si *p-n* junction can be related to the junction interface.

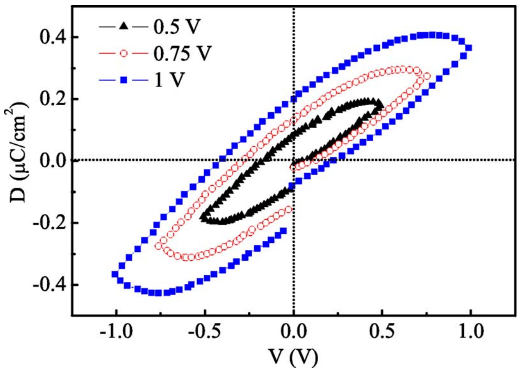

FIG. 3. (Color online) The *D-V* loops of $BaTiO_{3-\delta}$/Si *p-n* junction at three different applied voltages.

For $BaTiO_{3-\delta}$/Si *p-n* structure, it is well known that there should be a potential barrier region in the *p-n* interface due to the diffusion of carriers. Equal positive charges and negative charges appear in the *n* region and *p* region, respectively, inducing an electric field in the interface region in the direction from the *n* to the *p* region. The space charges due to charge transfer between $BaTiO_{3-\delta}$ and Si form electric dipoles at the $BaTiO_{3-\delta}$/Si interface. The dipole moments at the interface can give rise to polarization enhancement in $BaTiO_{3-\delta}$/Si *p-n* junction.[20,21] With increasing positive bias voltage, the positive polarization of $BaTiO_{3-\delta}$ increases and reaches to the maximum value when the voltage increases to its maximum value V_{max} ($V_{max} > 0$). Then, as the bias voltage decreases from V_{max}, the polarization of $BaTiO_{3-\delta}$ also decreases correspondingly. Thus, the process of sweeping voltage from 0 to V_{max} and from V_{max} to 0 is corresponding to the polarization and depolarization processes of $BaTiO_{3-\delta}$, respectively. As shown in Fig. 3, the magnitude of polarization in the polarization process (0 to V_{max}) is smaller than its counterpart in the depolarization process (V_{max} to 0) due to the hysteresis effect of polarization versus applied voltage. Larger *I-V* loop shown in the inset of Fig. 2 can arise from lager *D-V* hysteresis loop at larger V_{max} shown in Fig. 3. Noting that the *D-V* hysteresis loops cannot be observed in $BaTiO_{3-\delta}$ thin film on metallic substrate (SRO), we suspect that the interface of the heterostructure plays an important role in the obtaining of the hysteresis loop.

In conclusion, we have fabricated $BaTiO_{3-\delta}$/Si *p-n* junctions by epitaxially growing $BaTiO_{3-\delta}$ films on Si substrates. The resistance switching characteristic and *D-V* hysteresis loop have been observed at room temperature. Our experimental results indicate that the polarization enhancement by the interface can play a very important role in the ferroelectric response in $BaTiO_{3-\delta}$/Si *p-n* heterostructure. The resistance switching characteristic is related to the irreversibility of polarization of the junction. The interesting results suggest the possibility of a wide study on the resistance switching devices based on oxide and Si *p*-*n* junctions.

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[1] M. P. Singh, L. Méchin, W. Prellier, and M. Maglione, Appl. Phys. Lett. **89**, 202906 (2006).

[2] N. G. Subramaniam, J. C. Lee, and T. W. Kang, Appl. Phys. Lett. **87**, 212907 (2005).

[3] R. Oligschlaeger, R. Waser, R. Meyer, S. Karthäuser, and R. Dittmann, Appl. Phys. Lett. **88**, 042901 (2006).

[4] Y. D. Xia, W. Y. He, L. Chen, X. K. Meng, and Z. G. Liu, Appl. Phys. Lett. **90**, 022907 (2007).

[5] Y. Watanabe, Phys. Rev. B **59**, 11257 (1999).

[6] J. Rodríguez Contreras, H. Kohlstedt, U. Poppe, R. Waser, C. Buchal, and N. A. Pertsev, Appl. Phys. Lett. **83**, 4595 (2003).

[7] Y. Watanabe, Appl. Phys. Lett. **66**, 28 (1995).

[8] T. Fujii, M. Kawasaki, A. Sawa, H. Akoh, Y. Kawazoe, and Y. Tokura, Appl. Phys. Lett. **86**, 012107 (2005).

[9] P. W. M. Blom, R. M. Wolf, J. F. M. Cillessen, and M. P. C. M. Krijn, Phys. Rev. Lett. **73**, 2107 (1994).

[10] Y. H. Huang, K. Zhao, H. B. Lu, K. J. Jin, M. He, Z. H. Chen, Y. L. Zhou, and G. Z. Yang, Appl. Phys. Lett. **88**, 061919 (2006).

[11] C. C. Wang, M. He, F. Yang, J. Wen, G. Z. Liu, and H. B. Lu, Appl. Phys. Lett. **90**, 192904 (2007).

[12] K. Akiyama, S. Kaneko, Y. Hirabayashi, and H. Funakubo, Thin Solid Films **508**, 380 (1995).

[13] B. N. Mbenkum, N. Ashkenov, M. Schubert, M. Lorenz, H. Hochmuth, D. Michel, M. Grundmann, and G. Wagner, Appl. Phys. Lett. **86**, 091904 (2005).

[14] F. Mitsugi, Y. Yamagata, T. Ikegami, K. Ebihara, J. Narayan, and A. M. Grishin, Jpn. J. Appl. Phys., Part 1 **39**, 5418 (2000).

[15] T. Zhao, Z. H. Chen, F. Chen, H. B. Lu, G. Z. Yang, and H. S. Cheng, Appl. Phys. Lett. **77**, 4338 (2000).

[16] D. J. Fu, J. C. Lee, S. W. Choi, S. J. Lee, T. W. Kang, M. S. Jang, H. I. Lee, and Y. D. Woo, Appl. Phys. Lett. **81**, 5207 (2002).

[17] C. K. Wong and F. G. Shin, J. Appl. Phys. **96**, 6648 (2004).

[18] C. L. Chen, Y. Cao, Z. J. Huang, Q. D. Jiang, Z. Zhang, Y. Y. Sun, W. N. Kang, L. M. Dezaneti, W. K. Chu, and C. W. Chu, Appl. Phys. Lett. **71**, 1047 (1997).

[19] C. L. Hu, P. Han, K. J. Jin, H. B. Lu, and G. Z. Yang (unpublished).

[20] I. B. Misirlioglu, M. Alexe, L. Pintilie, and D. Hesse, Appl. Phys. Lett. **91**, 022911 (2007).

[21] C. G. Duan, R. F. Sabirianov, W. N. Mei, S. S. Jaswal, and E. Y. Tsymbal, Nano Lett. **6**, 483 (2006).