Journal of Alloys and Compounds 489 (2010) 519–522

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Growth of non-polar ZnO films on *a*-GaN/*r*-Al_2O_3 templates by radio-frequency magnetron sputtering

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ARTICLE INFO

Article history:
Received 31 May 2009
Received in revised form
17 September 2009
Accepted 18 September 2009
Available online 25 September 2009

Keywords:
Semiconductor
Thin film
Crystal growth
X-ray diffraction

ABSTRACT

In this work, non-polar (1,1,−2,0) ZnO thin films have been grown on *a*-GaN/*r*-Al_2O_3 templates by radio-frequency magnetron sputtering. By varying the substrate temperature, the ZnO thin films were transformed from polycrystalline structure to epitaxial one on *a*-GaN/*r*-Al_2O_3 templates. High-quality (1,1,−2,0) ZnO epitaxial thin films were grown on the *a*-GaN/*r*-Al_2O_3 template at the optimized condition of 300 °C, which was confirmed by X-ray diffraction. The full width at half maximum (FWHM) of the (1,1,−2,0) ω-rocking curve of the *a*-plane ZnO films grown on the *a*-GaN/*r*-Al_2O_3 template was 0.51°, indicating a small mosaicity and a low dislocation density in the ZnO film grown on the *a*-GaN/*r*-Al_2O_3 template. Its surface roughness observed by atomic force microscopy was about 2.32 nm. Furthermore, the comparative investigation results show that the ZnO films grown on *a*-GaN/*r*-Al_2O_3 templates are more likely to form in the (1,1,−2,0)-orientation than those directly grown on *r*-sapphire.

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1. Introduction

Zinc oxide (ZnO) has attracted increasing attention due to its various applications in light emitting diodes, transparent conductive electrodes, varistors, and so on [1–4]. Most of ZnO films ever reported are *c*-plane films grown on *c*-plane sapphire substrates, because the *c*-axis orientation perpendicular to the substrates has been found to be a preferable growth direction. However, non-polar ZnO is considered to be much desirable than *c*-plane ZnO in several cases. For example, ZnO has anisotropy along the *c*-axis, so non-polar ZnO films may be preferable for transverse acting devices such as surface acoustic wave devices [5]. Furthermore, in the development of ZnO-based UV light emitters with ZnO/ZnMgO quantum wells (QWs), one may meet the problem of quantum confined Stark effect due to the presence of piezoelectric polarizations in the strained QWs grown in the polar direction [6], which decreases the quantum efficiency of light emission from the QWs. Epitaxial growth of ZnO films along [1,1,−2,0] direction (*a*-plane) provides a promising solution to circumventing this problem.

Though considerable efforts have been made to grow *a*-plane ZnO [7–10], high-quality *a*-oriented ZnO films are still not available, mainly due to the lack of lattice-matched substrates, which limits their practical applications. Therefore, it is important to seek solutions to mitigate the large lattice mismatch between ZnO and sapphire to grow high-quality *a*-plane ZnO epilayers. The most promising one till now is to use GaN as the buffer layer on other substrates for the growth of ZnO epitaxial layers since GaN (a = 3.189 Å, c = 5.185 Å) and ZnO (a = 3.2498 Å, c = 5.2066 Å) [11] have the same crystal structure, close lattice constants (0.4% mismatch for *c*-axis and 1.9% mismatch for *a* axis) and a small difference between in-plane linear thermal expansion coefficients ($\alpha_{GaN} = 5.59 \times 10^{-6}\,K^{-1}$ and $\alpha_{ZnO} = 6.51 \times 10^{-6}\,K^{-1}$) [12].

In this paper, we report the fabrication of *a*-plane ZnO films by radio-frequency (RF) magnetron sputtering on *a*-GaN/*r*-Al_2O_3 templates, and compare the ZnO film on the *a*-GaN/*r*-Al_2O_3 template with that on the *r*-Al_2O_3 substrate, which reveals significant differences in structural and optical properties. To the best of our knowledge, this is the first report of the growth of the *a*-plane ZnO films on *a*-GaN/*r*-Al_2O_3 template and its comparison with those directly grown on *r*-Al_2O_3 by radio-frequency (RF) magnetron sputtering.

2. Experimental details

The *a*-GaN/*r*-Al_2O_3 templates on 2-in. *r*-Al_2O_3 (1,−1,0,2) substrates were prepared in a Thomas Swan close-coupled showerhead (CCS) metal organic chemical vapor deposition (MOCVD) reactor system [13]. About 2.0 μm GaN layers were grown on the *r*-Al_2O_3 using trimethylgallium (TMGa) and ammonia (NH_3) as Ga and N precursors, respectively. As-grown *a*-GaN/*r*-Al_2O_3 templates were directly

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doi:10.1016/j.jallcom.2009.09.098

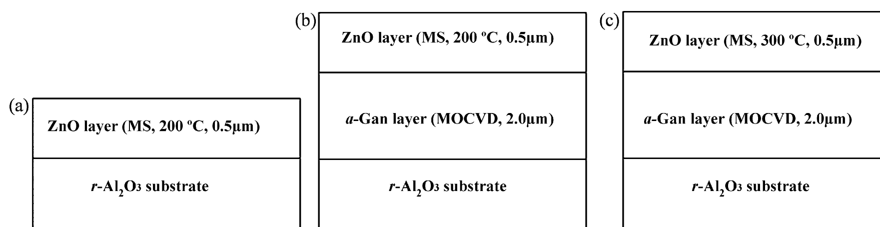

Fig. 1. Structure of the ZnO films in details grown on (a) r-Al_2O_3 substrate at 200 °C, (b) a-GaN/r-Al_2O_3 templates at 200 °C, and (c) a-GaN/r-Al_2O_3 templates at 300 °C by the magnetron sputtering (MS).

transferred into a RF magnetron sputtering system (Ulvac RFS-200) equipped with a ZnO target with purity of 99.999% and a diameter of 4 in. to deposit a-plane ZnO layers without preliminary cleaning and polishing procedures. The sputtering chamber was evacuated to 6×10^{-7} T before sputtering. Before deposition, the target was pre-sputtered for 10 min to remove possible contaminations. After that, the substrate temperature was elevated to 200 °C to deposit the ZnO films. During the film deposition, the ambient gases mixed were argon and oxygen (1:1), and the working pressure and the RF power were maintained at 1×10^{-2} T and 120 W, respectively. For a comparative analysis, the ZnO films grown directly on r-Al_2O_3 (1,−1,0,2) substrates were also prepared under the same conditions. To investigate the effects of substrate temperature on the properties of a-plane ZnO films grown on the a-GaN/r-Al_2O_3 templates, the ZnO samples grown at 300 °C were also prepared. The thickness of the a-plane ZnO thin film was determined to be around 0.5 µm. The detailed layer structures of the grown samples were shown schematically in Fig. 1.

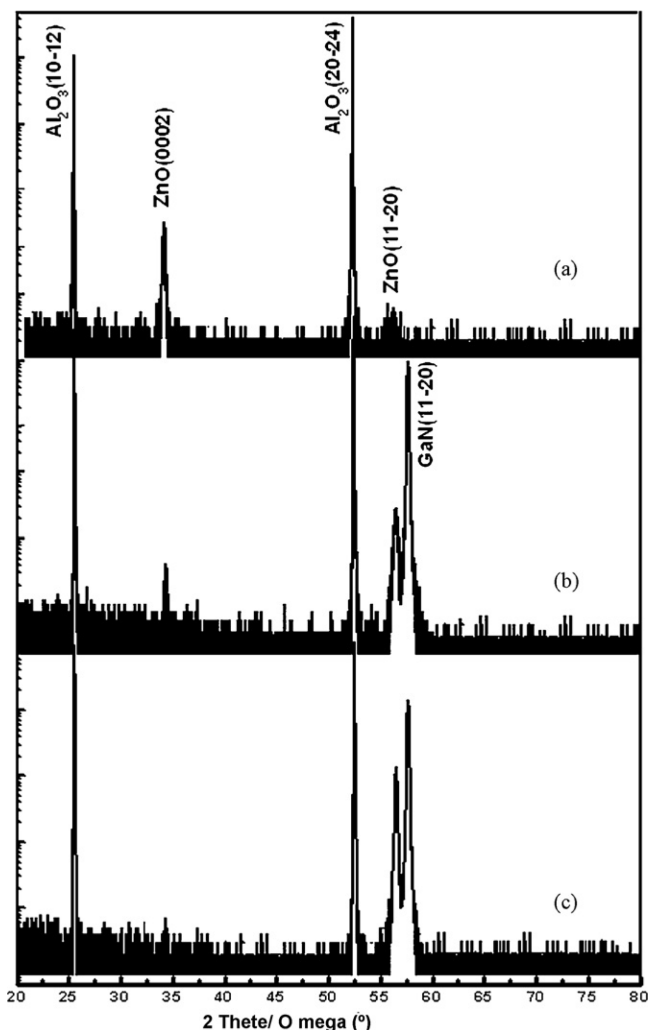

Fig. 2. XRD 2theta/omega scanning curves of the ZnO films grown on (a) r-Al_2O_3 substrate at 200 °C, (b) a-GaN/r-Al_2O_3 templates at 200 °C, and (c) a-GaN/r-Al_2O_3 templates at 300 °C.

The surface morphology of the samples was examined by atomic force microscopy (AFM) in contact mode (Veeco NanoScope MultiMode). The crystal structure and the orientations of GaN samples were investigated by X-ray diffraction (XRD, Panalytical X'pert PRO MRD, Holand) using Cu $K\alpha_1$ (λ = 1.54056 Å) as the source. Photoluminescence (PL) was performed to evaluate the optical properties of the samples by using the 325-nm line of a He–Cd laser (20 mW) as the excitation source. Raman spectra were recorded with a HR800UV Raman spectrometer using a 514 nm laser.

3. Results and discussions

The high-resolution X-ray diffraction (HRXRD) was performed using the symmetric 2theta/omega ($2\theta/\omega$) scan mode with the X-ray incident plane parallel to the c-axis of the a-plane ZnO film, and the results were shown in Fig. 2. As seen in Fig. 2(a), for the sample grown directly on r-Al_2O_3 at 200 °C, the (0 0 0 2) reflection is dominant, while the (1,1,−2,0) one is very weak, indicating the ZnO film is nearly c-oriented. On the other hand, as seen in Fig. 2(b), the (1,1,−2,0) peak becomes very strong for the sample grown on the a-GaN/r-Al_2O_3 template at the same temperature of 200 °C. Such observed phenomenon reveals that the ZnO films grown on a-GaN/r-Al_2O_3 templates are more likely to form in the (1,1,−2,0)-orientation than those directly grown on r-sapphire. The (0 0 0 2) peak for the film deposited on the a-GaN/r-Al_2O_3 template at 200 °C is much weaker but still noticeable, showing this film are polycrystalline with both (1,1,−2,0) and (0 0 0 2) orientations. It indicates that a low growth temperature like 200 °C is not high enough to achieve a pure ZnO[1,1,−2,0]//Al_2O_3[1,−1,0,2] epitaxy, and (0 0 0 1)-oriented ZnO grains are still present, which can be attributed to the fact that [0 0 0 1] is the natural growth direction of wurzite structure. In order to suppress the (0 0 0 1)-oriented phase, the substrate temperature was further raised up to 300 °C. As shown in Fig. 2 (c), the ZnO (0 0 0 2) peak eventually vanishes and a pure (1,1,−2,0)-oriented ZnO film is obtained on the a-GaN/r-Al_2O_3 templates, which indicates that increasing growth temperature can promote the ZnO[1,1,−2,0]//GaN[1,1,−2,0] epitaxy.

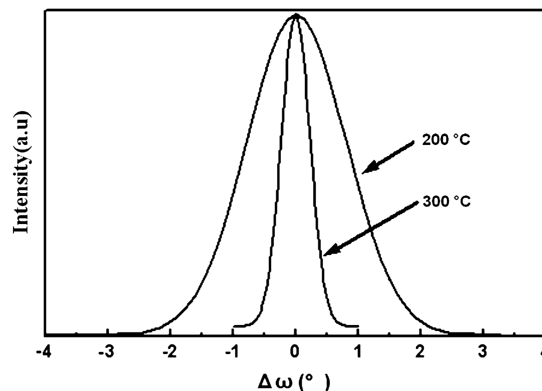

Fig. 3. The high-resolution XRD (1,1,−2,0) ω-scan rocking curves of the ZnO films grown on a-GaN/r-Al_2O_3 templates at 200 and 300 °C.

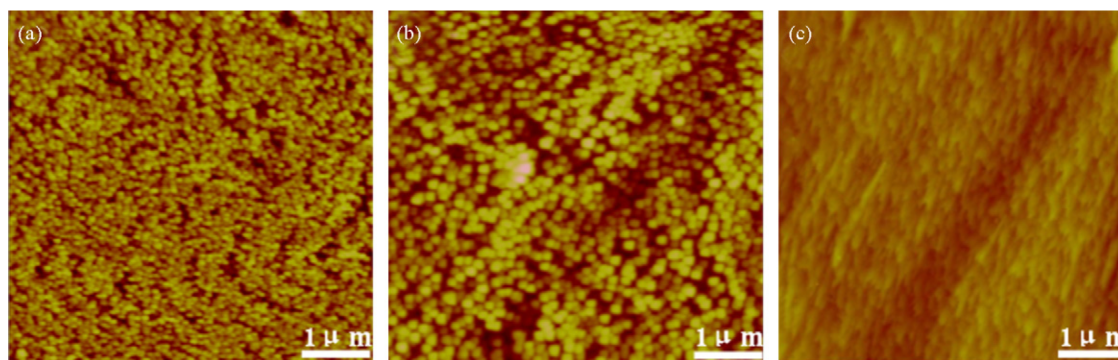

Fig. 4. AFM image of the ZnO films (5 μm × 5 μm) grown on (a) r-Al_2O_3 substrate at 200 °C, (b) a-GaN/r-Al_2O_3 templates at 200 °C, and (c) a-GaN/r-Al_2O_3 templates at 300 °C.

Fig. 3 shows the ω-scan rocking curve on ZnO (1,1,−2,0) peak with the X-ray incident plane parallel to the c-axis of the a-plane ZnO film. The FWHM of the ZnO (1,1,−2,0) rocking curve for the ZnO grown on the a-GaN/r-Al_2O_3 template at 200 °C is about 1.56°. When the growth temperature is further elevated to 300 °C, the FWHM of the ZnO (1,1,−2,0) rocking curve decreases to 0.51°, representing one of the lowest values of a-plane ZnO films grown on r-plane Al_2O_3 by RF magnetron sputtering [14,15]. Therefore, we can conclude that it is very effective to improve the structural quality of the a-plane ZnO film grown on the a-GaN/r-Al_2O_3 template by increasing the growth temperature from 200 to 300 °C.

Fig. 4 shows the AFM images of the a-plane ZnO films grown on the r-Al_2O_3 and the a-GaN/r-Al_2O_3 template in a scan area of 5 μm × 5 μm. From the Fig. 4(a), it was observed that the ZnO film grown on the r-Al_2O_3 at 200 °C has a relatively rough surface and the root mean square (RMS) roughness value is about 4.35 nm. The a-plane ZnO films grown on the a-GaN/r-Al_2O_3 template deposited at 200 °C has a very rough surface (Fig. 4(b)) and the RMS roughness value is 6.51 nm. This could be due to the fact that no solid epitaxy is established and a three-dimensional island growth mode dominates. In addition, the coexistence of the (0 0 0 1) and (1,1,−2,0)-oriented grains can result in severely misaligned growth fronts. As the growth temperature increases from 200 to 300 °C, the growth mode becomes progressively more epitaxy-like (Fig. 4(c)), and thus the surface gets increasingly smoother. The RMS roughness value is about 2.32 nm for the a-plane ZnO film grown on the a-GaN/r-Al_2O_3 template with growth temperature of 300 °C as determined by AFM.

For further insight into the quality of the ZnO epilayers, we investigated the optical properties by PL measurement. PL spectra for the three films were carried out at RT and are shown in Fig. 5. Strong near band edge emission at ∼378 nm could be observed in all samples, and the peak intensity increases from Fig. 5(a) to (c), showing strong correlation with the crystal quality as examined by XRD. The broad band emission at around 500–525 nm mainly due to deep-level impurities [16,17] is observed in the films grown on the r-plane Al_2O_3 and the a-plane GaN/r-plane Al_2O_3 template with the growth temperature of 200 °C. In contrast, this impurity-related peak is hardly seen in the film grown on the a-plane GaN/r-plane Al_2O_3 template at the temperature of 300 °C (Fig. 5(c)). Therefore, the growth temperature of 300 °C is necessary to achieve low impurity incorporation in a-plane ZnO films grown by RF magnetron sputtering in our current conditions.

In order to investigate the strain state in the (1,1,−2,0) a-plane ZnO films, Raman spectra were measured. Fig. 6 shows the Raman spectra of the ZnO films grown on the a-GaN/r-Al_2O_3 template and the r-Al_2O_3 substrate with the substrate temperature of 200 °C, respectively, together with the spectrum of the a-GaN/r-Al_2O_3 template for comparison. The sapphire A_{1g} and E_g modes at 418 and 748 cm^{-1} are clearly seen, which can be used as a frequency reference. Besides the phonon modes of the a-GaN/r-Al_2O_3 template, two apparent ZnO phonon modes were observed at 99.7 and 439.6 cm^{-1}, which are E_2 (low) and E_2 (high) phonon modes of ZnO, respectively [18]. The E_2 (low) mode has a very small pressure coefficient and is not suitable for strain calibration. On the other hand, the E_2 (high) mode is sensitive to the strain state, and can be used for accurate determination of the strain components [19,20]. The E_2 (high) mode in bulk ZnO occurs at 439.0 cm^{-1} according to the previously reported results [21,22]. As seen in Fig. 6(a), the E_2 (high) frequency (438.9 cm^{-1}) of the ZnO film grown on the r-Al_2O_3 substrate with growth temperature of 200 °C is very close to that of bulk ZnO, therefore the film is nearly unstrained. The E_2 (high) frequencies of the films grown on the a-GaN/r-Al_2O_3 templates with growth temperatures of 200 °C and 300 °C are 439.6 and 441.1 cm^{-1}, respectively. These two frequencies are almost the same in the measurement precision (<1 cm^{-1}), and are slightly up-shifted as compared with that of bulk ZnO. This means the films fabricated at 200 and 300 °C are under residual compressive stress. Compared to the film deposited at 300 °C, the smaller

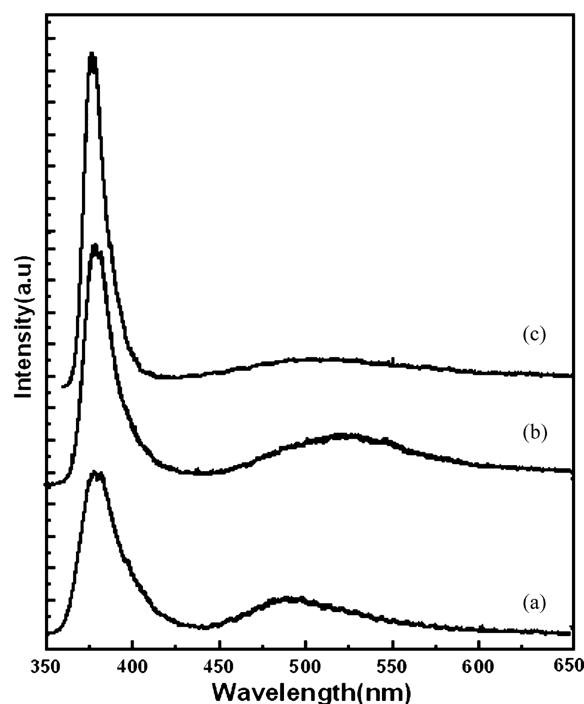

Fig. 5. Room-temperature PL spectra of the ZnO films grown on (a) r-Al_2O_3 substrate at 200 °C, (b) a-GaN/r-Al_2O_3 templates at 200 °C, and (c) a-GaN/r-Al_2O_3 templates at 300 °C.

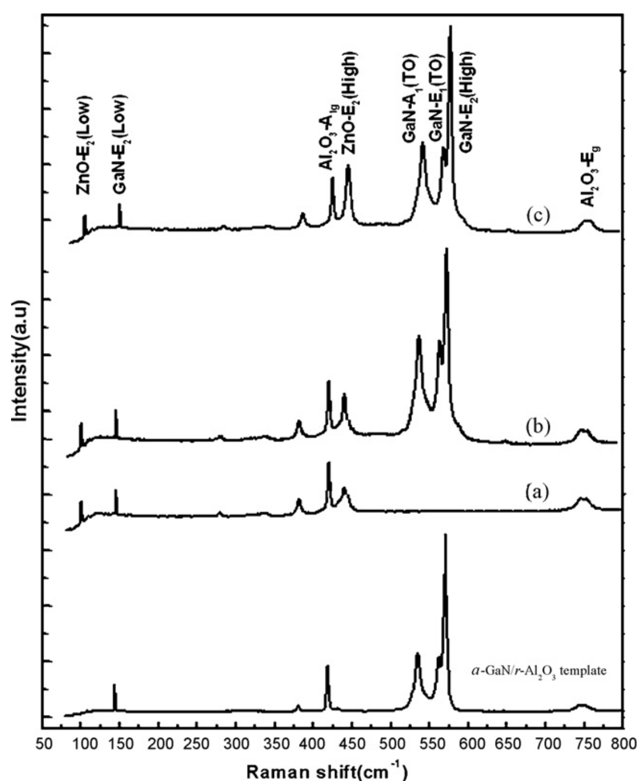

Fig. 6. Room-temperature Raman spectra of the ZnO films grown on (a) r-Al_2O_3 substrate at 200 °C, (b) a-GaN/r-Al_2O_3 templates at 200 °C, and (c) a-GaN/r-Al_2O_3 templates at 300 °C.

compressive strain state in the ZnO film deposited at 200 °C can be attributed to the fact that the film cannot be epitaxially grown on the a-GaN/r-Al_2O_3 template at such a low growth temperature and thus the grown layer has a smaller strain. In contrast, the stronger solid epitaxy growth mode promoted by the higher growth temperature like 300 °C allows for a good replication of lattice constant at the interface and the ZnO film is under compressive strain since a-GaN underneath has a smaller lattice constant: 0.4% smaller along the c-axis and 1.9% smaller along the a-axis. The peak of E_2 (high) mode becomes narrower as the growth temperature increases (Fig. 6(a)–(c)), and the FWHM values are 12.2, 8.3, and 4.7 cm^{-1} for the films deposited on the r-Al_2O_3 with the temperature of 200 °C, on the a-GaN/r-Al_2O_3 template with the temperature of 200 °C and on the a-GaN/r-Al_2O_3 templates with the temperature of 300 °C, respectively. This means the crystallinity of the films grown on the a-GaN/r-Al_2O_3 template gets better as the growth temperature increases, in agreement with the XRD results.

4. Conclusions

In conclusion, it has been demonstrated that a-plane ZnO films with high crystallinity can be grown on a-GaN/r-Al_2O_3 templates by radio-frequency magnetron sputtering. The deposition temperature has been shown to have strong effects on the growth mode and thus the crystal quality of the ZnO films. The structural change from a polycrystalline to a (1,1,−2,0) epitaxial one was observed by varying the substrate temperature. By a comparative study, the AFM and XRD investigation results show that a-oriented ZnO films are more easily achieved by using the a-GaN/r-Al_2O_3 template as the substrate than using the r-Al_2O_3. All these results indicate that a-plane GaN/r-Al_2O_3 templates are suitable substrates for growing high-quality a-plane ZnO films under appropriate substrate temperatures, which has potential applications in non-polar ZnO-based optoelectronic devices.

Acknowledgements

This work was supported by the Doctoral Program Foundation of Institutions of Higher Education of China (Grant No. 200804871144), the Program for New Century Excellent Talents in University(NCET-08-0214), the Hubei Province Science Fund for Distinguished Young Scholars (Grant No. 2008CDB334), the Key Programs of the Natural Science Foundation of Huazhong University of Science and Technology (Grant No. 20072008B), the National Science Foundation for Post-doctoral Scientists of China (Grant No. 20080430141), and the National Natural Science Foundation of China (Grant No. 60976042).

References

[1] Mariano A. Zimmler, T. Voss, C. Ronning, C. Federico, Appl. Phys. Lett. 94 (2009) 241120.
[2] Z. Yan, X.Y. Zhou, G.K.H. Pang, T. Zhang, W.L. Liu, J.G. Cheng, Z.T. Song, S.L. Feng, L.H. Lai, J.Z. Chen, Y. Wang, Appl. Phys. Lett. 90 (2007) 143503.
[3] M.-W. Ahn, K.-S. Park, J.-H. Heo, J.-G. Park, D.-W. Kim, K.J. Choi, J.-H. Lee, S.-H. Hong, Appl. Phys. Lett. 93 (2008) 263103.
[4] X.Y. Du, Y.Q. Fu, J.K. Luo, A.J. Flewitt, W.I. Milne, J. Appl. Phys. 105 (2009) 024508.
[5] S. Kumar, G.-H. Kim, K. Sreenivas, R.P. Tandon, J. Electroceram. 22 (2009) 198.
[6] T. Makino, A. Ohtomo, C.H. Chia, Y. Segawa, H. Koinuma, K. Kawasaki, Phys. E 21 (2004) 671.
[7] S.-R. Jian, J. S.-C. Jang, G.-J. Chen, H.-G. Chen, Y.-T. Chen, J. Alloys Compd. 479 (2009) 348.
[8] P. Pant, J.D. Budai, R. Aggarwal, R.J. Narayan, J. Narayan, Acta Mater. 57 (2009) 4426.
[9] D.-H. Cho, J.-H. Kim, B.-M. Moon, Y.-D. Jo, S.-M. Koo, Appl. Surf. Sci. 255 (2009) 3480.
[10] H. Lin, S. Zhou, J. Zhou, X. Liu, S. Gu, S. Zhu, Z. Xie, P. Han, R. Zhang, Thin Solid Films 516 (2008) 6072.
[11] Int. Center for Diffraction Data, PDF-2 card 36-1451.
[12] B.M. Ataev, W.V. Lundin, V.V. Mamedov, A.M. Bagamadova, E.E. Zavarin, J. Phys. Condens. Matter 13 (2001) L211.
[13] J. Dai, L. Zhang, Q. He, Y. Sun, C. Chen, Proc. SPIE 7279 (2008), pp. 72791B1–72791B6.
[14] Y.J. Kim, Y.T. Kim, H.K. Yang, J.C. Park, J.I. Han, Y.E. Lee, H.J. Kim, J. Vac. Sci. Technol., A 15 (1997) 1103.
[15] T. Yanagitani, M. Matsukawa, Y. Watanabe, T. Otani, J. Cryst. Growth 276 (2005) 424.
[16] B. Lin, Z. Fu, Y. Jia, Appl. Phys. Lett. 79 (2001) 943.
[17] D.C. Look, C. Coskun, B. Claflin, G.C. Farlow, Phys. B 340–342 (2003) 32.
[18] J.M. Calleja, M. Cardona, Phys. Rev. B: Condens. Matter 16 (1977) 3753.
[19] G.J. Exarhos, S.K. Sharma, Thin Solid Films 270 (1995) 27.
[20] S. Tripathy, S.J. Chua, P. Chen, Z.L. Miao, J. Appl. Phys. 92 (2002) 3503.
[21] K.A. Alim, V.A. Fonoberov, A.A. Balandin, Appl. Phys. Lett. 86 (2005) 053103.
[22] F. Decremps, J. Pellicer-Porres, A.M. Saitta, J.-C. Chervin, A. Polian, Phys. Rev. B: Condens. Matter 65 (2002) 092101.