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Effect of surface NH_3 anneal on the physical and electrical properties of HfO_2 films on Ge substrate

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Metal-oxide-semiconductor capacitors were fabricated on germanium substrates by using metalorganic-chemical-vapor-deposited HfO_2 as the dielectric and TaN as the metal gate electrode. It is demonstrated that a surface annealing step in NH_3 ambient before the HfO_2 deposition could result in significant improvement in both gate leakage current and the equivalent oxide thickness (EOT). It was possible to achieve a capacitor with an EOT of 10.5 Å and a leakage current of 5.02×10^{-5} A/cm^2 at 1 V gate bias. X-ray photoelectron spectroscopy analysis indicates the formation of GeON during surface NH_3 anneal. The presence of Ge was also detected within the HfO_2 films. This may be due to Ge diffusion at the high temperature ($\sim$400 °C) used in the chemical-vapor deposition process. © *2004 American Institute of Physics.*

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There have been extensive studies on high dielectric constant (high-κ) oxides as a possible replacement for conventional silicon oxide in complementary metal-oxide-semiconductor (CMOS) devices which require an equivalent oxide thickness (EOT) of below 2 nm. Among various high-κ materials, HfO_2 and Hf oxide-based compounds[1] have been identified as promising candidates to meet the scaling requirements stated in the International Technology Roadmap for Semiconductors. However, severe surface carrier mobility degradation has been observed in metal-oxide-semiconductor field-effect transistors using high-κ gate dielectrics.[1] This is one of the major challenges in the integration of high-κ dielectrics in CMOS technology. A potential solution to this problem is to use germanium as the substrate, where Ge has a higher hole and electron mobility than that of Si. However, changing the substrate from silicon to germanium will itself bring new challenges in the formation of high-κ gate stacks.

Rosenberg and Martin[2] have reported MOSFETs on Ge substrates using a pure Ge channel and a germanium oxynitride gate dielectric (GeON) layer of 25 nm thick. Recently, Shang *et al.*[3] reported well-behaved Ge MOSFETs with 6 nm GeON on top of a 3 nm low temperature oxide gate stack. However, the EOTs of the above dielectrics are too large for a modern device. On the other hand, high-mobility *p*-channel germanium MOSFETs with ultralow EOT (6–10 Å) have been reported with ultrathin ZrO_2 deposited by sputtering at room temperature.[4] Germanium-on-insulator (GOI) devices[5] have also been successfully demonstrated with Al_2O_3 gate dielectrics. CVD HfO_2 Ge MOS capacitors were first reported by Bai *et al.*[6] It was found that surface NH_3 annealing is effective in improving the electrical performance. However, physical characteristics were not evaluated for further understanding. Thus, it is of great importance to study the effect of surface NH_3 annealing on the Ge substrate, and to combine the physical and electrical characterization of the CVD HfO_2 layers on Ge substrates.

The experiment was carried out on *n*-type (100) Ge wafers (Sb doped, resistivity = 0.04–0.08 Ω cm). Ge substrates were dipped first in NH_4OH (1:4, 300 s) to remove the native Ge oxide, then in H_2O_2 (1:5, 60 s) to form a chemical oxide on the surface, and again in NH_4OH (1:4, 300 s) for chemical oxide removal.[7] Following that, annealing in a NH_3 ambient (purity = 99.999%) was performed inside a chamber with a base pressure of 5×10^{-6} Torr and at a constant temperature of 600 °C. After that, HfO_2 was deposited in another chamber using metalorganic chemical-vapor deposition (MOCVD), with Hf tert-butoxide as the metalorganic precursor in an N_2+O_2 ambient at 400 °C with a base pressure of 3×10^{-3} Torr. A vacuum load lock was used to store and transfer wafers. A postdeposition anneal (PDA) was then performed in a rapid thermal processor in N_2 ambient under 760 Torr at 600 °C for 30 s. After that, a layer of 150 nm TaN was sputtered at room temperature. This was followed by lithography and dry etching processes. The final step was an annealing in H_2+N_2 ambient at 300 °C. High-resolution *ex situ* x-ray photoelectron spectroscopy (XPS) analysis was performed with standard Al x-ray source. Capacitance–voltage (C–V) and leakage current–voltage (J–V) characteristics

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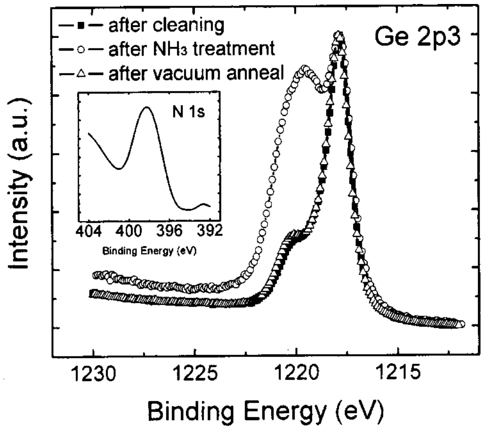


FIG. 1. *Ex situ* XPS analysis of the NH_3 annealing effect on the Ge substrates with the Ge $2p3$ spectra. The inset is the N $1s$ signal from the sample after NH_3 annealing. GeON is formed on the germanium surface.

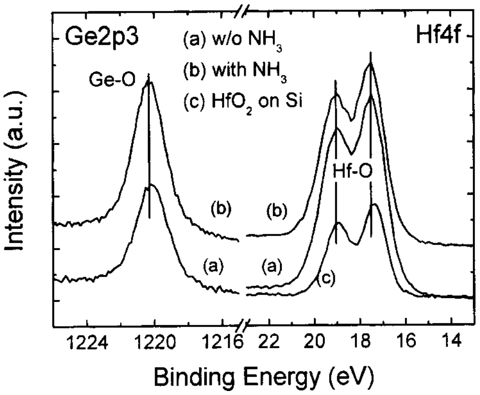


FIG. 2. High-resolution XPS spectra of Hf $4f$ and Ge $2p3$ for HfO_2 deposited on Ge substrates. Normal position of the Hf $4f$ signal implies chemically good quality of the film. Ge was detected to be incorporated in the as-deposited films.

were measured by an Agilent 4284A LCR meter and a HP4156A semiconductor parameter analyzer, respectively. High-resolution cross-sectional transmission electron micrographs (HR-XTEM) were also taken for physical characterization.

To study both the cleaning and surface nitridation effects on Ge substrates before HfO_2 deposition, the Ge $2p3$ core-level XPS spectra are characterized and shown in Fig. 1. The line with closed boxes is the signal of the Ge sample (sample A) right after the cleaning. The main peak located at 1217.8 eV is attributed to metallic Ge $2p3$ spectrum from the substrate. The shoulder, ranging from 1219 to 1221 eV, is attributed to GeO_x ($x \leq 2$) bonds,[8] which is believed to be introduced during sample transportation. The circle-dotted line, as shown in Fig. 1, is the signal of the Ge sample (sample B) annealed in NH_3 (10 min) after the same cleaning procedure. It is observed that the small shoulder in sample A has evolved to a broad peak (~1219.5 eV). Considering all the possible bonds that the Ge atoms may have, it is reasonable to infer that the broad peak consists of two types of Ge bonds: the Ge-O (1220.1 eV) and Ge-N (1218.9 eV). Detailed curve fitting was carried out with Shirley background and Gaussian-Lorentzian lines (not shown here). A Chi square of 4.151 is obtained, and the fitting result verifies that the whole Ge $2p3$ signal consists of three peaks which are identified as metallic Ge (1217.8 eV), Ge-N bond (1218.9 eV), and Ge-O bond (1220.1 eV), respectively.[8] The nitrogen existence is also confirmed by the N $1s$ spectrum (inset of Fig. 1). The concentrations of oxygen and nitrogen were quantified by integrating each peak area and subtracting the background, and a layer of $GeO_{0.83}N_{0.17}$ is found on top of the Ge substrate after surface nitridation. To clarify the oxygen source in the $GeO_{0.83}N_{0.17}$ during the NH_3 annealing, one more sample (sample C) was put in the NH_3 treatment chamber under same temperature without NH_3 flow for 10 min after the same cleaning procedure. The XPS result is also shown in Fig. 1 with the empty-triangle line. It clearly shows that, comparing to sample A, there is no substantial oxidation in the sample C. This means that the oxygen detected in the $GeO_{0.83}N_{0.17}$ of sample B is likely introduced by a NH_3 gas source, even though the NH_3 gas purity is 99.999% (with the main impurities of O_2, H_2O, and H_2). This high oxygen concentration in GeON after surface nitridation implies that Ge is easier to be oxidized than nitrified.

To investigate the effect of surface nitridation on the following deposited HfO_2, XPS spectra of Ge $2p3$ and Hf $4f$ for HfO_2 deposited on germanium with and without surface NH_3 annealing (30 s) are shown in Fig. 2. For comparison, the XPS spectrum of Hf $4f$ peak for HfO_2 deposited on Si with PDA is also plotted in Fig. 2. No substantial binding energy difference is observed in Hf $4f$ peaks between the Si and Ge substrates. On the other hand, Ge $2p3$ peaks at 1220.1 eV were detected and are identified as Ge-O bonds for both of the Ge samples with and without surface nitridation. Since there are no metallic Ge bonds found in these signals, the Ge signals are believed to be from the as-deposited HfO_2, which implies that Ge is incorporated in the HfO_2 films. This Ge incorporation phenomenon may result from the Ge diffusion from substrate during the CVD deposition process (~400 °C). Further, since no Ge-Hf bond is detected in both samples, the dielectrics are of good electrical insulating property in terms of chemical states. Considering the chemical similarities between Ge and Si,[9] two kinds of possible structures may exist for the Ge incorporated HfO_2 film. The first is that the dielectric film could be a mixture of HfO_2 and GeO_2. Another is that the film is hafnium germinate and the Hf $4f$ bonding is not affected by the vicinity of the Ge atom. However, this cannot be addressed by analyzing the O 1s signal in this experiment because it overlaps with the Ge *LMM* Auger signal.

Figure 3(a) shows the C-V characteristics of the HfO_2 Ge MOS capacitor (area $= 100\ \mu m \times 100\ \mu m$, sweeping from inversion to accumulation) with surface nitridation, and its J-V curve is plotted as inset. For comparison, both C-V and J-V characteristics of the HfO_2 Ge MOS capacitor without surface nitridation (same dimension) are also included. By fitting the C-V data in a computer while taking into account the quantum confinement effects, it is shown that a small EOT of 10.5 Å and a low leakage current of 5.02×10^{-5} A/cm^2 at $V_g = 1$ V can be achieved for the MOS capacitor with surface nitridation. While for the MOS capacitor without surface nitridation, an EOT of 16.8 Å is obtained with a leakage current of 1.01 A/cm^2 at $V_g = 1$ V. Figure 3(b) shows the gate leakage current density as a function of EOT together with published data.[4–6] Thus, though the Ge incorporation in HfO_2 films is observed for both samples with and

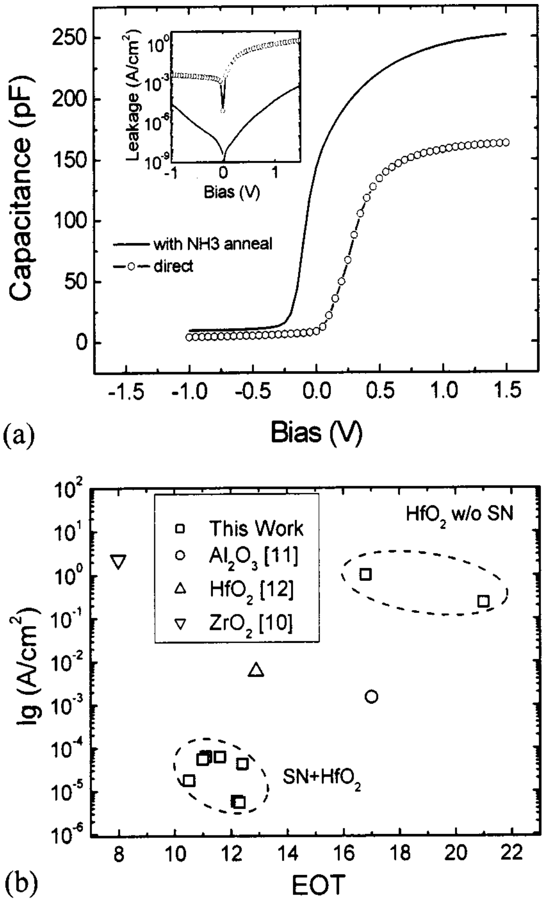
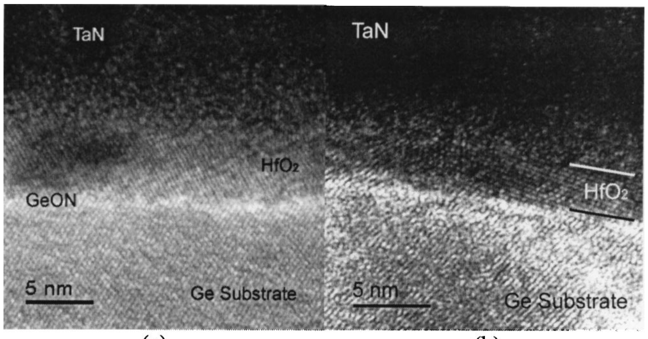


FIG. 3. (a) $C-V$ curves were measured at a frequency of 100 kHz and $J-V$ curves were plotted as inset. (b) Gate leakage currents at $V_g = 1$ V with respect to different EOTs were plotted together with published data.

without surface nitridation, and both samples show similar chemical states, the NH_3 annealing is very effective in improving the electrical properties of Ge MOS capacitors. The smaller EOT of the MOS capacitor with NH_3 annealing may indicate a smaller thickness of the dielectric and/or the interfacial layer than the capacitor without NH_3 annealing. However, the leakage current result is different from high-κ MOS capacitors on silicon substrates where a larger dielectric/interfacial layer usually yields a smaller gate leakage current. Considering together the fact that there is no significant chemical bonding difference in the dielectrics of both samples, the large difference of the leakage currents could be likely attributed to the interfacial layer. Therefore, the large leakage current of the Ge MOS capacitor implies the poor quality of interfacial layer (GeO_x) when there is no surface nitridation. Regarding the work function of TaN,[10] the device without NH_3 anneal has a closer flatband voltage to the ideal one than the device with surface nitridation. The negative shift of the flatband voltage of the surface nitridation device may be due to significant positive charge ($\sim 5.3 \times 10^{12}$ cm^{-2}) introduced by the NH_3 annealing.

HR-XTEM image of the Ge MOS capacitor with NH_3 anneal is presented in Fig. 4(a). The dielectric thickness measured from the TEM picture is ~51 Å and the dielectric constant of dielectric is ~18.9. From Fig. 4(a), it is also noticed that, unlike the interfacial layer on the Si substrate,[11] the interfacial layer on Ge substrate is crystallized. The crystallized interfacial layer may be related to its high oxygen concentration, since GeO_2 induced by gaseous O_2 on the Ge substrate was found to be polycrystalline.[12] It is also noted from the TEM picture that the dielectric film has recrystallized, which implies that the crystallization temperature of the HfO_2 film with Ge is lower than 600 °C. For comparison, the TEM image of the MOS stack without a NH_3 anneal is also presented in Fig. 4(b). A nonuniform interfacial layer is observed between the dielectric and the substrate. This could be due to the nonuniform oxidation behavior of the germanium,[12] which degrades the MOS leakage current.



(a) (b)

FIG. 4. HR-XTEM of the MOS structure of TaN/MOCVD HfO_2/Ge (a) with and (b) without surface NH_3 annealing.

In summary, the surface NH_3 annealing effects on the physical and electrical properties of MOCVD HfO_2 Ge MOS capacitors have been investigated. It is found that GeON is formed during surface nitridation (NH_3 annealing). Germanium is found to be incorporated within CVD HfO_2 films, in addition, the electrical characteristics of HfO_2 Ge MOS capacitors show that surface nitridation is very effective to improve the electrical properties in terms of I_g and EOT.

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[1] A. L. P. Rotondaro, M. R. Visokay, J. J. Chambers, A. Shanware, R. Khamankar, H. Bu, R. T. Laaksonen, L. Tsung, M. Douglas, R. Kuan, M. J. Bevan, T. Grider, J. McPherson, and L. Colombo, VLSI Tech. Dig. **2002**, 148 (2002).
[2] J. J. Rosenberg and S. C. Martin, IEEE Electron Device Lett. **12**, 639 (1988).
[3] H. Shang, H. Okorn-Schmidt, K. K. Chan, M. Copel, J. A. Ott, P. M. Kozlowski, S. E. Steen, S. A. Cordes, H.-S. P. Wong, E. C. Jones, and W. E. Haensch, Tech. Dig.-Int. Electron Devices Meet. **2002**, 441 (2002).
[4] C. O. Chui, H. Kim, D. Chi, B. B. Triplett, P. C. McIntyre, and K. C. Saraswat, Tech. Dig.-Int. Electron Devices Meet. **2002**, 437 (2002).
[5] C. H. Huang, M. Y. Yang, A. Chin, W. J. Chen, C. X. Zhu, B. J. Cho, M. F. Li, and D. L. Kwong, VLSI Tech. Dig. **2003**, 119 (2003).
[6] W. P. Bai, N. Lu, J. Liu, A. Ramirez, D. L. Kwong, D. Wristers, A. Ritenour, L. Lee, and D. Antoniadis, VLSI Tech. Dig. **2003**, 121 (2003).
[7] T. Akane, H. Okumura, J. Tanaka, and S. Matsumoto, Thin Solid Films **294**, 153 (1997).
[8] NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database 20, Version 3.3 (Web Version).
[9] G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **87**, 484 (2000).
[10] C. Ren, H. Y. Yu, J. F. Kang, Y. T. Hou, D. S. H. Chan, M.-F. Li, W. D. Wang, and D.-L. Kwong, IEEE Electron Device Lett. **25**, 123 (2004).
[11] H. Y. Yu, N. Wu, M. F. Li, C. X. Zhu, B. J. Cho, D.-L. Kwong, C. H. Tung, J. S. Pan, J. W. Chai, W. D. Wang, D. Z. Chi, C. H. Ang, J. Z. Zheng, and S. Ramanathan, Appl. Phys. Lett. **81**, 3618 (2002).
[12] F. L. Edelman, L. N. Alexandrov, L. I. Fedina, and V. S. Latuta, Thin Solid Films **34**, 107 (1976).