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Memristive characteristics in semiconductor/metal contacts tested by conductive atomic force microscopy

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Abstract
Memristive characteristics in semiconductor/metal contacts are studied by conductive atomic force microscopy. The ZnO/Au device shows excellent memristive characteristics under Pt and TiN tips and the resistances of the high-resistance state and the low-resistance state are almost unchanged with time. Unipolar resistive switching behaviour is observed when a positive voltage is applied. In addition, the pure Au film also shows resistive switching behaviour under the TiN tip which was used to test the ZnO/Au device, but this behaviour cannot be observed under a Pt tip. Our results suggest that the memristive characteristics existing in semiconductor/metal contacts are due to the formation of conducting filaments in the interior of the semiconductor and the change in the energy barrier at the interface between the conductive atomic force microscope tip and the ZnO film.

(Some figures may appear in colour only in the online journal)

1. Introduction

The concept of memristor was first suggested by Leon Chua in 1971 [1], which is considered to be the fourth passive element following the resistor, capacitor and inductor. It will have broad application prospects in artificial biological systems and nonvolatile random access memories (NVRAMs). Charge-based memory devices such as dynamic random access memory and flash memory have technological and physical limitations as device dimensions have shrunk. Thus, a resistive random access memory relying upon a resistive switching mechanism has attracted considerable attention as a promising next-generation NVRAM due to its simple structure [2], high density [3] and fast switching [4].

Since Strukov *et al* [2] succeeded in fabricating a memristor in 2008, many groups have been interested in this field. It is expected to be a new hot issue in the field of electronics and materials science applications [5]. The memory effect can be realized through the switching characteristic between the high-resistance state (HRS) and the low-resistance state (LRS), which has been observed in various material systems such as organic films [6–8], chalcogenides [9, 10] and metal oxides [11, 12]. Usually, ZnO is an n-type semiconductor, which is due to the presence of unintentionally introduced donor centres, usually identified as oxygen vacancies [13]. Although the resistive switching behaviour of ZnO films has been studied before [4, 14–16], the mechanism of this behaviour is still controversial. In this paper, memristive behaviour is observed in the ZnO/Au device tested by conductive atomic force microscopy (CAFM) without an electroforming process. Different AFM tips are used to analyse the memristive characteristics. We put forward a different point of view about the mechanism of the memristive behaviour: the Schottky-type interface plays an important role in this behaviour in addition to the filamentary mechanism.

2. Experiments

In the experiments, molecular beam epitaxy (MBE) (Sky Technology Development Co., Ltd) is used to fabricate the memory devices under a high vacuum of 2×10^{-7} Pa and a laser energy of 140 mJ. First, an Au film about 5 nm thick is deposited by MBE at room temperature on a Si substrate. Then a 15 nm thick ZnO film is deposited on a part of it

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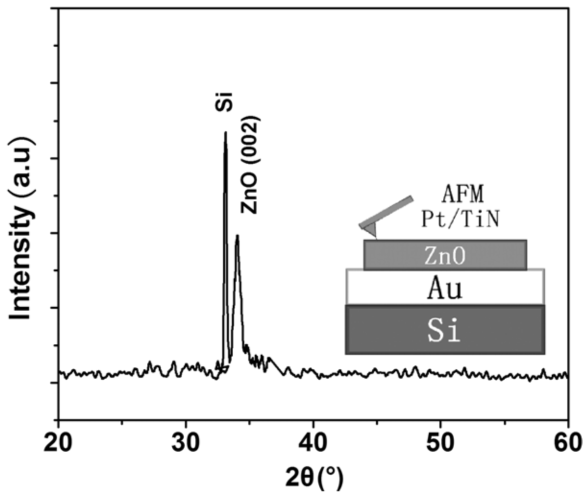

Figure 1. XRD spectrum of a ZnO/Au device fabricated on Si substrate. The inset shows the schematic view of the fabricated device.

with a circle metal mask so that the other part of the Au film is exposed. The diameter of the ZnO film is about 2 mm. The schematic view of CAFM tip/ZnO/Au/Si is shown in the inset of figure 1. The composition of the device is analysed by a D8 x-ray diffractometer (Bruker Co.). The film thicknesses are estimated using an M2000 spectroscopic ellipsometer (J A Woollam). Current–voltage (I–V) curves are obtained by CAFM (NT-MDT Co.), which is one of the best experimental tools to investigate the conductivity of a thin film due to the restricted interaction area of the tip and the film surface. During the electrical measurements, the sweeping voltage is applied to the Au bottom electrode while the AFM tip is grounded. The set point in contact mode is determined by a force versus z-directional displacement (F–Z) curve. DPE14-Pt and NSG11-TiN tips (NT-MDT Co.) are used in our experiment and the spring constants of the cantilevers are $5\,\mathrm{N\,m^{-1}}$ and $5.5\,\mathrm{N\,m^{-1}}$, respectively. The thickness of the Pt- or TiN-coated tip is 20–30 nm. The typical curvature radius of the tip is about 35 nm, which leads to the formation of a nanoscale contact between the top electrode (CAFM tip) and the ZnO film. All electrical measurements are carried out under ambient conditions. We fabricate tens of samples under the same conditions; each sample shows memristive behaviour, indicating that our device has excellent reproducibility.

3. Results and discussion

The x-ray diffraction (XRD) pattern of ZnO/Au/Si is shown in figure 1. The peak for Au film is not observed, which might be because the Au film is so thin that the intensity of diffraction is quite weak. The ZnO film exhibits a highly (0 0 2) textured orientation. A sharper peak reveals that the ZnO film prepared in this work has good crystallinity. As another paper reported [15], straight filaments are more likely to form along the flat grain boundary in the highly (0 0 2)-oriented ZnO film. Thus, the resistance of the ZnO film could decrease when the conducting filaments are formed.

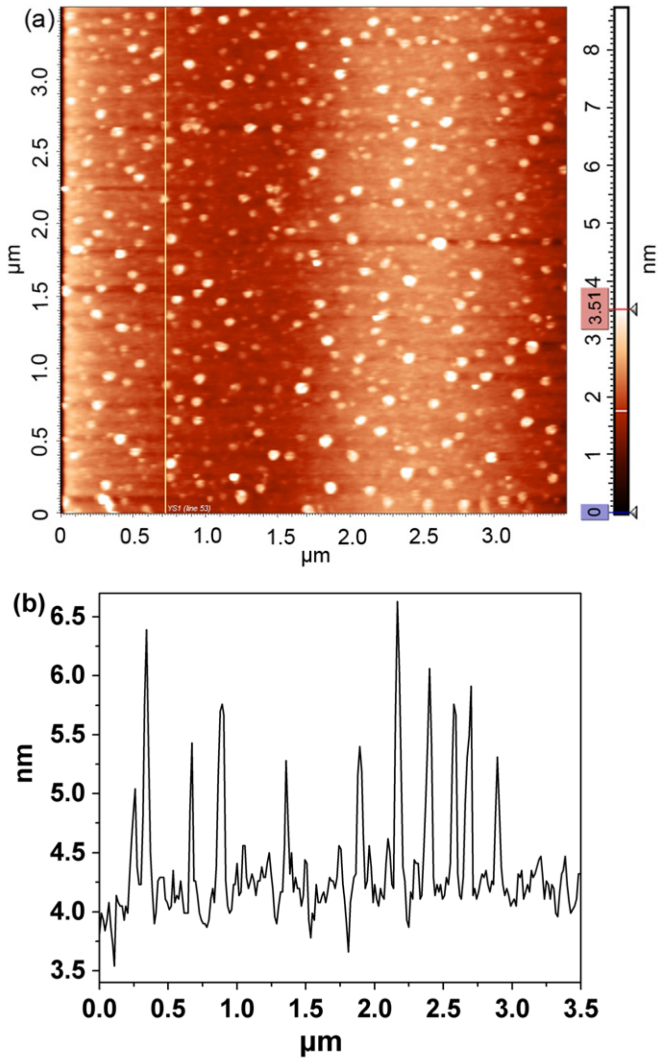

Figure 2. (a) Two-dimensional AFM image of the sample with a scanning area of $3.5\,\mu\mathrm{m} \times 3.5\,\mu\mathrm{m}$. ($b$) A height profile taken along the line marked in figure 2(a).

A two-dimensional (2D) AFM image of the ZnO film is shown in figure 2(a), with a scanning area of $3.5\,\mu\mathrm{m} \times 3.5\,\mu\mathrm{m}$. The white features in figure 2(a) delineate the ZnO grains and the sizes of these grains are about 30–50 nm. Figure 2(b) is a height profile taken along the line marked in the 2D image, with abscissa corresponding to the ordinate of figure 2(a), and the ordinate shows the relative height of the ZnO film. The AFM image shows a smooth surface, with a root mean square (rms) roughness of about 1.2 nm.

Figure 3(a) shows the I–V curves of the device tested by a fresh Pt tip in two sweeping cycles. The device is first in the HRS. When the bias applied to the Au film is swept from 0 to +10 V, a sudden resistance decrease from the HRS to LRS is observed at about 3 V. As the applied voltage is swept from +10 to 0 V and then from 0 to −10 V, the I–V curve does not retrace the same route because the LRS is maintained. When the bias is swept from −10 to 0 V, a resistance increase from the LRS to the HRS is obtained at about −1.3 V. The characteristics of the curves are consistent with the memristive behaviour [17], which is quite stable within hundreds of consecutive voltage

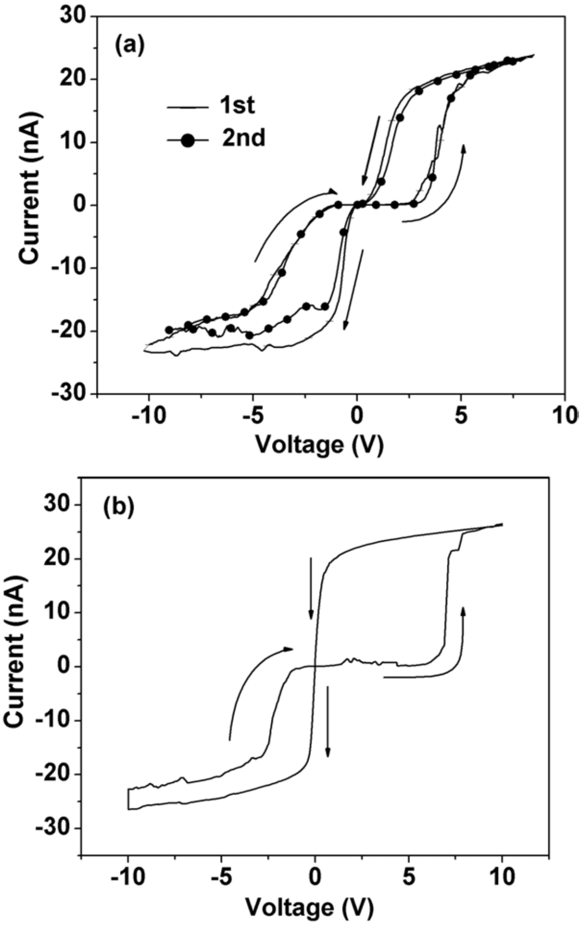

Figure 3. (*a*) Memristive characteristics of ZnO/Au tested by a fresh Pt tip in two sweeping cycles. (*b*) I–V characteristics tested by a fresh TiN tip.

sweepings. The high resistance is approximately $1.9 \times 10^{10}\ \Omega$, while the low resistance is about $1.8 \times 10^{8}\ \Omega$, which are both calculated at 1.6 V. In the experiments, the contact resistance can be neglected because it would not significantly affect the measured resistances, which are over one hundred megohms.

The experimental result changes when an AFM tip with different coating material is applied. Figure 3(*b*) shows the I–V curve tested by a fresh TiN tip. The results show a switching voltage (−1.2 V) from LRS to HRS similar to the result tested by the Pt tip. But a higher switching voltage (7.5 V) from HRS to LRS and a lower resistance in the LRS ($7 \times 10^{7}\ \Omega$) are observed. As another paper has reported, the TiN can contain significant amounts of oxygen due to exposure to air [18]. When the positive voltage sweep is applied to the bottom Au electrode, the TiN as an oxygen reservoir [4] could provide oxygen ions to neutralize the oxygen vacancies of the filaments, which would slow down the formation of conductive filaments, so a higher switching voltage is needed to switch the HRS to the LRS. However, once the filaments are formed, the resistance of the LRS becomes lower under the TiN tip than under the Pt tip. Since the work function of TiN (2.92 eV) is much lower than that of Pt (5.32 eV), it will be easier to form a good Ohmic contact between the TiN and the ZnO. In the experiments, we do not need to worry about the problem of measurement spots because the whole active region can be switched, which also implies that the whole ZnO film is equipotential.

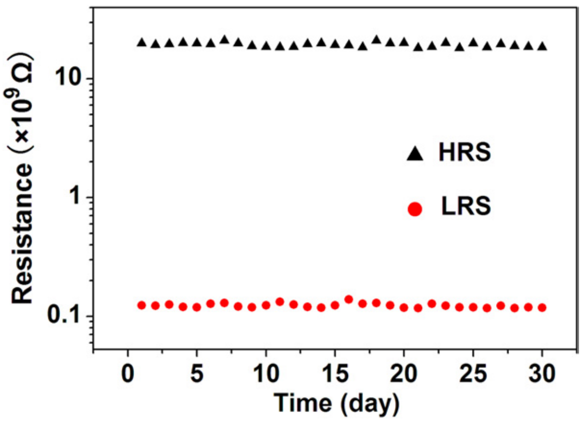

Figure 4. Variation of resistances of HRS and LRS versus time. The results are obtained by fresh Pt-coated tips and the resistances are all calculated at 1.6 V.

To study the data retention characteristics of the ZnO/Au device, the electrical properties are tested every day for one month. We use fresh tips in every testing in order to guarantee the same conditions. Figure 4 shows the resistance variation of the HRS and LRS over time, indicating that the resistance ratio is of about two orders of magnitude. The resistances of the HRS and the LRS are almost unchanged over one month, indicating that the data retention characteristic is very good, so nonvolatile application of the device is possible.

As reported by Waser and Aono [19], the electrode could be oxidized during the resistive switching process. In our experiments, the oxidation of TiN is observed when the TiN tip is used as the top electrode to test the I–V characteristics of the ZnO/Au device. Five hundred sweeping cycles were performed with the tip at the same place of the ZnO film. We found that the conductivity and stability become poor with the increasing of sweeping times. Figure 5(*a*) shows the I–V characteristic of the 500th sweeping cycle under a TiN tip. The current increases suddenly at about 8 V, but the maximum current is only 15 nA, which is much lower than the result tested by the fresh tip (figure 3(*b*)). In addition, the resistance in the LRS is quite unstable, which increases quickly as the voltage decreases from 10 to 0 V. The results indicate that the formed conductive filaments are quite weak. The reason should be that the tip is oxidized during the testing, resulting in deterioration of the conductivity of the tip, so that the electric field added on the device becomes much weaker. To verify the conclusion, we tested a pure Au film with a fresh TiN tip and a TiN tip that has been used to test the ZnO/Au device, respectively. The results show a good metallic conductive behaviour by a fresh tip, as shown in figure 5(*b*) (the black circle line), but the other one shows memristive characteristics. The phenomena could be related to the oxide (e.g. ZnO or TiO_x) on the tip. If the tip is only coated with ZnO during the repeated switching, the conductivity should not become so poor in figure 5(*a*). TiO_x could be formed once the TiN tip is oxidized during the repeated switching. When the oxidized TiN tip is used to test the conductivity of the pure Au film, a TiN/TiO_x/Au contact could be formed, in which TiN works as an electrode

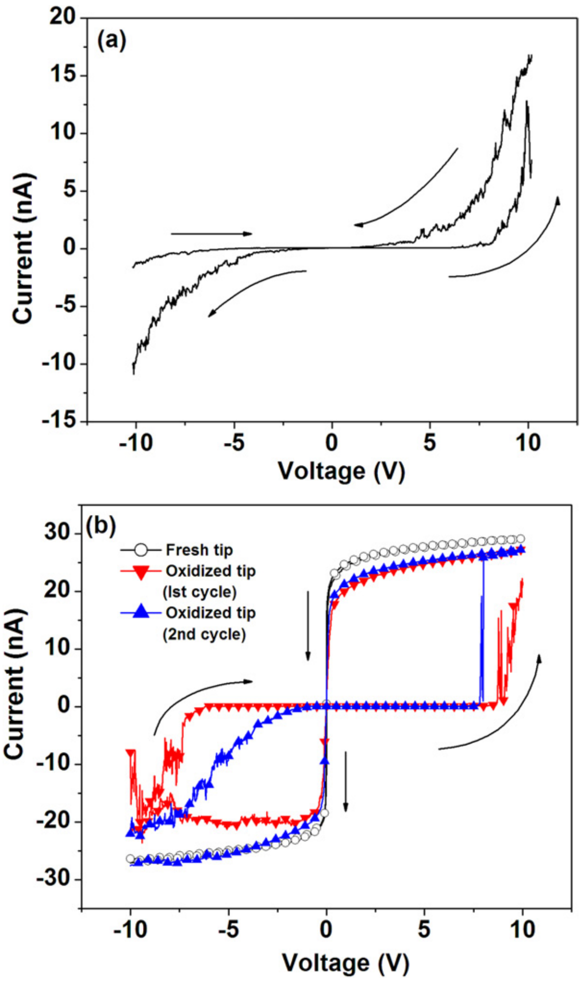

Figure 5. (*a*) I–V characteristics of the 500th sweeping cycle tested by a TiN tip. (*b*) I–V characteristics of an Au film tested by a TiN tip before and after the tip has been used to test the ZnO/Au device.

and TiO_x provides the oxygen vacancies [20]. In addition, we use the Pt tip to test the ZnO/Au device and find that the conductivity of the Pt tip also deteriorates after hundreds of sweeping cycles. Although Pt is a quite stable material, it can be oxidized under certain conditions [21, 22]. However, the memristive behaviour could not be observed by the oxidized Pt tip for the pure Au film, which might be because no oxygen vacancy exists in the oxidized Pt tip.

In order to exclude the effects of the conductive coating of the tip being worn away through repeated sweeping, a fresh TiN tip is used to test the pure Au film with a sweeping voltage from −0.1 to 0.1 V. We find that the conductivity is not affected after 500 sweeping cycles. So the effect of abrasion could be neglected in the experiments.

Although many mechanisms for memristive behaviour have been reported, such as insulator–metal transitions [23, 24], a boundary transport model [2], electronic spin blockade effects [25], conductive filaments [26] and redox reactions [7], the mechanisms for memristive behaviour are still controversial. We suggest there are two mechanisms to explain the behaviour in this work: the filamentary conduction and the interfacial effect [16]. The bipolar resistive switching in our device is quite stable. The conductive filament mechanism has been reported by many researchers. Waser and Aono [19] have reported a conductive path consisting of metal oxide with a metallic conducting phase. They noted that metal cations accommodate oxygen vacancies by trapping electrons emitted from the cathode, so the metal oxide is turned into a metallic conducting phase by a reduction reaction, which moves towards the anode and will finally form a conductive path. Although there has been no consensus about the nature of the conductive filaments, the idea that the deficiency plays an important role in the formation of conductive filaments has been consentient. Choi *et al* [3] found that the conductive path resulting from the aligning of oxygen vacancies should contribute to the resistive switching behaviour. Chang *et al* [15] and Xu *et al* [4] also attributed the resistive behaviour to the conductive filaments consisting of oxygen vacancies. In the present paper, the mechanism should be due to the formation of conductive filaments and the change of the Schottky barrier. When a positive voltage sweep is applied to the Au bottom electrode, the oxygen vacancies existing in the ZnO film align to form tiny conducting filaments in the HRS leading to a decrease in the resistance. Meanwhile, the oxygen vacancies move towards the Schottky-type interface between the CAFM tip and the ZnO film, which decreases the energy barrier. The two effects finally induce the device to switch to the LRS. Under a negative electric field, oxygen vacancies with positive charges migrate away from the Schottky interface, which increases the energy barrier, resulting in an increase in the resistance. Meanwhile, the strong current flowing through the existing filaments could cause the oxygen vacancies to be neutralized by the existing oxygen ions [4], or the filaments to be ruptured by Joule heating [3], so the original HRS appears again.

To further understand the mechanism of memristive behaviour, unipolar resistive switching characteristics under a Pt tip are studied. Memristive switching behaviour could be observed when a positive voltage sweep is applied, as shown in figure 6(*a*). Under a positive voltage sweep from 0 to 6 V, the oxygen vacancies align to form conductive filaments and the Schottky barrier is decreased so that the device is switched to the LRS. When the voltage is swept from 6 to 0 V, the HRS is observed again due to the oxygen vacancies of the filaments being neutralized by the existing oxygen ions or the filaments being ruptured by Joule heating. The resistance in the LRS becomes more stable during the second sweeping cycle than the first one. The unipolar resistive switching could be repeated hundreds of times. As a negative voltage sweep is applied to the device, the current begins to increase from −2.3 to −6 V. However, the second half-cycle almost coincides with the first one, indicating that the memristive behaviour could not be obtained when a negative voltage is applied, as shown in figure 6(*b*). This is because the Schottky barrier increases under a negative electric field and the barrier could not disappear as long as the negative voltage is applied to the device, which will obstruct the resistive switching from HRS to LRS. As the negative voltage increases, some electrons with enough energy pass through the energy barrier, which results in the formation of a current, but the resistance of the device has not decreased.

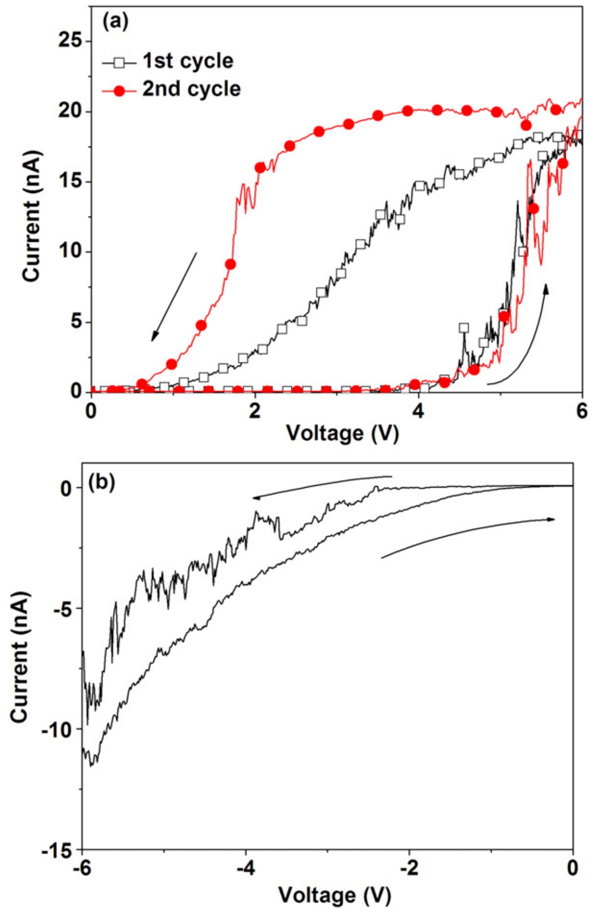

Figure 6. (*a*) I–V curves under positive voltage sweep with a Pt tip. (*b*) I–V curve under negative voltage sweep with a Pt tip.

4. Conclusions

We use the CAFM tip as one electrode to probe the memristive characteristics of a ZnO/Au device. The resistive switching remains stable over multiple sweeping cycles and the resistances of the HRS and the LRS are almost unchanged with time. The resistance ratio is of about two orders of magnitude. The memristive characteristics of the device are affected by the electrode materials. Unipolar resistive switching behaviour is also observed when a positive voltage sweep is applied to the device, while this behaviour could not be observed under a negative voltage sweep because of the increasing interface barrier. Our work provides a reference for studying the mechanism and the factors affecting the memristive behaviour.

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References

[1] Chua L O 1971 *IEEE Trans. Circuit Theory* **18** 507–19
[2] Strukov D B, Snider G S, Stewart D R and Williams R S 2008 *Nature* **453** 80–3
[3] Choi B J *et al* 2005 *Appl. Phys.* **98** 033715
[4] Xu N, Liu L F, Sun X, Chen C, Wang Y, Han D D, Liu X Y, Han R Q, Kang J F and Yu B 2008 *Semicond. Sci. Technol.* **23** 075019
[5] Tulina N A, Borisenko I Y and Sirotkin V V 2008 *Phys. Lett.* A **372** 6681–6
[6] Zhitenev N B, Sidorenko A, Tennant D M and Cirelli R A 2007 *Nature Nanotechnol.* **2** 237–42
[7] Plecenik A *et al* 2010 *Appl. Surf. Sci.* **256** 5684–7
[8] Scott J C and Bozano L D 2007 *Adv. Mater.* **19** 1452–63
[9] Bhadra R, Singh V N, Mehta B R and Datta P 2009 *Chalcogenide Lett.* **6** 189–96
[10] Liu X, Mayer M T and Wang D 2010 *Appl. Phys. Lett.* **96** 223103
[11] Yasuhara R, Fujiwara K, Horiba K, Kumigashira H, Kotsugi M, Oshima M and Takagi H 2009 *Appl. Phys. Lett.* **95** 012110
[12] Ielmini D, Nardi F, Cagli C and Lacaita A L 2010 *IEEE Electron Device Lett.* **31** 353–5
[13] Heluani S P, Braunstein G, Villafuerte M, Simonelli G and Duhalde S 2006 *Thin Solid Films* **515** 2379–86
[14] Villafuerte M, Heluani S P, Juarez G, Simonelli G, Braunstein G and Duhalde S 2007 *Appl. Phys. Lett.* **90** 052105
[15] Chang W Y, Lai Y C, Wu T B, Wang S F, Chen F and Tsai M J 2008 *Appl. Phys. Lett.* **92** 022110
[16] Peng H Y, Li G P, Ye J Y, Wei Z P, Zhang Z, Wang D D, Xing G Z and Wu T 2010 *Appl. Phys. Lett.* **96** 192113
[17] Tour J M and He T 2008 *Nature* **453** 42–3
[18] Mandl M, Hoffmann H and Kucher P 1990 *J. Appl. Phys.* **68** 2127–32
[19] Waser R and Aono M 2007 *Nature Mater.* **6** 833–40
[20] Shima H, Zhong N and Akinaga H 2009 *Appl. Phys. Lett.* **94** 082905
[21] Chau T D, Bocarme T V and Kruse N 2004 *Surf. Interface Anal.* **36** 528–32
[22] Klesper G and Rollgen F W 1999 *Surf. Sci.* **422** 107–17
[23] Fors R, Khartsev S I and Grishin A M 2005 *Phys. Rev.* B **71** 045305
[24] Driscoll T, Kim H T, Chae B G, Ventra M D and Basov D N 2009 *Appl. Phys. Lett.* **95** 043503
[25] Pershin Y V and Ventra M D 2008 *Phys. Rev.* B **78** 113309
[26] Jo S H, Kim K H and Lu W 2009 *Nano Lett.* **9** 870–4