

# Realization of controllable etching for ZnO film by NH<sub>4</sub>Cl aqueous solution and its influence on optical and electrical properties

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## Abstract

ZnO films were deposited on *c*-plane Al<sub>2</sub>O<sub>3</sub> substrates by pulsed laser deposition. The etching treatments for as-grown ZnO films were performed in NH<sub>4</sub>Cl aqueous solution as a function of NH<sub>4</sub>Cl concentration and etching time. It was found that NH<sub>4</sub>Cl solution is an appropriate candidate for ZnO wet etching because of its controllable and moderate etching rate. The influence of etching treatment on the morphology, optical and electrical properties of the ZnO films has been investigated systematically by means of X-ray diffraction, atomic force microscope, photoluminescence and Hall effect. The results indicated that the surface morphology and optical properties of the films were highly influenced by etching treatment.

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## 1. Introduction

ZnO has been of great interest recently because of its wide band gap (3.36 eV) and relatively large exciton binding energy (60 meV) at room temperature (RT), which make this material a promising candidate for light emitting devices and semiconductor lasers with low thresholds in the ultraviolet (UV) region [1,2]. Compared with GaN, ZnO possesses many unique properties mainly including the availability of high quality ZnO substrate and the simpler wet etching processing at safe temperature, these advantages are especially attractive for some device applications such as solar cells [3], photo detectors [4], acoustic devices [5], gases sensors, etc. [6]. Despite the difficulty in p-type doping, some ZnO based light emitting diodes (LEDs) have been reported recently [7–10]. For the fabrication of devices such as LED and laser diode (LD), mesa formation through controllable and uniform etching process is indispensable if nonconductive substrates were used. As yet,

most of the ZnO etch processing were dominated by dry etching because of its controllable etching rate [11–13]. Compared with the dry etch, the wet etch technique possesses the advantages of simplicity and low equipment cost. ZnO is easily etched in all acids and alkalis [14]. Nevertheless, the etching rate for ZnO in most single acids, mixed acids and alkalis is very fast, even if the solution concentration drastically reduced [15]. There has been no report on the systematic investigation of the influence of wet etching on morphology, optical and electrical properties of ZnO films.

In this paper, ZnO films grown by pulsed laser deposition (PLD) were etched in NH<sub>4</sub>Cl aqueous solution of different concentrations at RT. The dependences of surface morphologies, optical and electrical properties of ZnO films on the etching time were systematically investigated. The results suggested that NH<sub>4</sub>Cl is a promising etchant candidate for ZnO because of its controllable etching rate and the relatively low cost.

## 2. Experimental procedures

ZnO thin films were deposited on *c*-plane Al<sub>2</sub>O<sub>3</sub> substrates by ablating a ceramic ZnO target (99.99%) using a KrF excimer

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laser (248 nm, 5 Hz). The substrate surface was sequentially degraded in ultrasonic baths of methylbenzene, acetone and ethanol, then etched by a mixture of  $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4$  (3:1) at  $160^\circ\text{C}$  for 15 min. During film deposition, the laser energy density was kept at  $2.5\text{ J/cm}^2$ . The distance between the substrate and target was 5 cm. The substrate holder was rotated at a rate of 20 rpm to obtain uniform films. ZnO films were grown at  $650^\circ\text{C}$  for 200 min under 60 Pa in oxygen ambient. The thickness of all the samples was about 500 nm.

$\text{NH}_4\text{Cl}$  aqueous solutions of different concentrations were prepared by dissolving high-purity (99.99%)  $\text{NH}_4\text{Cl}$  powder in deionized water ( $\rho > 18\text{ M}\Omega\text{ cm}$ ). For investigation of the dependence of etching rate on the concentration, ZnO films were etched in  $\text{NH}_4\text{Cl}$  aqueous solutions with different concentrations in the range of 1–15 wt%. In order to study the relationship between etching thickness and etching time, ZnO films were etched by a selected concentration of 5%  $\text{NH}_4\text{Cl}$  solution for different time and then washed by deionized water immediately.

The crystalline quality of the as-deposited ZnO films was determined by X-ray diffraction (XRD) with a  $\text{Cu K}\alpha$  radiation (0.15418 nm). The etching depth was measured by profilometer (ET 4000M). The influence of etching treatment on the morphology, optical and electrical properties of the ZnO films has been investigated systematically. The morphology was observed with a BENYUAN CSPM-2000 atomic force microscope (AFM). The photoluminescence (PL) measurement was carried out using a He–Cd laser (325 nm, 30 mW). The optical absorption spectra were recorded using a Shimadzu UV160 spectrometer. The electrical properties were measured by Hall system (Bio-Rad HL5500) using Van de Pauw method. All the measurements were performed at RT. Furthermore, the experiments have been repeated several times.

### 3. Results and discussions

The crystalline quality of the samples is evaluated by XRD measurements. Fig. 1 shows the XRD pattern of the film deposited on *c*-plane  $\text{Al}_2\text{O}_3$  substrate. In Fig. 1, the intense ZnO

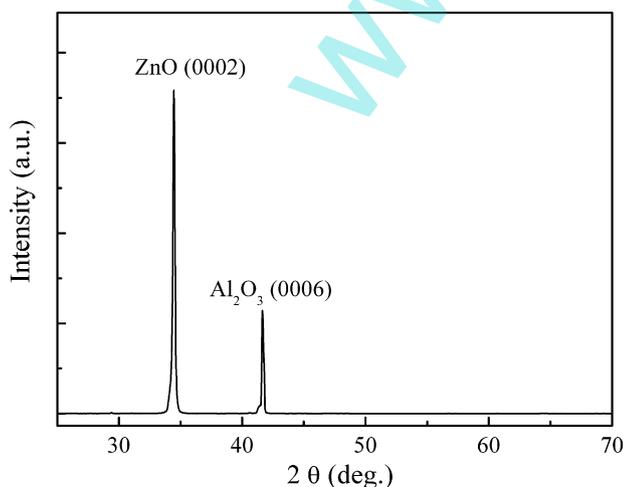


Fig. 1. XRD pattern of the as-deposited ZnO film.

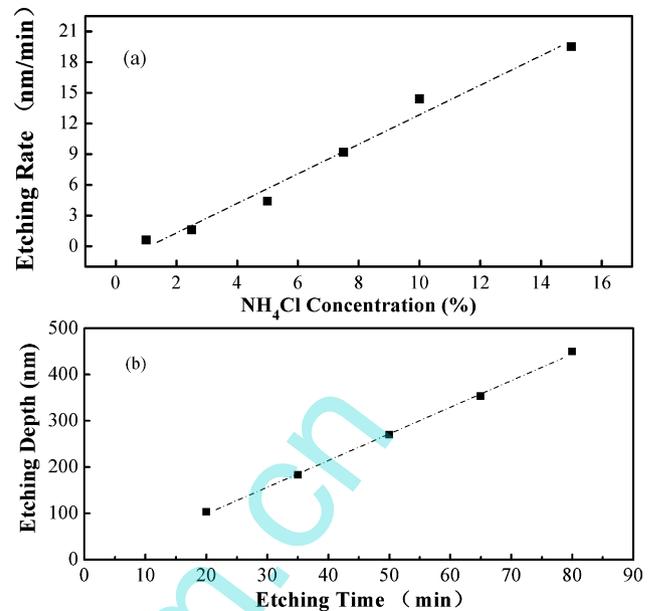
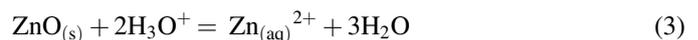
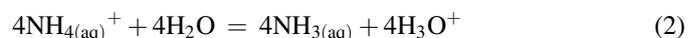
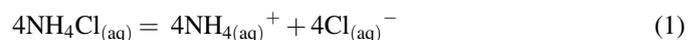


Fig. 2. (a) The etching rate of ZnO etched by  $\text{NH}_4\text{Cl}$  solution with different concentrations. (b) The etching depth of ZnO etched by  $\text{NH}_4\text{Cl}$  solution with 5% concentration for different time.

(0 0 0 2) diffraction peak can be observed, indicating that the ZnO films are strongly *c*-axis-oriented with high crystalline quality. The dependence of etching rate for ZnO film on the concentration of  $\text{NH}_4\text{Cl}$  is shown in Fig. 2(a). Etching depth measurements were made with the profilometer scanning in a direction perpendicular to substrate surface. In our work, the optimum *c*-axis-oriented ZnO thin films were obtained, as described in Fig. 1. Therefore, the etch direction discussed here is along the ZnO (0 0 0 2). It can be easily found that the etching rate has a nearly linear relationship with the etching concentration of the  $\text{NH}_4\text{Cl}$  aqueous solution. When the solution concentration varied from 1 to 15%, the calculated etching rate increased from 1.4 to 19.0 nm/min accordingly. The reaction of ZnO (solid state) with  $\text{NH}_4\text{Cl}$  solution (liquid state) can be described by the following equations from (1) to (3) [15]:



It can be concluded that the linear relationship between etching rate and  $\text{NH}_4\text{Cl}$  concentration is attributed to the linear increasing of the  $\text{H}_3\text{O}^+$  number with thickening of the  $\text{NH}_4\text{Cl}$  aqueous solution. Fig. 2(b) shows the dependence of depth on etching time for the film etched in 5%  $\text{NH}_4\text{Cl}$  aqueous solution. The good linear dependence indicated that the etching depth is controllable in our process.

Moreover, ZnO is a semiconducting material with a strong polarity. Generally, the etch rate is dependent on the polarity of grown ZnO thin films. Some researchers have discussed the relationship between the etch rate and the polarity of ZnO thin

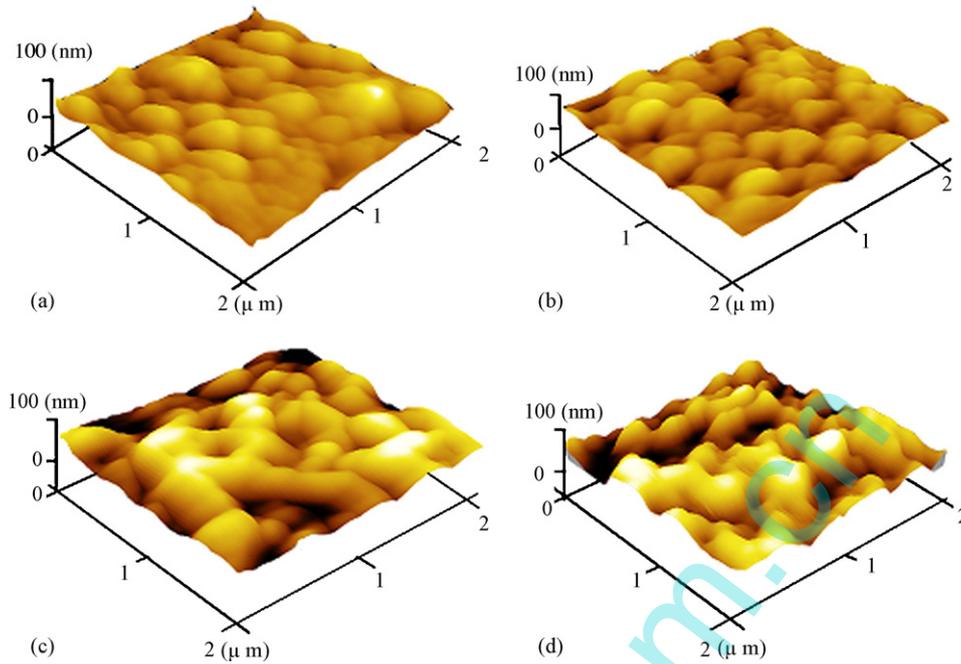


Fig. 3. The AFM images of ZnO films etched by 5%  $\text{NH}_4\text{Cl}$  solution for different time: (a) as-deposited sample, (b) 3 min, (c) 10 min and (d) 30 min.

film. Jo et al. found that O-terminated  $(000\bar{1})$  surface ( $-c$  surface) is etched rapidly and uniformly, while the etching of the Zn-terminated  $(0001)$  surface ( $+c$  surface) is non-uniform and slow [16]. Ohnishi et al. found that the polarity of ZnO epilayers is  $(000\bar{1})$  (O face) for growth on  $c$ -plane  $\text{Al}_2\text{O}_3$  substrates [17], while Kaidashev et al. found that surface polarity of the PLD ZnO films on  $c$ -plane  $\text{Al}_2\text{O}_3$  is Zn-face [18]. So, the accurate polarity of the ZnO film fabricated by laser molecular beam epitaxy (L-MBE) or pulsed laser deposition remains controversial. As for the polarity of ZnO film, the further research work is still needed.

Fig. 3 shows the AFM surface images of unetched film and the films etched by 5%  $\text{NH}_4\text{Cl}$  solution for different time. The scan area is  $2\ \mu\text{m} \times 2\ \mu\text{m}$ . After etching, the surface morphologies become rougher and the root mean square (RMS) surface roughness of the film increased from 44.8 to 101.0 nm gradually while the etching time increased to 30 min. Simultaneously, the grain size reduced from 119.5 to 70.1 nm, as listed in Table 1. It indicates that the surface morphologies of the film had been greatly influenced by etching time. Owing to a significant lattice mismatch between ZnO and  $\text{Al}_2\text{O}_3$  (18.4%), ZnO films deposited on  $\text{Al}_2\text{O}_3$  contain large quantity of dislocation [14], and the etching operation occurring at the dislocation and boundary was preferable [19]. The etching rate

along boundary was faster than that in the grain, as a result, the surface morphologies become rougher and rougher with the increasing etching time.

The PL measurement was performed to investigate the effect of etching treatment on the optical properties of ZnO thin film, as shown in Fig. 4. As can be seen in the spectra, all the PL spectra show two peaks. For the as-deposited film, the near band edge (NBE) emission around 380 nm is relatively strong and is accompanied by a rather weak deep level (DL) emission band at around 500 nm. The NBE emission is generally ascribed to the exciton emission [20], and the DL emission is attributed to oxygen vacancies [21] or zinc interstitials [22]. PL measurement suggested that the as-grown films are of optical high quality with minor defects. It was found that the intensity of NBE emission becomes weaker and the intensity of the DL emission becomes stronger with increasing of the etching time.

Table 1  
Grain size and RMS surface roughness of ZnO samples

Etching time (min)	Grain size (nm)	RMS surface roughness (nm)
0	119.5	44.8
3	94.9	51.1
10	78.2	69.1
30	70.1	101.0

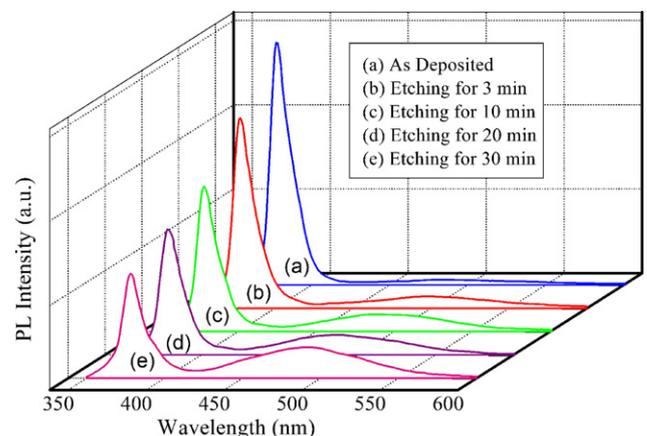


Fig. 4. The PL of ZnO films etched by 5%  $\text{NH}_4\text{Cl}$  solution for different time: (a) as-deposited sample, (b) 3 min, (c) 10 min, (d) 20 min and (e) 30 min.

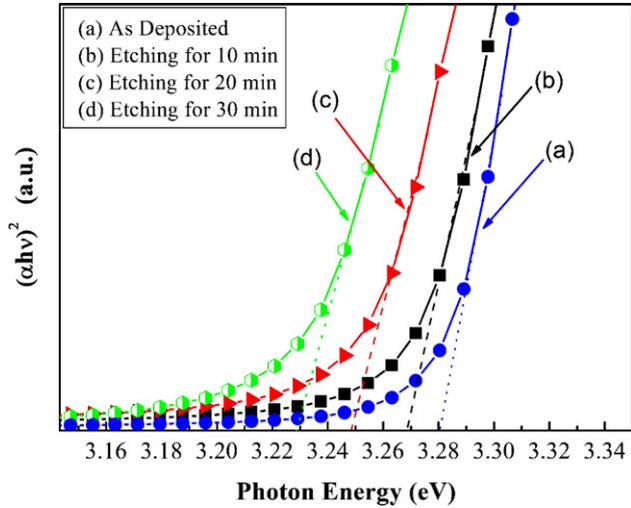


Fig. 5. Plot of  $(\alpha hv)^2$  vs. photon energy ( $h\nu$ ) for ZnO films etched by 5%  $\text{NH}_4\text{Cl}$  solution for different time: (a) as-deposited sample, (b) 10 min, (c) 20 min and (d) 30 min.

Table 2  
Estimated optical band gap of ZnO film

Etching time for samples (min)	Number of measurements ( $N = 3$ )	
	$\bar{E}_g$ (eV)	S.D. (eV)
As-deposited	3.28	0.00
3	3.26	0.01
10	3.25	0.01
30	3.22	0.01

$\bar{E}_g$ , average band gap; S.D., standard deviation.

For convenience a parameter  $K$  is defined, which is the integrated intensity ratio of the NBE emission to DL emission. The value  $K$  is about 8.5, 3.2, 1.7, 1.2 and 0.9 for the curves a–e in Fig. 4, respectively. It is believed that the surface states originated from large surface-to-volume ratios seriously influence the PL process [23,24]. The number of photon-generated carrier in surface states in a grain is proportional to the number of atoms on the surface. After etch, the number of atoms on the surface per unit volume increased [24]. Consequently, the DL emission increased. Godlewski et al. conclude that poor morphology and granular features is the key reason why the NBE emission may become weak [25].

Table 3  
Electrical parameters for the ZnO samples obtained from Hall measurements

Etching time for samples (min)	Number of measurements ( $N = 3$ )					
	Resistivity		Hall mobility		Carrier concentration	
	$\bar{R}$ ( $\Omega$ cm)	S.D. ( $\Omega$ cm)	$\bar{\mu}$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	S.D. ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$\bar{n}$ ( $\text{cm}^{-3}$ )	S.D. ( $\text{cm}^{-3}$ )
As-deposited	0.41	0.02	9.37	0.07	$1.62 \times 10^{18}$	$7.49 \times 10^{16}$
3	0.58	0.07	6.59	0.34	$1.65 \times 10^{18}$	$2.48 \times 10^{17}$
10	0.69	0.10	5.56	0.57	$1.64 \times 10^{18}$	$9.15 \times 10^{16}$
30	0.83	0.13	5.04	0.34	$1.51 \times 10^{18}$	$1.60 \times 10^{17}$

$\bar{R}$ , average resistivity; S.D., standard deviation;  $\bar{\mu}$ , average mobility;  $\bar{n}$ , average carrier concentration.

In addition, the optical absorption spectra were measured (figure not shown). To determine the optical band gap, the model for direct interband transitions was used:  $\alpha hv = A \times (hv - E_g)^{1/2}$  where  $A$  is a constant,  $h\nu$  the photon energy,  $E_g$  the optical band gap and  $\alpha$  is the absorption coefficient. In this approximation,  $(\alpha hv)^2$  is a linear function of  $h\nu$ . The  $E_g$  value can be obtained by extrapolating the linear portion to the photon energy ( $h\nu$ ) axis and a sample is illustrated in Fig. 5. Reproducibility studies have been carried out for three samples. The number of measurements ( $N$ ) and average optical band gap values ( $\bar{E}_g$ ) of the samples are summarized in Table 2. The band gap redshifted gradually with the increasing of etching depth. In order to verify the reliability of the redshift, the standard deviation (S.D.) was utilized. We found that the S.D. is very small (less than 0.4%) from sample to sample. This suggested that the results were not occasional. As for the redshift of the band gap for the ZnO films, some researchers believed that it was associated with the relaxing of compressive stress. Because of the large lattice mismatch between ZnO and  $\text{Al}_2\text{O}_3$ , ZnO films grown on  $\text{Al}_2\text{O}_3$  always contain large quantity dislocation and tend to exhibit intensive compress stress [26,27]. The band gap due to strain-induced confinement displayed a redshift that increases with etching time, this may be because of the strain relaxation along the dislocation and grain boundary [28,29]. Macht et al. verified direct influence of dislocations on the photoluminescence bands utilizing low temperature (4 K) PL measurement in their experiment [29]. In addition, the increasing defects such as point defects around the surface resulting from the etching process may contribute to the redshift of the band gap.

The electrical parameters of ZnO films were investigated by Hall effect measurement. Moreover, reproducibility investigations have also been performed for three samples. The number of measurements, average value and standard deviation are listed in Table 3. As the etching time increased, the resistivity ( $\bar{R}$ ) increased slightly, at the same time the Hall mobility ( $\bar{\mu}$ ) decreased. After being etched for 30 min, the mobility decreased from 9.37 to 5.04  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  and the carrier concentration ( $\bar{n}$ ) did not change obviously within this range. We also found that the S.D. is comparatively small. The electrical parameters were the statistical measuring results from the whole film (including the surface and under layer). The thickness of the film decreased with the increasing of etching time and the surface scattering contributing to the mobility became noticeable accordingly. After etching, ZnO films got

rougher and the defects resulting from the etching treatment increased. All these factors strengthened the surface scattering, as a result the Hall mobility reduced and the resistivity increased accordingly. The exact origin and mechanism for the obtained electrical parameters have to be verified by further research.

#### 4. Conclusion

In summary, ZnO thin films were deposited on Al<sub>2</sub>O<sub>3</sub> substrates using the PLD technique. The etching treatments for as-grown ZnO films in NH<sub>4</sub>Cl aqueous solution were investigated. The good linear dependence of etching depth on etching time indicated that the etching rate is controllable in etching process. The influence of etching treatment on the morphology, optical and electrical properties of the ZnO films has been investigated systematically. With the increasing of etching time, surface morphologies of ZnO films become rougher, and the NBE emission decreased and the DL emission increased.

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#### References

- [1] Y. Gu, I. Kuskovsky, M. Yin, S. O'Brien, G.F. Neumark, *Appl. Phys. Lett.* 85 (2004) 3833.
- [2] J. Zhao, L.Z. Hu, Z.Y. Wang, Y. Zhao, X.P. Liang, M.T. Wang, *Appl. Surf. Sci.* 229 (2004) 311.
- [3] U. Rau, M. Schmidt, *Thin Solid Films* 387 (2001) 141.
- [4] S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu, H. Shen, *J. Cryst. Growth* 225 (2000) 110.
- [5] T. Mitsuyu, S. Ono, K. Wasa, *J. Appl. Phys.* 51 (1980) 2646.
- [6] Q. Wan, Q.H. Li, Y.J. Chen, T.H. Wang, X.L. He, J.P. Li, C.L. Lin, *Appl. Phys. Lett.* 84 (2004) 9654.
- [7] X.L. Guo, J.H. Choi, H. Tabata, T. Kawai, *Jpn. J. Appl. Phys., Part 2* 40 (2001) L177.
- [8] D.K. Hwang, S.H. Kang, J.H. Lim, E.J. Yang, J.Y. Oh, J.H. Yang, S.J. Park, *Appl. Phys. Lett.* 86 (2005) 222101.
- [9] S.J. Jiao, Z.Z. Zhang, Y.M. Lu, D.Z. Shen, B. Yao, J.Y. Zhang, B.H. Li, D.X. Zhao, X.W. Fan, Z.K. Tang, *Appl. Phys. Lett.* 88 (2006) 031911.
- [10] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, M. Kawasaki, *Nat. Mater.* 4 (2005) 42.
- [11] S.W. Na, M.H. Shin, Y.M. Chung, J.G. Han, N.E. Lee, *J. Vac. Sci. Technol. A* 23 (2005) 898.
- [12] J.S. Park, H.J. Park, Y.B. Hahn, G.C. Yi, A. Yoshikawa, *J. Vac. Sci. Technol. B* 21 (2003) 800.
- [13] J.M. Lee, K.M. Chang, K.K. Kim, W.K. Choi, S.J. Park, *J. Electrochem. Soc.* 148 (2001) G1.
- [14] Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.J. Cho, H. Morkoç, *J. Appl. Phys.* 98 (2005) 041301.
- [15] S.C. Chang, D.B. Hicks, R.C.O. Laugal, Technical digest, in: *IEEE Solid-State Sensor and Actuator Workshop, Fifth Technical Digest*, 1992. p. 41.
- [16] W. Jo, S.J. Kim, D.Y. Kim, *Acta Mater.* 53 (2005) 4185.
- [17] T. Ohnishi, A. Ohtomo, M. Kawasaki, K. Takahashi, M. Yoshimoto, H. Koinuma, *Appl. Phys. Lett.* 72 (1998) 824.
- [18] E.M. Kaidashev, M. Lorenz, H. von Wenckstern, A. Rahm, H.-C. Semmelhack, K.-H. Han, G. Benndorf, C. Bundesmann, H. Hochmuth, M. Grundmann, *Appl. Phys. Lett.* 82 (2003) 3901.
- [19] L.W. Zhao, C.C. Liu, X.Y. Teng, S.L. Sun, W. Zhang, J.S. Zhu, Y.C. Feng, B.P. Guo, *Mater. Sci. Semicond. Process.* 9 (2006) 403.
- [20] Y. Sun, J.B. Ketterson, G.K.L. Wong, *Appl. Phys. Lett.* 77 (2000) 2322.
- [21] E.G. Bylander, *J. Appl. Phys.* 49 (1978) 1188.
- [22] D.C. Look, J.W. Hemsky, J.R. Sizelove, *Phys. Rev. Lett.* 82 (1999) 2552.
- [23] H. Shalish, H. Temhin, V. Narayanamurti, *Phys. Rev. B* 69 (2004) 245401.
- [24] X.F. Wang, F.L. Zhao, P.B. Xie, S.Z. Deng, N.S. Xu, H.Z. Wang, *Chem. Phys. Lett.* 423 (2006) 361.
- [25] M. Godlewski, E.M. Goldys, M.R. Phillips, R. Langer, A. Barski, *Appl. Phys. Lett.* 73 (1998) 3686.
- [26] Z.Y. Zhang, Y. Zhang, L. Duan, B.X. Lin, Z.X. Fu, *J. Cryst. Growth* 290 (2006) 341.
- [27] H.K. Yadav, K. Sreenivas, V. Gupta, *J. Appl. Phys.* 99 (2006) 083507.
- [28] I. Tan, D. Lishan, R. Mirin, V. Jayaraman, T. Yasuda, E. Hu, J. Bowers, *Appl. Phys. Lett.* 59 (1991) 875.
- [29] L. Macht, J.L. Weyher, A. Grzegorzczak, P.K. Larsen, *Phys. Rev. B* 71 (2005) 073309.