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Citation: [Applied Physics Letters](#) **89**, 012905 (2006); doi: 10.1063/1.2219347

View online: <http://dx.doi.org/10.1063/1.2219347>

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Thermochemical reaction of $ZrO_x(N_y)$ interfaces on Ge and Si substrates

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(Received 11 December 2005; accepted 2 June 2006; published online 6 July 2006)

We have studied the thermochemical characteristics of $ZrO_x(N_y)/Ge$ and Si interfaces by employing postdeposition annealing. We found that Ge oxide species severely desorbed from the inherent interfacial layer, which was speculated to retard the formation of Zr germanate during high-temperature processing. These unique features enable $ZrO_x(N_y)/Ge$ gate stack to show a better equivalent-oxide-thickness scalability as compared to $ZrO_x(N_y)/Si$ gate stack. However, the volatilization of GeO_x -contained interfacial layer also caused the formation of small pits and/or holes in the overlying $ZrO_x(N_y)$ gate dielectrics, which was expected to cause deterioration in the electrical properties of fabricated high- k/Ge devices. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2219347]

There have been extensive studies on several promising high-permittivity (high- k) candidates—including HfO_2 ,^{1,2} ZrO_2 ,³ and Al_2O_3 (Ref. 4)—deposited on Ge because of the application of its higher low-field carrier mobility; the admirable capacitance properties and transistor performances were continually demonstrated in recent years.^{5,6} However, it seems essential to clarify what other advantages and/or disadvantages of Ge as a replacement of Si. For instance, the thinner lower-permittivity interfacial layer (IL) was observed in high- k/Ge system,⁷ which is beneficial in further scaling the equivalent oxide thickness (EOT) below 1 nm. This finding also implies that fundamental dissimilarities exist between the thermochemical properties of the Ge and Si; distinct thermal decomposition pathway of their oxides was ever reported.⁸ To date, detailed material analysis of high- k/Ge interfaces using x-ray photoelectron spectroscopy (XPS), however, remains quite rare. In the former studies,^{9,10} the authors confirmed that a substoichiometric Ge oxide layer, in which the amount of Ge oxide was dependent upon the ZrO_2 overlayer thickness, did form at the ZrO_2/Ge interface. But, the influences of thermal instability of GeO_x -contained IL on the properties of the overlying high- k dielectrics seem to be still insufficient. The purpose of this work is to study thermal stability of high- k/Ge interface with respect to high- k/Si interface through a comprehensive comparison of the photoemission spectra.

Two different high- k thin films were deposited on the bare Ge and Si wafers by reactive sputtering chamber, which are precleaned by cyclic rinse of diluted HF dip and deionized water; ZrO_2 was deposited in an Ar+ O_2 ambient [$O_2/Ar+O_2=0.2$] with a high-purity Zr target, while ZrO_xN_y was deposited in an Ar+ N_2 ambient [$N_2/Ar+N_2=0.33$] with residual oxygen. For studying the interfacial reaction be-

tween the IL and Zr high- k dielectrics on Ge and Si substrates, we analyzed the effect of N_2 postdeposition annealing (PDA) on the chemical configuration by *ex situ* XPS using an Al $K\alpha$ source (1486.6 eV). We also employed secondary ion mass spectroscopy (SIMS), high-resolution transmission electron microscopy (HRTEM), and atomic force microscopy (AFM) to characterize the entire structures and surface morphology, respectively.

Figure 1 shows the SIMS depth profiles of elements in the ultrathin ZrO_xN_y film on the Si and Ge substrates. The overall thicknesses of the as-deposited films were estimated to be ca. 30 Å and ca. 35 Å, respectively. We found that the nitrogen, which mainly accumulated at the interface, exhibited peak concentrations of ca. 2.3×10^{21} at./cc and ca. 5.3×10^{20} at./cc, corresponding to the maximum atomic percentages of ca. 3.8% and ca. 0.85% in the as-deposited ZrO_xN_y film on Si and Ge substrates, respectively. Lower nitrogen level in ZrO_xN_y/Ge system can be reasonably attributed to the fact that Ge is more easily oxidized than nitrated.¹¹ With 600 °C annealing, most of the nitrogen content was lost in Ge case, which may be perhaps due to the lower thermal stability of Ge–N bonds.¹² Also, it can be observed that such a high temperature can significantly push the Ge into the ZrO_xN_y film bulk; the outdiffusion mechanism and the chemical states of incorporated Ge atoms will be discussed in further detail below.

Figure 2(a) displays the XPS core-level spectra for the ZrO_2 and ZrO_xN_y ultrathin films on Si substrates before and after 600 °C PDA, respectively. As seen from Zr 3d spectra, a Zr–O–Si intermediate layer inclined to emerge in the as-deposited film prepared in an Ar/ O_2 ambient; while ZrO_xN_y was the main composition in the film deposited in an Ar/ N_2 ambient. Interestingly, we observed that the spectra both shifted to higher binding energy and became almost identical after 600 °C PDA; this finding indicates that high-

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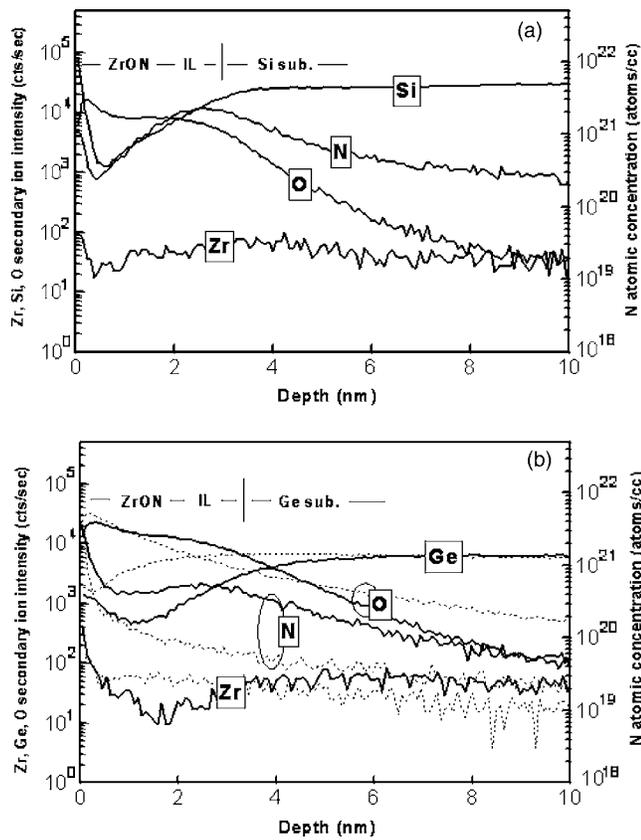


FIG. 1. SIMS profiles of the ZrO_xN_y on (a) Si and (b) Ge substrates before (solid lines) and after (dash lines) 600 °C PDA. The PDA time is 1 min.

temperature annealing tends to convert both the Zr–N and Zr–O bonds into the configuration of Zr–O–Si bond.^{13,14} From the O 1s broad spectra, we confirm this tendency by observing the shifting toward higher binding energy and the increased peak intensity, which is also consistent with the findings of the Si 2p spectra. A N_2 ambient instead of an O_2 ambient facilitates to minimize the thickness of the IL during sputtering and suppress the further growth due to a few SiN_x bond (the N 1s spectra) against the overoxidation.

Pronouncedly, the resultant high- k films on Ge substrate depicted several noteworthy distinct features with respect to their counterparts, as presented in Fig. 2(b). First, from the Zr 3d spectra, there is no evidence of the emergence of interfacial Zr–O–Ge bonding albeit the films deposited in an Ar/ O_2 ambient. The subsequent 600 °C annealing still cannot prompt the occurrence of Zr germanate, i.e., $ZrGeO_x$; indeed, the spectrum profiles even slightly move backward to lower binding energy, implying poor intermixing and alloying in Ge and Zr systems. Next, a broad band consisting of Ge dioxides and suboxides was observed both in Ge 2p3 and Ge 3d spectra. Through the curve fitting for these two Ge core levels with mixed Gaussian-Lorentzian line shapes, the amounts of three components—including element Ge, GeO , and GeO_2 —were extracted. The reduced intensity ratio of GeO_x ($x \leq 2$) to Ge substrate is illustrated in Fig. 3; the inset displays the HRTEM image of as-deposited ZrO_2 /Ge gate stack, in which an IL of ca. 22 Å can be equivocally seen, showing agreement with the estimated thickness of ca. 20 Å by XPS calculation.^{15,16} Upon the increasing PDA temperature, thermally induced transformation of GeO_x into GeO gaseous species led to severe IL desorption through the top high- k films. In addition, residual oxygen in a N_2 ambient

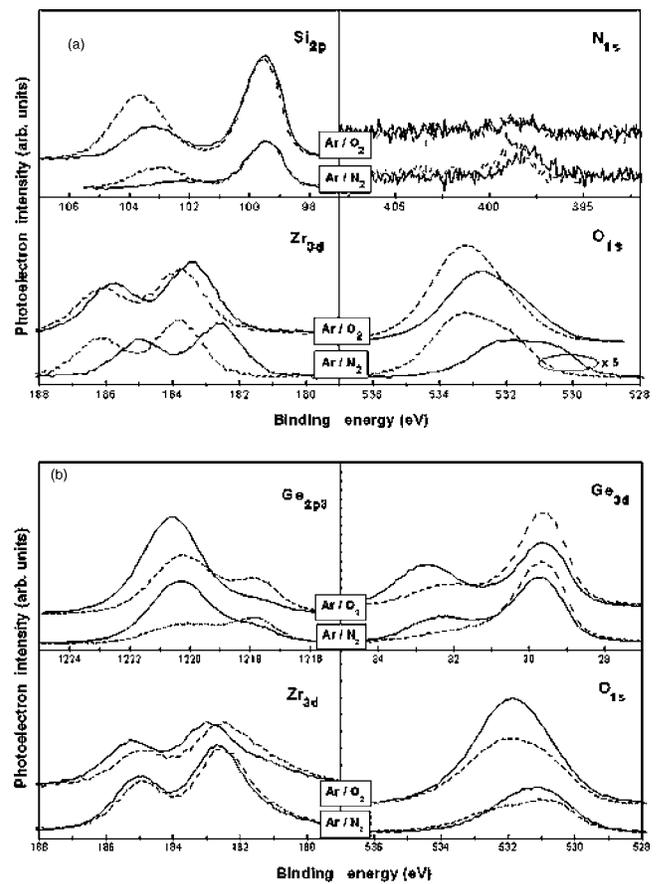


FIG. 2. Zr 3d, Si 2p, Ge 2p3, Ge 3d, N 1s, and O 1s core-level spectra of ZrO_xN_y and ZrO_2 thin films on (a) Si and (b) Ge substrates before (solid lines) and after (dash lines) 600 °C PDA.

can readily oxidize the entire Ge substrate and incur the formation of volatile GeO as well. Therefore, after 600 °C thermal annealing, the GeO_x -contained IL certainly revealed acute volatilization, which was also evidenced by the reduced intensities of the corresponding O 1s spectra. In our previous study, such an IL shrinking tendency after N_2 annealing has also been observed from the TEM images of the HfO_xN_y /Ge gate stacks.¹⁷ We also noticed that the Ge–N and/or Zr–N bonds were undetected in the N 1s spectra (not

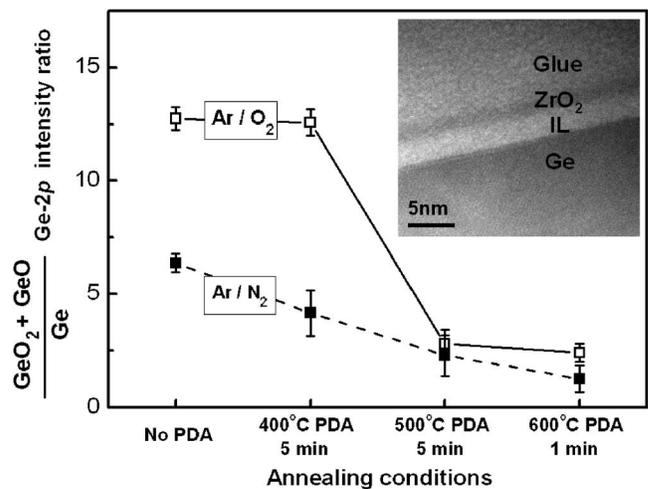


FIG. 3. The ratio of GeO_x to Ge substrate vs annealing conditions for ZrO_xN_y /Ge and ZrO_2 /Ge gate stacks. Inset: Cross-sectional TEM image of ZrO_2 /Ge before the PDA.

shown), which may be owing to the detection limit for lower nitrogen concentration in $\text{ZrO}_x\text{N}_y/\text{Ge}$ structure.

From the viewpoint of aggressive EOT scaling, it is delighted to see an IL contraction on the Ge system. From the AFM images (not shown), the smooth surface morphology of as-deposited ZrO_2 overlayer on Ge was found ($R_{\text{rms}} \sim 1 \text{ \AA}$), but, the outdiffused species led to small pits and/or holes on the top surface of Zr high- k dielectrics after 600°C annealing for 1 min ($R_{\text{rms}} \sim 3 \text{ \AA}$); this in turn possibly created a considerably high defect density and then severely jeopardized the insulating properties of high- k/Ge capacitors.¹⁷ Extending the annealing time to 5 min even resulted in the tremendous surface roughness ($R_{\text{rms}} \sim 26 \text{ \AA}$) and the distortion of Zr $3d$ spectra (not shown), indicative of the destruction of overlying high- k dielectrics. With above examinations, we speculate that the desorption of GeO_x -contained IL is the possible origin of why we did not observe the formation of Zr germanate after high-temperature annealing on Ge. In this study, we showed that the thermal stability of high- $k/\text{substrate}$ interface on Ge is not as good as that on Si due to inherent poor quality of Ge native oxide. Seeking for the means of restraining the Ge-mixed oxides at the interface will be indispensable in pursuit of high-performance high- k gate dielectrics on Ge substrates or epitaxial Ge films.

Thermal stability of $\text{ZrO}_x(\text{N}_y)/\text{Si}$ and Ge interfaces has been studied through the physical characterization. We found that the IL has distinct thermochemical properties on these two substrates. High-temperature processing aids the IL growth and the formation of Zr silicate in $\text{ZrO}_x(\text{N}_y)/\text{Si}$ gate stack. On the contrary, severe IL volatilization and the inhibition of Zr germanate were found in $\text{ZrO}_x(\text{N}_y)/\text{Ge}$ system; these features are expected to possess a better EOT scalability with respect to $\text{ZrO}_x(\text{N}_y)/\text{Si}$ system. However, the generated localized pits in deposited high- k films owing to the desorption of the underlying IL may severely degrade the electrical properties of fabricated high- k/Ge devices.

This study was mainly sponsored by Taiwan Semiconductor Manufacturing Company, Ltd. and partly supported by the National Science Council of Taiwan under Contract No. NSC94-2215-E009-066. One of the authors (C.-C.C.) is grateful to Dr. Fu-Liang Yang and Dr. Chien-Chao Huang for fruitful discussions and to Dr. Ming-Yi Yang for technical assistance.

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