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Hf-Aluminate Films With and Without an Interfacial Layer during Growth and Postannealing

Structural and Electrical Characteristics

K. B. Chung,[a,b] H. S. Chang,[b] S. H. Lee,[b] C. N. Whang,[a] D.-H. Ko,[c] H. Kim,[d] D. W. Moon,[b] and M.-H. Cho[b,z]

[a]*Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea*
[b]*Nano Surface Group, Korea Research Institute of Standards and Science, Daejeon 305-600, Korea*
[c]*Department of Ceramics Engineering, Yonsei University, Seoul 120-749, Korea*
[d]*Department of Ceramic Engineering, Sungkyunkwan University, Suwon 440-746, Korea*

The structural and electrical characteristics resulting from an interfacial layer of Hf-aluminate films grown by atomic layer deposition were investigated using medium energy ion scattering spectroscopy and electrical measurements. The Hf-aluminate films with an interfacial layer of SiO_2 grew with higher Hf contents and lower interdiffusion of Si than the film without an interfacial SiO_2 layer. In Hf-aluminate films with an interfacial layer of SiO_2, the thickness of HfO_2 decreased slightly after postannealing as a result of crystallization. In films without an interfacial layer of SiO_2, the structural rearrangement was observed due to the interdiffusion of Si with no change in thickness. The structural changes affected electrical properties such as the oxide trap charge and the interfacial trap charge. Moreover, reoxidation of the Hf-aluminate films without an interfacial layer of SiO_2 caused a dramatic increase in the thickness of the interfacial region. This resulted in a positive shift of flatband voltage.
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As the sizes of silicon-based devices have decreased and higher switching speeds have been required, the conventional SiO_2 gate dielectric thickness has been pushed below 15 Å for submicrometer complementary metal-oxide-semiconductor (CMOS) transistors.[1,2] However, as the gate dielectric thickness decreases, the leakage current through direct tunneling across the gate dielectric increases.[3] As a result, research has focused recently on investigating high-k gate dielectrics, which potentially may replace SiO_2 in advanced CMOS technologies.[4] Conventional high-k candidates, such as Al_2O_3, ZrO_2, HfO_2, and silicates of either Hf or Zr, have been considered as alternative gate dielectric materials.[5,6] Such materials should have high dielectric properties and satisfy thermal stability requirements, for example, by not undergoing interfacial reactions and structural changes after postannealing treatment under the integration process. Unfortunately, the high dielectric oxide films do not have sufficient thermal stability because they can easily change from an amorphous structure to a polycrystalline structure and can react with the Si substrate. To overcome these problems, researchers have attempted to create nanolaminates and their oxide alloys.[7,8] Some authors have reported that nanolamnates and alloys composed of HfO_2 and Al_2O_3 have enhanced thermal stability and therefore could sustain a high dielectricity.[8] Previous studies have focused on the change in chemical state and the interfacial reaction between the HfO_2–Al_2O_3 laminate and the Hf–Al–O alloy during post-treatment.[9-11] Many reports show that high-k oxides have a high interfacial trap charge density (D_{it}) during film growth and postannealing, which may affect their reliability.[8,12] Generally, an interfacial layer of SiO_2 is used to increase the interfacial stability and reduce the interface trap charge density.[10,11] Therefore, it is important to understand the properties of Hf-aluminate films depending on the presence of an interfacial layer of SiO_2.

In this study, we investigated the structural and electrical characteristics of Hf-aluminate films with and without an interfacial layer of SiO_2 during growth and postannealing. In addition, the reoxidation of Hf-aluminate films was examined to gain better understanding of changes in the interface region according to the presence of an interfacial layer.

Experimental

Samples were prepared on (100)-orientated p-type Si wafers with two different surface conditions: surfaces with and without an interfacial layer of SiO_2. Si surfaces were cleaned chemically by the standard Radio Corporation of America (RCA) method to remove organic and metallic residues.[13,14] Immediately after RCA cleaning, the Si wafers were dipped in a dilute solution of HF to remove the chemical oxide formed by the cleaning. Finally, the wafers were divided into two groups. One group was introduced into the deposition chamber without additional surface treatment and terminated with hydrogen bonds. The other group was preprocessed to grow an interfacial layer of SiO_2 with a thickness of approximately 1 nm by rapid thermal oxidation (RTO). The metal oxides were grown by an atomic layer deposition (ALD) system, which has a vertical warm-wall reactor with a showerhead and a heated susceptor. The Hf-aluminate films composed of HfO_2 and Al_2O_3 with 3-nm thickness, were grown at 300°C using $HfCl_4$ and $Al(CH_3)_3$, respectively, as precursors. Water vapor served as the oxygen source, and nitrogen was supplied as the purge and carrier gas. To investigate interfacial reactions and structural changes resulting from the presence of an interfacial layer, postdeposition annealing of the samples was performed by a rapid thermal process in an atmosphere of nitrogen and oxygen at 950 and 800°C, respectively, for 2 min.

Interfacial and structural characteristics were investigated using medium-energy ion scattering (MEIS). The kinematic scattering energy analysis gives the elemental and quantified information in the depth direction. The MEIS analysis was accomplished with a 100 keV proton beam in double alignment, which reduced contributions from the crystalline Si substrates and allowed the spectra to be deconvoluted into the Al_2O_3 and interfacial Si contributions.[15] The electronic energy loss of 100 keV protons was measured precisely with an electrostatic energy analyzer. The incident ions were along [111], and the scattered ions were along [001], giving a scattering angle of 125°. Quantitative analysis of the different species was carried out with a depth resolution of 3–5 Å in the near surface. During the MEIS experiments, the sample was exposed to a minimum H^+ beam dose to avoid beam damage. To investigate the dielectric characteristics related to the structural changes, MOS capacitors with Pt electrodes of $9 \times 10^{-6}\ cm^2$ were produced by photolithography and etching for electrical measurements. Capacitance–voltage (C–V) measurements were performed using the HP4284A instrument as a probe station.

Results and Discussion

Figure 1a shows the backscattering energy spectrum for Hf measured by MEIS for the as-deposited and annealed Hf-aluminate films in an atmosphere of nitrogen at 950°C for 2 min. For the Hf-

[z] E-mail: mhcho@kriss.re.kr

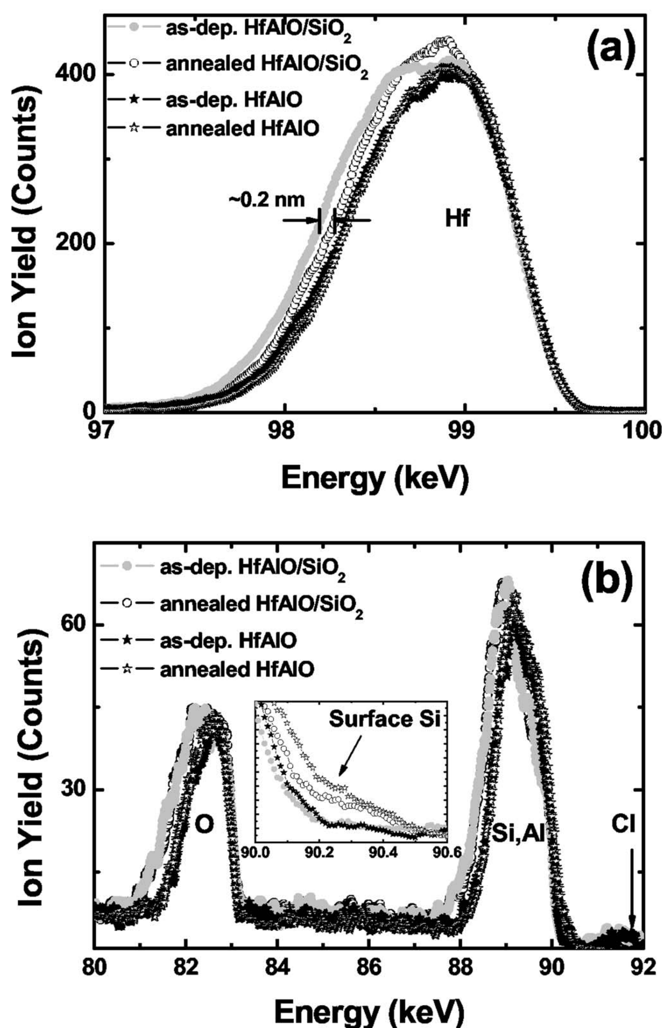

Figure 1. (a) MEIS energy spectra of Hf for the as-deposited and postannealed Hf-aluminate films with and without an interfacial layer of SiO_2 in a nitrogen atmosphere at 950 °C for 2 min. The width of the Hf peak decreases after postannealing in the Hf-aluminate films with an interfacial SiO_2 layer; this is estimated to represent a decrease in HfO_2 thickness at the interface of approximately 0.2 nm. (b) MEIS energy spectra of Si, Al, and O for the as-deposited and postannealed Hf-aluminate films with and without an interfacial layer of SiO_2 in a nitrogen atmosphere at 950 °C for 2 min. The inset shows the enlargement of the Si surface region.

aluminate films with an interfacial layer of SiO_2, a decrease in film thickness is clearly observed after postannealing. The shape and width of the Hf peak indicate that the thickness of about 2 Å, which was calculated from energy deviation of Hf peak, was approximately reduced as a result of postannealing. Moreover, an interesting finding is that the area of Hf peak was not changed, while the width was slightly decreased. Generally, the density for crystalline films is higher than that for amorphous films.[16] Thus, the decrease in film thickness may be attributed to the crystallization of Hf-aluminate films resulting from annealing at a temperature above the decomposition temperature of interfacial SiO_2 as shown in a previous study.[17-19] Although crystallization of the Hf-aluminate films was suppressed by incorporating Al_2O_3 into the pure HfO_2, changes in structure depending on the stack structure of Al_2O_3 and HfO_2 are inevitable at temperatures above 900°C.[8,10,11] Another interesting finding is that Hf-Aluminate films with an interfacial layer of SiO_2 have higher Hf content after the same ALD cycles. It has been reported that HfO_2 films grow faster on the SiO_2 layer than on an

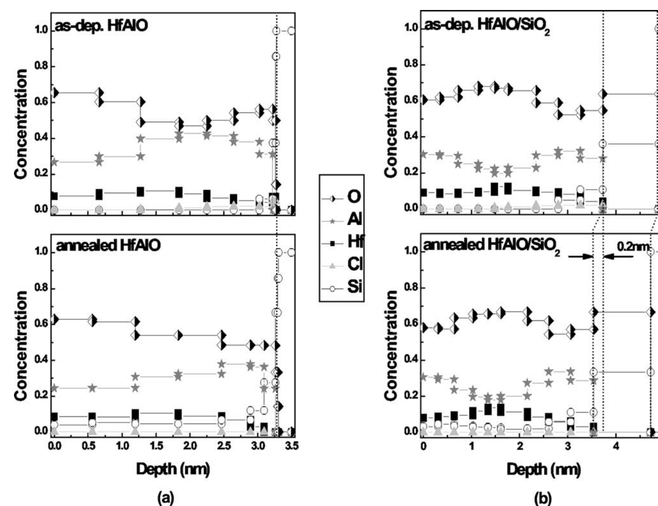

Figure 2. (a) Compositional depth profile for the as-deposited and postannealed Hf-aluminate films (a) without and (b) with an interfacial layer of SiO_2.

H-terminated surface because the surface disturbs the reaction between $HfCl_4$ and water.[20,21] Therefore, a difference in Hf content is caused by the initial surface conditions depending on the presence of an interfacial layer of SiO_2.

Figure 1b shows the MEIS energy spectra of Si, Al, and O for the samples shown in Fig. 1a. An interfacial layer of SiO_2 with a thickness of approximately 1 nm, which was preprocessed before the growth of Hf-aluminate films is clearly demonstrated by the wider Si and O peaks of Hf-aluminate films grown on an interfacial SiO_2 layer. A Cl element of small amounts was observed at the interface region of Hf-aluminate films with and without an interfacial layer of SiO_2. It is thought that a Cl element related to $HfCl_4$ remained in the initial growth stage due to the incomplete surface exchange reaction. However, the Cl was not detected after postannealing below detectible limits because Cl content was outdiffused during the annealing treatment. In addition, the concentration of Al in the Hf-aluminate films without an interfacial layer of SiO_2 was higher than that in films with an interfacial SiO_2 layer. An important point is that a high-energy shoulder ($\sim$90.2 keV) caused by scattering from Si on the deposited films was revealed for both of the annealed films, indicating the presence of Si at the film surface, as shown in the inset of Fig. 1b. The amounts of Si in the Hf-aluminate films with an interfacial layer of SiO_2 are lower than those in the films without an interfacial SiO_2 layer. Although the annealing temperature was higher than the decomposition temperature of SiO_2, relatively lower contents of Si were observed in the films with an interfacial layer of SiO_2. These results suggest that the Si on the film surface is generated by interdiffusion from the Si substrate and not from the interfacial layer of SiO_2. The interfacial layer of SiO_2 prevents contact between the film and the Si substrate, hindering interdiffusion of Si from the Si substrate to the film. In addition, the incorporation of Al_2O_3 into HfO_2 introduces a compressive strain on the Si lattice at the interface region during film growth.[22] The relaxation of this compressive strain during high-temperature annealing can affect the degree of interdiffusion and intermixing with the underlying layer at the interface.[23]

For the further information for a detailed quantity, MEIS spectra were simulated using the Kido program.[24] Figure 2 shows the compositional depth profile for the as-deposited and annealed Hf-aluminate films depending on an interfacial layer of SiO_2. The total thickness for Hf-aluminate films without an interfacial layer of SiO_2 was maintained at 33 Å during postannealing. However, the total thickness was reduced from 37 to 35 Å in the Hf-aluminate films grown on an interfacial layer of SiO_2 similar to the result of the

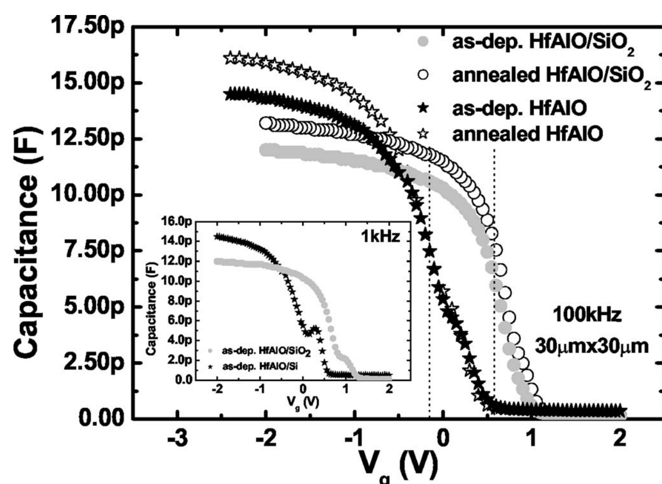

Figure 3. C–V curves for the as-deposited and postannealed Hf-aluminate films with and without an interfacial layer of SiO_2 in a nitrogen atmosphere at 950 °C for 2 min. The dotted lines indicate the flatband voltage of each sample, which selects the midgap energy in the depletion region. The inset shows the C–V characteristics at low frequency.

MEIS spectrum shown in Fig. 1a. The areal density, which corresponded to the amounts of Hf was extracted in the Hf-aluminate films without an interfacial layer of SiO_2: 1.99×10^{15} Hf atom/cm^2, and that in the films with interfacial layer of SiO_2: 2.22×10^{15} Hf atom/cm^2. Similarly, the amounts of Al atom were 8.55×10^{15} and 6.83×10^{15} Al atom/cm^2 for the samples without and with an interfacial layer of SiO_2, respectively. The total thickness was almost the same despite the difference of concentration in the Hf and Al atoms. This can be explained by the difference between molecular density of HfO_2 (2.49×10^{22} atom/cm^3) and that of Al_2O_3 (2.34×10^{22} atom/cm^3).[25] The Hf-aluminate films without an interfacial layer of SiO_2 have a higher amounts of total elements because the difference in the amounts of Al atom is higher than that of Hf atom. However, the density of Hf-aluminate films which determine the total thickness is subject to the molecular density of HfO_2 density having the relatively higher composition value with oxygen. The amounts of surface Si interdiffused were 3% in the Hf-aluminate films with an interfacial layer of SiO_2 and 5% in the films without an interfacial SiO_2 layer. In addition, there is almost no change in an interfacial layer of SiO_2 with thickness of 12 Å after postannealing treatment. This implies that the Si incorporated during the postannealing is diffused out from Si substrate as previously explained in Fig. 1b. Another important finding is that the distribution of elemental concentration in the depth direction was changed in Hf-aluminate films without an interfacial layer of SiO_2 after postannealing, although the total thickness did not change. The distribution of elemental concentration was preserved in the films with an interfacial layer of SiO_2, even if the total thickness was slightly shrunk. It is regarded that the interdiffusion of higher Si in the Hf-aluminate films without an interfacial layer of SiO_2 affects the structural rearrangement. Thus, it is concluded that the elemental amounts and distribution of Hf-aluminate films have a difference depending on the presence or absence of an interfacial layer of SiO_2.

To investigate the changes in electrical characteristics resulting from the structural changes, C–V measurements were carried out using an MOS capacitor fabricated with a Pt electrode of 9×10^{-6} cm^2. Figure 3 shows the C–V characteristics of Hf-aluminate films with and without an interfacial layer during postannealing. The difference in the accumulation capacitance of the as-deposited films is attributed to the interfacial layer of SiO_2. The accumulation capacitance increases in both types of film after postannealing. In the films with an interfacial layer of SiO_2, the increase in accumulation capacitance is caused by the decrease of film thickness resulting from the crystallization indicated by the results in Fig. 1a (the reduction in the width of the Hf peak). Another reason is the formation of silicate through intermixing with small amounts of Si interdiffused from Si substrate. The films without an interfacial layer of SiO_2 have a change of elemental distribution owing to the greater interdiffusion of Si, as shown in Fig. 2. This intermixing variation contributes to the increase in accumulation capacitance, because the change of elemental distribution incorporated such as Al_2O_3 and SiO_2, into HfO_2 can change the molar volume, which affects the dielectric constant.[8] A shift of flatband voltage was observed in the film with an interfacial layer of SiO_2 but not in the film without an interfacial SiO_2 layer. Hf-aluminate alloys generally exhibit electron trapping related to the charge at the interface between the Al_2O_3 film and the interfacial layer of SiO_2.[26] Therefore, the positive shift in flatband voltage in the films with an interfacial layer of SiO_2 is probably a consequence of negative charge trapping between Al_2O_3 and the interfacial layer of SiO_2. In addition, a slightly more positive shift in flatband voltage was observed after postannealing in the films with an interfacial layer of SiO_2. This result is attributed to the change in the density of Hf-aluminate films due to crystallization during postannealing as shown in the MEIS results. C–V curves at the low-frequency of 1 kHz (inset of Fig. 3) show the characteristics of interfacial trap charge at the interface between as-deposited films and the Si substrate. We found that Hf-aluminate films that were in direct contact with the Si substrate had higher interfacial trap charges than films with an interfacial layer of SiO_2. A detailed analysis of interfacial trap charge density (D_{it}) was performed by the conduction method.[27] The estimated D_{it} of as-deposited films was 1.97×10^{12} cm^2/eV for the films with an interfacial layer of SiO_2 and 5×10^{12} cm^2/eV for films without an interfacial SiO_2 layer. As shown by the C–V results at low frequency (inset in Fig. 3), the films without an interfacial layer of SiO_2 have higher interfacial trap charge densities. The D_{it} of Hf-aluminate films with an interfacial layer of SiO_2 decreases to approximately 1×10^{12} cm^2/eV after postannealing. The slight reduction of interfacial trap charge density results from the elimination of the impurities such as a Cl element in the interface region through postannealing. However, the D_{it} of the films without an interfacial layer of SiO_2 after the annealing treatment increased slightly to about 5.18×10^{12} cm^2/eV. This may be because the interdiffusion of more Si, relative to the films with an interfacial layer of SiO_2, results in a little increase in interfacial trap charge density. Therefore, the electrical characteristics are strongly related to the structural changes depending on the presence of an interfacial layer of SiO_2.

To assess the structural and electrical changes resulting from the inclusion of an interfacial layer of SiO_2, the Hf-aluminate films were reoxidized in an atmosphere of oxygen at 800°C for 2 min. Figure 4 shows the MEIS energy spectra for the as-deposited and annealed films. The main finding is that the interfacial oxide is dramatically thicker (approximately 2.5 nm) in the Hf-aluminate films without an interfacial layer of SiO_2. In the films with an interfacial layer of SiO_2, the growth of interfacial oxide is remarkably suppressed during the post-reoxidation. A decrease in accumulation capacitance was observed in both types of film, while the original C–V characteristics were maintained after postannealing in an ambient of oxygen at 800°C, despite the increase in the interfacial oxide (inset of Fig. 4). However, the decrease in accumulation capacitance was somewhat small in the films with an interfacial layer of SiO_2. This is consistent with the MEIS results, which show that the growth of interfacial oxide is suppressed. The flatband voltage tends to shift positively in both types of film after post-reoxidation. The growth of an oxide at the interface between Al_2O_3 and SiO_2 results in negative charge trapping similar to that seen in the as-deposited films with an interfacial layer of SiO_2 (Fig. 3).

Conclusion

The structural and electrical characteristics resulting from the presence or absence of an interfacial layer in Hf-aluminate films

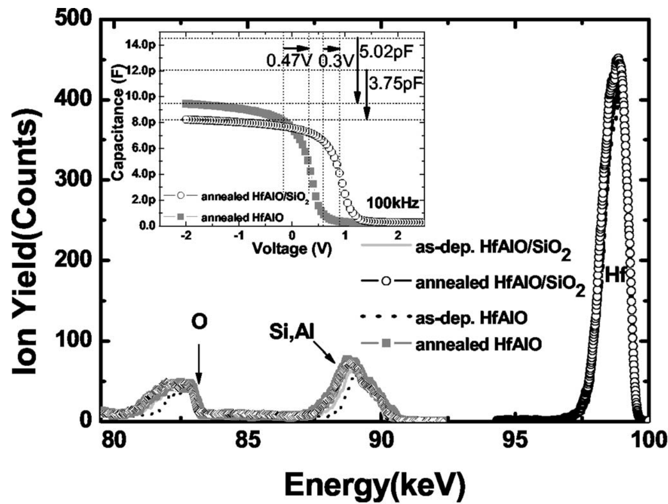

Figure 4. MEIS energy spectra for the as-deposited and postannealed Hf-aluminate films with and without an interfacial layer of SiO_2 in an oxygen atmosphere at 800 °C for 2 min. The inset shows the C–V curves after post-annealing in an oxygen atmosphere. The parallel and perpendicular arrows in the inset indicate the positive shift of flatband voltage and the decrease in accumulation capacitance as compared with the as-deposited films, respectively.

during growth and postannealing were investigated. The interdiffusion of Si from the substrate was suppressed in Hf-aluminate films with an interfacial layer of SiO_2, relative to films without an interfacial SiO_2 layer. Hf-aluminate films with an interfacial layer of SiO_2 showed a slight crystallization and that without an interfacial SiO_2 layer showed the structural rearrangement caused by the interdiffusion of Si. Reoxidation of Hf-aluminate films without an interfacial layer of SiO_2 resulted in a dramatic thickening of the interfacial region. The presence of an interfacial layer caused a positive shift in flatband voltage.

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References

1. *International Technology Roadmap for Semiconductors*, Semiconductor Industry Association, San Jose, CA 2001.
2. A. I. Kingon, J.-P. Maria, and S. K. Streiffer, *Nature (London)*, **406**, 1032 (2000).
3. G. D. Wilk and R. W. Wallace, *Appl. Phys. Lett.*, **76**, 112 (2000).
4. G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.*, **89**, 5243 (2001).
5. G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.*, **87**, 484 (2000).
6. G. B. Alers, D. J. Werder, Y. Chabal, H. C. Lu, E. P. Gusev, E. Garfunkel, T. Gustafsson, and R. S. Urdahl, *Appl. Phys. Lett.*, **73**, 1517 (1998).
7. M.-Y. Ho, H. Gong, G. D. Wilk, B. W. Busch, M. L. Green, W. H. Lin, A. See, S. K. Lahiri, M. E. Loomans, P. I. Raisanen, and T. Gustafsson, *Appl. Phys. Lett.*, **81**, 4218 (2002).
8. M.-H. Cho, Y. S. Roh, C. N. Whang, K. Jeong, H. J. Choi, S. W. Nam, D.-H. Ko, J. H. Lee, N. I. Lee, and K. Fujihara, *Appl. Phys. Lett.*, **81**, 1071 (2002).
9. H. S. Chang, H. Hwang, M.-H. Cho, D. W. Moon, S. J. Doh, J. H. Lee, and N. I. Lee, *Appl. Phys. Lett.*, **84**, 28 (2004).
10. M.-H. Cho, H. S. Chang, Y. J. Cho, D. W. Moon, K.-H. Min, R. Sinclair, S. K. Kang, D.-H. Ko, J. H. Lee, J. H. Gu, and N. I. Lee, *Appl. Phys. Lett.*, **84**, 571 (2004).
11. M.-H. Cho, K. B. Chung, H. S. Chang, D. W. Moon, S. A. Park, Y. K. Kim, K. Jeong, C. N. Whang, D. W. Lee, D.-H. Ko, S. J. Doh, J. H. Lee, and N. I. Lee, *Appl. Phys. Lett.*, **85**, 4115 (2004).
12. H. Kim, P. C. Mclntyre, and K. C. Saraswat, *Appl. Phys. Lett.*, **82**, 106 (2003).
13. W. Kern, *RCA Rev.*, **31**, 207 (1970).
14. W. Kern, *RCA Rev.*, **31**, 235 (1970).
15. J. F. van der Veen, *Surf. Sci. Rep.*, **5**, 199 (1985).
16. M. A. Alam and M. L. Green, *J. Appl. Phys.*, **94**, 3403 (2003).
17. H. Watanabe, K. Fujita, and M. Ichikawa, *Appl. Phys. Lett.*, **70**, 1095 (1997).
18. Y. Kobayashi and K. Sugii, *J. Vac. Sci. Technol. A*, **10**, 2308 (1992).
19. K. E. Johnson and T. Engel, *Phys. Rev. Lett.*, **69**, 339 (1992).
20. M. L. Green, M.-Y. Ho, B. Busch, G. D. Wilk, T. Sorsch, T. Conard, B. Brijs, W. Vandrvorst, P. I. Räisänen, D. Muller, M. Bude, and J. Grazul, *J. Appl. Phys.*, **92**, 7168 (2002).
21. K. B. Chung, H. S. Chang, C. N. Whang, D. W. Moon, and M.-H. Cho, *J. Appl. Phys.*, In preparation.
22. H. S. Chang, H. Hwang, M.-H. Cho, H. K. Kim, D. W. Moon, *J. Vac. Sci. Technol. A*, **22**, 165 (2004).
23. T. Emoto, K. Akimoto, Y. Yoshida, A. Ichimiya, T. Nabatame, and A. Toriumi, *Appl. Surf. Sci.*, **244**, 55 (2005).
24. Y. Kido and T. Koshikwa, *J. Appl. Phys.*, **67**, 187 (1990).
25. J. R. Tesmer and M. Nastasi, *Handbook of Modern Ion Beam Materials Analysis*, Materials Research Society, Warrendale, PA.
26. R. S. Johnson, J. G. Hong, C. Hinkle, and G. Lucovsky, *J. Vac. Sci. Technol. B*, **20**, 1126 (2002).
27. E. M. Vogel, W. K. Henson, C. A. Richter, and J. S. Suehle, *IEEE Trans. Electron Devices*, **47**, 601 (2000).