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Laser annealed $Hf_xZr_{1-x}O_2$ high-*k* dielectric: Impact on morphology, microstructure, and electrical properties

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The impact of microsecond laser annealing at 1325 °C on physical and electrical characteristics of $Hf_xZr_{1-x}O_2$ is compared to films annealed at 1000 °C for 5 s by a conventional rapid thermal process (RTP). Atomic force microscopy analysis shows that laser annealed $Hf_xZr_{1-x}O_2$ is smoother and void free, while RTP annealed $Hf_xZr_{1-x}O_2$ exhibits void formation and is rough. The x-ray diffraction analysis revealed higher degree of tetragonality on laser annealed film, particularly for $Hf_{0.5}Zr_{0.5}O_2$ and ZrO_2. Furthermore, laser annealed $Hf_xZr_{1-x}O_2$ devices have good electrical properties (well behaved *CV*, low gate leakage, and good mobility) whereas RTP annealed devices are not functional. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2898710]

As transistor size continues to shrink, the scaling of SiO_2 gate dielectrics reaches its limit. In the past decades, the semiconductor industry has expended much effort to find replacement materials for SiO_2 gate oxide. In recent years, the industry has converged on hafnium-based high-dielectric constant (high-*k*) materials as the most promising SiO_2 replacement.[1–5] Encouraging results on hafnium-based devices (HfO_2, $Hf_xZr_{1-x}O_2$, and HfSiON) have been reported by many groups.[2–5] Crystallization properties of these films have been widely studied using conventional rapid thermal process (RTP) anneals. Recently, however, microsecond laser annealing of high-*k*/metal gate devices has been reported to have advantages over conventional RTP annealing.[6] However, the impact of laser annealing on properties of hafnium-based high-*k* films has not been studied in detail. In this letter, we report the impact of laser annealing on hafnium-based high-*k* films.

Among the various methods used to deposit thin high-*k* dielectrics, atomic layer deposition (ALD) provides some advantages such as excellent thickness control, conformality, and low temperature deposition. Recently, ALD has been used to deposit thin high-*k* films to manufacture dynamic random access memory.[7] In this letter, we report physical and electrical characteristics of microsecond laser annealed films and compare them to films given conventional RTP anneal. We found that laser annealing is a favorable method of annealing ALD high-*k* films compared to RTP anneal.

HfO_2 and $Hf_xZr_{1-x}O_2$ films were fabricated by ALD using $HfCl_4$, $ZrCl_4$, and D_2O precursors at a deposition temperature of 300 °C as previously reported.[8,9] All films were either annealed at 1000 °C for 5 s in a nitrogen ambient or laser annealed.[6] The laser anneals were performed using the Ultratech LSA platform,[10–13] rastering the subject wafer on a heated chuck under a high power of 10.6 μm wavelength laser beam incident upon the wafer's surface near Brewster's angle. The beam was rastered using an 800 μs beam dwell time with a beam width on the order of 100 μm. The laser power was adjusted to determine the peak anneal temperature to be between 1275 and 1325 °C. The laser anneal peak temperature was calibrated relative to the melt temperature

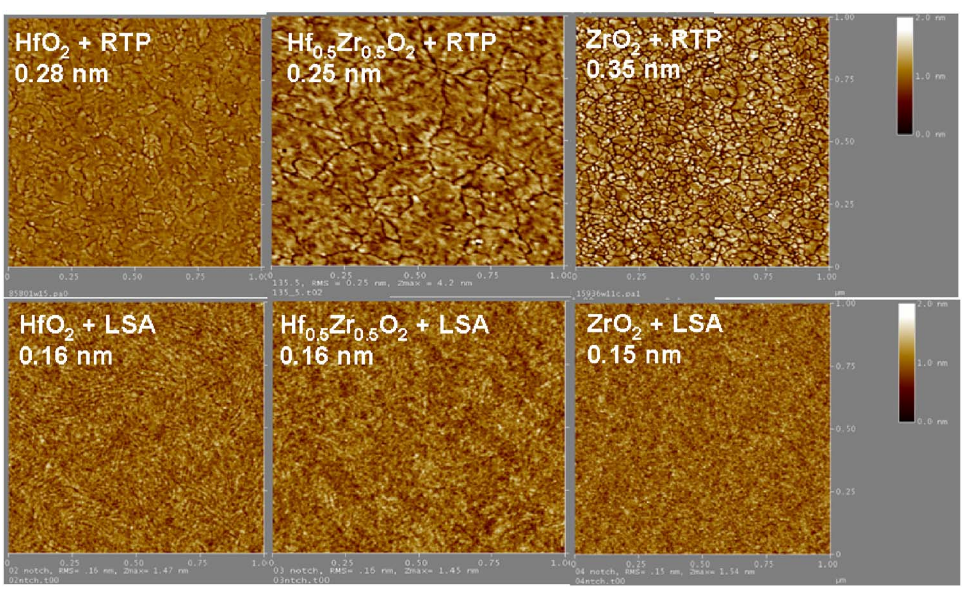

FIG. 1. (Color online) AFM of laser annealed vs RTP annealed $Hf_xZr_{1-x}O_2$ films.

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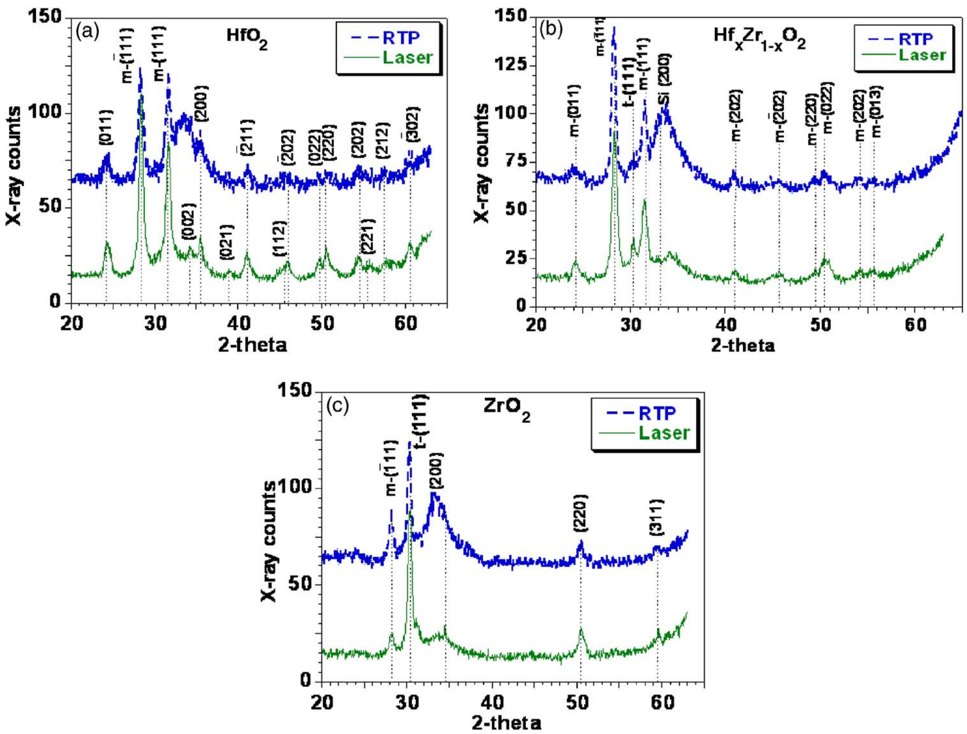

FIG. 2. (Color online) XRD of laser anneal vs RTP annealed (a) HfO_2, (b) $Hf_{0.5}Zr_{0.5}O_2$, and (c) ZrO_2 films.

of silicon. Rutherford backscattering spectroscopy analysis was performed to determine the composition of $Hf_xZr_{1-x}O_2$ alloy and to confirm that film composition does not change significantly after annealing.[9,14,15] Film roughness was measured by atomic force microscopy (AFM) operated in tapping mode. The root mean square roughness values were calculated on 1×1 μm^2 images. X-ray diffraction (XRD) in powder mode was used to determine the preferred orientation of the films. Instrumentation consisted of a Rigaku Rotaflex RU-200BH with Cu $K\alpha$ rotating anode and Dmax-B-goniometer. For electrical characterization, ~30 Å high-*k* dielectric deposition was followed with a TaC_y metal gate electrode and capped with poly-Si. The high-*k* dielectric films were deposited on "cake oxide" wafers with pregrown SiO_2 thickness. Transistors were fabricated using conventional complementary metal-oxide semiconductor integration with sidewall liners and spacers, implants to the Si cap/source/drain, 1000 °C activation anneal, cobalt-salicide contacts, and forming gas anneal. Equivalent oxide thickness was extracted using the HAUSER program, while mobility was determined using MOB2D as previously reported.[6,16]

Figure 1(a) shows AFM images of 3 nm $Hf_xZr_{1-x}O_2$ (x=0, 0.5, and 1) after a microsecond laser anneal or a conventional RTP anneal. All laser annealed films are void free,

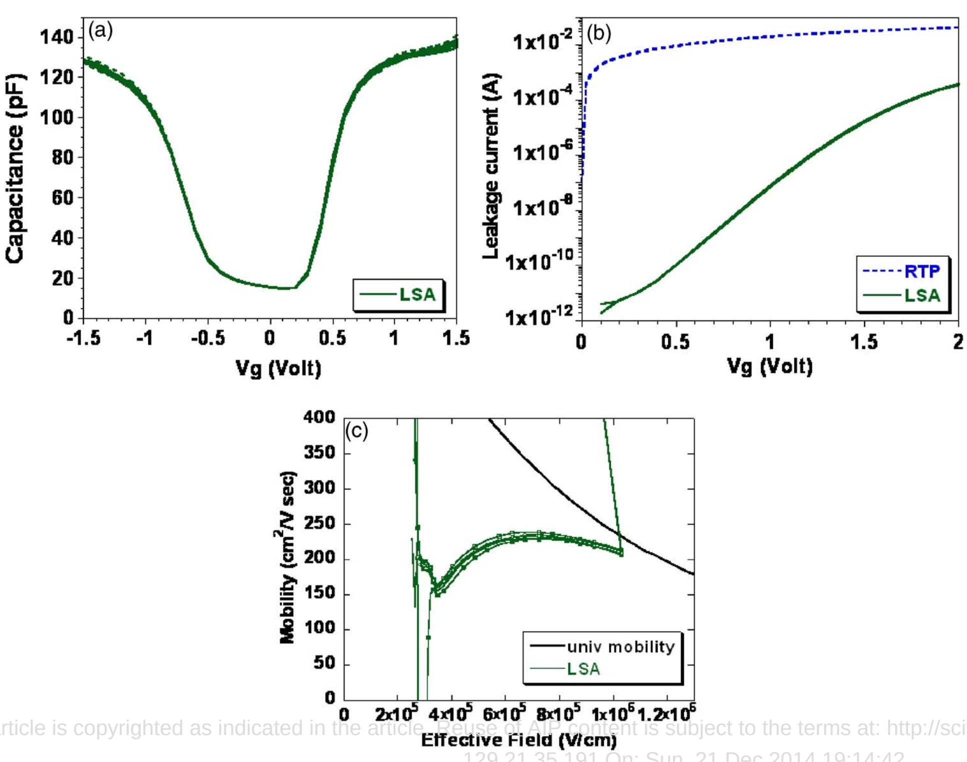

FIG. 3. (Color online) (a) Capacitance-voltage, (b) gate leakage current-voltage, and (c) mobility of laser annealed vs RTP annealed $Hf_xZr_{1-x}O_2$ devices. Device size is 85×80 μm^2.

TABLE I. Summary of impact of LSA on $Hf_{0.5}Zr_{0.5}O_2$ film morphology, microstructure, and device properties.

	$Hf_{0.5}Zr_{0.5}O_2$	
	RTP	LSA
AFM-roughness (nm)	0.25	0.16
XRD-tetragonality (%)	0	12.5
Well-behaved CVs?	No	Yes
$J_g(A)$ at 1 V	2.1×10^{-2}	7.2×10^{-8}
Peak G_m compared to SiO_2	⋯	90.3%

(as opposed to the RTP annealed film, which show evidence of void formation) and are smoother than the RTP annealed films. It appears that the ultrashort duration of the laser anneal helps us to significantly reduce void formation that occurs when these ALD high-*k* films are exposed to high temperature annealing for times on the order of seconds. To further investigate the microstructure of these films, XRD spectra were recorded for ~200 Å $Hf_xZr_{1-x}O_2$ (x=0, 0.5, and 1) after both annealing conditions. Figure 2(a) shows XRD spectra of ~20 nm HfO_2 films after a 1000 °C anneal for 5 s in a nitrogen ambient compared to laser annealed films. Both films are monoclinic and exhibit strong (111) or $(\bar{1}11)$ texture. Figure 2(b) shows XRD spectra of $Hf_{0.5}Zr_{0.5}O_2$ films after RTP or laser annealing. The spectra reveal that the RTP film is mostly monoclinic with perhaps a slight hint of tetragonal phase (broad peak at 30° theta), whereas the laser annealed $Hf_xZr_{1-x}O_2$ film has a more pronounced peak at 30° indicating tetragonal phase. The XRD spectra in Fig. 2(c) show that the laser annealed film has greater tetragonality than the RTP annealed films as evidenced by stronger peak at 30° and relatively weaker monoclinic peaks. The evidence that tetragonal phase stabilization is more pronounced in the laser annealed material is encouraging because tetragonal phase $Hf_xZr_{1-x}O_2$ with its higher-*k* value is more desirable phase than monoclinic phase material.[4,9,15–19] It is known that the driving force for the tetragonal to monoclinic transformation is smaller when ZrO_2 is alloyed into the HfO_2. This is more exaggerated in the case of millisecond anneal. Microstructure modification due to laser annealing has also been recently reported for La_2O_3 system.[20] Laser annealing results in a significantly higher-*k* value for La_2O_3 than those obtained by conventional anneal.[20,21]

To investigate electrical properties of laser annealed films, long channel transistors and capacitors were fabricated. Figure 3(a) shows capacitance voltage characteristics of laser annealed devices. *CV* curves from multiple sites are coplotted and show very little site to site variation, indicating good uniformity. No functional *CV* were obtained for RTP annealed devices. RTP annealed devices are very leaky, as shown in Fig. 3(b). This is not surprising as AFM images show evidence of void formation in $Hf_xZr_{1-x}O_2$ films after high temperature RTP annealing. Figure 3(c) plots mobility of laser annealed $Hf_xZr_{1-x}O_2$ devices showing excellent mobility compared to the universal SiO_2 curve. Table I summarizes electrical and material properties of $Hf_xZr_{1-x}O_2$ after RTP or laser anneal.

In summary, the impact of laser annealing versus conventional RTP annealing on physical and electrical properties of hafnium-based dielectrics is studied. Results show that laser annealed films have significantly improved material and device properties when compared to RTP annealed films. Not only the films are smoother and void free, these films crystallize more in the tetragonal phase which has a higher-*k* value than the monoclinic phase. Electrically, laser annealed films yield good devices, whereas RTP annealed $Hf_xZr_{1-x}O_2$ devices are leaky and not functional.

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[1]G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).
[2]P. D. Kirsch, M. A. Quevedo-Lopez, S. A. Krishnan, C. Krug, H. AlShareef, C. S. Park, R. Harris, N. Moumen, A. Neugroschel, G. Bersuker, B. H. Lee, J. G. Wang, G. Pant, B. Gnade, M. J. Kim, R. M. Wallace, J. S. Jur, D. J. Lichtenwalner, and A. I. Kingon, and R. Jammy, Tech. Dig. - Int. Electron Devices Meet. **2006**, 4.
[3]H.-H. Tseng, P. J. Tobin, S. Kalpat, J. K. Schaeffer, M. E. Ramon, L. R. C. Fonseca, Z. X. Jiang, R. I. Hegde, D. H. Triyoso, and S. Samavedam, IEEE Trans. Electron Devices **54**, 3267 (2007).
[4]R. I. Hegde, D. H. Triyoso, P. J. Tobin, and B. E. White, Jr., J. Appl. Phys. **101**, 074113 (2007).
[5]W. J. Taylor, Jr., C. Capasso, B. Min, B. Winstead, E. Verret, K. Loiko, D. Gilmer, R. I. Hegde, J. Schaeffer, E. Luckowski, A. Martinez, M. Raymond, C. Happ, D. Triyoso, S. Kalpat, A. Haggag, D. Roan, J.-Y. Nguyen, L. B. La, L. Hebert, J. Smith, D. Jovanovic, M. Foisy, S. B. Samavedam, N. Cave, B. E. White, Jr., and S. Venkatesan, Tech. Dig. - Int. Electron Devices Meet. **2006**, 625.
[6]D. C. Gilmer, J. K. Schaeffer, W. J. Taylor, G. Spencer, D. H. Triyoso, M. Raymond, D. Roan, J. Smith, C. Capasso, R. I. Hegde, and S. B. Samavedam, Proceedings of the 36th European Solid-State Device Research Conference, 2006 (unpublished), p. 351.
[7]See http://www.micromagazine.com/archive/05/07/chipworks.html for article on ALD high-*k* DRAM.
[8]H.-H. Tseng, M. E. Ramon, L. Hebert, P. J. Tobin, D. Triyoso, J. M. Grant, Z. X. Jiang, D. Roan, S. B. Samavedam, D. C. Gilmer, S. Kalpat, C. Hobbs, W. J. Taylor, O. Adetutu, and B. E. White, Tech. Dig. - Int. Electron Devices Meet. **2003**, 4.1.1.
[9]D. H. Triyoso, P. J. Tobin, B. E. White, Jr., R. Gregory, and X.-D. Wang, Appl. Phys. Lett. **89**, 132903 (2006).
[10]A. Shima and A. Hiraiwa, Jpn. J. Appl. Phys., Part 1 **45**, 5708 (2006).
[11]S. K. H. Fung, H. T. Huang, S. M. Cheng, K. L. Cheng, S. W. Wang, Y. P. Wang, Y. Y. Yao, C. M. Chu, S. J. Yang, W. J. Liang, Y. K. Leung, C. C. Wu, C. Y. Lin, S. J. Chang, S. Y. Wu, C. F. Nieh, C. C. Chen, T. L. Lee, Y. Jin, S. C. Chen, L. T. Lin, Y. H. Chiu, H. J. Tao, C. Y. Fu, S. M. Jang, K. F. Yu, C. H. Wang, T. C. Ong, Y. C. See, C. H. Diaz, M. S. Liang, and Y. C. Sun, *2004 Symposium on VLSI Technology: Digest of Technical Papers* (IEEE, Piscataway, NJ, 2004), pp. 92–93.
[12]L. M. Feng, Y. Wang, and D. A. Markle, International Workshop on Junction Technology, 2006 (unpublished), pp. 1–5.
[13]S. Chen, J. Hebb, A. Jain, S. Shetty, and Y. Wang, Proceedings of the 15th IEEE International Conference on Advanced Thermal Processing of Semiconductors 2007 (unpublished).
[14]D. H. Triyoso, R. I. Hegde, J. K. Schaeffer, D. Roan, P. J. Tobin, S. B. Samavedam, B. E. White, R. Gregory, and X.-D. Wang, Appl. Phys. Lett. **88**, 222901 (2006).
[15]D. H. Triyoso, R. I. Hegde, J. K. Schaeffer, R. Gregory, X.-D. Wang, M. Canonico, D. Roan, E. A. Hebert, K. Kim, J. Jiang, R. Rai, V. Kaushik, and S. B. Samavedam, J. Vac. Sci. Technol. B **25**, 845 (2007).
[16]D. H. Triyoso, R. I. Hegde, J. Jiang, J. K. Schaeffer, and M. V. Raymond, IEEE Electron Device Lett. **29**, 57 (2008).
[17]X. Zhao and D. Vanderbilt, Phys. Rev. B **65**, 233106 (2002).
[18]X. Zhao and D. Vanderbilt, Phys. Rev. B **65**, 075105 (2002).
[19]C. Fachmann, L. Frey, S. Kudelka, T. Boescke, S. Nawka, E. Erben, and T. Doll, Microelectron. Eng. **84**, 2883 (2007).
[20]P. Darmawan, P. S. Lee, Y. Setiawan, J. Ma, and T. Osipowicz, Appl. Phys. Lett. **91**, 092903 (2007).
[21]S. Ohmi, M. Takeda, H. Ishiwara, and H. Iwai, J. Electrochem. Soc. **151**, G279 (2004).