Surface & Coatings Technology 231 (2013) 563–566

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Effect of ITO electrode with different oxygen contents on the electrical characteristics of HfO_x RRAM devices

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

[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, Minghsin University of Science and Technology, Hsinchu, 340, Taiwan, ROC
[e] Electronics and Optoelectronics Research Laboratory, Industrial Technology Research Institute, Hsinchu, 310, Taiwan, ROC

ARTICLE INFO

Available online 20 July 2012

Keywords:
Indium tin oxide (ITO)
Transparent-RRAM (TRRAM)
Oxygen content

ABSTRACT

In this study, the influence of indium tin oxide (ITO) top electrodes with different oxygen contents on the resistive switching characteristics of HfO_x/TiN capacitor structure is investigated. Switching parameters, including set and reset voltage values, and high and low resistance values are highly related to the properties of ITO thin films. Higher resistance values in both states can be obtained when ITO thin films with higher oxygen contents are used as top electrodes; such values are accompanied by larger set voltages and fluctuating transient currents during the reset process. Based on the proposed filament model, we suggest that the switching mechanism of HfO_x/TiN structure is attributed to the formation and rupture of conducting filamentary paths near the anodic side, which is highly correlated with the properties of the top electrode. The top electrode must be well determined to obtain reliable switching properties.
Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

1. Introduction

Resistive random access memory (RRAM) devices based on the different resistances of oxide materials have been extensively investigated in recent years. Because of their advantages, such as small cell size [1], fast switching speed [2], low power consumption [3], and compatibility with standard complementary metal oxide semiconductor (CMOS) technologies [4], thus RRAM devices have become one of several candidates that may potentially be utilized for the next generation of nonvolatile memory devices. To this end, a transparent electronic device with a fully transparent ITO/ZnO/ITO capacitor structure, called a transparent-RRAM (T-RRAM), has been achieved [5]. The realization of T-RRAM is a milestone in memory technology and demonstrates the high potential of RRAM device compatibility. The use of indium-tin-oxide as a top electrode is highly applied to optical-electronic devices, such as solar cells and organic light-emitting diodes (OLEDs). Transparent conducting oxides (TCOs) are highly degenerate n-type semiconductors and high carrier concentration materials that exhibit low electrical resistivities of up to 2×10^{-4} Ω-cm [6]. It has been reported that the degeneracy observed in TCO stems from oxygen vacancies and substitution of tin dopants within the ITO film that occur during deposition. However, the electrical properties of ITO films depend on the film composition and deposition parameters [7]. Because switching properties are highly correlated with the properties of the electrode materials, variations in ITO thin film properties may cause different switching characteristics in RRAMs.

In this paper, the electrical switching behavior of an ITO/HfO_x/TiN capacitor is investigated. HfO_x-based memory cells have been proposed to be candidates for nonvolatile memory applications due to their excellent switching characteristics, including low operation current, large resistance ratio, fast switching speed, reliable switching endurance, and data retention [8]. We previously investigated the effect of top electrodes on the electrical characteristics of HfO_x/TiN RRAM devices [9]. Here, the effect of different oxygen contents within the ITO electrode on the switching properties of the HfO_x/TiN structure is discussed to provide a better understanding of the behavior of the intermediate state. Based on the reported filament model, we suggest that the intermediate state during the RESET process is attributed to the partial rupture of the conducting filamentary paths near the anodic side, which is highly dominated by the oxygen contents of the top electrode.

2. Experimental method

A TiN bottom electrode was deposited on a 100 nm SiO_2/Si substrate layer by dc sputtering at room temperature (RT). The thickness and sheet resistance of the electrode were 30 nm and 50–60 Ω/□, respectively. A 20-nm HfO_x thin film was deposited by atomic layer deposition on a TiN/SiO_2/Si structure at 300 °C. Hafnium tetrachloride and water were used as reactants for HfO_x deposition. A 1000 Å-thick TCO ITO was used as a top electrode, and deposited by rf-magnetron sputtering

* Corresponding author. Tel.: +886 32118800x3152; fax: +886 32118507.
E-mail address: jacobliu@mail.cgu.edu.tw (K.-C. Liu).

0257-8972/$ – see front matter. Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2012.07.039

at RT through a shadow mask with a diameter of 200 μm. The sputtering target was a 3 inch ITO target which composed of In_2O_3:SnO_2 = 9:1 in weight ratio (high-purity of 99.99%). To understand the effect of ITO oxygen contents on the switching characteristics of the device, three concentrations of oxygen with partial pressures of 0%, 15%, and 33% were sampled by controlling the O_2 sputtering gas from 0 to 12 sccm during ITO deposition. For 15% and 33% samples, we only added the oxygen contents at an initial thickness of 100 Å, then the oxygen flow was controlled to 0% during the following 900 Å-thick ITO film deposition. The flow rate of the Ar sputtering gas was maintained at 24 sccm during deposition. A deposition power of 100 W and a process pressure of 5 mTorr were used for all samples under the same conditions. The electrical characteristics of the HfO_x/TiN RRAM device were analyzed with an Agilent 4156C semiconductor parameter analyzer. A bias voltage was applied to the top electrode with a grounded TiN bottom electrode. All measurements were performed at RT.

3. Results and discussion

The resistive switching characteristics of RRAM devices require electroforming with a current compliance (10 μA) to activate the switching behavior. After initial electroforming, RRAM devices switch to a low resistance state (LRS). As the applied voltage sweeps from 0 V to a certain positive voltage, the state switches back to a high resistance state (HRS), afterward the applied voltage sweeps from 0 V to a certain positive voltage, the HRS switches to low resistance state (LRS), the operation and voltage are denoted as RESET process/voltage and SET process/voltage respectively. This is called unipolar switching. We abbreviated our ITO/HfO_x/TiN structure as IHT, and the different oxygen partial pressures for ITO deposition are listed as IHT—0%, IHT—15%, and IHT—33%. Electroforming current–voltage (I–V) curves of the IHT samples are shown in Fig. 1. The three samples exhibit almost similar leakage current values, a leakage current about 50 pA at 1 V and a breakdown voltage of about 5.5–6 V. No clear differences are observed between the electroforming processes of the three samples.

Fig. 2(a)–(c) shows the resistive switching characteristics of HfO_x/TiN devices with ITO top electrodes fabricated under different oxygen partial pressures of 0%, 15%, and 33%, respectively. A sequence of 5 cycles is shown to exhibit reproducible and reversible conducting behaviors. The figures show that the SET voltage increases slightly with increasing oxygen pressure. The above phenomenon maybe cause by formed a new HfO_x thin film during formation of ITO top electrode which the oxygen remained at initial thickness of 100 Å, the new HfO_x thin film is less oxygen-related defect, oxygen vacancy, causing extra

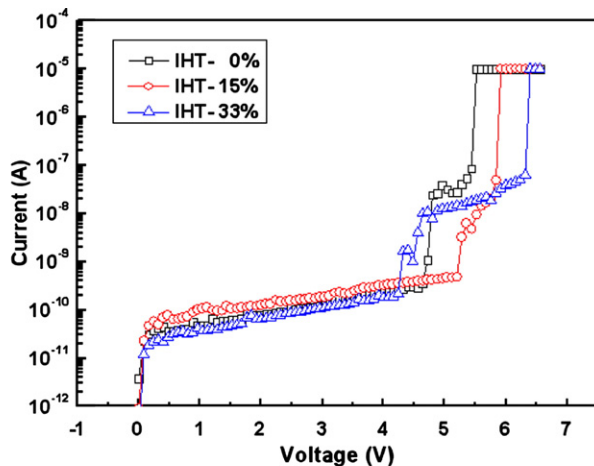

Fig. 1. I–V curves of the electroforming process of the ITO/HfO_x/TiN device with 0%, 15%, 33% oxygen content, respectively.

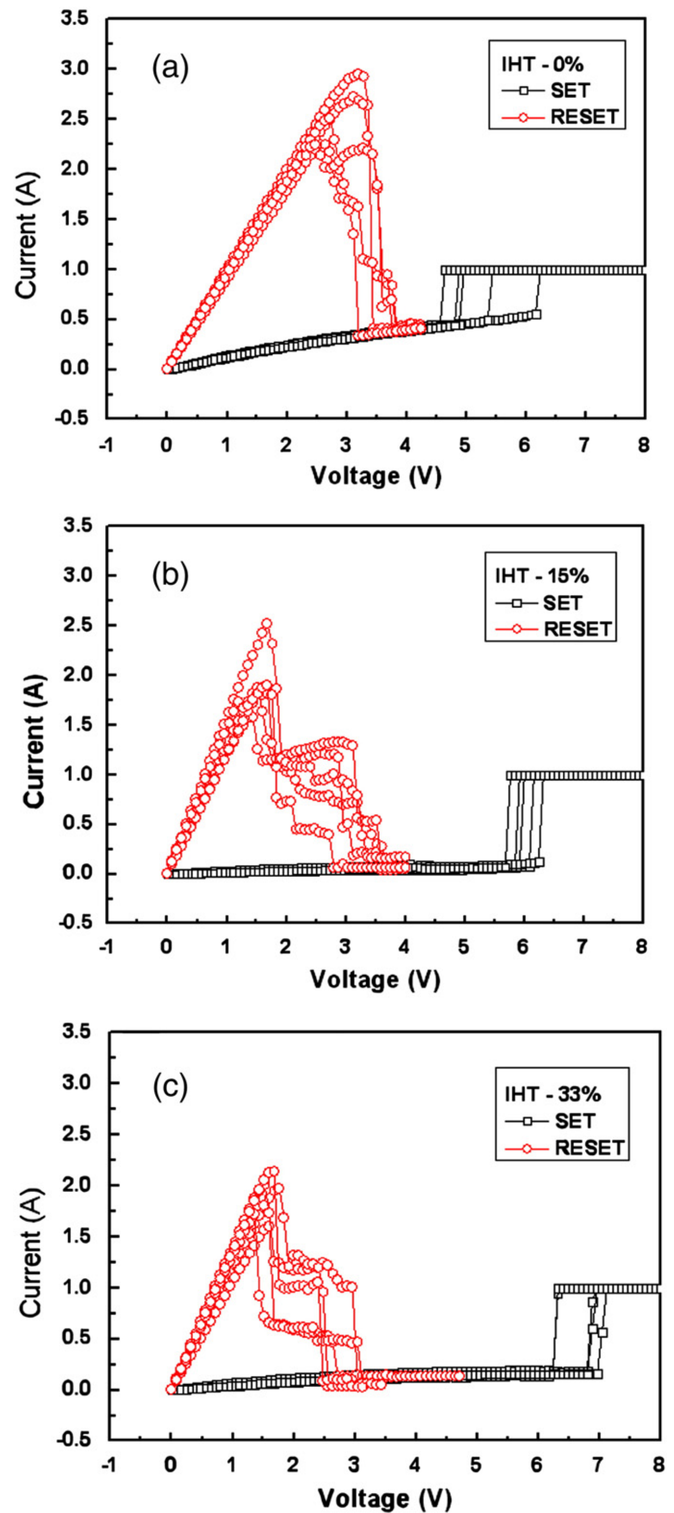

Fig. 2. Switching characteristics of the I–V curve of an HfO_x/TiN capacitor with a top electrode of (a) ITO—0%, (b) ITO—15%, and (c) ITO—33% in 5 consecutive cycles.

oxygen diffused into HfO_x thin film which improves binding strength so it need more energy to form conductive filament. In addition, distinct conducting behaviors at the RESET operation are clearly observed. With increasing oxygen pressure of the ITO, an intermediate state during RESET becomes obvious. The intermediate state causes by random conductive filaments are partial ruptured so the conduction current doesn't decrease abruptly in the intermediate state. When high enough energy

ruptures remaining conductive filament the intermediate state is changed to high resistance state (HRS). The random conductive filament is a major issue for device reliability. In the IHT—33% sample, the electrical characteristics first switch to the intermediate state, and then maintain almost the same current with increasing voltage. When the voltage reaches a large enough value, about 3 V, the second switch to the HRS occurs. The intermediate state number is usually 1 or 2. This phenomenon is observed less in the IHT—0% sample and even less in the IHT—15% sample. We define that the voltage value corresponding to I_{max} is called V_m, and V_{reset} is defined as the voltage at which the state completely switches back to the HRS. The set voltage is defined as V_{set}. This definition is different from that in other reports because of the specific electrical characteristics of our IHT device. Table 1 lists the V_{set}, V_m, and V_{reset} of the IHT samples. The respective average values for V_{set}, V_m, and V_{reset} are about 4.59, 2.35, and 4 V for IHT—0%, 5.02, 1.87, and 4 V for IHT—15%, and 5.90, 1.81, and 4.03 V for IHT—33%. It is obvious that IHT—33% has the highest V_{reset} and the lowest V_m. The V_{reset} is almost the same for all samples. Larger V_{set} values indicate that the SET operation experiences difficulties in forming a conducting filament within the TMO film, and lower V_m values indicate that the conducting filament is easier to rupture during the RESET operation. We suggest that the shift in the operating voltage is related to the influence of the oxygen contents within the ITO film.

Fig. 3 compares the endurance of the IHT—0% and IHT—33% devices. The poor high-to-low resistance ratio of the IHT—0% device limits the application of this ITO film as the top electrode for RRAM devices and confines the development of T-RRAM. Fortunately, device performance is greatly improved in the IHT—33% sample. Compared with IHT—0%, the IHT—33% sample shows higher resistance values in both the HRS and LRS, and larger resistance ratio (1 order of magnitude), which may be attributed to the higher resistivity of the ITO film. The incorporation of oxygen will lead to a decrease in oxygen vacancies in the ITO films and hence an increase in the resistivity. The larger the amount of oxygen ions that could be supplied from the ITO electrode of the IHT—33% device, the easier it is for filament rupture during the RESET operation. Therefore, switching stability could be improved.

It has been reported that oxygen contents play an important role in the resistive switching of RRAM devices [2,10,11]. Studies on RRAM devices based on HfO_x/TiN substrates under unipolar switching indicate that the switching mechanism may be attributed to the filament model [12]. In the filament model, the formation and rupture of the conducting filaments are the main switching mechanisms. The switching process occurs near the anode electrode was proposed by Kim et al. [13] and Lee et al. [14]. We suggest that the intermediate state is highly dependent on the oxygen content of the electrode, implying that the filaments are influenced by oxygen ions within the ITO film. Schematic diagrams of the electrode effect are shown in Fig. 4(a)–(e). During the SET operation, oxygen ions are extracted to the top electrode, contributing to oxygen vacancies within the HfO_x film, and the injected electrons conduct under positive bias. This causes a switch to the LRS, as shown in Fig. 4(a). Larger V_{set} values are observed in the IHT—33% sample; this may be attributed to oxygen ion migration difficulties due to the higher resistivity of the ITO—33% film at the anodic interface, as shown in Fig. 4(c). Given a positive bias, electrons transported through oxygen vacancies contribute to the current in the LRS. As the dc sweep voltage increases, larger amounts of electrons are transported through a tiny filament, which induced the Joule heating effect and the rearrangement of atoms. Then, the state was switched back to the HRS. In our previous report, we concluded that rupture of the conducting filaments occurs at the anodic side of HfO_x films because switching characteristics are highly correlated with electrode properties. During the RESET process as shown in Fig. 4(e), large amounts of non-lattice oxygen within the ITO—33% film could influence the rearrangement of atoms during Joule heating. The intermediate state may be attributed to the inconsistent rupture of conducting filaments, as shown in Fig. 4(d). These findings match the smaller V_m of IHT—33% well because larger amounts of non-lattice oxygen ions could be easily triggered under thermal Joule heating. This may lead to fluctuations in the diameter of the conducting filaments and the intermediate states in a dispersed phenomenon. Since the switching properties of the IHT film are highly correlated with the number of oxygen ions or vacancies within the electrode and insulator thin film, a well-packaged fabricated RRAM device free from such is necessary to promote the reliable switching behavior of ITO/HfO_x/TiN RRAM devices.

Table 1
Operation voltages of the HfO_x film obtained from ITO top electrodes with different oxygen contents.

	V_{set}	V_m	V_{reset}
IHT—0%	4.59	2.35	4
IHT—15%	6.02	1.76	4
IHT—33%	6.75	1.54	4.03

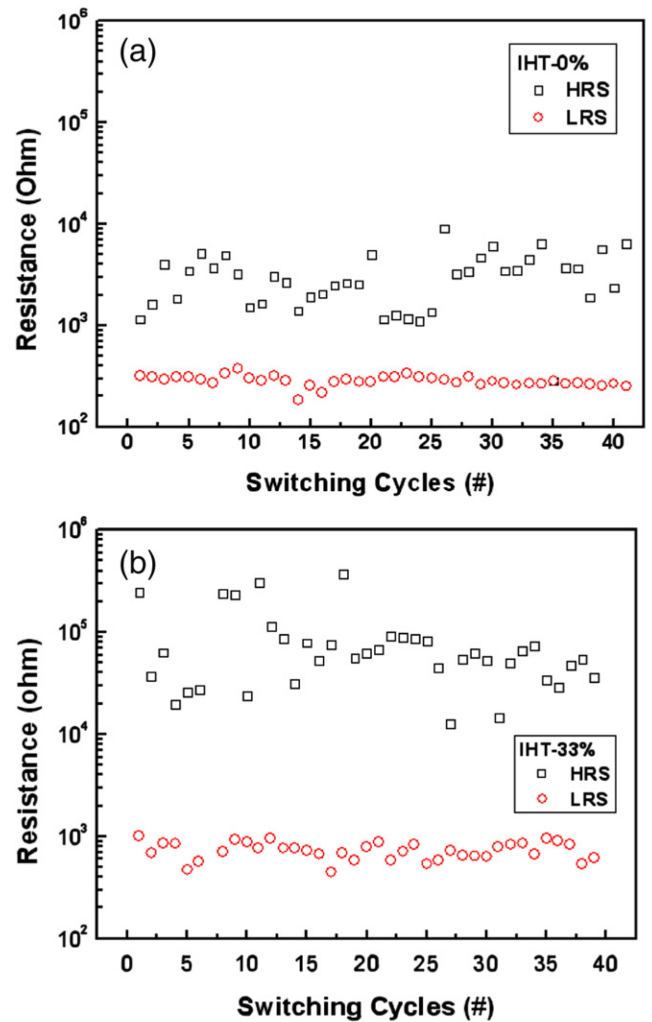

Fig. 3. Endurance tests of the (a) ITO—0%/HfO_x/TiN and (b) ITO—33%/HfO_x/TiN capacitor structures.

4. Conclusion

We conclude that ITO top electrodes with different oxygen contents play significant roles in the switching characteristics of an HfO_x/TiN structure. The RESET behavior changes from the abrupt type to the

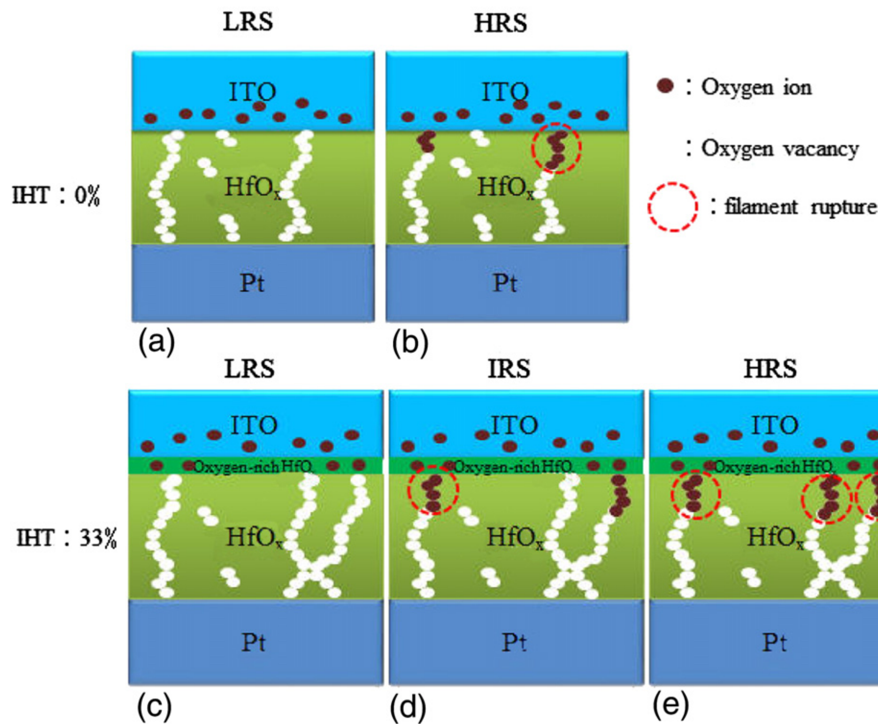

Fig. 4. Schematic pictures of the HfO$_x$/TiN structure at (a) LRS and (b) HRS with ITO—0% as the top electrode, and (c) LRS, (d) IRS, and (e) HRS with ITO—33% as the top electrode. Solid and empty circles represent the oxygen ions and oxygen vacancies, respectively.

gradual or two-step types, and the high and low resistance increases with increasing oxygen content in the ITO thin film. In addition, the high-to-low resistance ratio and set voltage values all increase when ITO films with higher oxygen contents are used as top electrodes. From the reported filament model, we propose a possible switching mechanism based on the formation and rupture of conducting filaments inside the HfO$_x$ films to elucidate distinctions between the switching parameters of different samples. Top electrodes with larger oxygen contents may increase the resistivity of ITO thin films, resulting in the set voltage increased during the SET process. Larger amounts of non-lattice oxygen ions are easily reoxidized by oxygen vacancies under Joule heating, which is related to transitions between resistance states during the RESET process. An adequate top electrode may improve the switching characteristics of a device during operation.

Acknowledgment

This work was supported by J. P. Lin in Nanya Technology Corporation and by M. J. Tsai, P. S. Chen and H. Y. Lee in the Electronics and Optoelectronics Research Laboratory of Industrial Technology Research Institute and by the National Sciences Council (NSC 97_2221_E_182005).

References

[1] M. Lundstrom, Science (2003) 210.
[2] M. Fujimoto, H. Koyama, M. Konagai, Y. Hosoi, K. Ishihara, S. Ohnishi, N. Awaya, Appl. Phys. Lett. 89 (2006) 223509.
[3] K. Tsunoda, K. Kinoshita, H. Noshiro, Y. Yamazaki, T. Iizuka, Y. Ito, A. Takahashi, A. Okano, Y. Sato, T. Fukano, M. Aoki, Y. Sugiyama, IEDM Tech. Dig. (2007) 767.
[4] A. Chen, S. Haddad, Y.C. Wu, Z. Lan, T.N. Fang, S. Kaza, Appl. Phys. Lett. 91 (2007) 123517.
[5] J.W. Seo, J.W. Park, K.S. Lim, J.H. Yang, S.J. Kang, Appl. Phys. Lett. 93 (2008) 223505.
[6] C. Park, Y. Seo, J. Jung, D.W. Kim, J. Appl. Phys. 103 (2008) 054106.
[7] C.Y. Lin, C.Y. Wu, C.Y. Wu, T.C. Lee, F.L. Yang, C. Hu, T.Y. Tseng, IEEE Electron Device Lett. 28 (2007) 366.
[8] H.Y. Lee, P.S. Chen, T.Y. Wu, Y.S. Chen, C.C. Wang, P.J. Tzeng, C.H. Lin, F. Chen, C.H. Lien, M.J. Tsai, IEDM Tech. Dig. (2008) 297.
[9] K.M. Chang, W.H. Tzeng, K.C. Liu, W.R. Lai, ECS Trans. 28 (2010) 119.
[10] S. Seo, M.J. Lee, D.H. Seo, E.J. Jeoung, D.S. Suh, Y.S. Joung, I.K. Yoo, I.R. Hwang, S.H. Kim, I.S. Byun, J.-S. Kim, J.S. Choi, B.H. Park, Appl. Phys. Lett. 85 (2004) 5655.
[11] D.C. Kim, M.J. Lee, S.E. Ahn, S. Seo, J.C. Park, I.K. Yoo, I.G. Baek, H.J. Kim, E.K. Yim, J.E. Lee, S.O. Park, H.S. Kim, U-In Chung, J.T. Moon, B.I. Ryu, Appl. Phys. Lett. 88 (2006) 232106.
[12] H.Y. Lee, P.S. Chen, C.C. Wang, S. Maikap, P.J. Tzeng, C.H. Lin, L.S. Lee, M.J. Tsai, Jpn. J. Appl. Phys. 46 (2007) 2175.
[13] K.M. Kim, B.J. Choi, Y.C. Shin, S. Choi, C.S. Hwang, Appl. Phys. Lett. 91 (2007) 012907.
[14] H.Y. Lee, P.S. Chen, T.Y. Wu, C.C. Wang, P.J. Tzeng, C.H. Lin, F. Chen, M.J. Tsai, C. Lien, Appl. Phys. Lett. 92 (2008) 142911.