Thin Solid Films 520 (2012) 3415–3418

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Resistive switching characteristics of multilayered $(HfO_2/Al_2O_3)_n$ n = 19 thin film

Wen-Hsien Tzeng [b], Chia-Wen Zhong [b], Kou-Chen Liu [a,*], Kow-Ming Chang [b,c], Horng-Chih Lin [b], Yi-Chun Chan [a], Chun-Chih Kuo [a], Feng-Yu Tsai [d], Ming Hong Tseng [d], Pang-Shiu Chen [e], Heng-Yuan Lee [f], Frederick Chen [f], Ming-Jinn Tsai [f]

[a] Institute of Electronics Engineering, Chang Gung University, Tao-Yuan, 33302, Taiwan, ROC
[b] Institute of Electronics, Department of Electronics Engineering, National Chiao Tung University, HsinChu, 30010, Taiwan, ROC
[c] Department of Electronic Engineering, I-Shou University, No. 1, Sec. 1, Syuecheng Rd., Kaohsiung, 840, Taiwan, ROC
[d] Department of Material Science and Engineering, National Taiwan University, Taipei, Taiwan, ROC
[e] Department of, Minghsin University of Science and Technology, Hsinchu, 340, Taiwan, ROC
[f] Electronics and Optoelectronics Research Laboratory, Industrial Technology Research Institute, Hsinchu, 310, Taiwan, ROC

ARTICLE INFO

Available online 4 November 2011

Keywords:
Multilayer
Stacked oxide
Resistive memory
RRAM

ABSTRACT

A transparent resistive random access memory used as Indium Tin Oxide (ITO) electrode, ITO/HfO_2/Al_2O_3/…/HfO_2/Al_2O_3/ITO capacitor structure is fabricated on glass substrate by atomic layer deposition. The unipolar resistive switching characteristics can be performed by applying the positive- or negative-bias through top electrode, however, the differences of switching and stability in the two different operations can be observed. The diversities of electrical property are attributed to different oxide/ITO interface materials, which influence the current flow of the injected electrons.

1. Introduction

Recently, the non-volatile resistive switching phenomenon in the metal/oxide/metal structure has attracted great attention due to its potential for nonvolatile resistive random access memory (RRAM) applications. As the device is getting stressed from memory switching cycling, one could observe broad dispersions of these parameters [1–5]. It is well known that various bulk materials exhibit a variety of electronic properties, such as insulating, semiconducting, metallic, and even superconducting behavior [6–9]. Combining the two different layers together by fabricating the stacked multilayer can provide diversified electronic properties. One of the main goals is to improve the resistive switching characteristics. Seo et al. [10] reduced the reset current by introducing multilayers consisting of NiO layers with different resistance values. It beneficially reduced the reset current by two orders of magnitudes. Choi et al. [11] studied the resistive switching characteristics of the double layer (NiO/SiO_2) by controlling the SiO_2 thickness. They observed the switching parameters of the device depended on the thickness of SiO_2 layer. Chen et al. [12] provided the excellent memory switching behavior of a NbAlO film with a thin Al_2O_3 buffer layer for a possible candidate nonvolatile memory application. According to previous reported discussion, resistive switching properties can be more stable and reliable for practical applications if the switching regions occur can be controlled, which can be achieved by fabricating the multilayer to confine the formation and rupture in a localized spot.

In this study, we investigate the use of HfO_2/Al_2O_3 stacked thin films for RRAM device application by atomic layer deposition. A bulk HfO_2 thin film with the similar thickness was fabricated for comparison. The thin film morphology, electrical properties, and resistive switching characteristics were investigated and discussed. The electric property's diversities which are caused by the different oxide-layer materials were also discussed. We observe that the switching stability depends on the oxide thin layer where the conduction electron was injected.

2. Experimental method

The Al_2O_3/HfO_2 bi-layer oxide film was deposited by Savannah 100 atomic layer deposition system (Cambridge Nanotech Inc.) at 100 °C on a commercially-available Indium Tin Oxide glass (ITO film is 300 nm thick). During the deposition, the chamber pressure was 13.3 Pa and high-purity N_2 (flow rate = 20 sccm) was used as the carrier gas for the precursors. The trimethylaluminum (TMA) and H_2O were used as the precursors of Al_2O_3; whereas the Tetrakis (dimethylamino) hafnium (TDMAHf) and H_2O were used as precursors of HfO_2. The sequence of pulses for one cycle deposition of Al_2O_3 was TMA (0.03 s)/ purge (5 s)/ H_2O (0.05 s)/ purge (5 s), whereas that of HfO_2 was TDMAHf (1 s)/ purge (5 s)/ H_2O (0.05 s) purge (5 s). A cycle produced ~1 Å as determined by ellipsometry (EP3, Nanofilm Tech.). The HfO_2/Al_2O_3 bi-layer film was repetitively deposited until the 19 period was accomplished then it was stopped. A control

* Corresponding author. Tel.: +886 3 2118800 3152; fax: +886 3 2118507.
E-mail address: jacobliu@mail.cgu.edu.tw (K.-C. Liu).

0040-6090/$ – see front matter. Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.10.118

sample with only HfO_2 thin film as insulator film was also experimented. Then top electrode ITO was deposited by dc sputtering system with a shadow mask in a diameter of 200 μm. 10 minute pre-sputtering was worked under pressure of 4 Pa and 5 W power and then ITO film with thickness of 100 nm was deposited in Ar gas of 15 sccm at room temperature. The resistive switching behavior of the multi-bi-layer film was measured by an HP4156C semiconductor parameter analyzer at room temperature. Each of the voltage sweeps started from 0 V. Cross-sectional high resolution transmission electron microscopy (HR-TEM) was employed to examine the microstructure. Model of HR-TEM is JEOL-2100F and operation voltage is 200 kV. Preparation with HR-TEM of multi-bi-layer samples used a focus ion beam (SMI 3050) that was manufactured by SII NanoTechnology Inc. Tokyo Office. The near-infrared (NIR) spectrometer (PerKin Elmer Lamda 900) is used for transmittance measurement.

3. Results and discussion

Fig. 1 (A) shows the schematic cross-section structure of the device of multi-bi-layer binary transition metal oxide. It reveals the multi-bi-layer binary transition metal oxide made by the 19 periods and each period is composed of HfO_2 (12 Å)/Al_2O_3 (2 Å) bi-layer. The transmittance of the multi-bi-layer metal oxide is shown in Fig. 1 (B). It is measured by irradiating the ultraviolet–visible light from the top electrode side and receiving at the bottom electrode side ranging from 400 to 800 nm wavelength. High transmittance of about 80% in the average value and 85% in the maximum wavelength can be observed, which reaches nearly fully transparent electronic device. The cross sectional structures of the nanolaminate multi-bi-layer devices were characterized by HR-TEM, as shown in Fig. 1 (C). This figure clearly demonstrates the multi-bi-layer of the ITO/HfO_2/Al_2O_3/…/HfO_2/Al_2O_3/ITO capacitor structure with a thickness of 27 nm, which is fairly consistent with the deposition rate. This kind of transparent resistive random access memory [13–15] has drawn attention of widespread applications in consumer devices such as cell phones, computers, TV monitors, and watches.

Before the resistive switching (RS) operation, forming process is needed in the beginning to activate the RS properties. As shown in Fig. 2 (A), it compares the electroforming current–voltage (I–V) curves of the control and multi-bi-layer-cell sample. A large forming voltage of about −26.4 V was observed on the HfO_2 sample, while only about −7.8 V was needed to turn on the multi-bi-layer-cell device. However, if positive bias was used to forming process, the device cannot show predictable or consistent switching characteristics. We speculate that this asymmetric behavior was caused by interface property difference between top and bottom side ITO/TMO (Transition Metal Oxide). The top side ITO was deposited by sputtering. During sputtering process, impinging In, Sn or O atom will destroy original well arranged HfO_2/Al_2O_3 Bi-layer growth by atomic layer deposition. The damage interface used as anode during electroforming process can provide many possible filamentary conducting paths resulting irreproducible and unreliable switching characteristics. As negative bias used for forming process, the anode now is at the bottom side ITO/TMO interface which has more stable filamentary conducting paths than that of the top interface. The thickness 3–10 nm near the anode plays the important role of the resistive switching property, reported by C. S. Hwang's group [16]. In addition, the leakage current is significantly different between these two samples. It is below 10 pA for the control device and 10 nA for multi-bi-layer-cell device at −2 V respectively. A multi-bi-layer structure may induce some defects such as oxygen vacancies or interstitials inside the insulator film, which can contribute on the leakage current by forming conducting filamentary paths. Fig. 2 (B) and (C) shows the typical unipolar I–V curves of multi-bi-layered stacked sample on linear scale, where positive and negative voltage value was applied to the ITO top electrode, respectively. No switching characteristics can be

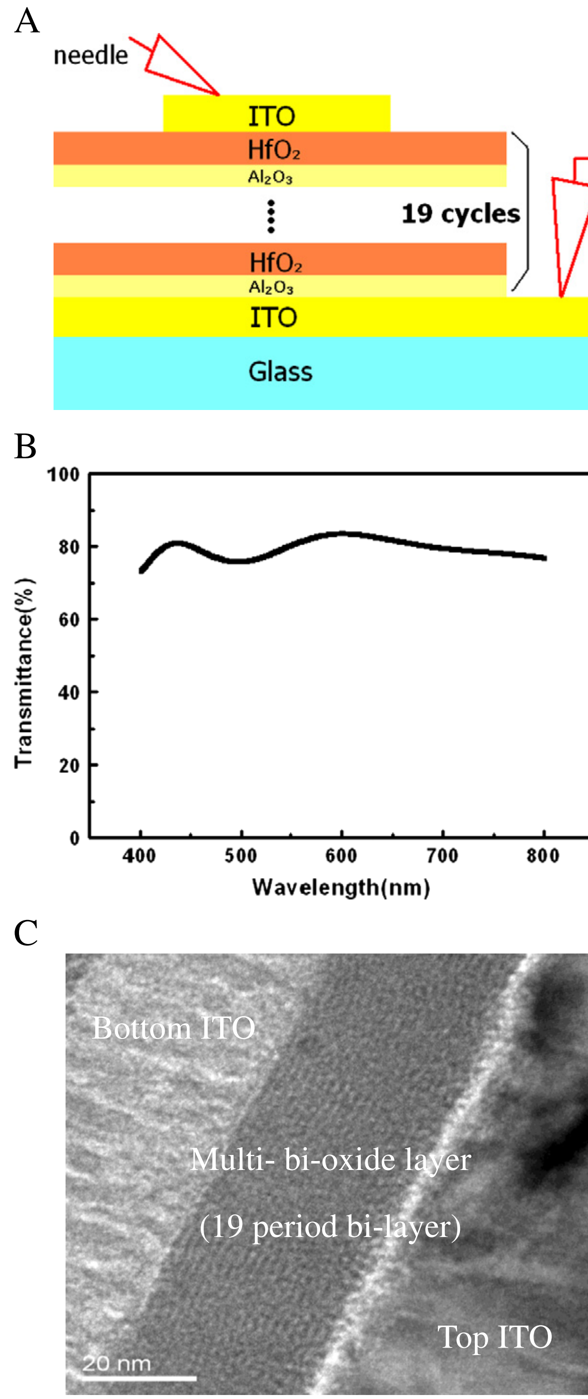

Fig. 1. (A) Schematic cross-section structure of the multi-bi-layer device composed of HfO_2/Al_2O_3/…/HfO_2/Al_2O_3 layer, (B) transmittance of the multi-bi-layer device, and (C) cross-sectional TEM image of the multi-bi-layer device.

observed on HfO_2 control samples after electroforming operation, while the multi-bi-layer stacked sample exhibits the repeated RS characteristics under both bias polarities. We suggest that the RS characteristics may depend on the defect density inside insulator thin film. In Fig. 2 (B) and (C), the voltage sweeps from zero bias toward a certain positive or negative bias until the current value increased sharply. This bias is defined as V_{set} and the state is switched to low resistance state (LRS). During the next positive bias operation, much larger conducting current mediates through the generated defects inside the stacked oxide. The voltage value when the current abruptly decreased is defined as V_{reset}, and the state is switched to

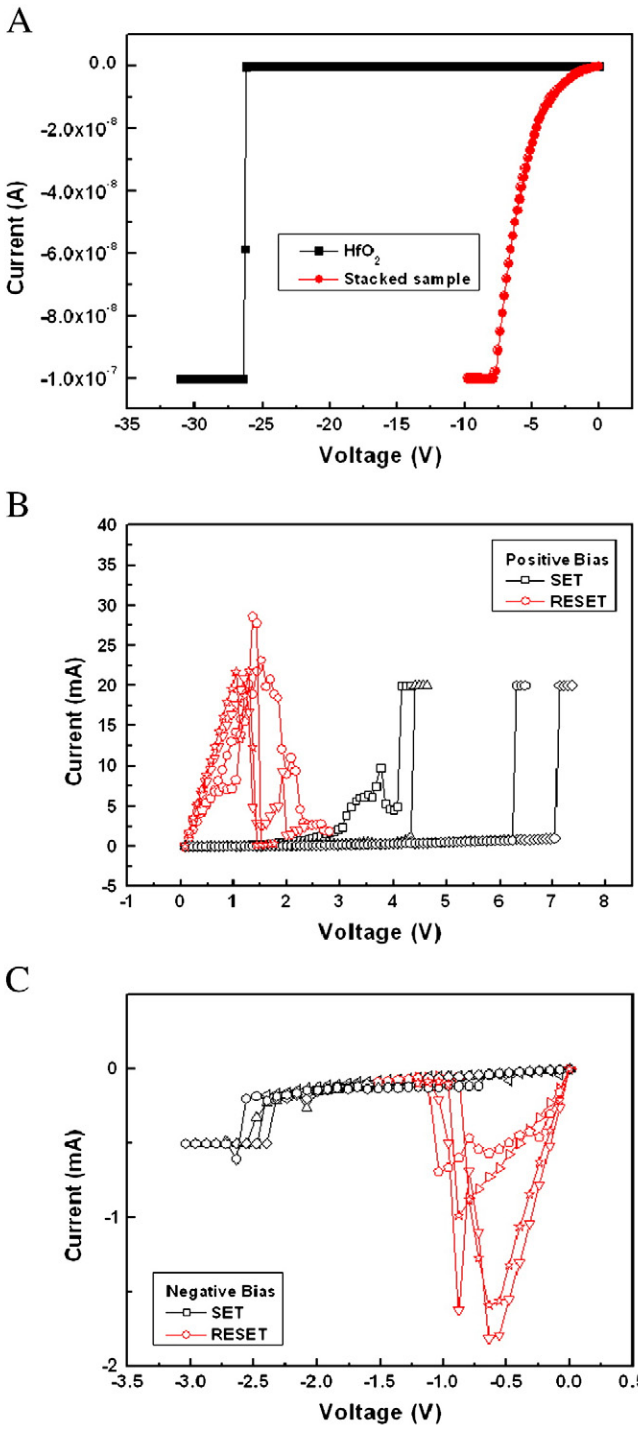

Fig. 2. (A) The forming characteristics of the HfO_2 film and HfO_2/Al_2O_3 stacked samples. The I–V curves in continuous resistive switching for 5 times under (B) positive bias, and (C) negative bias on top electrode.

high resistance state (HRS). Observation on the I–V curves finds that V_{set} and V_{reset} are variable in their voltage value from different applied polarities, which was influenced by operation polarity. The V_{set} and V_{reset} values disperse in the range of 4–7 V and 1–3 V for positive operation, while concentrate on −0.3 to −1.3 V and −2 to −3.5 V for negative operation. We refer the difference to the asymmetry of the multi-bi-layered stacked structure. The ITO/oxide interface influencing the flow of current, i.e. electron injecting into dielectric film, is easier to pass through ITO/HfO_2 interface. This factor influences not only the switching voltage values but also the resistance values on HRS and LRS.

The conducting behaviors of the positive and negative operation I–V curves are fitted, as shown in Fig. 3 (A)–(C), respectively. The positive switching I–V curve can be well fitted to space-charge-limited current with a slope of 1 in LRS and at the low voltage bias in HRS and a slope of 2 at the high voltage bias in HRS, as shown in Fig. 3 (A). Oppositely, the negative switching I–V curve was fitted to a different conducting behavior. An ohmic conduction behavior with a linear slope of 1 was also

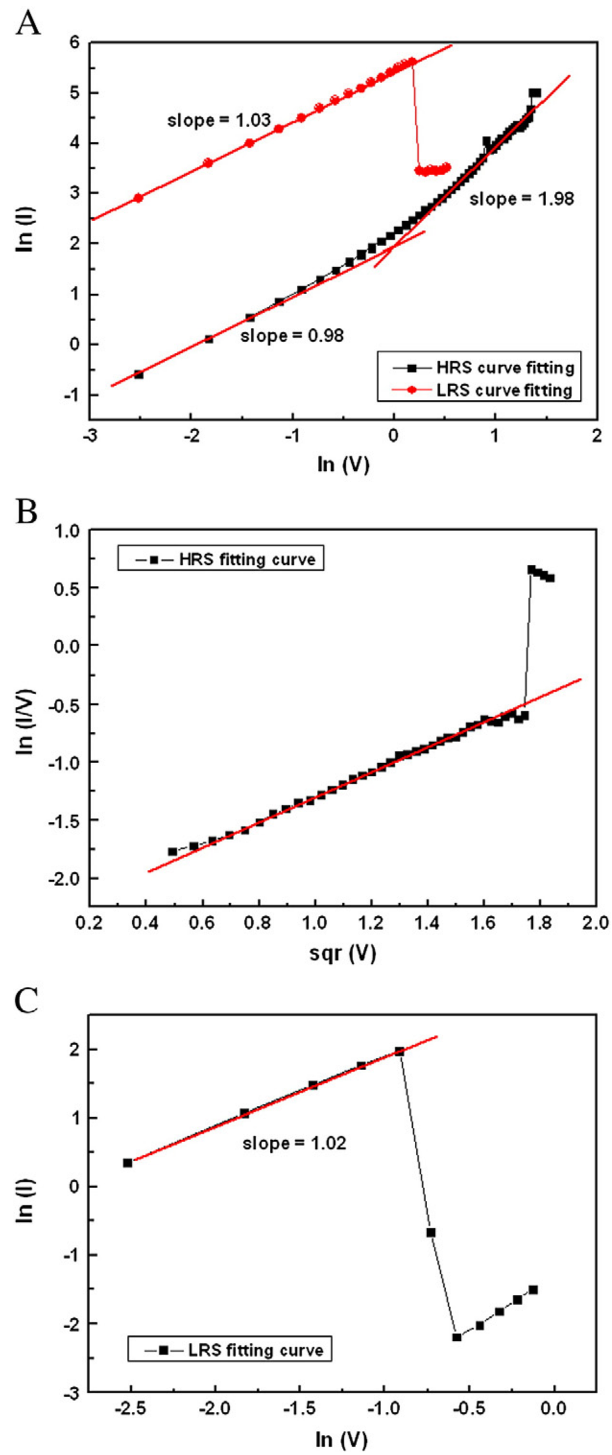

Fig. 3. Both HRS and LRS I–V curves can be well fitted to ln (I)–ln (V) curve under positive bias operation. (B) HRS I–V curve under negative bias operation was fitted to ln (I/V)–ln (V) curve. (C) LRS I–V curve under negative bias operation was fitted to ln (I)–ln (V) curve.

observed in LRS, while changes to Frenkel–Poole emission in HRS. Different conducting behaviors may be responsible for different switching characteristics, as shown in Fig. 2 (B) and (C). We suggest that the ITO/oxide interface is a critical factor to determine the injected electron to conduction. According to Shiiki et al. [17] and Martinez et al. [18], the bandgap of HfO_2 and Al_2O_3 thin film is about 5.9 and 2.6 eV for ultrathin film. Difference on the bandgap may modulate the band offset between the oxide and ITO film, which dominates the injected electron conduction behavior. For the positive operation, the electron injected from the Al_2O_3/ITO interface via the defects inside the thin Al_2O_3 insulator. The Al_2O_3 layer is too thin to sustain a good insulator film blocking the leakage current, thus much injected electrons mediate through the random defects inside the insulator film. Therefore, the electrons conduct by ohmic conduction in the beginning, then followed by the trap-limited and trap-free conduction. For the negative operation, large bandgap of HfO_2 thin film effectively blocks the injected electrons, thus causing the conducting behavior changes to Frenkel–Poole emission. In addition, the thin defect-riched Al_2O_3 layer can confine the reproducible formation and rupture of a conducting path at a fixed point through the defective structure [19], thus obtaining reliable switching characteristics. Further investigation is needed to elucidate in detail the possible mechanism for the multi-bi-layer stacked structure, leading to better uniformity and reliability of RRAM characteristics.

4. Conclusion

A multi-bi-layer stacked structure based on ITO/HfO_2/Al_2O_3/…/HfO_2/Al_2O_3/ITO capacitor is fabricated on a glass substrate to form a transparent resistive random access memory device. The resistive switching characteristics were only observed on the multi-bi-layer stacked structures, which may be attributed to induce more defects or vacancies inside the insulator film. The unipolar resistive switching properties can be demonstrated by both positive and negative operations. The differences of switching and stability in the two different operations may be caused by the different oxide-layer materials toughing the top and bottom electrodes. We refer the difference to the asymmetry of the multi-bi-layered stacked structure, which influences the current flow of the injected electrons.

References

[1] I.G. Baek, M.S. Lee, S. Seo, M.J. Lee, D.H. Seo, D.-S. Suh, J.C. Park, S.O. Park, H.S. Kim, I.K. Yoo, U.-In. Chung, J.T. Moon, IEDM Tech. Dig. (2004) 587.
[2] T. Fujii, M. Kawasaki, A. Sawa, H. Akoh, Y. Kawazoe, Y. Tokura, Appl. Phys. Lett. 86 (2005) 012107.
[3] R. Waser, M. Aono, Nat. Mater. 6 (2007) 833.
[4] C. Rohde, B.J. Choi, D.S. Jeong, S. Choi, J.S. Zhao, C.S. Hwang, Appl. Phys. Lett. 86 (2005) 262907.
[5] S. Kim, I. Byun, I. Hwang, J. Kim, J. Choi, B.H. Park, S. Seo, M.J. Lee, D.H. Seo, D.S. Suh, Y.S. Joung, I.K. Yoo, Jpn. J. Appl. Phys. 44 (2005) L345.
[6] K.C. Liu, W.H. Tzeng, K.M. Chang, Y.C. Chan, C.C. Kuo, C.W. Cheng, Microelectron. Reliab. 50 (2010) 670.
[7] N. Das, S. Tsui, Y.Y. Xue, Y.Q. Wang, C.W. Chu, Phys. Rev. B 78 (2008) 235418.
[8] J.W. Park, M.K. Yang, K. Jung, J.K. Lee, IEEE Trans. Electron. Dev. 55 (2008) 782.
[9] C.Y. Liu, P.H. Wu, A. Wang, W.Y. Jang, J.C. Young, K.Y. Chiu, T.Y. Tseng, IEEE Electron Dev. Lett. 26 (2005) 351.
[10] S. Seo, M.J. Lee, D.H. Seo, S.K. Choi, D.S. Suh, Y.S. Joung, I.K. Yoo, I.S. Byun, I.R. Hwang, S.H. Kim, B.H. Park, Appl. Phys. Lett. 86 (2005) 093509.
[11] J.H. Choi, S. Nath Das, J.M. Myoung, Appl. Phy. Lett. 95 (2009) 062105.
[12] L. Chen, Y. Xu, Q.Q. Sun, H. Liu, J.J. Gu, S.J. Ding, D.W. Zhang, IEEE Electron Dev. Lett. 31 (2010) 356.
[13] J.W. Seo, J.-W. Park, K.S. Lim, S.J. Kang, Y.H. Hong, J.H. Yang, L. Fang, G.Y. Sung, H.K. Kim, Appl. Phys. Lett. 95 (2009) 133508.
[14] J.W. Seo, J.-W. Park, K.S. Lim, J.H. Yang, S.J. Kang, Appl. Phys. Lett. 93 (2008) 223505.
[15] K.C. Liu, W.H. Tzeng, K.M. Chang, Y.C. Chan, C.C. Kuo, Microelectron. Eng. 88 (7) (2011) 1586.
[16] K.M. Kim, B.J. Choi, C.S. Hwang, Appl. Phys. Lett. 90 (2007) 242906.
[17] K. Shiiki, M. Igarashi, H. Kaijyu, Jpn. J. Appl. Phys. 42 (2003) 5185.
[18] F.L. Martinez, M. Toledano-Luque, J.J. Gandia, J. Carabe, W. Bohne, J. Rohrich, E. Strub, I. Martil, J. Phys. D: Appl. Phys. 40 (2007) 5256.
[19] R. Jung, M.J. Lee, S. Seo, D.C. Kim, G.S. Park, K. Kim, S. Ahn, Y. Park, I.K. Yoo, J.S. Kim, B.H. Park, Appl. Phys. Lett. 91 (2007) 022112.