Band Alignment and Optical Properties of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ Gate Dielectrics Thin Films on *p*-Si (100)

Dahlang Tahir[1], Hee Jae Kang[2] & Sven Tougaard[3]

[1]Dep. of Physics, Hasanuddin University, Makassar, Indonesia
[2]Dep. of Physics, Chungbuk National University, Cheongju, Korea
[3]Dep. of Physics and Chemistry, University of Southern Denmark, Denmark
Email: d.tahir@fmipa.unhas.ac.id

Abstract. $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric films on p-Si (100) were grown by atomic layer deposition method, for which the conduction band offsets, valence band offsets and band gaps were obtained by using X-ray photoelectron spectroscopy and reflection electron energy loss spectroscopy. The band gap, valence and conduction band offset values for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric thin film, grown on Si substrate were about 5.34, 2.35 and 1.87 eV respectively. This band alignment was similar to that of ZrO_2. In addition, the dielectric function $\varepsilon(k, \omega)$, index of refraction n and the extinction coefficient k for the $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ thin films were obtained from a quantitative analysis of REELS data by comparison to detailed dielectric response model calculations using the QUEELS-ε (k,ω)-REELS software package. These optical properties are similar with ZrO2 dielectric thin films.

Keywords: *Band alignment; band gap; gate dielectrics; REELS; XPS.*

1   Introduction

High-k dielectric materials have been intensively investigated as alternative gate dielectric to SiO_2 for application in advanced semiconductor devices in recent years [1]. Among prominent candidates in high-k materials, amorphous Zr and Hf based complex oxides have been largely studied due to their composition-tunable structure and electrical properties [2,3]. In contrast to the transition metal (TM) and rare-earth (RE) silicates and aluminates, the single binary alloy and the compound binary alloy between TM and RE oxide, or two different TM or RE oxides had also been investigated to improve electrical properties. Both terminated oxides have high-k and suitable wide band gap [4-6]. The $(ZrO_2)_x(HfO_2)_{1-x}$ dielectrics also attracted attention and were frequently explored [7]. It has been reported that HfO_2 addition into ZrO_2 exhibited improved electrical properties. There are some benefits of Hf addition into ZrO_2, e.g., HfO_2 has a chemical structure similar to ZrO_2 and completely miscible in ZrO_2 [8]. The primary goal of using high-k dielectrics as alternatives

to SiO_2 is to reduce tunneling currents through the gate oxide. Thus band alignment is one of the most fundamental physical properties in characterizing the gate dielectrics. An adequate large band gap and sufficient barrier height are necessary for any alternative high-*k* material [9]. An asymmetry barrier height in holes and electrons is a potentially significant limitation in the operation of CMOS devices and their reliability. We need to identify the band gap and band offsets for the dielectrics on a nanometer scale special resolution. How the energy band structure of Zr compounds aligns with Si is of fundamental importance because it affects the performance of transistors, e.g., electrical properties. In addition, quantitative optical properties are playing an increasingly important role in electronic structure studies of materials. The study of optical properties for the nano scale dielectrics is also necessary.

In this paper, we shall present results of the electronic and optical properties of Zr based dielectrics with the thickness in nanometer range. We compared the band gap and band alignment of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ with ZrO_2 by combining reflection electron energy loss spectroscopy (REELS) and X-ray photoelectron spectroscopy (XPS) measurement to gain more insight into the band alignments for these dielectrics. Furthermore, we obtained the dielectric function and optical properties of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ and ZrO_2 thin film for comparison by quantitative analysis of REELS spectra.

2   Experiment

$(ZrO_2)_{0.66}(HfO_2)_{0.34}$ were grown on *p*-Si (100) substrate by atomic layer deposition (ALD) method. Prior to growing the mixed oxide film, a *p*-type Si substrate was cleaned using the Radio Corporation of America (RCA) method. $HfCl_4$ and $ZrCl_4$ were used as precursors, and H_2O vapor served as oxygen source. The films were grown in N_2 ambient, which was supplied as the purge and carrier gas. The substrate temperature was below 300 ^{o}C during the thin film deposition. The physical thickness of deposition was 7nm. XPS and REELS spectra were obtained by using the VG ESCALAB 210 spectroscopy with LaB_6 electron gun. XPS spectra were measured using Mg $K\alpha$ source and with the pass energy of 20 eV. XPS binding energies were referenced to C 1*s* peak of hydrocarbon contamination at 285 eV. The incident and take-off angles of electrons for both REELS and XPS were 55° and 0° from the surface normal, respectively. The composition of compounds was determined via XPS analysis using sensitivity factors. REELS were measured with the primary electron energy of 1500 eV for excitation and with the constant analyzer pass energy of 20 eV. The full width at half maximum (FWHM) of the elastic peak was 0.8 eV.
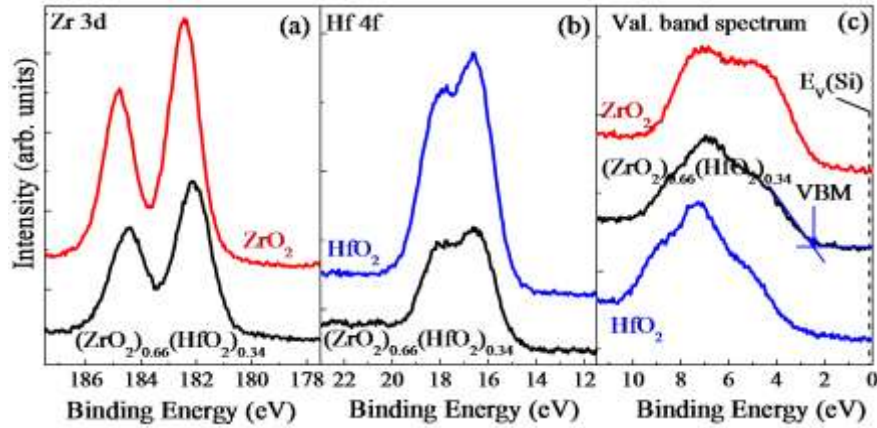
3   Results and Discussion

Figure 1 X-ray photoelectron spectroscopy spectra for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$, HfO_2, and ZrO_2 dielectrics (a) Zr *3d* core level photoelectron spectra, (b) Hf *4f* core level photoelectron spectra, and (c) valence band spectra.

Figure 1 shows XPS spectra, (a) the Zr *3d* photoelectron spectra, (b) the Hf *4f* photoelectron spectra, and (c) the valence band spectra for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$, HfO_2 and ZrO_2 thin films was included for comparison. One of Zr *3d* spectra was characteristic of fully oxidized state of Zr^{4+} for ZrO_2. It had the binding energies of Zr $3d_{5/2}$ and Zr $3d_{3/2}$ peaks measured at 182.4 and 184.8 eV, respectively. Two peaks have the spin-orbital splitting of 2.4 eV [10]. For $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ thin film the Zr *3d* peak, located at 182.1 eV, was at lower side relative to that of ZrO_2. Since the electronegativity difference between Hf (1.30eV) and O (3.44eV) is larger than that between Zr (1.33eV) and O(3.44) [11], the formation of Hf-O bond would be preferred rather than the formation of Zr-O bond for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$. This resulted in a shift of Zr *3d* core level in $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ to a lower binding energy relative to ZrO_2 (see Figure 1(a)) and there is no shift for Hf *4f* (see Figure 1 (b)).

To obtain the valence band offset at the dielectric and Si interface, the valence band spectra were measured to determine the valence band maximum (VBM). The valence band spectra are shown in Figure 1 (b). The VBM was determined using the same method in some of previous work [10,12-15]. From the energy difference between the VBM of gate dielectric and Si, the valence band offset was obtained. Valence band maximum of *p*-Si bulk is positioned at 0.24 eV. Here we do not take into account any possible band bending in the silicon with the oxide grown on top of the Si. The valence band offset of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ shows same valence band offset as that of ZrO_2 with an accuracy of 0.05 eV.
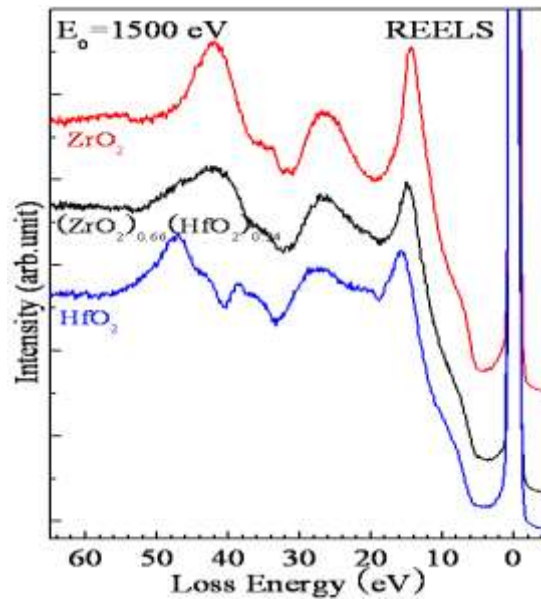
Figure 2 Reflection electron energy loss spectra for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$, ZrO_2, and HfO_2 dielectrics at the primary beam energy of 1500 eV.

REELS is a useful technique in the surface and interface analysis of nanostructure with primary energies less than several keV. We make use of the REELS measurement to find the electronic structure near the band gap. Figure 2 shows REELS spectra for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric thin films. The band gap values were determined from the onset of energy loss spectrum. The method was already described in some of the previous papers [10,12-15].The obtained band gap values for these high-k gate dielectric films are around 5.30 eV. Even if we added Hf elements in ZrO_2 within certain ranges, $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ band gap value was almost not changed. For comparison, we add the REELS spectrum of ZrO_2 and HfO_2 given in our previous works [10,12,16]. For the loss spectra of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric, it appeared to be a superposition of the loss spectra of ZrO_2 and HfO_2 thin film.

Using the band gap and valence band offset we can determine the conduction band offset (ΔE_c) [10,12]. For $(ZrO_2)_{0.66}(HfO_2)_{0.34}$, the conduction band offset was 1.87 eV, which is similar to that of ZrO_2 thin films and higher than that of HfO_2 at 1.54 eV. A sufficiently large barrier height for the electrons was obtained in $(ZrO_2)_{0.66}(HfO_2)_{0.34}$. The band alignments for these dielectrics are shown in Figure 3. We also gave the band alignment of ZrO_2 and HfO_2, which were published previously [10,12]. Through the identification of band alignment for these gate dielectrics, we noticed that the barrier heights for electrons and holes were more symmetric for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ and ZrO_2.

Adequate large barrier heights for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ suggests it could be a better alternatives to SiO_2. The band alignment of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ and ZrO_2 dielectrics were similar. A roughly symmetrical offsets at the valence and conduction bands were found for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric, which is desirable for an idea gate dielectric.
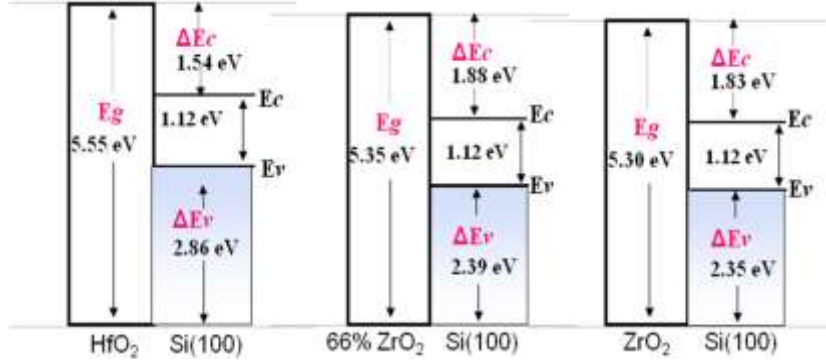

Figure 3 Band alignment for HfO_2, $(ZrO_2)_{0.66}(HfO_2)_{0.34}$, and ZrO_2 dielectrics gate oxide films.

We have also studied the optical properties of the $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric thin films by quantitative analysis of the REELS spectrum by using the Tougaard-Yubero QUEELS-ε (k,ω)-REELS software package [17]. The experimental inelastic scattering cross section from the measured REELS spectra was obtained from the QUASES-XS-REELS software. Comparison of the theoretical inelastic cross section to the experimental one allows us to determine the dielectric function of the $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ thin films. The theoretical inelastic-scattering cross section was calculated from the dielectric response theory [18]. In this model, the response of the material to a moving electron is described by the dielectric function ε, which is conveniently described by the energy loss function (ELF) Im (-1/ε). To evaluate the ELF, we parameterized it as a sum of Drude-Lindhard type oscillators [18,19],which is given by:

$$\text{Im}\{\frac{-1}{\varepsilon(\text{k},\omega)}\} = \theta(\hbar\omega - \text{E}_g) \cdot \sum_{i=1}^{n} \frac{A_i\gamma_i\hbar\omega}{(\hbar^2\omega_{0ik}^2 - \hbar^2\omega^2)^2 + \gamma_i^2\hbar^2\omega^2} \qquad (1)$$

where the dispersion relation is given in the form:

$$\hbar\omega_{0ik} = \hbar\omega_{0i} + \alpha_i\frac{\hbar^2k^2}{2m} \qquad (2)$$

Here, A_i, γ_i, $\hbar\omega_i$ and α_i are the oscillator strength, damping coefficient, excitation energy and momentum dispersion coefficient of the ith oscillator, respectively. The step function $\theta(\hbar\omega\text{-}E_g)$ is included to simulate a possible energy gap, E_g, which was estimated from the onset of energy loss in the REELS data (Figure 2). The parameters in the ELF were determined via a trial-and-error procedure, until a satisfactory quantitative agreement between the experimental and theoretical inelastic scattering cross section was reached. The parameters were determined from the REELS spectra for primary energies of 1.0, 1.5 and 1.8 keV.
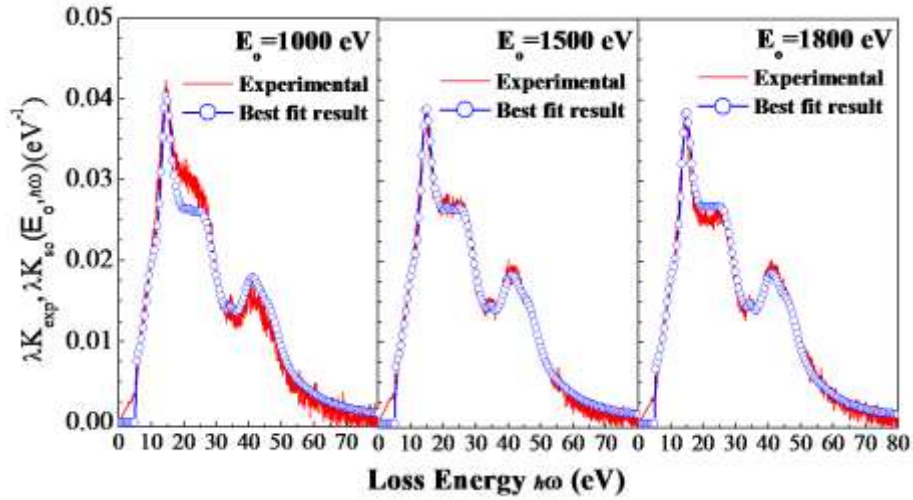

Figure 4 Experimental inelastic cross section λK_{exp} (line) obtained from REELS data of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ thin films compared to theoretical inelastic cross section λK_{sc} (symbol) evaluated using the simulated energy loss function.

Figure 4 shows the experimental λK_{exp} (line) from REELS spectra, which is compared with the theoretical λK_{sc} (symbol) by using the QUEELS-$\varepsilon(k,\omega)$-REELS software. The parameters in the ELF were determined via a trial-and-error procedure, until a satisfactory quantitative agreement is reached. Note that in all the calculations, the same ELF was used for all energies and only the ELF (not the SELF) is used as an input parameter to calculate the λK_{SC} value for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ on Si substrate in Figure 3, because the algorithm ([18,20]) in the software calculates the quantitative influence of surface excitation and its interference with the bulk excitation. The dielectric loss functions for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric thin films were obtained from REELS spectra for the primary electron energies of 1.0, 1.5 and 1.8 keV.

Table 1   Parameters in the model energy loss functions of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ thin films on *p*-Si (100) substrate that give the best fit overall to the experimental cross sections at 1.0, 1.5, and 1.8 keV.

	i	$\hbar\omega_{0i}$ (eV)	A_i (eV^2)	γ_i (eV)
$(ZrO_2)_{0.66}(HfO_2)_{0.34}$	1	10.5	6.0	5.0
(E_g=5.35)	2	15.3	35.2	3.3
(a_i=0.02)	3	18.0	21.1	5.0
	4	21.5	46.4	7.0
	5	26.7	162.9	9.5
	6	34.5	6.7	2.5
	7	41.0	173.8	8.5
	8	46.5	83.4	7.0
	9	57.0	12.0	10.0

The resulting oscillator parameter of ELF for the $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectrics thin film are listed in Table I. The corresponding ELF is plotted in Figure 4(a) for a wide energy range (0 to 80 eV). We see from Table I that the ELF for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric has 9 oscillators in the vicinity of 10.5, 15.3, 18.0, 21.5, 26.7, 34.5, 41.0, 46.5 and 57 eV. For the ELF of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric, it appeared similar to that of ZrO_2 thin film (see Table 1 in [21]). The main different are peaks at energy loss between 40 eV to 50 eV, which is contributed from HfO_2 loss function at 46.5 eV [16]. For energy lower than 40 eV the ELF of ZrO_2 and HfO_2 are similar (see Figure 5 (a)) [16,21]. There is a shift for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric at energy lower than 40 eV compared to that of, indicated these peak overlapping with ELF of HfO_2 thin films. From this analysis, we conclude that the electronic structure of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric is contributed from that of ZrO_2 and HfO_2 as shown by previous works [16,21]. The loss function $Im\{-1/\varepsilon\}$ allows us to perform a Kramers-Kronig transformation to obtain the real part $Re\{1/\varepsilon\}$ of the reciprocal of complex dielectric functions. Then, we can obtain the real part ε_1 and imaginary part ε_2 by using $Im\{-1/\varepsilon\}$ and $Re\{1/\varepsilon\}$ [18]. The real and imaginary parts of the dielectric function are as follows;

$$\varepsilon_1 = \frac{Re\{1/\varepsilon\}}{\left(Re\{1/\varepsilon\}\right)^2 + \left(Im\{1/\varepsilon\}\right)^2} \tag{3}$$

$$\varepsilon_2 = \frac{Im\{1/\varepsilon\}}{\left(Re\{1/\varepsilon\}\right)^2 + \left(Im\{1/\varepsilon\}\right)^2} \tag{4}$$

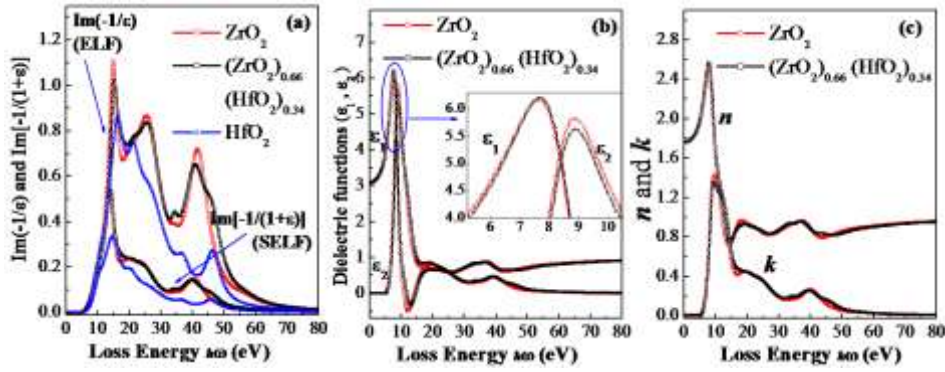**Figure 5** Dielectric function and optical properties of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectrics. (a) Energy loss function (ELF) and surface energy loss function (SELF), we included HfO_2 ([16]) and ZrO_2 ([21]) dielectrics for comparison, (b) Real part (ε_1) and imaginary part (ε_2) of dielectric functions (ZrO_2 dielectrics for comparison), and (c) Refractive index (n) and extinction coefficient (k) (ZrO_2 dielectrics for comparison).

Figure 5(b) shows the values of the real part ε_1 and imaginary part ε_2 (corresponding to the absorption spectrum) of dielectric functions. As can be seen in the insert figure in Figure 5(b), the main peak position of dielectric function of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric are same to that of ZrO_2. In the absorption spectrum ε_2, the strong absorption below 9 eV was associated with a transition of the valence band electrons into the unoccupied d states in the conduction bands [20-22].

We also determined the optical properties (see Figure 5 (c)) such as the index of refraction n, and the extinction coefficient k from the ELF. The index of refraction n and the extinction coefficient k are given in terms of the dielectric function as follows [19];

$$n = \sqrt{\frac{1}{2}\left(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1\right)} \qquad (5)$$

$$k = \sqrt{\frac{1}{2}\left(\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1\right)} \qquad (6)$$

As can be seen in Figure 5 (b) and (c) there are no different in energy loss of the peaks in ε_1, ε_2, n, and k for $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric compared with that of ZrO_2 thin films. These results lead to the conclusion that ZrO_2 have a strong effect on the dielectric function and optical properties of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric thin films.

4   Conclusions

We investigated the band alignments and optical properties for ZrO_2 and $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectrics. The band alignments were investigated by using REELS and XPS analysis. The results showed that the $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ has same barrier heights as those of ZrO_2. $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric should exhibit good electronic properties with this sufficient barrier heights. Through a quantitative analysis of REELS spectra of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric thin films, we found that the optical properties of $(ZrO_2)_{0.66}(HfO_2)_{0.34}$ dielectric thin films obtained by analyzing the ELF with Kramer-Kronig relations are similar to that of ZrO_2 dielectric thin films. Hence, a quantitative analysis of REELS provides us with a straightforward way to determine the electronic and optical properties of high-k dielectrics materials.

References

[1]   http://www.itrs.net/Links/2010ITRS/Home2010.htm,   (last   accessed July 12, 2010).

[2]   E. Bersch, S. Rangan, R.A. Bartynski, E. Garfunkel & E. Vescovo, *Band Offsets of Ultrathin High-k Oxide Films with Si*, Phys. Rev., **B78**, 085114, 2008.

[3]   J.I. Beltran & M.C. Munos, *Ab Initio Study of Decohesion Properties in Oxide/Metal System,* Phys. Rev., **B78**, 245417, 2008.

[4]   D. Tahir, H.L. Kwon, H.C. Shin, S.K. Oh, H. J. Kang, S. Heo, J. G. Chung, J. C. Lee, and S. Tougaard, *Electronic and Optical Properties of Al_2O_3/SiO_2 Thin Films Grown on Si Substrate,* J. of Physics D: Appl. Phys.*,* **43,** 255301, 2010.

[5]   Y. Yamamoto, K. Kita, K. Kyuno, and A. Toriumi, *Structural and Electrical Properties of $HfLaO_x$ Films for an Amorphous High-K Gate Insulator*, Appl. Phys. Lett., **89**, 032903, 2006.

[6]   V.V. Afanas'ev and A. Stesmans, *Internal Photoemission at Interfaces of High-k Insulator with Semiconductors and Metals*, J. Appl. Phys., **102**, 081301, 2007.

[7]   D.H. Triyoso, R.I. Hedge, J.K. Schaeffer, D. Roan, P.J. Tobin, S.B. Samavedam, B.E. White Jr., R. Gregory & X.D. Wang, *Impact of Zr Addition on Properties of Atomic Layer Deposited HfO_2*, Appl. Phys. Lett., **88**, 222901, 2006.

[8]   R.I. Hegde, D.H. Triyoso, S.B. Samavedam & B. E. White Jr., *Hafnium Zirconate Gate Dielectric for Advance Gate Stack Applications*, J. Appl. Phys., **101**, 074113, 2007.

[9]   J. Robertson, J. *Maximizing Performance for Higher K Gate Dielectrics,* Appl. Phys., **104**, 124111, 2008.

[10] D. Tahir, E. K. Lee, S. K. Oh, T. T. Tham, H. J. Kang, H. Jin, S. Heo, J. C. Park, J. G. Chung & J. C. Lee, *Band Alignment of Atomic Layer Deposited $(ZrO_2)_x(SiO_2)_{1-x}$ Gate Dielectrics on Si (100)*, Appl. Phys. Lett., **94,** 212902, 2009.

[11] http://www.webelements.com/electronegativity.html, (last accessed July 5, 2010).

[12] H. Jin, S.K. Oh, H.J. Kang & M.-H. Cho, *Band Gap and Band Offsets for Ultrathin $(HfO_2)_x(SiO_2)_{1-x}$ Dielectrics on Si (100)*, Appl. Phys. Lett., **89**, 122901, 2006.

[13] S. Miyazaki, *Characterization of High-k Gate Dielectric/Silicon Interfaces,* Appl. Surf. Science, **190**, 66-74, 2002.

[14] S. Miyazaki, M. Narasaki, M. Ogasawara, M. Hirose, *Chemical and Electronic Structure of Ultrathin Zirconium Oxide Films on Silicon as Determined by Photoelectron Spectroscopy*, Solid State Elect., **16**, 1679-1685, 2002.

[15] S. Miyazaki, M. Narasaki, A. Suyama, M. Yamaoka & H. Murakami, *Electronic Structure and Energy Band Offsets for Ultrathin Silicon Nitride on Si(100)*, Appl. Surf. Science, **216**, 252-257, 2003.

[16] H. Jin, S. K. Oh, H. J. Kang, and S. Tougaard, *Electronic properties of ultrathin $(HfO_2)_x(SiO_2)_{1-x}$ dielectrics on Si (100)*, J. Appl. Phys., **102**, 053709, 2007.

[17] S. Tougaard, F. Yubero, *QUEELS-ε(**k**, ω)-REELS: Software Package for Quantitative Analysis of Electron Energy Loss Spectra; Dielectric Function Determined by Reflection Electron Energy Loss Spectroscopy*, Ver. 3.0, 2008. See http://www.quases.com.

[18] S. Hajati, O. Romanyuk, J. Zemek & S. Tougaard, *Validity of Yubero-Tougaard Theory to Quantitatively Determine the Dielectric Properties of Surface Nanofilms,* Phys. Rev., **B77**, 155403, 2008.

[19] F. Wooten, *Optical Properties of Solid*, Academic Press New York and London, pp. 42-185,1972.

[20] L. K. Dash, N. Vast, P. Baranek, M. C. Cheynet, and L. Reining, *Electronic Structure and Electron Energy Loss Spectroscopy of ZrO_2 Zirconia,* Phys. Rev., **B70**, 245116, 2004.

[21] D. Tahir, E. K. Lee, S. K. Oh, H. J. Kang, S. Heo, J. G. Chung, J. C. Lee & S. Tougaard, *Dielectric and Optical Properties Zr-Silicates Thin Films Grown on Si (100)by atomic layer deposition,* J. Appl. Phys., **106,** 084108, 2009.

[22] D. Tahir, E. K. Lee, H. L. Kwon, S. K. Oh, H. J. Kang, S. Heo, E. H. Lee, J. G. Chung, J. C. Lee & S. Tougaard, *Electronic and Optical Properties of GIZO Thin Film Grown on SiO_2/Si Substrate*, Surf. and Interf. Anal., **42,** 906-910, 2010.