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Atomic layer etching of ultra-thin HfO_2 film for gate oxide in MOSFET devices

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Abstract
Precise etch depth control of ultra-thin HfO_2 (3.5 nm) films applied as a gate oxide material was investigated by using atomic layer etching (ALET) with an energetic Ar beam and BCl_3 gas. A monolayer etching condition of 1.2 Å/cycle with a low surface roughness and an unchanged surface composition was observed for ultra-thin, ALET-etched HfO_2 by supplying BCl_3 gas and an Ar beam at higher levels than the critical pressure and dose, respectively. When HfO_2-nMOSFET devices were fabricated by ALET, a 70% increase in the drain current and a lower leakage current were observed compared with the device fabricated by conventional reactive ion etching, which was attributed to the decreased structural and electrical damage.

1. Introduction

As the critical dimensions of the metal-oxide-semiconductor field effect transistor (MOSFET) undergo further miniaturization to nanoscale, the thickness of the gate oxide also needs to be reduced [1]. Currently, with the use of SiO_2 as the gate oxide having reached its physical and electrical limits, various efforts have been made to replace SiO_2 with high-k oxides such as Al_2O_3, HfO_2, ZrO_2 and TiO_2 [2–4]. Among these oxides, considerable research attention has focused on the potential of HfO_2 as a next-generation gate dielectric material due to many advantages in comparison with SiO_2, such as a high dielectric constant (15–25), good thermal stability, wide band gap (5.6 eV) and large band offsets (1.5 eV) [5, 6].

In micro-sized integrated devices, reactive ion etching (RIE) has been successfully applied to transfer the mask pattern to the substrate. However, with the continuing miniaturization of the integrated semiconductor devices, novel etching processes capable of satisfying the new requirements resulting from the nanoscale components need to be developed due to the thin thickness and the high surface-to-volume ratio of the materials to be etched. Therefore, in the gate dielectric etch processing of nanoscale MOSFET devices, precise control of the etch rate (depth) has become a greater prerequisite than achieving a high etch rate due to the extreme thinness of the gate dielectric material. In addition, the etched surface and the gate dielectric material must remain undamaged for the gate dielectric processing of nanoscale devices [7, 8]. However, conventional RIE tends to cause electrical and physical damage to the surface of the devices due to use of energetic reactive ions and the difficulty in the precise etch rate (depth) control at an atomic scale. For the etching of ultra-thin HfO_2 gate dielectrics in nanoscale MOSFET devices, atomic layer etching (ALET) may be the most suitable method because it is capable of etching materials with atomic-scale etch controllability while avoiding etch damage [7, 9]. In this study, HfO_2 (3.5 nm) was etched on the SiO_2/Si (p-type substrate) by ALET using an Ar neutral beam and BCl_3 gas and the resulting etch characteristics and the electrical properties of the devices formed were investigated.

2. Experimental details

One cycle of HfO_2 ALET was composed of four steps, as shown in figure 1. The first step was the adsorption step where BCl_3 gas was chemically adsorbed on the HfO_2 surface by 20 s exposure. The third step was the desorption step where the chemisorbed chlorine compound was removed by the irradiation of an energetic Ar beam. The second and fourth steps were the purging steps, where the remaining BCl_3 gas, which had not been adsorbed on the substrate surface, and the chlorine compounds desorbed by the energetic Ar beam were removed by pumping for 20 s, respectively. During the desorption step, an Ar neutral beam, instead of an Ar ion beam, was used to eliminate possible charge-related damage to the substrate. The details of the neutral beam used in this experiment are described elsewhere [10–13]. The energy and the flux of the Ar neutral beam were about 73 eV and 1.51×10^{15} atoms s^{-1} cm^{-2}, respectively. HfO_2 (3.5 nm) was deposited on the SiO_2/Si (p-type substrate) by atomic layer deposition (ALD). X-ray photoelectron spectroscopy (XPS; Thermo VG, MultiLab 2000, Mg K source) was used to observe the change in the surface composition during the etching. Transmission electron microscopy (TEM; Tecnai F20) was used to observe the etch depth of HfO_2. The electrical properties of the HfO_2-MOSFET devices fabricated after the etching of HfO_2 by ALET and a conventional inductively coupled plasma (ICP) were measured using a semiconductor parameter analyzer (HP, 4155B).

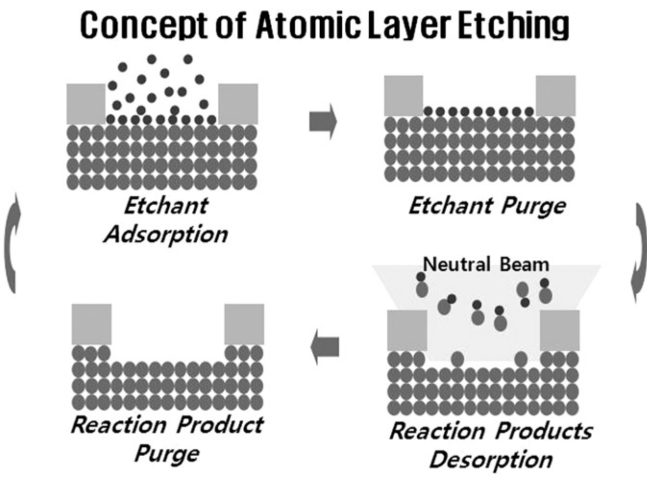


Figure 1. Concept of the four-step ALET process.

3. Results and discussion

A previous study on the etching of HfO_2 by ALET using BCl_3 gas and an Ar beam has shown that a saturated HfO_2 monolayer etching of 1.2 Å/cycle is obtained by supplying BCl_3 gas at a pressure higher than 0.22 mTorr and Ar neutral beam (73 eV) irradiation at a dose higher than 1.48×10^{17} atoms cm^{-2} [9]. In this study, 3.5 nm thick HfO_2 was etched on SiO_2 (1.7 nm)/Si by ALET and the etch characteristics of HfO_2 were observed. The results shown in figure 2 indicate the percentages of SiO_2, Si and HfO_2, as estimated by XPS, on the etched HfO_2 (3.5 nm)/SiO_2 (1.7 nm)/Si (p-type substrate), measured as a function of (a) an Ar neutral beam irradiation dose (atoms cm^{-2}) at a BCl_3 gas pressure of 0.33 mTorr and (b) BCl_3 gas pressure at an Ar beam irradiation dose of 2.11×10^{17} atoms cm^{-2} (140 s). Thirty etch cycles were used for the etch cycling because 3.5 nm thick HfO_2 can be etched in full when the monolayer etching condition of 1.2 Å/cycle is obtained. The percentages of SiO_2, Si and HfO_2 were estimated by measuring the bonding peak intensities of Si_{2p} relative to Si–O at 103.3 eV, of Si_{2p} relative to Si–Si at 99.3 eV and of $Hf_{4f7/2}$ relative to Hf–O at 14.3 eV, respectively. As shown in figure 2(*a*), when the Ar beam irradiation dose was increased from 3.02×10^{16} atoms cm^{-2} (20 s) to 1.51×10^{17} atoms cm^{-2} (100 s), the percentage of HfO_2 on the etched substrate measured by XPS was decreased from 43.9% to 0.0%, that of Si was increased from 28.6% to 80% and that of SiO_2 was not changed significantly. The increase in the Ar beam irradiation dose from 1.51×10^{17} atoms cm^{-2} (100 s) to

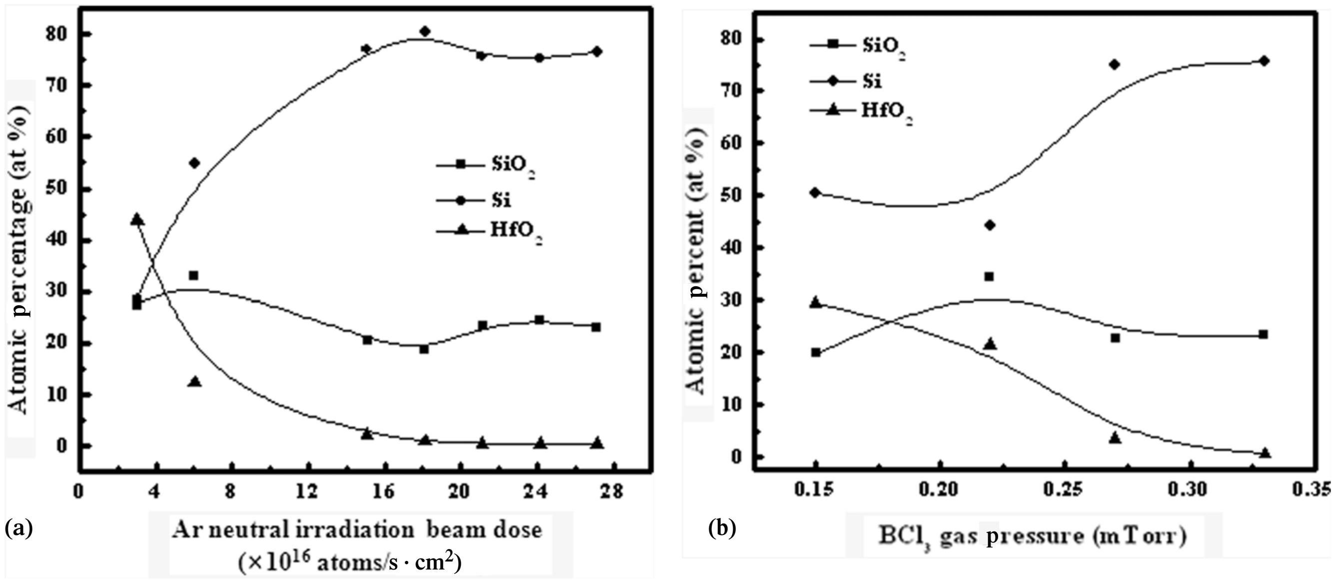
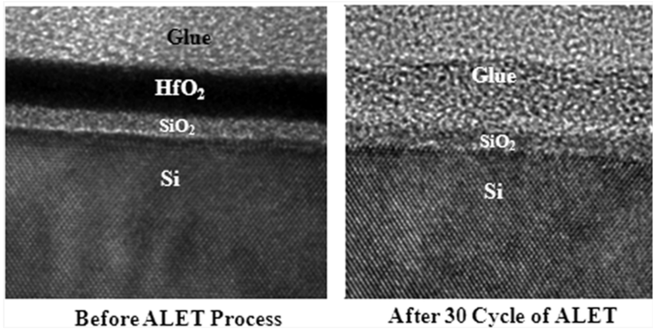


Figure 2. HfO_2, SiO_2 and Si percentages (%) by ALET etching as a function of (*a*) the Ar neutral beam irradiation dose and (*b*) the BCl_3 gas pressure. Process conditions: (*a*) BCl_3 pressure: 0.33 mTorr and (*b*) Ar beam irradiation dose: 2.11×10^{17} atoms cm^{-2} (140 s). For (*a*) and (*b*), the Ar beam energy was 73 eV with 30 cycles.

2.72×10^{17} atoms cm^{-2} (180 s) did not change the percentages of HfO_2, Si and SiO_2. XPS detects the components at a depth of about 10 nm when an escape angle of 0° was used. When the 3.5 nm thick HfO_2 layer on the SiO_2 (1.7 nm)/Si (p-type substrate) was removed, the percentages of HfO_2 and Si measured by XPS were decreased and increased, respectively, but if the SiO_2 layer on Si was not etched, the percentage of SiO_2 remained the same because the SiO_2 layer was within the XPS detection thickness during the etching. Therefore, the decrease in HfO_2 from 43.9% to 0.0% and the lack of any significant change in SiO_2 at an Ar beam irradiation dose higher than 1.51×10^{17} atoms cm^{-2} (100 s) indicated that the HfO_2 layers were precisely removed without etching of the SiO_2 layer at 30 cycles by using the monolayer etching condition of 1.2 Å/cycle. The variation in the percentages of HfO_2, Si and SiO_2, measured as a function of the BCl_3 gas pressure at an Ar beam irradiation dose of 2.11×10^{17} atoms cm^{-2} (140 s), also indicated the decrease in the HfO_2 percentage from 30.0% to 0.0% and the increase in the Si percentage from 50% to 80% as the BCl_3 gas pressure was increased from 0.15 to 0.27 mTorr. However, the further increase in the BCl_3 gas pressure to 0.33 mTorr did not change the percentages significantly. The SiO_2 percentage was not significantly affected by the change in the BCl_3 gas pressure. Therefore, at BCl_3 pressures higher than 0.27 mTorr, complete removal of the HfO_2 layer and the monolayer etching condition of 1.2 Å/cycle was observed.

The monolayer etching condition of 1.2 Å/cycle obtained in our experiment for HfO_2 etching was attributed to the monolayer adsorption of the BCl_3 gas at a pressure higher than the critical pressure during the adsorption stage and to the desorption of all the compounds formed on the substrate surface without sputtering of the substrate material during the desorption stage [9, 14]. When the operating pressure was lower than the critical pressure of 0.27 mTorr, one monolayer of volatile chlorine compound was not formed on the surface due to insufficient surface coverage ($\theta_{HfO_2\text{–boron oxychloride}}$) of the BCl_3 gas on the substrate surface. Furthermore, when the Ar beam flux was lower than the critical dose of 1.51×10^{17} atoms cm^{-2} (100 s), the monolayer compound formed on the substrate surface could not be etched, due to insufficient removal of the volatile compounds formed on the substrate surface, even though a monolayer chorine compound was formed because the BCl_3 gas pressure was higher than the critical pressure during the adsorption step. Therefore, when the BCl_3 gas pressure during the adsorption step was lower than the critical pressure or/and when the Ar beam dose during the desorption step was lower than the critical dose, an etch rate lower than one monolayer per cycle (<1.2 Å/cycle) was obtained.

Thirty etch cycles were required to remove the 3.5 nm thick HfO_2 layer on the SiO_2 (1.7 nm)/Si substrate if the monolayer etching condition of 1.2 Å/cycle was obtained for HfO_2 etching. Using HRTEM, the etch amount of HfO_2 in the HfO_2 (3.5 nm)/SiO_2 (1.7 nm)/Si substrate was investigated and the results are shown in figure 3. Figure 3(*a*) shows the as-received sample having the structure of an HfO_2 (3.5 nm)/SiO_2 (1.7 nm)/Si (p-type substrate) and figure 3(*b*) shows the sample after the 30-cycle etching with one of the monolayer etching conditions (Ar neutral beam irradiation dose: 2.11×10^{17} atoms cm^{-2} (140 s), BCl_3 gas pressure: 0.33 mTorr). As shown in the figures, after the 30-cycle etching, all of the HfO_2 was etched away and a 1.6 nm thick SiO_2 layer was left on the silicon substrate. The root mean square (RMS) surface roughness of the sample after the 30-cycle etching, as measured by atomic force microscopy (AFM), was in the range 0.12–0.26 nm, which was close to the surface roughness of the as-received sample (0.17 nm).



(a) (b)

Figure 3. TEM image of (*a*) as-received: HfO_2 (3.5 nm)/ SiO_2 (1.7 nm)/Si and (*b*) ALET processed device. (Process conditions: ALET—Ar beam energy: 60 V, Ar neutral beam irradiation dose: 2.11×10^{17} atoms cm^{-2} (140 s), BCl_3 pressure: 0.33 mTorr and number of etch cycles: 30.)

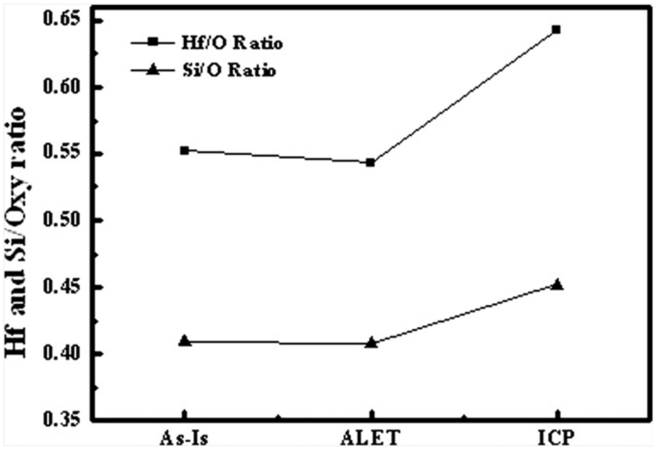


Figure 4. Composition ratios of Hf/O and Si/O measured by XPS for HfO_2 and SiO_2 samples etched by ALET and ICP. (Process conditions: ALET—1st grid voltage: 60 V, Ar neutral beam irradiation dose: 2.11×10^{17} atoms cm^{-2} (140 s), BCl_3 pressure: 0.33 mTorr, number of cycles: 30, ICP etching-inductive power: 300 W, dc bias voltage: −60 V, BCl_3 (50 sccm)/Ar (50 sccm) and working pressure (12 mTorr), process time: 20 s.)

During ALET of HfO_2, the surface composition was maintained by removing one surface layer of the sample per etch cycle, whereas conventional ICP changes the surface composition by the preferential etching of more volatile compounds during the etching. Figure 4 shows the Hf/O and Si/O ratios during ALET etching and during the conventional ICP condition of HfO_2. For the former, the condition in figure 3 was used while the experimental conditions for the latter were 300 W of 13.56 MHz RF power to the ICP source, −60 V of substrate biasing and 12 mTorr of the BCl_3(50 sccm)/Ar(50 sccm) gas mixture. As shown in the

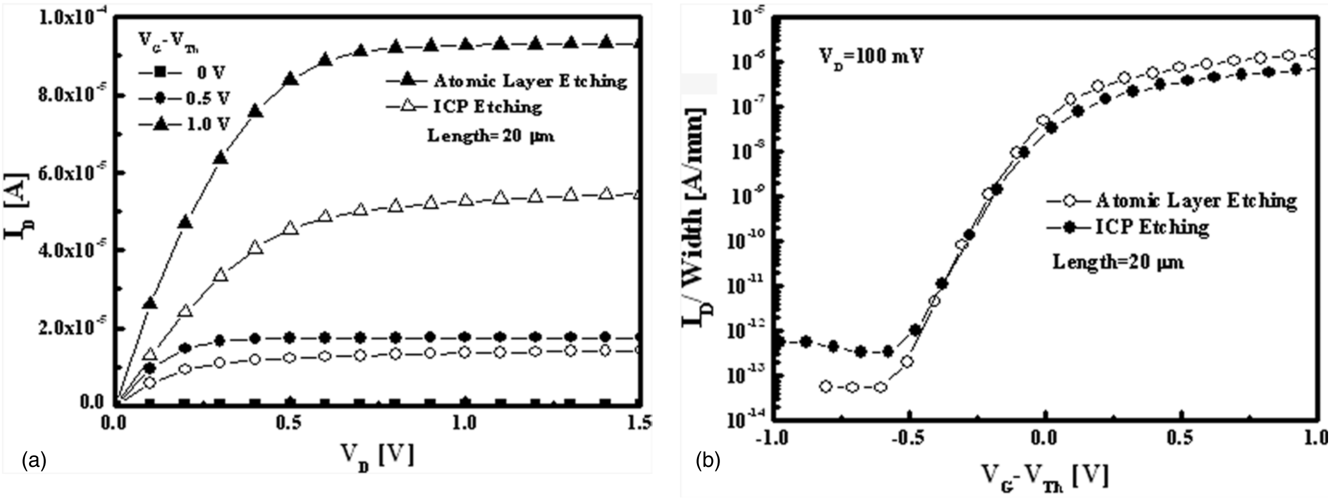


Figure 5. (*a*) I_D–V_D curves and (*b*) threshold voltage characteristic of HfO_2-nMOSFET devices fabricated by ALET etching and ICP etching of gate dielectric material composed of HfO_2 (3.5 nm)/SiO_2 (0.8 nm). (Process conditions are the same as those in figure 4.)

figure, the ICP-etched HfO_2 and SiO_2 showed a change in the surface composition ratio due to the preferential removal of one component of oxides from the surface layers during etching due to the higher or lower vapour pressure of Hf (or Si) chlorides compared with BCl_xO_y [15] formed on the surface. However, the surface compositions of the ALET-etched HfO_2 and SiO_2 were similar to those of the as-received samples, as shown by the peeling of the exact amount of the surface layer per etch cycle. In fact, during SiO_2 etching using the ALET condition of HfO_2, about 1.2 Å/cycle, which is higher than one monolayer etching per cycle for SiO_2 etching (3.67 Å/cycle), was obtained. It is considered that, with the ALET condition of HfO_2 used in this experiment, more than atomic layer is etched during each cycle for SiO_2 etching possibly due to the sputtering of surface atoms during the desorption step (that is, for the ALET of SiO_2, a lower Ar irradiation beam energy appears to be required). However, possibly due to the removal of every cycle of certain surface layers, the surface composition of SiO_2 etched by the ALET condition of HfO_2 was similar to that of the as-received SiO_2.

Through the fabrication of HfO_2-nMOSFETs with a TaN metal gate by using ALET and the ICP etching shown in figure 4, the device characteristics were compared and the results for the characteristics of V_D–I_D and V_G–I_D are shown in figures 5(*a*) and (*b*), respectively. A bilayer gate dielectric composed of HfO_2 (3.5 nm)/SiO_2 (0.8 nm) grown by ALD was used and these gate dielectric materials were etched by the ALET condition for 35 cycles and by the ICP etching condition for 20 s, as shown in figure 4. After the etching of the gate dielectric materials, source/drain metallization was conducted by depositing Ti (30 nm)/Al (200 nm) by sputtering, followed by conventional forming gas annealing at 400 °C for 30 min. As shown in figure 5(*a*), the device etched using ALET exhibited an improvement in the drain current of about 70% at $V_D = 1$ V compared with that etched by ICP. In addition, as shown in figure 5(*b*), the I_{off} leakage current for the device etched using ALET was lower than that etched by using ICP. The higher drain current and the lower leakage current obtained by ALET were attributed to the decreased structural and electrical damage to the gate dielectric material and the substrate material during Ar beam ALET etching. Moreover, ALET facilitates exact etch depth control by determining the exact etch depth per etch cycle, which minimizes the overetching of the shallow doped source/drain silicon area.

4. Conclusion

In this study, 3.5 nm thick HfO_2 was etched by ALET using an Ar neutral beam and BCl_3 gas and the effects of the ALET conditions on the etch characteristics and the electrical properties of the nMOSFET devices were investigated. For the ultra-thin HfO_2 (3.5 nm) deposited on the SiO_2 (1.7 nm)/Si substrate, the monolayer etching condition of 1.2 Å/cycle for HfO_2 was observed by supplying BCl_3 gas at a pressure higher than the critical pressure of 0.27 mTorr during the adsorption step and by supplying an Ar beam at a dose higher than the critical dose of 1.51×10^{17} atoms cm^{-2} (100 s). No significant increase in the surface roughness and no change in the surface composition of HfO_2 and SiO_2 were observed during ALET etching. When HfO_2-nMOSFET devices were fabricated by ALET, the drain and leakage currents of the devices were significantly improved by the etching of the gate dielectric materials composed of HfO_2 (3.5 nm)/SiO_2(0.8 nm), compared with those attained by conventional ICP etching, due to the decreased structural and electrical damage induced by the ALET etching using the Ar neutral beam.

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References

[1] Wu E Y, Nowak E J, Vayshenker A, Lai W L and Harmon D L 2002 *IBM J. Res. Dev*. **46** 287
[2] Lin Y S, Puthenkoviloakam R and Chang J P 2002 *Appl. Phys. Lett.* **81** 2041
[3] Chang J P, Lin Y S, Berger S, Kepten A, Bloom R and Levy S 2001 *J. Vac. Sci. Technol.* B **19** 2137
[4] Copel M, Gribelyuk M and Gusev E 2000 *Appl. Phys. Lett.* **76** 436
[5] Wu W C, Lai C S, Wang Z M, Wang J C, Hsu C W, Ma M W and Chao T S 2008 *Electrochem. Solid-State Lett.* **11** H15
[6] Wu W C, Lai C S, Wang J C, Chen J H, Ma M W and Chao T S 2007 *J. Electrochem. Soc.* **154** 561
[7] Zhang Y 2007 *Dry Process Int. Symp. (Tokyo)* vol 1-01, p 1
[8] Hussain M M, Song S C, Barnett J, Kang C Y, Gebara G, Barry Sassman and Moumen N 2006 *IEEE Electron Device Lett.* **27** 972
[9] Park S D, Lim W S, Park B J, Lee H C, Bae J W and Yeom G Y 2008 *Electrochem. Solid-State Lett.* **11** H71
[10] Lee D H, Chung M J, Hwang H K and Yeom G Y 2003 *Mater. Sci. Eng.* C **23** 221
[11] Park B J, Min K S, Park S D, Bae J W, Vozniy O and Yeom G Y 2007 *Solid State Phenom.* **124** 275
[12] Park B J *et al* 2008 *J. Phys. D: Appl. Phys.* **41** 024005
[13] Lee D H, Bae J W, Park S D and Yeom G Y 2001 *Thin Solid Films* **398** 647
[14] Čermáková J Ř, Marković A, Uchytil P and Seidel-Morgenstern A 2008 *Chem. Eng. Sci.* **63** 1586
[15] Park S D, Lim J H, Oh C K, Lee H C and Yeom G Y 2006 *Appl. Phys. Lett.* **88** 094107