

Low-temperature Atomic Layer Deposition of TiO_2 , Al_2O_3 , and ZnO Thin Films

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(Received 28 April 2011, in final form 30 May 2011)

We studied low-temperature atomic layer deposition (LT-ALD) of TiO_2 , Al_2O_3 , and ZnO thin films at temperatures down to room temperature, mainly focusing on the growth characteristics and the film's properties. Here, two kinds of ALD deposition systems were introduced. Initially, for the thermal ALD (T-ALD) process using a commercial ALD system, a very long purging time of up to ~ 300 s was required to entirely evacuate the remaining H_2O vapors at room temperature due to the large volume and the complicated inner structure of the commercial ALD chamber. For the realization of LT-ALD with a short process time, a plasma-enhanced ALD (PE-ALD) process using O_2 plasma was employed, which enabled us to effectively remove the residual reactants at temperatures down to room temperature. As another method, we specifically designed a homemade ALD system with a small volume and a simple inner structure, thereby being able to use T-ALD to synthesize TiO_2 , Al_2O_3 , and ZnO thin films by using H_2O with very short H_2O purging times even at room temperature, which reveals that the chamber size and design are the critical factors enabling LT-ALD with a short process time. The LT-ALD processes produced highly-pure Al_2O_3 , TiO_2 , and ZnO films without any C and N impurities by complete elimination of ligands and exhibited excellent conformality in 3-dimensional nanoscale via holes.

PACS numbers: 68.55.Jk, 68.55.Nq, 81.15.Gh

Keywords: Low-temperature atomic layer deposition, TiO_2 , Al_2O_3 , ZnO, Growth characteristics, Film properties

DOI: 10.3938/jkps.59.452

I. INTRODUCTION

As modern integrated devices are scaling down, the need for a deposition technique to produce high-quality films with atomic-thickness controllability is tremendous. Among various thin-film deposition methods, atomic layer deposition (ALD) is being considered as a promising deposition method with great benefits, such as good conformality, good uniformity, atomic-scale thickness controllability, and low impurity contamination even at low growth temperatures due to its growth mechanism being controlled by a self-limited surface reaction [1,2].

Due to its several advantages, ALD has received a great deal of attention for its potential to play a major role for applications in flexible electronics such as flexible displays, wearable computers, and portable solar cells [3,4]. Especially, low-temperature depositions of various ALD oxides, such as TiO_2 , Al_2O_3 , and ZnO,

have enabled them to be applied for dielectric, channel and TCO contact layers for plastic-substrate-based transparent and flexible thin-film transistors [3,5,6]. Besides, ALD Al_2O_3 has been employed to passivate surface defects, acting as an excellent charge-recombination barrier on solar cells [7,8]. Above conventional electronic device applications, the functional coating of thermally fragile substrates becomes interesting for new applications of ALD oxides such as TiO_2 , Al_2O_3 , and ZnO in diverse areas, including food packaging, photocatalysts and biomaterials [9–11]. Regarding all these applications, the ALD process with low growth temperatures below 150°C is a crucial prerequisite to be researched. Although ALD of oxide thin films at low growth temperatures can be found in previous publications [4,10,12], comprehensive and systematic studies on various oxide films have still not been carried out, as far as we know, in spite of their potential importance. In particular, the effects of the process chamber and the deposition method on effective LT-ALD with a short process time appli-

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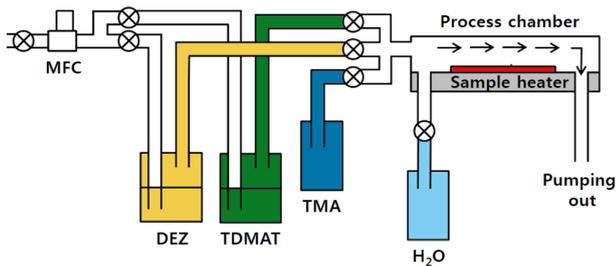


Fig. 1. (Color online) Schematic drawing of our own homemade ALD system.

cable industry have not been reported yet. Therefore, it would be the valuable to comprehensively investigate low-temperature ALD (LT-ALD) of various oxide thin films such as TiO₂, Al₂O₃, and ZnO to enable potential applications in diverse areas.

In this study, we have systematically investigated the growth characteristics and the film properties of LT-ALD TiO₂, Al₂O₃, and ZnO, mainly focusing on the chamber design and the process method. Hence, we employed two kinds of ALD systems and deposition methods to realize the LT-ALD process effectively. The growth features were studied as a function of key growth parameters, including growth temperature, reactant exposure and purging time. Furthermore, the crystallinity, chemical composition and conformality of the LT-ALD TiO₂, Al₂O₃, and ZnO films were examined by using several analysis techniques.

II. EXPERIMENTAL DETAILS

In this work, two kinds of ALD systems were employed for LT-ALD. Initially, a commercial PE-ALD chamber (SNTEK Co., ALD5008) with large volume (8" wafer level) was utilized. This system has a vertical double shower head system for good uniformity with plasma capability and consists of two pieces laid in a fold: the upper one for the precursor dose and the lower one for the reactant exposure. The lower showerhead part was connected to a radio-frequency (RF) plasma generator with matching network. Thus, the specimen on the substrate heater was directly exposed to the plasma generated during the reactant pulse. Further information on the same type of chamber configuration can be found in our previous publications [13,14]. The other system is our own homemade ALD chamber with a simple laminar gas flow, which is specifically designed for LT-ALD. A schematic drawing of the homemade ALD system is shown in Fig. 1. The chamber volume is small (80 cc) enough to prevent any residual reaction, even with a very short purging time, through effective evacuation during the ALD process.

Here, tetrakis (dimethylamino) titanium (TDMAT), trimethylaluminum (TMA), and diethylzinc (DEZ) were

employed as precursors for ALD TiO₂, Al₂O₃, and ZnO, respectively. For thermal and the plasma-enhanced ALD (T-ALD and PE-ALD, respectively), H₂O and O₂ plasma reactants were used as the oxidants. The TDMAT and the DEZ vapors contained in stainless-steel bubblers were delivered to the reaction chamber by using Ar carrier gas at 10 sccm; the flow rate was elaborately controlled by using a mass flow controller (MFC). The TDMAT-containing bubbler was heated to 50 °C to produce a high enough vapor pressure whereas the TMA-containing bubbler was maintained at room temperature (RT). However, the DEZ-containing bubbler was cooled to 0 °C to suppress the vapor pressure. The growth temperatures were changed within various ranges from 300 °C down to RT. For T-ALD, H₂O vapors in the water container were directly evaporated and delivered to the main chamber without any carrier gas. On the other hand, for PE-ALD, oxygen gas, controlled by a MFC, was flowed into the showerhead, where the plasma was turned on only during the O₂ exposure step with a constant plasma power of 300 W.

The film's thickness and the refractive index of the oxide thin films were measured by using spectroscopic ellipsometry. The film's morphology and conformality were observed by using field-emission scanning electron microscopy (FE-SEM). The microstructure of the films was analyzed by using X-ray diffraction (XRD). The chemical composition and the impurity level were analyzed by using X-ray photoelectron spectroscopy (XPS) with an Al $K\alpha$ monochromatic source of 1486.6 eV.

III. RESULTS AND DISCUSSION

As an initial study toward LT-ALD of TiO₂ and Al₂O₃, we used the commercial ALD system as described above. Figure 2 shows the growth rate per cycle as a function of the growth temperature for TiO₂ and Al₂O₃. For both cases, good saturation and linearity were observed at growth temperatures from 100 to 200 °C. The saturated growth rates of TiO₂ and Al₂O₃ grown by using T-ALD were 1.35 and 1.5 Å/cycle, respectively. However, with decreasing growth temperature to RT, the rate of TiO₂ grown by using T-ALD abruptly increased by over seven times under the saturation condition in Fig. 2(a). Similarly, the growth rates of Al₂O₃ grown by using T-ALD were greatly increased at low temperatures below 100 °C, being essentially identical to that of TiO₂ in Fig. 2(b). These results indicate that sufficient purging time was not ensured due to the residual H₂O vapors in the reaction chamber for both the T-ALD processes. Regarding this, Hausmann et al. reported that the H₂O vapor required a very long purge time at growth temperatures lower than 100 °C [15,16]. Hence, we increased the purging time to 300 s to completely eliminate the residual H₂O vapors. Nevertheless, remaining H₂O vapors resulted in slightly high growth rates due to a

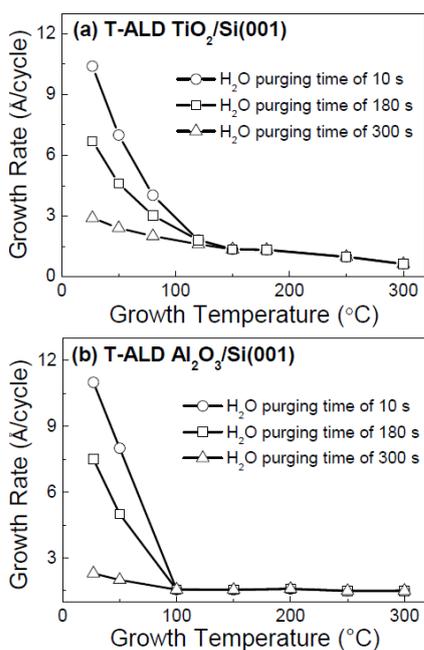


Fig. 2. Growth rate per cycle as a function of growth temperature for (a) TiO_2 and (b) Al_2O_3 grown by using T-ALD.

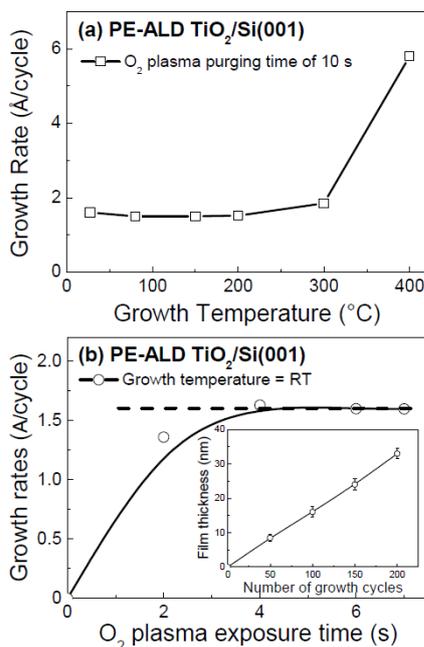


Fig. 3. Growth rate per cycle as a function of (a) growth temperature and (b) O_2 plasma exposure time [inset: dependence of TiO_2 film thickness on deposition cycles] for TiO_2 grown by using PE-ALD.

chemical vapor deposition (CVD)-like reaction. The requirement of very long purging time is believed to be due to the large volume and the complicated inner structure of the commercial ALD system.

This problem can be alleviated by using other reac-

ants instead of water. For instance, the use of an appropriate plasma reactant is one good solution. Therefore, we carried out a PE-ALD process using oxygen plasma with the same process equipment. Figure 3(a) shows the growth rate per cycle as a function of the growth temperature for TiO_2 by using PE-ALD with an O_2 plasma reactant purging time of 10 s. Nearly constant growth rates of 1.5 ~ 1.6 Å/cycle were observed within the temperature range from RT to 300 °C, which is similar to previous reports on TiO_2 grown by using PE-ALD [17]. In particular, it should be noted that compared to T-ALD in Fig. 2, no significant increase in growth rate is observed at low temperatures, even for very short purging time. Furthermore, in Fig. 3(b), a saturated growth rate of 1.6 Å/cycle and a linear growth feature according to the reaction cycle were still observed even at a low growth temperature of RT. Similar growth characteristics were also observed for Al_2O_3 grown by using PE-ALD (data not shown). This suggests that the current PE-ALD process has a very high efficiency of reactant purging, in contrast to T-ALD using water. However, the growth rate increases sharply at temperatures over 300 °C, which is attributed to the disturbance of self-limitation by thermal decomposition of the TDMAT precursor, leading to a partially CVD-like growth [1,18].

Meanwhile, we specifically developed our own homemade ALD system with small volume and simple inner structure as a promising solution enabling LT-ALD even with water. Figure 4 shows the growth rate per cycle of TiO_2 , Al_2O_3 , and ZnO grown by using T-ALD as a function of purging time at a low growth temperature of RT. While the growth rate of the ZnO was nearly constant over a purging time of 10 s, the purging time for TiO_2 and Al_2O_3 was good enough for the ALD growth mode over 6 s. This indicates that our mini-ALD chamber, as compared to the commercial chamber above effectively evacuated residual H_2O vapors even with a very short purging time. Under these conditions, saturated growth characteristics occurred for the three ALD processes. It is worthy to note that the chamber size and design are the critical factors for the realization of H_2O -based LT-ALD with a short process time.

Under the current ALD conditions, the growth rate per cycle was investigated at various growth temperatures from RT to 200 °C for the TiO_2 , Al_2O_3 , and ZnO grown by using T-ALD, as shown in Fig. 5. The growth rates of Al_2O_3 and ZnO grown by using T-ALD slightly decreased with decreasing growth temperature to RT. Actually, for most cases, the growth rate decreases with decreasing growth temperature to a low growth temperature. This is mainly because the precursor adsorption or reaction between the precursor and surface species is a thermally-activated process [1]. Previously, similar trends have been reported elsewhere [4,10]. On the other hand, the growth rate of TiO_2 grown by using T-ALD was slightly increased at low temperatures down to RT. This seems to be related to the concentration of surface OH groups. The surface OH groups become

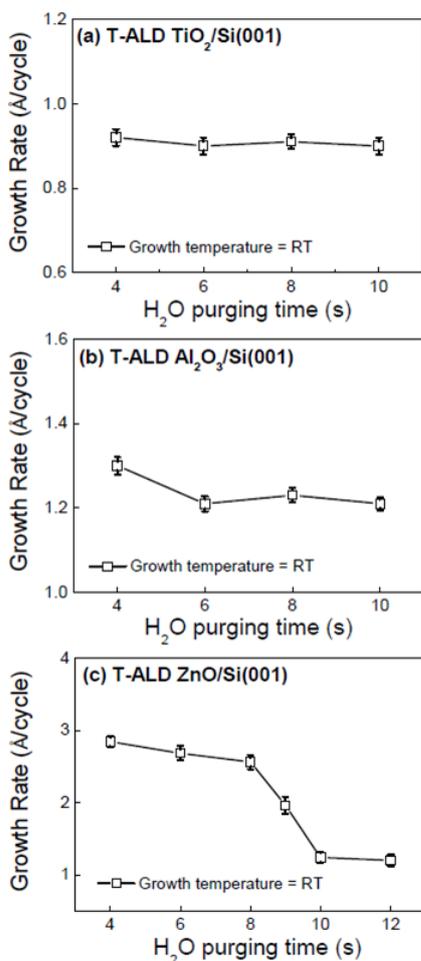


Fig. 4. Growth rate per cycle as a function of H₂O purging time for (a) TiO₂, (b) Al₂O₃, and (c) ZnO grown by using T-ALD.

higher with decreasing growth temperature, which leads to a large number of active sites, resulting in a slightly higher growth rate at low growth temperatures [19,20]. Moreover, Xie *et al.* reported similar results exhibiting high growth rates at low temperatures [12]. According to their energetic model based on a density functional theory calculation, the growth rate per cycle at low temperatures is determined by the reaction energy barrier. The initially adsorbed TDMAT precursors are prone to the high reaction with H₂O at RT, which means that the energy barrier is small enough to replace the ligands even at very low temperatures, thereby inducing high growth rates. Although the reactivity between the two increases with increasing growth temperature, in this case, the intermediate product desorption, as well as reduced surface OH groups, becomes more severe. Hence, a further increase in growth temperature results in a slightly decreased growth rate. Therefore, we revealed that there are the differences in deposition features depending on the precursor ligand, either alkylamide or alkyl group, at low growth temperatures.

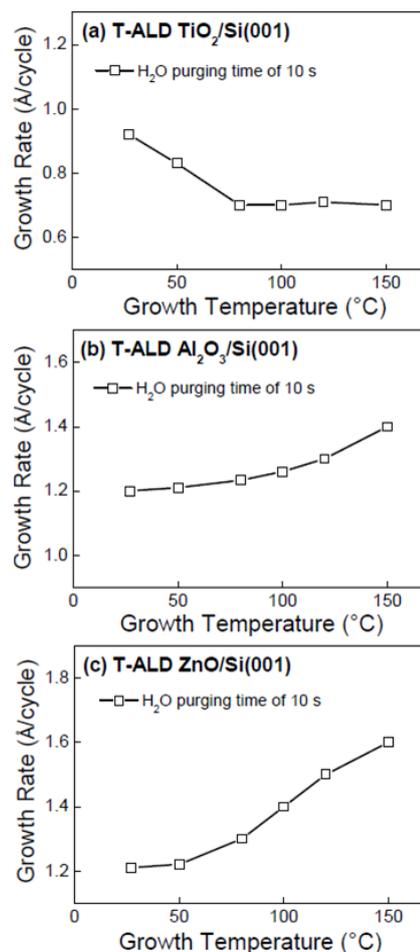


Fig. 5. Growth rate per cycle as a function of growth temperature for (a) TiO₂, (b) Al₂O₃, and (c) ZnO grown by using T-ALD.

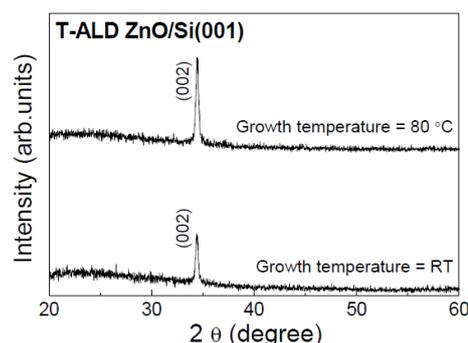


Fig. 6. XRD patterns of ZnO films grown at (a) 80 °C and (b) room temperature by using T-ALD.

The crystallinity of the TiO₂, Al₂O₃, and ZnO films grown at RT by using T-ALD were examined by using XRD. Here, the TiO₂ and Al₂O₃ films showed the absence of any significant diffraction features, indicating an amorphous-like structure (data not shown), which agrees well with previous reports [10,21]. In contrast to the two

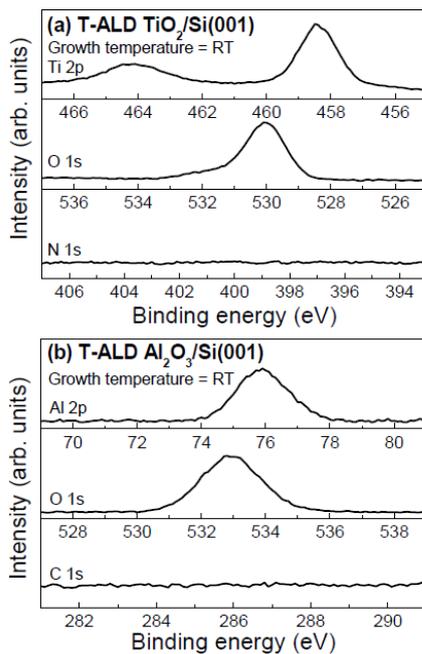


Fig. 7. XPS spectra of (a) TiO₂ (Ti 2p, O 1s, and N 1s) and (b) Al₂O₃ (Al 2p, O 1s, and C 1s) grown at room temperature by using T-ALD.

films, the ZnO film had a strong tendency to grow with a *c*-axis lattice orientation perpendicular to the Si(001) substrate even at very low temperatures down to RT as shown in Fig. 6. In other words, both the ZnO films grown at temperatures below 100 °C by using LT-ALD exhibited a single phase of the (002) plane, identifying the hexagonal wurtzite structure. Previously, ZnO grown by using LT-ALD at temperatures down to 100 °C exhibited crystalline diffraction patterns, depending on the deposition temperature and other process parameters such as the pulsing and the purging times [4]. By considering the full width at half maximum (FWHM) value, we calculated the average crystallite size (*D*) of both samples by using the Scherrer formula: $D = 0.9\lambda/\beta\cos\theta$, where λ is the X-ray wavelength (Cu K α = 1.54 Å), and β and θ are the FWHM and the diffraction angle of the (002) peak, respectively. The estimated average crystallite size along the *c* axis was about 27 nm, which is not significantly changed, at least, in the temperature region below 100 °C.

In order to examine the chemical composition and the impurity level, we used XPS to analyze the 30-nm-thick TiO₂ and Al₂O₃ films grown at RT, as shown in Fig. 7. The peak locations of Ti 2p_{3/2} (458.5 eV, spin orbit splitting between the two peaks: 5.7 eV) and O 1s (532.7 eV) in Fig. 7(a) are consistent with those in the XPS handbook and previous publications [22,23]. No N signal is observed in the TiO₂ film, indicating that the Ti-N bonding in the TDMAT precursor is fully broken. Besides, the binding energies of the Al 2p (75.8 eV) and O 1s (532.7 eV) in Fig. 7(b) are well matched with previously re-

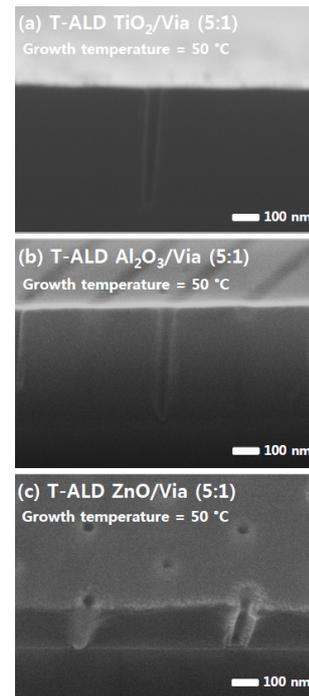


Fig. 8. Cross-sectional FE-SEM images of (a) TiO₂, (b) Al₂O₃, and (c) ZnO grown at 50 °C in nanoscale contact hole vias with an aspect ratio of 5:1 (depth of 450 nm and diameter of 90 nm) by using T-ALD.

ported values [24]. After surface cleaning by sputtering, no C signal was detected in the Al₂O₃ film, which indicates that the carbon concentration is at least below the detection limit of XPS. Therefore, the current LT-ALD processes produce very high purity films without any impurity contamination.

Figure 8 shows cross-sectional FE-SEM images of TiO₂, Al₂O₃ and ZnO films grown at 50 °C in nanoscale contact hole vias with an aspect ratio of 5:1 (depth of 450 nm and diameter of 90 nm) by using T-ALD. Excellent conformality over 90% was achieved for all three oxide films. Therefore, the current LT-ALD is envisaged to be applicable for functional coatings, as well as future electronic devices with three-dimensional complex structures.

IV. CONCLUSION

In this study, we systematically investigated the growth characteristics and film properties of TiO₂, Al₂O₃, and ZnO grown by LT-ALD with two kinds of ALD systems and deposition methods. T-ALD processes for the growth TiO₂ and Al₂O₃ by using a commercial ALD chamber required a very long H₂O purging time up to 300 s to avoid a CVD-like reaction at growth temperatures below 100 °C, which is attributed to the large volume and the complicated inner structure of the ALD

system. To overcome this problem, we employed a PE-ALD process using an O₂ plasma. For TiO₂ grown by using PE-ALD, a saturated growth rate and a linear growth feature were achieved even at a low growth temperature of RT. As another solution, a homemade ALD system with a small volume and simple inner structure was specifically developed. The ALD growth characteristics for TiO₂, Al₂O₃, and ZnO grown by using T-ALD with H₂O at temperatures down to RT were successfully attained with a very short purging time within 10 s, indicating effective evacuation of the residual H₂O vapors. However, the growth rates per cycle of TiO₂, Al₂O₃, and ZnO grown at low temperatures below 150 °C by using T-ALD exhibited differences that mainly depended on the ligand groups, either alkylamide or alkyl. In any case the LT-ALD processes produced highly pure N- and C-free TiO₂ and Al₂O₃ films by complete elimination of ligands, and excellent conformality was observed in 3-dimensional nanoscale via holes for all the films. Therefore, the current LT-ALD is envisaged to be a viable option with eco-environmental and biological applications in micro- and macroelectronics in the near future.

ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0024066) and by the Future-based Technology Development Program (Nano Fields) through the NRF funded by the Ministry of Education, Science and Technology (2010-0020230).

REFERENCES

- [1] H. Kim, *J. Vac. Sci. Technol.*, B **21**, 2231 (2003).
- [2] H. Kim, H. B. R. Lee and W. J. Maeng, *Thin Solid Films* **517**, 2563 (2009).
- [3] J-M. Kim, T. W. Nam, S. J. Lim, Y. G. Seol, N. E. Lee, D. Y. Kim and H. Kim, *Appl. Phys. Lett.* **98**, 142113 (2011).
- [4] E. Guziewicz, I. A. Kowalik, M. Godlewski, K. Kopalko, V. Osinniy, A. Wojcik, S. Yatsunenko, E. Usakowska, W. Paszkowicz and M. Guziewicz, *J. Appl. Phys.* **103**, 033515 (2008).
- [5] J-M. Kim, S. J. Lim, T. W. Nam, D. Y. Kim and H. Kim, *J. Electrochem. Soc.* **158**, J150 (2011).
- [6] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano and H. Hosono, *Nature* **432**, 488 (2004).
- [7] J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M. Sanden and W. Kessels, *Prog. Photovoltaics Res. Appl.* **16**, 461 (2008).
- [8] T. W. Hamann, O. K. Farha and J. T. Hupp, *J. Phys. Chem. B.* **112**, 19756 (2008).
- [9] C-S. Lee, J. Kim, J. Y. Son, W. Choi and H. Kim, *Appl. Catal., B* **91**, 628 (2009).
- [10] M. Groner, F. Fabreguette, J. Elam and S. George, *Chem. Mater.* **16**, 639 (2004).
- [11] S.-M. Lee, G. Grass, G.-M. Kim, C. Dresbach, L. Zhang, U. Gosele and M. Knez, *Phys. Chem. Chem. Phys.* **11**, 3608 (2009).
- [12] Q. Xie, Y.-L. Jiang, C. Detavernier, D. Deduytsche, R. L. Van Meirhaeghe, G.-P. Ru, B.-Z. Li and X.-P. Qu, *J. Appl. Phys.* **102**, 083521 (2007).
- [13] W-H. Kim, S. J. Park, J. Y. Son and H. Kim, *Nanotechnology* **19**, 045302 (2008).
- [14] H. B. R. Lee, G. H. Gu, J. Y. Son, C. G. Park and H. Kim, *Small* **4**, 2247 (2008).
- [15] D. M. Hausmann, E. Kim, J. Becker and R. G. Gordon, *Chem. Mater.* **14**, 4350 (2002).
- [16] G. T. Lim and D. H. Kim, *Thin Solid Films* **498**, 254 (2006).
- [17] Q. Xie, J. Musschoot, D. Deduytsche, R. L. Van Meirhaeghe, C. Detavernier, S. Berghe, Y. L. Jiang, G. P. Ru, B. Z. Li and X. P. Qu, *J. Electrochem. Soc.* **155**, H688 (2008).
- [18] W. J. Maeng and H. Kim, *Electrochem. Solid-state Lett.* **9**, G191 (2006).
- [19] J. Aarik, A. Aidla, V. Sammelselg, H. Siimon and T. Uustare, *J. Cryst. Growth* **169**, 496 (1996).
- [20] R. L. Puurunen, *Chem. Vap. Deposition* **9**, 327 (2003).
- [21] J. Aarik, A. Aidla, T. Uustare and V. Sammelselg, *J. Cryst. Growth* **148**, 268 (1995).
- [22] J. Moulder and J. Chastain, *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer, Physical Electronics Division, Eden Prairie, MN, 1992).
- [23] G. Hopfengärtner, D. Borgmann, I. Rademacher, G. Wedler, E. Hums and G. W. Spitznagel, *J. Electron Spectrosc. Relat. Phenom.* **63**, 91 (1993).
- [24] A. Nylund and I. Olefjord, *Surf. Interface Anal.* **21**, 283 (1994).